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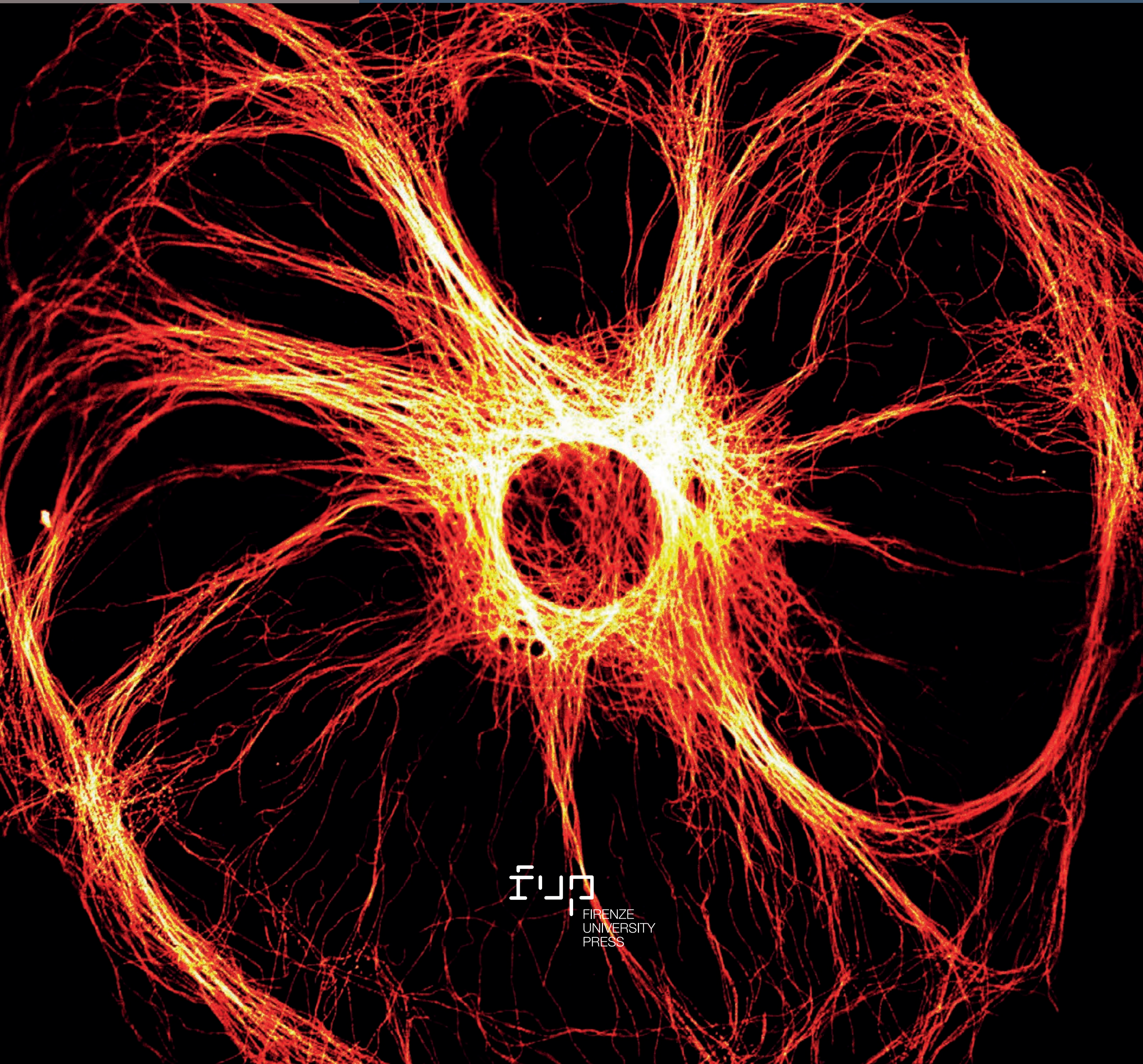

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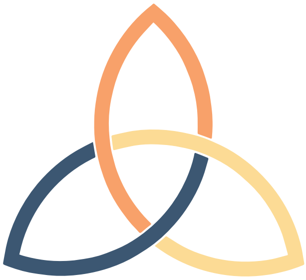

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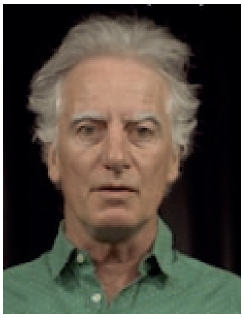

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Editorial

Artificial Intelligence *vs.* Natural Stupidity

Pierandrea Lo Nostro

Department of Chemistry "Ugo Schiff", University of Florence, 50019 Sesto Fiorentino (Firenze), Italy
E-mail: pierandrea.lonostro@unifi.it

The number of articles, contributions, TV reports and tweets, squeaks and cheeps on the social networks that deal with the emerging and invasive role of artificial intelligence (AI) in several aspects of our life is increasing enormously, day by day.

Like for other hot issues, the use of AI has bright and dark sides. Some are sincerely excited by the potential beneficial outcomes of its applications, others are scared by the potential drawbacks, including some challenging limitations to human freedom. Others are just making their wallet fuller and fuller with AI.

Apparently it is the same story depicted so amusingly in the movies "Frankenstein junior" (1974) or "Blade Runner" (1982). Humans create their own creatures – usually to make them work hard at very low costs or to commit criminal activities – that in turn revolt and threaten their makers. The literature is replenished with similar stories.

This time with AI of course the situation is pretty different.

AI is an incredibly powerful machine. It can make calculations and infer conclusions starting from huge datasets and with such a speed that is absolutely inconceivable for a human being. However the history of technology teaches us that the problem is always in the mind and in the hands of the user and, particularly in this case, of the developer.

It is not necessary to be sluggishly reluctant to accept innovations and changes to advance serious doubts on the consequences of AI. Some of these effects are, at the moment, unforeseeable.

Some applications are certainly very useful and valuable. For example AI helped find a new drug to cure drug-resistant infections [1]. *Acinetobacter baumannii* is a very nasty bug that often colonizes hospitals and can lead to pneumonia, meningitis, and other potentially deadly infections. Well, a machine-learning model was able to identify a new drug starting from a set of 7,000 potential compounds. The machine-learning model was trained to evaluate whether a chemical compound would inhibit the growth of *A. baumannii* [1].

AI can be convenient in other very different cases: assisting a doctor in diagnosing a disease (especially with rare diseases), in remote medical visits, for first (non specialized) assistance in call centers, in assisting elderly people, and several others.

AI is also helpful in writing and texting. Most of us use T9 or other more recent chatbots when composing a Whatsapp message to friends or colleagues. And Gmail uses a similar learning system for anticipating the words we are about to type in an email. It is certainly useful to save time and to avoid typos, but probably this habit will lead to an even lower level of knowledge of a language: teenagers will not need to know how to spell words any more, as AI will do it for them. As they will probably use a calculator to calculate Log(10).

So, AI will make us lazier, more ignorant and superficial. That's for sure.

Apparently, according to an ACS publication, AI is particularly poor in chemistry, so it is quite uncertain whether AI could help students in studying chemistry or not [2].

AI will use a rather boring and monochromatic language, certainly politically correct, flavorless and soft. I don't believe it can reach the infinite complexity of human expressions with double meanings and ambiguities.

On the other hand, AI will certainly be a very tough and valid opponent in a chess play.

In this intricate muddle of Pros and Cons we cannot forget the production of fake news. About 50 news websites are generated by AI: an interesting article published

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in *The Guardian* wonders whether we would be able to find out promptly it is just garbage [3].

It has to be recalled that AI may also help fight fake news, although this process is more complicated and slower than creating misinformation, and requires also a vigilant filter from the targets of the information release [4].

But I would like to stress here the few positive and the many negative aspects of using AI in scientific publishing.

Some big publishers started using AI during the different stages of publication [5]. By using some machine-learning algorithms to "replicate" human intelligence, AI can actually replace or assist the journal editor in reading the submitted manuscript, identifying the reviewers, compile the received reviews, text analyze the paper, decide whether the content "sells" or not (to increase views, downloads and citations), detect plagiarism and self-plagiarism, detect false statistical analyses, and get a final decision on the suitability of the paper for publication.

I believe we all agree that the selection of reviewers is probably the most important and delicate step of the entire publication process. When we accept and perform a review we willingly become part of a huge database from which some algorithms catch the data they want. A similar thing happens with conference invitations: we all receive hundreds of invitations to strange conferences, some of which do not even address our scientific interests. No surprise the invitation often starts with the acknowledgement of one of our most recent papers. Well, in these cases the learning machine is really stupid and would invite me to a geology conference mentioning one of my papers on soft matter…

With *Substantia*, we are proud of our willing, reliable and skilled reviewers. With them we built a strong sense of the journal's purpose. In a relatively short time (only 8 years) we established *human* relationships with authors and reviewers that represent the real pillar of our journal.

The pervasive introduction of AI within editorial systems reflects also an awful ontological prejudice that entails the belief that human judgment in the publication process is a polluting player, a source of bias and inefficiencies. While AI is supposed to provide an impartial evaluation of research quality. This is a trivial nonsense, as we don't know how the algorithms are made.

In the perennial opposition between quality and quantity, AI can only adopt the latter for its own assessments. This means for example that in the selection of a reviewer parameters like the H-index, number of publications, number of citations, IF of the journal, etc. will be considered (probably using the ORCID, the Scopus identification number or the Clarivate code), with the potentially dangerous consequence to perpetuate the *status quo* and breed inbox thinking, preventing new contributions from younger or other scientists in a specific field.

As an author: my personal private opinion is that writing a paper is an extraordinary, exciting and absolutely creative activity I do with my set of data that my coworkers and I collected in the lab. Then, why should I let a learning machine write even a draft of my paper [6]? Human creativity must be fueled and not depressed. Different scientists will probably discuss and even interpret the same set of data in different ways. Why should we abandon this pleasure and sophisticated capability we have to represent and describe reality?

In the end, cloud computing, IoT (Internet of Things), Big Data, and the most advanced artificial intelligence algorithms are nothing but the result of our attempts to improve computation execution time and data availability [7]. If you are interested, follow up on the developments of the new "algorhetics" [7].

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Research Article

Chemical Demulsification of Oil-in-Water Emulsion from Gas Condensate Field

Habineswaran Rajan[1,2,*], Nur'aini Raman Yusuf[2], Dzeti Farhah Mohsim[1], Nor Hadhirah Bt Halim[3]

[1] *Department of Petroleum Engineering, Universiti Teknologi PETRONAS, 32610, Seri Iskandar, Perak, Malaysia*
[2] *Center of Enhanced Oil Recovery, Institute of Hydrocarbon Recovery, Universiti Teknologi Petronas, 32610 Bandar Seri Iskandar, Perak Darul Ridzuan, Malaysia*
[3] *PETRONAS Research Sdn Bhd, Jln Ayer Hitam, Kawasan Institusi Bangi, 43000 Bandar Baru Bangi, Selangor, Malaysia*
*Corresponding author. E-mail: habines17@gmail.com

Abstract. Produced water, also known as oily wastewater, is one of the major wastes in the oil and gas industry. During the hydrocarbon production, formation of emulsion takes place such as oil-in-water emulsion which has a huge financial effect on the sector. Oil and gas industry seeks highly effective and reasonable demulsifying chemicals to separate the oil-in-water emulsions into water and crude oil. Thus, in this publication, resin alkoxylate, cationic polyamine, cationic surfactant and ethylene oxide/propylene oxide (EO/PO) block copolymers are utilized to resolve the oil-in-water emulsion from a gas condensate field. According to the findings of preliminary screening, a unique demulsifier DB was formulated by incorporating resin alkoxylate and cationic surfactant at an optimal weight percentage ratio. Demulsification efficiency (D_e) of 96 % based on measurement of turbidity was attained after treating the oil-in-water (O/W) emulsion with demulsifier DB at a dosage of 7 ppm. To determine the demulsifier's efficiency further, the oil-in-water content (OiW) of the produced water was evaluated after the treatment with demulsifier DB. Oil removal efficiency (OR_e) of 90% was achieved as the formulated demulsifier DB reduced the oil-in-water content (OiW) of O/W emulsion from 1008.3 ppm to 97.1 ppm within 15 minutes at the dosage of 7 ppm. Furthermore, interfacial tension (IFT) and Turbiscan analysis were performed to further study the demulsification process of blank sample and the addition of the demulsifier DB at the optimized dosage of 7 ppm. At demulsifier DB dosage of 7 ppm, the interfacial tension between oil and water reduced significantly compared to blank sample from 24.98 mN/m to 9.38 mN/m. The produced water sample after treatment with 7 ppm of demulsifier DB resulted in a significant increase of Turbiscan Stability Index (TSI) value of 8 which indicates the rate at which the separation of oil and water occurred. The attained results of IFT and Turbiscan analysis further validate that mixed surfactant system is more efficient than single surfactant system. By combining surfactants with different functional groups, mixed surfactant systems can exhibit greater surface activity than single surfactants.

Keywords: emulsion, produced water, demulsifier, demulsification, Oil-in-Water content (OiW), demulsifier OA-KX.

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1. INTRODUCTION

The development of alternative energy sources is a significant challenge in today's world, given environmental contamination and the constant need for fresh water. Nevertheless, petroleum is still one of the prominent sources of energy for transportation fuels in most countries. Therefore, there is a steady need to supply the continuous demand for the oil and gas industry. As a result of exploration and development activities, excessive amount of water known as produced water is lifted from the subsurface formations to the earth surface (Veil *et al.*, 2004). Produced water can be present in the form of emulsions which can be harmful to the aquatic organism if it was discharged untreated into the sea. In order to preserve the environment from contamination, these excessive amounts of water should be treated before it can be discharged into the environment. When economically feasible, it is recommended to recycle produced water within the upstream oil and gas sector as it offers several benefits, such as minimizing the need for external water sources, reducing liability concerns associated with managing produced water, and limiting the overall management of produced water. Prior to recycling, specific substances like insoluble oil, microorganisms, iron, and boron are typically removed using fit-for-purpose treatment trains consisting of oil-water separations, solids separation, disinfection, and iron removal methods (Liden *et al.*, 2017). Conventional oil and gas wells are drilled into geological formations where oil and natural gas flow easily to the wellbore. In contrast, unconventional oil and gas wells are drilled into previously unconventional geological sources, such as coalbed methane (CBM), shale gas, tight oil, shale oil, and oil sands. With conventional production, the produced water is often recycled by injecting back into medium-to-high permeability reservoirs to maintain pressure of the reservoir or enhanced oil recovery (EOR) (Scanlon *et al.*, 2019). However, in the case of unconventional production, the excessive produced water cannot be injected back into the low-permeability reservoirs. Therefore, treating produced water is a practical approach for managing the large volumes of water generated during oil and gas exploration and production. The primary objectives of produced water treatment are to remove dispersed oil and grease, desalinate the water, remove suspended solids, eliminate soluble organics, remove dissolved gases, reduce naturally occurring radioactive materials (NORM), disinfect the water, and soften it (Liden *et al.*, 2019). De-oiling is a process of removing any remaining oil and grease that can be harmful to the environment if discharged untreated. Desalination process done using desalters removes any salt from the water to prevent damage to the environment and equipment.

Generally, combination of two non-miscible liquid phases is known as emulsion in which one phase is dispersed in the other phase (Tadros, 2013). An emulsion contains a continuous phase and a dispersed phase which are also known as external and internal phase respectively. The oil droplets are the dispersed phase in the continuous phase which is water or vice versa. Regardless of the phase volume ratio, dispersed phase always has the smaller phase volume compared to the other phase (Schramm, 1992). A water-in-oil (W/O) emulsion is a type of emulsion in which the dispersed and continuous phase is water and oil respectively. Oil-in-water (O/W) emulsion is a form of emulsion in which continuous phase or the dispersion medium is water and the dispersed phase is oil (Auflem, 2002). Multiple emulsions have a more complicated structure, with microscopic droplets suspended in large droplets in a continuous phase. Oil-in-water-in-oil (O/W/O) and water-oil-in-water (W/O/W) emulsions are two types of multiple emulsions (Israelachvili, 1994; Sjoblom, 2001) as shown in the Fig. 1.

Oil refining, also known as petroleum refining, is the process of transforming crude oil into a range of useful products such as gasoline, diesel, jet fuel, heating oil, lubricants, and various other chemicals. Crude oil is a complex mixture of hydrocarbons, impurities, and contaminants, and refining is necessary to convert this raw material into usable products that meet spe-

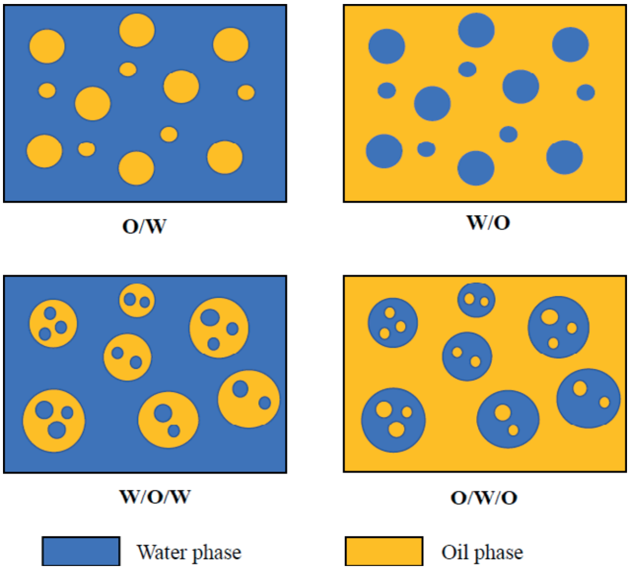


Figure 1. Types of emulsions.

cific quality and performance standards. The refining process typically involves several stages of processing, each of which is designed to remove different impurities and contaminants from the crude oil. Desalination process done using desalters removes any salt from the water to prevent damage to the environment and equipment. De-oiling is a process of removing any remaining oil and grease that can be harmful to the environment if discharged untreated. These processes of oil refinery are often aided by demulsifier where it helps to separate water and other impurities from the oil more effectively, reducing the amount of contaminants in the final products. Demulsifiers involve desalters and deoilers, which is considered to be about 40% approximately the world oilfield production chemicals market.

Demulsification is the process of segregating an emulsion into two different phases which are water and crude oil. Crude oil can be sent directly to refineries utilising less complex emulsion breakers and chemical technology when crude oil had little to no water during its production in oil and gas industry. Emulsion droplets can range in size from rather big (visible) to sub-micron. Some emulsions are extremely stable and require a demulsification technique to be treated. Destabilization of emulsion is carried out by using either four main methods such as mechanical, chemical, thermal, or electrical (Coca *et al.*, 2011). Chemical method is one of the common approaches applied in the process of demulsification where demulsifiers are added into the emulsion to assist the emulsion breaking process (Razi *et al.*, 2011). Chemical additives' primary role is to counteract the stabilizing impact of emulsifying agents which are asphaltenes and resins (Daniel-David *et al.*, 2008). Demulsifiers are surfactants that helps to separate O/W and W/O emulsions into two phases respectively at low concentrations of dosage. Produced water include a significant amount of oil droplets during the production of hydrocarbon. To minimise complications during the refining process, these oil droplets should be removed from the produced water or viceversa. Asphaltenes and resins are naturally occurring compound of crude oil which can form a stabilizing layer around the water droplets, preventing them from coalescing and separating from the oil (Feitosa *et al.*, 2019). The surface-active chemicals known as demulsifier are absorbed to the oil/water interface and it weaken the rigid film of the droplets. Addition of demulsifier reduces the surface tension of the droplets, which in turn destabilizes the emulsion particles (or droplets). Eventually, it leads to the rupturing of rigid film and enhance coalescence of water droplet (Mhatre *et al.*, 2018). As a result, the particles within the emulsion have a natural tendency to agglomerate and form larger masses which leads to the separation of oil and water. Demulsifiers or surfactants are organic particles comprising of two parts: the polar portion that is attractive to the water phase (hydrophilic) and the non-polar portion that is attractive to the oil phase (hydrophobic) as shown in Fig. 2. Effective emulsion breaking using a demulsifier needs a chemical that is appropriately selected for the specific emulsion, a suitable amount of dosage, appropriate stirring of chemical in the emulsion, and an adequate time for the droplets to settle down (Yi *et al.*, 2017). It may also be necessary to rise the temperature of the system to aid the demulsification process, however, it might increase the cost of treatment.

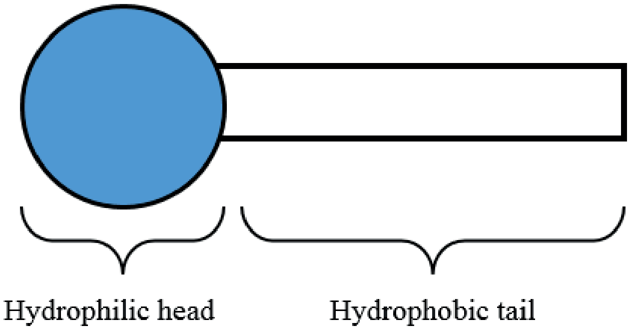


Figure 2. Basic structure of demulsifier (Porter, 1991).

There are previous study and research on the types of demulsifiers tested which is important for improving the understanding of emulsions, developing more effective treatments, optimizing their usage, and minimizing their environmental impact. Poly aluminium chloride and quaternary ammonium salt (PAC-QAS), polyamine (PA), and the compound of polyamine and poly aluminium chloride (PA-PAC) were investigated for the treatment of oily produced water in 2020 (Shu *et al.*, 2021). Shu discovered that PA and PA-PAC at 60 mg/L and 90 mg/L respectively showed better performance than PAC-QAS in terms of oil removal efficiency, achieving around 60% and 70%. Due to the cationic polyamine's high positive charge, the stability of emulsified oil droplets was disrupted as the negatively charged oil droplets was counteracted by the chemical and making it surface active (Shu *et al.*, 2021).Wang *et al.* examined the demulsification of O/W emulsions using block copolymers of ethylene oxide (EO) and propylene oxide (PO), which has amphiphilic characteristics in aqueous solution (Wang *et al.*, 2010). When the concentration of PAE82 and PAE102, which are dendritic copolymers and synthesised by propylene oxide and ethylene oxide reactions, reached 150 mg/L, their demulsification ratios were 91.92% and 91.23% at 15 minutes respectively. This shows that EO/PO block copolymers is capable of a good demulsifier for O/W emulsion. Furthermore, according to the study conducted by Acostal *et al.*, a member of the resin alkoxylate family, C6 have demonstrated remarkable performance in accordance with industrial norms when tested for the demulsification of W/O emulsion, enabling more than 80% water separation (Acosta *et al.*, 2020). A feasible substitute to the hydrophilic–lipophilic balance (HLB) approach for evaluating the hydrophilic-lipophilic balance of surfactants is the Relative Solubility Number (RSN). RSN has found extensive applications in the surfactant chemical industry for aiding in product selection, quality control, and formulation. It is also beneficial in emulsion research as it facilitates the choice of demulsifiers and stabilizers (Wu *et al.*, 2004). The demulsifier C6 has a relative solubility number (RSN) value of 11. This constant, which is frequently used for screening and benchmarking, categorises demulsifiers as water or oil-soluble. High RSN numbers (>13) are associated as water-soluble demulsifier, whereas low RSN numbers (< 13) numbers are associated with oil-soluble demulsifiers (Marquez-Silva *et al.*, 1997). Intriguingly, C6 lies in the region close to the region of oil-soluble demulsifier which shows that it could be effective in resolving in O/W emulsion. For the O/W emulsions demulsification, water-soluble demulsifiers are typically utilized whereas oil-soluble demulsifiers are commonly utilized to destabilise water-in-oil emulsions (Raya *et al.*, 2020). Hirasaki *et al.* observed that certain amphoteric and cationic surfactants were efficient at segregating O/W emulsions, which were produced when surfactant/polymer (SP) method was used for enhanced oil recovery (Hirasaki *et al.*, 2011). In his study, adding roughly 200 ppm of cationic surfactant, n-octyltrimethylammonium bromide (C_8TAB) caused a distinct segregation of the oil and water phase. The cationic surfactant decreased electrostatic repulsion between droplets and altered system phase behaviour leading to a balanced state of lipophilic and hydrophilic effects which reduces the emulsion stability. In this article, various types demulsifiers such as resin alkoxylate, cationic polyamine, cationic surfactant and EO/PO block copolymers were evaluated for the demulsifcation of O/W emulsion. The impact of various demulsifiers on the O/W emulsion was investigated based on the turbidity and OiW content of the treated sample. The main objective of this work is to minimize the OiW content of the O/W emulsion from gas condensate field by developing a new formulation using selected effective demulsifiers based on the screening conducted.

2. MATERIALS AND METHODS

2.1 Materials

PETRONAS Research Sdn. Bhd. (PRSB) provided the essential materials for the experiment purpose from gas condensate field such as produced water and condensate. They were selected for the preparation of emulsion as they were raw material obtained from a gas condensate field without undergoing any treatment. The characteristics of the condensate and produced water are shown in Table 1 and Table 2. Several types of chemicals were provided by PETRONAS Research Sdn. Bhd. (PRSB) were used for the treatment of O/W emulsion of gas condensate field are shown in Table 3. Demulsifier A, B, C and D are used in this experiment and the chemicals are industrial grade.

2.2 Emulsion preparation

For the preparation of O/W emulsion, the condensate and produced water from gas condensate field were

Table 1. Characteristics of the condensate.

Characteristics	Value
Density @15°C	0.8857 g/cm^3
API Gravity @15°C	28.2°
Wax appearance temperature (WAT)	10.7 °C
Kinematic viscosity @60 °C	1.438 mm^2/s
Saturates	52.77 %
Aromatics	46.77 %
Resins	0.41 %
Asphaltenes	0.12 %

Table 2– Characteristics of produced water

Characteristics	Value
Salinity	100 mg/L
pH	3.7

Table 3. Types of demulsifier.

Demulsifier	Type
A	Cationic polyamine
B	Resin alkoxylate
C	EO/PO block copolymers
D	Cationic surfactant

used as oil and water phases respectively. The O/W emulsion was prepared by using the produced water and condensate at a volume ratio of 85:15. Using a 100 ml beaker, produced water and condensate were added into the beaker at a volume of 34 ml and 6 ml respectively. The total mixture of condensate and produced water was 40 ml in the beaker. In order to form a stable O/W emulsion, the produced water and condensate was then homogenized for 10 mins at 4000 rpm using IKA Ultra-Turrax T-50 Homogenizer.

2.3 Emulsion characterization

The type of emulsions whether O/W or W/O emulsion and the typical size was confirmed visually using a Leica DM LB2 microscope at 40X magnifications. Furthermore, zeta potential (z-potential) gives more information on the O/W emulsion stability, and it is measured by measuring the charged droplets or colloids' velocity in a specified electrical potential field. Zeta-potential of the emulsion were measured to study the electrical charge of any droplet present in the emulsion. Malvern Zetasizer Nano-ZSP was used to test the zeta-potential of emulsion that had no chemical compounds added.

2.4 Bottle test screening

The prepared emulsion according to the experimental procedure mentioned above was then transferred to a bottle. In order to stimulate the real field condition, the bottle containing the emulsion was then immersed in water bath for 30 minutes at 60 °C. After that, the demulsifiers was injected into the bottle using pipette at various dosages and the bottles were shaken 100 times by hand to ensure that the demulsifier was uniformly distributed throughout the emulsion. For the segregation of oil and water to take place, the emulsion was then allowed to settle down for 15 minutes by placing the bottles in water bath. The water sample from the bottom of the bottle was obtained at the end of the retention time. The water sample's turbidity and OiW content were also determined.

2.5 Turbidity measurement

Turbidity is a liquid's relative clarity measurement that has long been used as a fundamental and straightforward indication of water quality. It is an optical property of water in which the amount of light scattered by material in the water is measured when a light is shone on a water sample. The turbidity of the emulsion and treated sample was measured with HACH 2000 turbidimeter at 0.001 NTU, maximum sensitivity. The efficiency of the demulsifier was determined by calculating the demulsification efficiency, D_e (%), using the formula below:

$$\textit{Demulsificatian efficency, } D_e\ (\%) = \frac{T_o - T}{T_o} \times 100 \tag{1}$$

where T_o and T are the initial and final turbidities of the produced water.

2.6 Oil-in-water content (OiW) measurement

For the measurement of oil concentration of the sample, TD-500D Handheld Oil in Water Meter from HMA INSTRUMENTATION was utilized. Using infrared detection, the TD-500D Handheld Oil in Water Analyzer determines solvent extractable substances (hydrocarbons, oil, and grease) in water or wastewater. The standard procedure to measure oil concentration is by transferring the produced water to a tube and add hexane solution at a volume of 10% to the total amount of produced added initially. The tube was then shaken for 2 minutes and the top layer of the tube was taken using a pipette. The solution will be then injected on the surface of the oil analyzer to measure the OiW content. The amount of oil removed from the produced water was evaluated based on the oil removal efficiency, OR_e (%), calculated using the formula below:

$$\textit{Oil removal efficency, } OR_e\ (\%) = \frac{OiW_o - OiW}{OiW_o} \times 100 \tag{2}$$

where OiW_o and OiW are the initial and final OiW contents of produced water sample.

2.7 Interfacial tension (IFT) measurement

The force between two distinct phases that can be liquid-solid, liquid-liquid, gas-solid or gas-liquid contact is known as interfacial tension (IFT). The interfacial tension of two non-miscible liquids, oil and produced water, was measured at 60°C using the Rame Hart Model 260 by the pendant drop method. Pendant drop is an optical method to measure interfacial and surface tensions of fluid system. They are determined through the drop shape using the following equation:

$$\textit{Surface tension, } \gamma = \frac{\Delta\rho g {R_0}^2}{\beta} \tag{3}$$

where γ is the surface tension, g is the gravitational constant, Δρ is the difference of densities between liquids, R_0 is the curvature's drop radius at the apex, and β is the shape factor. β is defined as three dimensionless first-order equations through the Young-Laplace equation expressed.

2.8 Turbiscan Lab® Expert demulsification analysis

Turbiscan™ AGS High Throughput Stability Analyzer from Formulaction (France) is intended for examining destabilization mechanisms of emulsions and dispersions. Besides, it characterizes physical properties of substances, or identifies the particle size and concentration in a sample more importantly (Mengual *et al.*, 1999; Paweł *et al.*, 2020). The Turbiscan apparatus utilizes a near-infrared light source with a wavelength (λ) of 880 nm, emitting pulsed signals, in combination with synchronized dual detectors – a transmission (T) detector and a backscattering (BS) detector – to aid in the optical evaluation of dispersion destabilization. At a degree of 0° from the incident beam, the transmission (T) detector detects light that passes through the sample. The light will be then reflected back by the sample at degree of 135° from the incident beam and it will be detected by the back scattering (BS) detector (Celia *et al.*, 2009). This equipment can detect destabilisation by creaming before it is apparent to the human eye. Emulsion destabilisation was investigated utilising profiles of transmission (T) and backscattering (BS) by scanning the sample of emulsion at a wavelength of 880 nm every 5 minutes for 1 hour at 60 °C. It analyses all variances in each sample and generates a unique number that indicates a specific sample's destabilization. TurbiSoft Lab can be utilised to compute the Turbiscan Stability Index (TSI) and analyse any quantity of samples. This will provide an analysis of the sample's stability. This coefficient, TSI is calculated as follows (Zheng *et al.*, 2018; Zhu *et al.*, 2015):

$$\textit{Turbiscan stability index, TSI} = \sqrt{\frac{\sum_{i=1}^{n}(x_i - x_{bs})^2}{n-1}} \qquad (4)$$

where n is the scans number, $\boldsymbol{x_i}$ is the mean backscattering measurement for every minute and $\boldsymbol{x_{bs}}$ is the average value of $\boldsymbol{x_i}$.

3. RESULT AND DISCUSSION

3.1 Emulsion characterization

The microscopy image of the prepared emulsion is shown in Fig. 3. Based on the observation, the continuous phase occupies most of the area which indicates that the phase with the smaller volume is the dispersed phase. Therefore, O/W emulsions were formed based on the emulsion preparation procedure which involved mixing produced water and condensate in a volume ratio of 85:15. The surface charge of particle is linked to the zeta potential. Large readings of z-potential (negative or positive) improve emulsion stability and signify difficulties in droplet coalescence, although z-potential is often pH-dependent, and other important parameters must be addressed for coalescence prediction (Coca *et al.*, 2011). This is a vital parameter for studying the chemistry taken place in evaluating whether an emulsion will remain stable in its intended environment. The prepared emulsion recorded a zeta potential measurement of -29.8 mV that represent a stable emulsion has formed. When the zeta potential is in the range of +5 m to -5 mV, colloidal particles are quite unstable due to agglomeration and it is highly stable when the zeta potential reading is around -30 mV or more negative (Schramm, 1992). A zero-zeta potential implies that the conditions for flocculation of emulsion droplet are at optimum meaning it has a potential for easier emulsion separation. Emulsions are classified as macro-, micro-, and nano-emulsions based on size of droplet and its stability (Komaiko & McClements, 2016). Based on visual observation obtained under microscope, the average size of oil droplets ranges from 20 μm to 5 μm. This shows that the prepared emulsion is a macroemulsion which is also known as conventional emulsion. The typical droplet size of macro-emulsion ranges from 1 – 100 μm and it has a turbid optical property which is the same as the prepared emulsion. Micro- and nano-emulsions has a droplet size of 10 – 100 nm and < 200 nm respectively

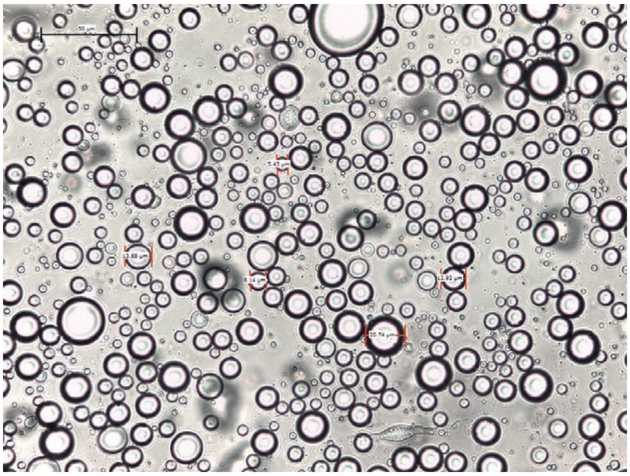


Figure 3. Photography of prepared emulsion under microscope.

(Aswathanarayan & Vittal, 2019). Macro-emulsions will lead to a separation of two-phase over time as it is thermodynamically unstable (Yao *et al.*, 2021).

3.2 Impact of demulsifier on produced water turbidity

The bottle test screening was conducted according to the experimental procedures on the prepared emulsion. The dosage of demulsifier used are 7 ppm, 10 ppm and 20 ppm. Fig. 4 illustrate the results obtained from the experiment after the injection of chemicals and immersed in water bath for 15 minutes at 60 °C. The impact of demulsifier on the changes in the turbidity reading of the treated produced water sample was studied. The turbidity of the produced water is mainly caused by the presence of oil droplets dispersed in the produced water. The greater the turbidity reading, the greater the intensity of scattered light. As a result, clear water has a low turbidity value, indicating that there are less oil droplets suspended in the produced water. Based on the results shown in Table 4, demulsifier A showed no impact on the turbidity of the produced water as a constant 1000 NTU reading were recorded. As for demulsifier C, a slight change in the turbidity reading of 966 NTU recorded at a dosage of 10 ppm. The impact of demulsifier C is not significant as the reading of turbidity is still high. It can be said that the cationic polyamine and EO/PO block copolymers demulsifer are ineffective in treating O/W emulsion of the gas condensate field. However, as compared to the blank sample, the demulsifiers D and B significantly reduced the turbidity reading of the treated sample. The addition of demulsifier B resulted in a constant decrement of turbidity reading as the dosage increased from 7 ppm to 20 ppm where the lowest reading of turbidity reading of 210 NTU at 20 ppm. A slight increment in the turbidity reading was recorded as the dosage increased to 30 ppm which is unfavourable. Besides, at a dosage of 7 ppm, demulsifier D had the lowest turbidity reading (181 NTU) with the least dosage of demulsifier. The reading of turbidity started to increase when the dosage of demulsifier was increased to 20 ppm where a turbidity measurement of 593 NTU was recorded. The significant reduction in turbidity reading of demulsifiers D is due to the highly active molecules of the demulsifier which can attach to the oil/water interface and lower the stability of dispersed oil droplets. At a dosage of 7 ppm, the adsorption behaviour of demulsifier D molecules on the oil/water interface was remarkable which resulted in a low turbidity reading. Further increase of the dosage of demulsifier D has caused the turbidity reading to increase as the demulsifier D has reached the saturation or optimal point at 7 ppm. The molecules of demulsifier starts to form micelles due to aggregation when the demulsifier dosage exceeded the micelle concentration (CMC) which increased the turbidity of treated produced water sample (Huang *et al.*, 2019). The demulsification efficiency (D_e) of the demulsifiers were calculated based on Eq. 1. Based on the results, demulsifier D recorded the highest demulsifcation efficiency up to 82% at a minimum dosage of demulsifier which is 7 ppm. Demulsifier B was able to achieve a demulsification efficiency of 79% at a dosage of 20 ppm. Therefore, demulsifier D and demulsifier B were further optimized to treat the O/W emulsion of produced water from the gas condensate field.

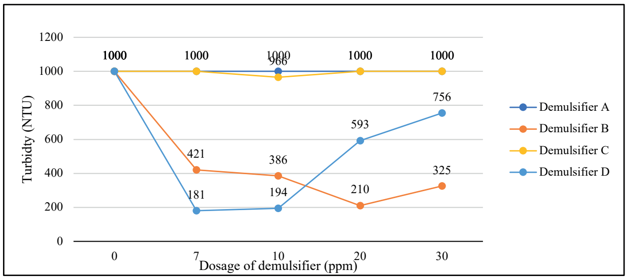


Figure 4. Impact of demulsifier on the turbidity of treated produced water sample at 60 °C.

Table 4. Turbidity result of various demulsifiers.

	Type of demulsifer	Chemical dosage (ppm)				
		0	7	10	20	30
Turbidity (NTU)	Demulsifier A	1000	1000	1000	1000	1000
	Demulsifier B	1000	421	386	210	325
	Demulsifier C	1000	1000	966	1000	1000
	Demulsifier D	1000	181	194	593	756

3.3 Development of demulsifier (DB) formulation

A unique demulsifier was formulated by incorporating demulsifier D with demulsifier B. The unique demulsifier is prepared by adding 10 ml of demulsifier D and 10 ml of demulsifier B into a tube. The mixture is then stirred at 1200 rpm for 10 minutes using Barnstead Thermolyne Maxi Mix II Vortex Mixer as shown in Fig. 5. The unique demulsifier DB was then used to conduct bottle test screening at dosage of 7 ppm, 10 ppm and 20 ppm for treating the O/W emulsion. Fig. 6 illustrate the turbidity results obtained after addition of demulsifier DB. According to the outcome of the testing, the newly formulated demulsifier DB decreased the turbidity read-

Figure 5. Preparation of demulsifier DB using Barnstead Thermolyne Maxi Mix II Vortex Mixer.

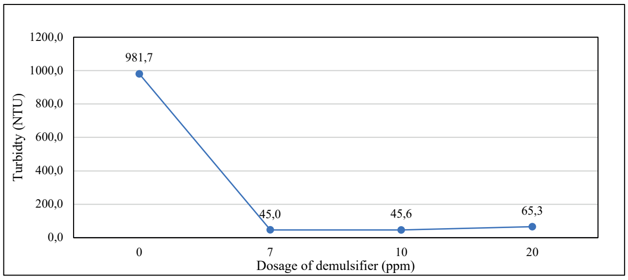


Figure 6. Impact of demulsifier DB on the turbidity of treated produced water sample at 60 °C.

ing of treated produced water sample to 45 NTU which is lesser than results attained by the addition of demulsifier D alone (181 NTU). Based on Eq. 2, the demulsification efficiency (D_e) of 96% was attained at 7 ppm of demulsifier DB. The water clarity of the produced water sample is much clearer after the addition of demulsifier DB when compared with blank sample which is very turbid as shown in Fig. 7.

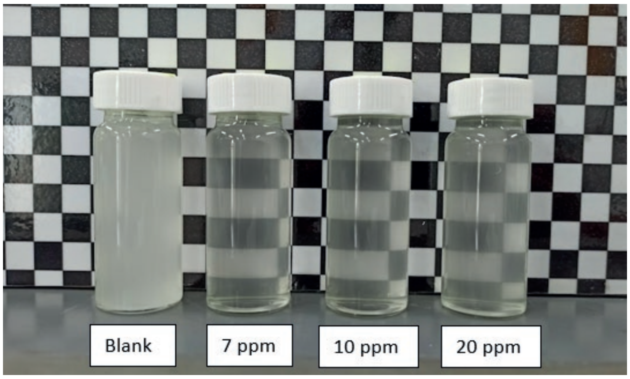


Figure 7. Produced water after the addition of demulsifier DB.

3.4 Impact of demulsifier DB on oil-in-water content (OiW)

The OiW content of the treated produced water sample with demulsifier DB were measured using TD-500 TD-500D Handheld Oil in Water Analyser and the results are shown in Fig. 8. Based on the results obtained, the blank sample without any addition of demulsifier recorded an OiW content of 1008.3 ppm. At a dosage of 7 ppm, OiW content reading of 97.1 ppm which is the lowest reading was obtained with demulsifier DB. When the unique demulsifier DB was applied, the results demonstrate a substantial drop in OiW content at an oil removal efficiency (OR_e) of 90%. As the dosage of demulsifier was increased after 7 ppm, the OiW content gradually increased. demulsifier DB helps to neutralise the negatively charge oil droplets and reduce zeta potential, lowering repulsion and weakening the oil droplets stability. However, excessive amounts of demulsifier DB may cause the flocs to become positively charged, preventing the production of big flocs from tiny ones. As a result, an excess of the demulsifier DB impedes the oil removal from wastewater which can

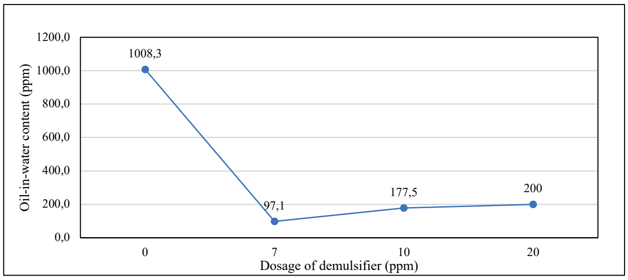


Figure 8. Impact of demulsifier DB on the OiW content of treated produced water sample at 60 °C.

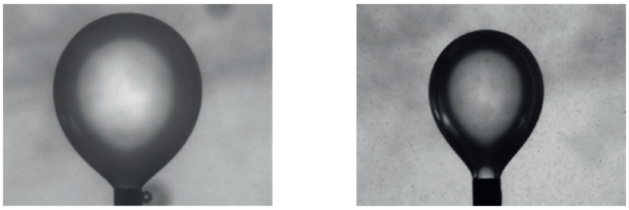
be seen by the increase of OiW content from 97.1 ppm to 200 ppm as the dosage increase to 20 ppm. Therefore, the optimum dosage of demulsifer DB is 7ppm to achieve the lowest reading of OiW content. The treated produced water sample is further validated with interfacial measurement and Turbiscan analysis to show that the demulsifier DB helps in the demulsification of O/W emulsion.

3.5 Impact of demulsifier DB on interfacial tension (IFT)

Produced water was the aqueous phase and condensate was the drop phase in this IFT analysis. The blank sample without addition of chemical has a high IFT value (24.98 mN/m) indicates that a steady emulsion is still present as shown in Fig. 9. A high IFT results indicates a highly stable emulsion (Kumar & Mandal, 2018). With the addition of demulsifier DB, it can be seen that the newly formulated demulsifier was able to minimize the interfacial tension at oil/water interface. The interfacial tension between oil and water reduced significantly from 24.98 mN/m to 9.38 mN/m at demulsifier DB dosage of 7 ppm. Demulsifiers can significantly lower interfacial tension, which weakens the oil droplets' stability as the rigid film surrounding the oil droplets tends to breakdown readily. The oil droplet with the addition of demulsifier DB has a smaller shape compared to the untreated sample as the demulsifier DB neutralize the natural surfactant present on the oil droplet film. Minimizing the droplets' stability leads to the coalescence of oil droplets which leads to the separation of condensate and produced water (Huang *et al.*, 2019). Demulsifier DB was able to decrease the IFT at the oil/water interface, leading to an increased separation rate of oil and water via enhanced flocculation and coalescence process.

3.6 Demulsification analysis using Turbiscan Lab® Expert

In order to demonstrate how the emulsion ageing process influences the oil droplets, the sample can be be optically analysed by the Turbiscan equipment. The Turbiscan Stability Index (TSI), which is used to characterise physical stability, is determined by adding changes in transmission (T) or backscattering (BS) of light over the course of several measurements as a function of sample height (Paweł *et al.*, 2020). The main advantages of TSI measurement are the ability to analyse opaque systems (such as crude oil emulsions) over a short period of time and the samples are undisturbed during TSI measurement from transmission/backscattering data as no dilution is required. TSI measurement has the advantages over several typical stability determination techniques, such as conductivity measurements, and ageing tests (Xu *et al.*, 2013). The TSI value will trend upward for any destabilization occurrence, including coalescence, creaming, sedimentation, flocculation, or Ostwald ripening, because the back-scattered signal and the photon transport mean free route are inversely related ($\text{BS} \approx 1/\sqrt{\lambda^{*}}$) (Acosta *et al.*, 2020). In short, Turbiscan Stability Index (TSI) measurements are utilized to determine how stable an emulsion is. Based on Fig. 10a and 10b, it



(a) (b)

Figure 9. Image of oil droplet without demulsifier DB (a) and after the addition of demulsifier DB dosage at 7ppm (b).

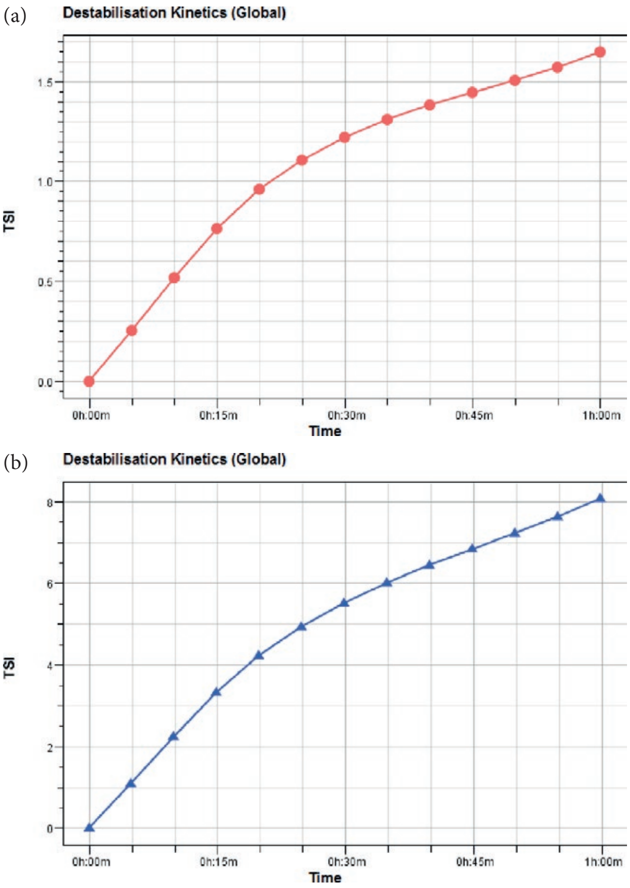


Figure 10. Comparison of Turbiscan analysis of sample without demulsifier DB (a) and after the addition of demulsifier DB dosage at 7ppm (b) conducted at 60 °C.

Table 5. Turbiscan analysis of DB demulsifier conducted at 60 °C.

Dosage of demulsifier DB (ppm)	TSI value
0	1.6
7	8

can be observed that there is a rise in the slope and TSI value after the addition of demulsifier DB compared to blank sample. Over the period of 30 minutes, the slope of the treated sample with demulsifier DB showed a rapid increase which indicates a steady increase of TSI values. The rate of slope change indicates how quickly separation occurs in which higher instability is implied by higher TSI value. (Liu *et al.*, 2011; Mengual, 1999). Compared to TSI value of blank sample without the addition of demulsifier DB which is 1.6, the treated produced water sample with 7 ppm of demulsifier DB resulted in a significant increase of TSI value of 8 as shown in Table 5. The emulsion's stability is considered weaker when the TSI value is high (Li *et al.*, 2019). This shows that the demulsifier DB helps in the demulsification of the emulsion efficiently in a short period of time compared to the blank sample without any chemical additives.

3.7 Demulsification mechanism of O/W emulsion using mixed surfactant system

Generally, chemical demulsification, as performed in this study, is a process in which an optimum amount of demulsifier is added to emulsions and the emulsion is rapidly agitated to separate the oil and water. Ostwald ripening happens when the dispersed phase which is the oil droplets may readily diffuse in a continuous phase which is the water to come together for flocculation. The demulsifier molecules of a mixed surfactant solution will be absorbed to the oil droplets' surface, thus lowering interfacial tension and rupturing interfacial film strength which holds the oil in droplets form. This will indirectly minimize the oil droplets' stability and allow the oil droplets to accumulate. The accumulation of oil droplets is referred to as the flocculation process in which the oil droplets cluster together in the water continuous phase. This causes the droplets of oil to coalesce and form larger droplets. Finally, depending on the phase density of emulsion's dispersed, the creaming or sedimentation processes take place when the denser phase settles down below the less dense phase (Abdulredha *et al.*, 2020). Since combinations of various surfactant types typically demonstrate synergism in their impact on the characteristics of the system, utilising a mixed surfactant system is more effective than using conventional method of single surfactant (Holland & Rubingh, 1992). Mixed surfactant demulsifiers have been shown to be more effective than single-surfactant demulsifiers in breaking oil-water emulsions. By combining different surfactants with different mechanisms of action, mixed surfactant demulsifiers can more effectively reduce the interfacial tension, provide steric hindrance, and neutralize electrostatic repulsion between the droplets (Kronberg *et al.*, 2014). Besides, mixed surfactant demulsifiers can improve the stability of the demulsification process by providing a broader range of surface activity and surface coverage (Kronberg *et al.*, 2014). This leads to a more complete destabilization of the emulsion, resulting in faster and more efficient separation of the oil and water phases. After analysing the experimental data, considerable impacts at interfaces with the solution can be noticed even at low concentrations of mixed surfactants in the emulsion sample. The most noticeable result is a reduction in interfacial tension caused by adsorption of surfactant molecules at oil droplets interface, as seen in Fig. 11.

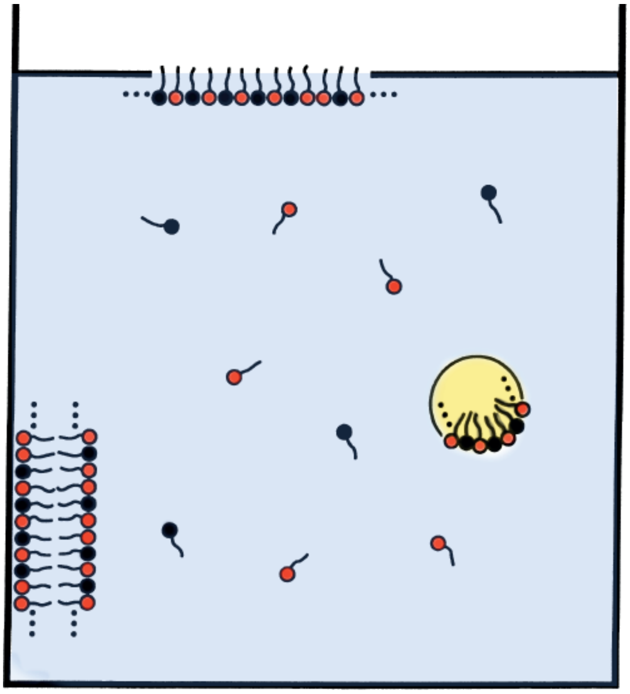


Figure 11. Occurrence in a mixed surfactant system of two surfactant types.

4. CONCLUSION

The O/W emulsion of gas condensate field was treated through demulsification in the present study. Various types of demulsifiers were studied by bottle test and based on the study, the demulsifiers D and B reduced turbidity substantially higher when in comparison with demulsifier A and C. Therefore, an unique demulsifier DB was formulated at an optimal weight percentage ratio of D/B. The unique demulsifier DB exhibited the highest efficiency in removing the dispersed oil droplets of the produced water compared to single demulsifier use. The demulsifier DB was able to neutralize the charge around the dispersed oil droplets leading to coalesces of oil droplets and reduced the OiW content in the produced water. At a temperature of 60 °C, the optimum dosage of demulsifier DB was determined at 7 ppm. An oil removal efficiency (OR_e) of 90% was achieved where the OiW content of the treated produced water sample reduced from 1008.3 ppm to 97.1 ppm under 15 minutes. Moreover, the IFT and Turbiscan analysis exhibited that the utilization of demulsifier DB further validates the results obtained for the OiW content measurements in which the demulsifier helps in minimizing the interfacial tension at oil/water interface and reduce the stability of the produced water sample for the separation of water and condensate to occur. This shows that the resin alkoxylate (Demulsifier B) and cationic surfactants (Demulsifier D) work together well to treat the O/W emulsion from gas condensate field.

Nomenclature

D_e	[%]	Demulsification effieciency
T_o	[NTU]	Intial turbidity
T	[NTU]	Final turbidity
OR_e	[%]	Oil removal efficency
OiW_o	[ppm]	Initial oil-in-water content
OiW	[ppm]	Final oil-in-water content

Sub- and Superscripts

o	Initial
e	Efficiency

Abbreviation

OiW	Oil-in-water content
IFT	Interfacial tension
W/O	Water-in-oil
O/W	Oil-in-water
W/O/W	Water-oil-in-water
TSI	Turbiscan stability index
HLB	Hydrophilic–lipophilic balance

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Research Article

Demulsifier Selection Guideline for Destabilizing Water-in-Oil Emulsion for both non-EOR and EOR Application

Nor Hadhirah Halim[1,*], Ismail M Saaid[2], Sai Ravindra Panuganti[1]

[1] *PETRONAS Research Sdn Bhd, Jln Ayer Hitam, Kawasan Institusi Bangi, 43000 Bandar Baru Bangi, Selangor*

[2] *Department of Petroleum Engineering, Universiti Teknologi PETRONAS, 32610, Seri Iskandar, Perak, Malaysia*

*Corresponding author. E-mail: norhadhirah@petronas.com

Abstract. The most common method for resolving water-in-oil (W/O) emulsion is chemical demulsification. Bottle test is a recommended procedure to analyze a combination of essential parameters such as the demulsifier dosage, residence time, heat, degree of agitation to generate the emulsion and agitation effects after demulsifier injection. It is an extensive and time-consuming selection procedure. Furthermore, the previous demulsifier selection guideline reported in the literature had limitations and was not suitable for the Southeast Asia region. This study describes the development of a new demulsifier selection guideline that relates the demulsifier properties to the crude oil characteristics and is more representative for resolving emulsions in Southeast Asia environment. In developing the selection guideline, four types of synthetic crude were used, with the crude API ranging from 27° to 40°. Sixteen demulsifiers with a relative solubility number (RSN) ranging from 11 to 21 were evaluated comprising resin alkoxylate and modified polyol base demulsifiers. An emulsion test matrix was developed by creating emulsions with different wax contents, asphaltene content and solid contents in the crude oil; then, the demulsifier was screened for all the matrices. Based on the demulsification bottle test completion for all the test matrices, the demulsifier selection guideline was developed and then validated with the blind test in resolving emulsions from the actual crude. The validation results achieved an 86.7% match rate between the guideline output and the lab experimental result. This proved that good agreement had been established between the demulsifier properties and the crude characteristics.

Keywords: emulsion, demulsifier selection guideline, Relative Solubility Number (RSN).

1. INTRODUCTION

The most common type of emulsions in the petroleum industry are water-in-oil (W/O) emulsion. Once formed, W/O emulsion can adversely impact petroleum dehydration and desalination processes. They cause corrosion, scaling, and mechanical changes in gas-oil separation units, affect the operation of the pumping systems due to the elevated viscosity, influence raw material processing quality and increase energy consumption (Binks and Rocher, 2009). Crude oil emulsions must be separated almost completely before the oil can be transported and processed further.

W/O emulsion is strongly stabilized by native crude oil emulsifiers (surfactants), which tend to migrate and concentrate at the W/O interface, forming a film that reduces the interfacial tension between the phases, preventing droplet coalescence. Asphaltenes, resins, waxes and fine solid particles are generally considered to be natural emulsifiers and are thought to be responsible for the emulsion stability (Zaki *et al.*, 2000). On the other hand, the use of chemicals such as alkali, surfactants, and polymers in the injected water in EOR technologies not only interacts with rock to change the wettability conditions, but also reacts with oil to form emulsions that improve oil recovery. However, the natural oil–water interfacial properties are also altered, which possibly makes the W/O emulsions much more stable. Thus, while oil field emulsion might possess beneficial effects for oil recovery during oil reservoir Enhanced Oil Recovery (EOR) flooding processes, they create challenging conditions in the subsequent oil processing operations and must be neutralized, reduced, or removed. Therefore, for many decades, understanding their causes, both chemically and physically, and predicting their formation and how to mitigate them, has been a very important technical development objective in the petroleum industries.

Chemical methods are the most common mitigation approach for emulsion resolution in both the oil fields and the refinery (Angle, C.W., 2001). The application of chemicals designed to neutralize the effects of emulsifying agents has the great advantage of being able to break the interfacial film effectively without the addition of new equipment or modification of existing equipment. However, due to the great number of different types of crude oils and EOR process conditions, development, and selection of effective demulsifiers for regional crude oils has become a serious challenge.

Currently, in the oil industry, the selection of a demulsifier is still based mainly on trial and error after some preliminary screening such as bottle testing (Wu *et al.*, 2003). Normal bottle testing duration in screening the demulsifier raw chemicals is very time consuming as there are a lot of raw chemicals to be tested which sometimes can reach 40 to 50 types of raw chemical. There should be a systematic process for selecting a suitable demulsifier based on the increasing knowledge of demulsifier chemistry. Marques-Silva *et al.* developed a model that relates the crude oil acidity number, water salinity and demulsifier relative solubility number. Correlation between the crude oil nature, the associated water salinity and the demulsifier hydrophilicity (RSN) are described as per Eq. (1) below (Marques-Silva *et al.*, 1997):

$$\ln S = -0.77A - 0.28\ \text{RSN} + 8.17 \tag{1}$$

where S is the associated water salinity and A is the crude oil acidity number.

This model is proposed as a method for demulsifier selection of crude oil/ water systems in which the acidity number and water salinity are easy parameter to be measured in the laboratory.

Cooper *et al.* studied the hydrophilic–lipophilic balance (HLB) of the demulsifier used to break an emulsion of heavy oil, water, and clay. The degree of demulsification was found to correlate with the HLB of the surfactant. The most effective agents for dewatering had HLB values between either 4 and 6, or 13 and 15. For clay removal, the most useful surfactants had HLB values above 20 (Cooper at al., 1980). Grenoble and Trabelsi agreed on the relationship of HLB with demulsifier performance by mentioning that the initial selection of the most suitable surfactant or surfactant combination based on the intrinsic HLB may be a valid starting point but should not be limiting for fine-tuning the system (Grenoble and Trabelsi, 2018).

Temple-Heald *et al.* reported that because the RSN of a demulsifier is a measure of its solubility properties, it is a key factor in demulsifier selection because solubility properties dictate whether the chemical will perform effectively as a surface-active agent at the oil/water interface. Demulsifier molecular weight, RSN and functional groups are the keys to provide good separation of the water from the oil emulsion for heavy oil applications. In terms of the RSN evaluation, all demulsifiers < 8 RSN did not exhibit any separation whilst surfactants with RSN > 11 showed an improvement in the emulsion separation. In terms of the level of alkoxylation levels, the products that had highly mixed alkoxylation levels had better demulsification properties than single alkoxylated products (Temple-Heald *et al.*, 2014). Al-Sabagh and Noor El-Din stated that the optimum demulsification efficiency, with 80% water separation, was obtained by a demulsifier with a high RSN value of 22 (Al-Sabagh and Noor El-Din, 2014).

Many studies have been carried out to evaluate the stability and demulsification of crude oil emulsions. A.A. Pena *et al.* carried out research on the effect of alkylphenol polyalkoxylated resins and polyurethanes on the stability and properties of brine-in-crude oil emulsions. The phenolic resins promoted coalescence of droplets, supplemented by the cross-linked polyurethanes, which may act as "bridges" between droplets, thus increasing the probability for collisions leading to successful coalescence events. A mixture of 200 ppm of polymer polyurethane and 40 ppm of phenolic resin managed to achieve complete water separation in less than 2 hours at 30 °C (Pena *et al.*, 2005)**.** F. Zhang *et al.* described that one of the main challenges in demulsifier research and application is the demulsification of Alkali Surfactant Polymer (ASP) flooding produced liquid, because the ASP application induces oil-in-water, water-in-oil and multiple emulsions which are very complex. To tackle this, there is a need to study dual function demulsifiers which can provide demulsification of both O/W and W/O emulsions at the same time (Zhang *et al.*, 2017).

As reported in other literature, the efficiency of a surfactant to act as a demulsifier depends on a few factors related to the surfactant structure, namely, the distribution of the demulsifier molecules throughout the bulk volume of the emulsion, the partition of the demulsifier between the phases, the process temperature, pH, and the salt content of the aqueous phase (Auflem, 2002). In other literature, molecular dynamic simulation software Materials Studio was used to determine the effectiveness of the demulsifier. The simulation results show that the demulsifier with ethylene oxide (EO) and propylene oxide (PO) values of 21 (EO) and 44 (PO) achieved the highest water removal amount of 7.21 ml with an overall error less than 1.83 in which the predicted results are consistent with the experimental screening results (Gent *et al.*, 2022).

This paper will discuss the establishment of a demulsifier selection guideline based on the demulsifier characteristics of Relative Solubility Number (RSN) with the crude oil characteristics including asphaltene content, wax content, and solid content. These three elements are the emulsion stabilizing agents and the impact of them in the emulsion behavior is discussed further in this paper. The previous demulsifier selection guidelines were focusing on the crudes from Northern America (Canada), Europe (UK and France) and Middle East (Egypt) whereas this study are meant for Southeast Asia region which the crudes have higher crude API but some of the fields may contain high wax and solid content as describes in Table 1. Nevertheless, the guideline can be used outside Southeast Asia boundary as well since the synthetic crude of API 27 included in this study resembles the heavy crude behavior which is not from this Southeast Asia region.

Relative solubility number (RSN) is an empirically determined value that characterizes water solubility and the hydrophobic–hydrophilic character of a surfactant. It is commonly used to distinguish demulsifiers from emulsifiers. A demulsifier with an RSN value < 13 is considered insoluble in water or hydrophobic, while 13 <RSN>17 is dispersible at low concentrations, and demulsifiers with an RSN > 17 are soluble in water or hydrophilic (Grenoble and Trabelsi, 2018). RSN has similarities with HLB as such that it measures the combined affinity of the hydrophobic part and lipophilic part of the surfactants to oil or aqueous phase. RSN has been widely used by surfactant manufacturers due to the simplicity of the testing in determining the RSN value (Wu *et al.*, 2003).

Table 1. Physical properties of Southeast Asia crude oil.

No	Properties	Value
1	Asphaltene	0.1–2 %
2	Wax content	1–10 %
3	Crude API	30–46 %
4	Solid content	0–0.2%

Two demulsifier groups were studied, namely resin alkoxylate and a modified polyol type of demulsifiers. The resin alkoxylate demulsifier is a versatile demulsifier for covering all emulsion treatment aspects and is usually used as the major portion in demulsifier formulations. It is a fast water dropper, which separates the emulsion quickly, while modified polyol is a good demulsifier for treating emulsions from heavy oil or low API crude oil. In term of resin alkoxylate demulsifier application, Mohammed *et al.* (1994) has evaluated that the ethylene oxide: propylene oxide mixes and resin: alkoxylate ratio are more important for assessing demulsifier performance than the type of resin used. From this paper as well, nonylphenol resin alkoxylates showed the best performing products in treating emulsion for heavy oil application. Normal demulsifier screening may took 2 or 3 months to obtain the formulation. After the guideline has been developed, team took only around 2 weeks in average to obtain the suitable demulsifier formulation in resolving the emulsion.

2. MATERIALS AND METHODS

2.1 Materials

As the basis for developing the demulsifier selection guideline for non EOR emulsion, four types of synthetic crude oil were used in the demulsifier bottle test with crude oil API ranges from 26˚ to 40˚. Lower API indicates a heavier crude oil. Non EOR emulsion means that the emulsion stabilization is not caused by the EOR chemical surfactant. The synthetic crude oil recipe was developed based on the crude True Boiling

Table 2. Physical properties of synthetic crude oil.

Properties	Crude Oil API 27	Crude Oil API 34	Crude Oil API 37	Crude Oil API 40
Wax (wt%)	2.18	6	11.55	2.85
Asphaltene (wt%)	1.6	0.18	0.72	0.36
Saturate (wt%)	29.8	30.1	52.1	37.4
Aromatic (wt%)	4.5	29.1	20.7	28.0
Solid (wt%)	0.1	0.1	0.1	0.1

Point (TBP) from the crude assay. Light components would involve TBP from C5-150 °C, the intermediate components include TBP of 150-370°C distillate and the heavy components TBP ranging from 370-540°C. Under light components of C5-150°C TBP, the components that need to be included were naphthene and aromatics solvent. For intermediate component, naphthalene needs to be introduced while under heavy components, asphaltene and wax were added into the synthetic crude oil. All these components need to be incorporated to a certain ratio to produce the four (4) types of synthetic crude. The physical properties of the synthetic crude oil are described in Table 2 below. The synthetic crude oil was used to vary the amount of wax, resin, and solid particles in the crude oil in producing various kind of emulsion behaviors.

In the bottle test, 16 different base demulsifiers supplied by CRODA with RSN ranges from 11 to 21 were used, comprising resin alkoxylate and modified polyol groups. The chemical structures are illustrated in Fig. 1 and Fig. 2. For the resin alkoxylate demulsifier, the resins have some aromatic hydroxyl groups that react with ethylene oxide/propylene oxide. For the modified polyol demulsifier, the alkoxylated polyol compound is modified by a quaternary amine capping unit to give the desired characteristics of demulsifier (Scheibel and Menkhaus, 2005).

For the emulsion-stabilizing agent, asphaltenes were introduced into the synthetic oil by adding vacuum residue in the range of 3 wt% to 26 wt% that had been collected from the distillation process at the PETRONAS Malaysian Refining Company Sdn Bhd (MRCSB). The vacuum residue contained 28% saturate, 37% aromatic, 29% resin and 6% asphaltene. For the effect of solid particles, this study used Aerosil R974, a moderately hydrophobic solid nanoparticle, provided by Evonik Inc. For evaluating the effect of wax on the emulsion stability, 2 wt% to 12 wt% of paraffin wax, namely ACROS organic type, which has a melting point of 42 °C and boiling point of 370 °C, was incorporated into the synthetic oil.

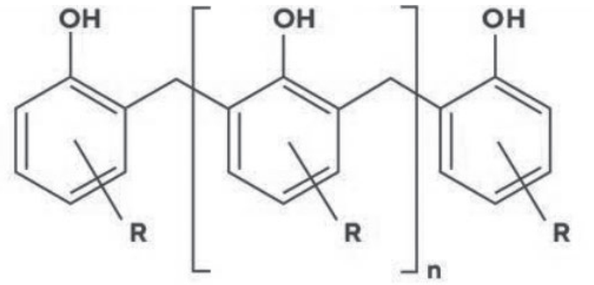


Figure 1. Chemical structure of resin alkoxylate demulsifier.

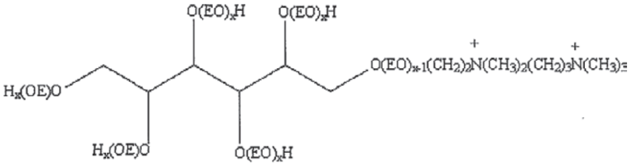


Figure 2. Chemical structure of modified polyol demulsifier.

2.2 Emulsion Tendency Test for non-EOR emulsion

Before performing the demulsification test, an emulsion tendency test was conducted for the blank sample without any demulsifier injected to evaluate the stability of the emulsion produced. The formation of the emulsion and observation of the emulsion stability of each synthetic crude oil was performed in the laboratory following the inhouse standardized protocol as below:

1. Place 50 ml of synthetic crude oil and 50 ml of 2% NaCl water and warm to 60 °C in a 100 ml centrifuge tube.
2. Manually shake 100 times to create a homogeneous emulsion.
3. Place the tube in a water bath maintained at 60 °C, except when taking photographic images.
4. Observe, photograph, and record the volume of emulsion left at 5, 10, 15, 20 and 30 minutes.
5. Record the appearance of the emulsion.

2.3 Demulsification Test

For the demulsification bottle test to evaluate non-EOR emulsion, 2% NaCl was used as the synthetic water. This represents the average salinity of the produced water in Malaysian offshore fields. The bottle test is conducted by mixing the crude oil and brine in a 50:50 ratio, because the emulsion behavior is usually at a maximum at this water to crude oil ratio. Each sample was manually shaken 100 times to produce a homogeneous emulsion. A total of 100 ppm of each base demulsifier was dosed into the emulsion mixture. This is the baseline concentration that is normally applied during the demulsifier screening process. After dosing the demulsifier, the samples were shaken by hand for another 20 times before placing the tubes back in the water bath. Monitoring of the emulsion separation was recorded at 30 minutes. The demulsifier bottle tests were performed at two different operating temperatures of 60 °C and 35 °C. These temperature points were selected in accordance with the operating temperature of the demulsifier injection in the Malaysia offshore fields. Table 3 presents the test matrix of the bottle tests that were conducted to study the relationship between the demulsifier performance and crude oil properties for a non-EOR emulsion.

For the EOR induced emulsion demulsification guideline development, crude oils from three EOR fields were used, namely from Field A, Field D and Field B. The test matrix of the EOR demulsification test is illustrated in Table 3. For Field A, a chemical EOR (CEOR) application was implemented using a proprietary formulation of surfactant S which is an amphoteric type of surfactant. For Field D and Field B, an enhanced water alternate gas (EWAG) application using surfactant E was implemented, which is a foam surfactant comprising a mixture of anionic and amphoteric surfactants.

Table 3. Test matrix of non-EOR demulsification test.

Parameter	Testing Condition
Crude Oil API (°)	27, 34, 37 and 40
Temperature (°C)	35 and 60
Asphaltene content (wt %)	0.09–1.8
Wax content (wt%)	2.85–11.55
Solid effect (wt%)	0.1 and 0.2

Table 4. Test matrix of EOR demulsification test.

Parameters	Field A	Field D	Field B
EOR Method	CEOR	EWAG	EWAG
EOR Surfactant	Amphoteric type	Mixture of Anionic and Amphoteric type	Mixture of Anionic and Amphoteric type
EOR Surfactant Concentration (ppm)	250 750	900 2700	900 2700
Process Temperature (°C)	65	55	40
Watercut (%)	60 and 80	80	60 and 80
Demulsifier Concentration (ppm)	20–100	1000–3000	1000–3000

During the demulsification bottle testing, an amount of EOR surfactant as shown in Table 4 was mixed with the synthetic produced water following the water composition from each field. The low concentration (LC) of the surfactant refers to the probable case of the emulsion which will be produced at the surface facilities, allowing for some surfactant adsorption into the rock in the reservoir. The high concentration (HC) of surfactant considers the worst-case scenario of the produced emulsion. The water with surfactant was then mixed with the actual crude oil following the water cut for each field and a test was conducted as per the field process temperature. To produce the emulsion, the mixtures were manually shaken 100 times, and the demulsifiers were dosed at the concentration described in Table 3. After 30 minutes of heating in a water bath, the emulsion separation for each sample was monitored.

2.4. Blind Test for Demulsifier Validation

Once all the demulsification data sets were completed, the demulsifier selection guideline was established. In validating the guideline, a blind test was conducted in testing the demulsifier performance with the actual crude oil. For the blind test, 15 crude oil samples from 5 fields were tested with base demulsifiers in which their RSN were matched with their crude oil property data. The demulsifiers were tested using the bottle test method to evaluate whether they could resolve the emulsion from these actual crude oil samples.

3. RESULT AND DISCUSSION

3.1 Emulsion Tendency Test (Non-EOR Emulsion)

When crude oil and water are mixed, there is an intrinsic risk that they will stabilize and create an emulsion. The purpose of this emulsion tendency test is to create a stable and robust emulsion in the middle phase of the prepared synthetic crude oil for each individual API. Fig. 3 shows the emulsion produced from each of the synthetic crude oils when mixed with 2% NaCl at 50:50 crude oil: water volume ratio after 30 minutes at 60 °C; and Fig. 4 illustrates the emulsion separation times within the 30-minute time, with respect to different crude oil APIs. As can be observed from the graph, for the low crude oil API of API 27 and API 34,

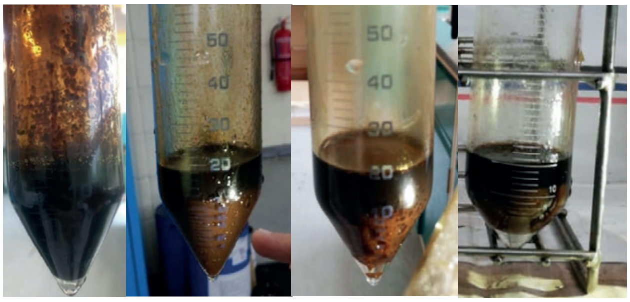


Figure 3. Test matrix of non-EOR demulsification test.

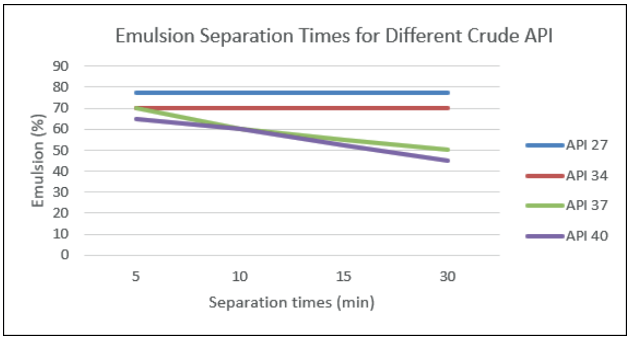


Figure 4. Emulsion separation time of crude oil API 27, API 34, API 37, and API.

the emulsion was stable, which means no separation at all after 30 minutes. The most stable emulsion was from the crude oil of API 27, and the least emulsion produced from the crude oil of API 40. This is due to the increasing amount of vacuum residue in the heavy crude oil of API 27. It contained the highest asphaltene and saturate content, which are the stabilizing agents for the emulsion. The content of the vacuum residue in each of the crude oil were 26.2% for crude oil of API 27, 5.5% for crude oil of API 34, 4.4% for crude oil of API 37 and 3% for crude oil of API 40.

3.2 Demulsification Test (Non-EOR Emulsion)

After completing the emulsion tendency test, the next step was to conduct the demulsification test by dosing a certain concentration of demulsifier into the emulsion. In this case, 100 ppm demulsifier concentration was used to resolve the produced emulsion. The effect of different crude API, wax content, asphaltene content and solid content to the emulsion and demulsification behavior are discussed further in each subsection.

3.2.1 Effect of Crude API and Wax Content

From the demulsification test result, the most effective demulsifier in terms of their RSN for variation of crude oil API and wax content at 60 °C, are tabulated in Fig. 5. The demulsifiers are defined as working when they can completely resolve the emulsion or there is 1% or less remaining in the solution. The demulsification result from the two demulsifier chemistry groups shows that on average, the demulsifier with the high RSN, which is from 19 to 21, works best in resolving the emulsion compared to the low RSN demulsifiers. Increase in HLB/ RSN value increases the solubility of the demulsifier in the aqueous phase which is water. When the demulsifier is initially introduced to the water in oil emulsion, it will be thermodynamically stable at the interface of water droplets. Accordingly, the surfactants possessing high RSN migrate faster to the interface than those having low RSN. As a result of such enhanced migration toward the interface, the surfactant forms a continuous hydrophilic pathway between the dispersed water droplets. This leads to a rapture of the interfacial film surrounding the water droplets (Atta *et al.*, 2009).

The high RSN demulsifier is a water soluble demulsifier which worked well in resolving the water-in-oil emulsion of this emulsified synthetic crude oil. Compared to this high RSN demulsifier, the demulsifier with RSN 19 was the most effective demulsifier in resolving the emulsion for all the crude oil APIs except for crude oil API 37. The crude oil of API 37 had the highest wax content, 11.55%, and that required a higher RSN, of RSN 21, for it to work effectively.

The demulsification data, based on each demulsifier chemistry group at 60 °C for all the crude oil APIs are illustrated in Fig. 6. As determined by the demulsifier

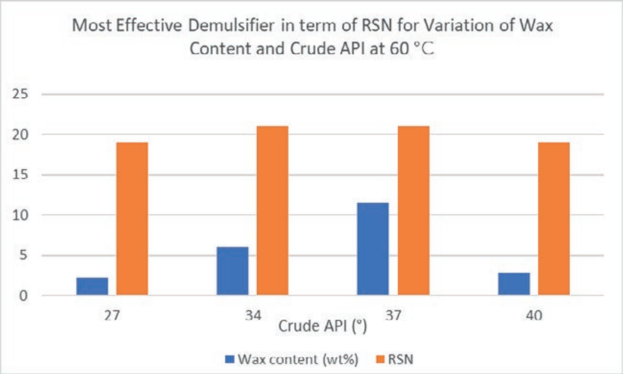


Figure 5. Most effective demulsifier based on the RSN for variation in crude oil API and wax content at 60 °C.

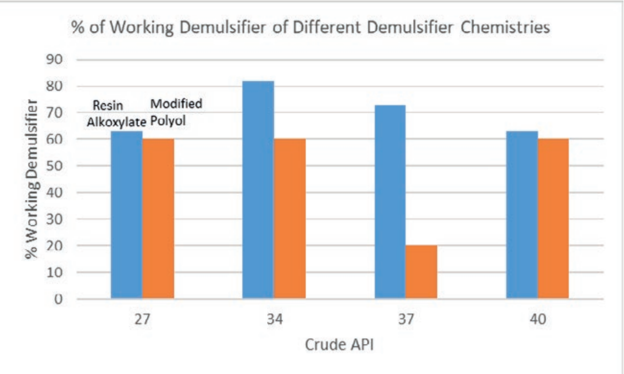


Figure 6. Percentage (%) of working demulsifier at 60 °C based on different demulsifier chemistries.

chemistry trend, the resin alkoxylate type was better in dehydrating the crude oil compared to the modified polyol type especially for crude oil API 37 where the crude oil was a bit waxy and the wax content was high, up to 11.55%. The percentage of the working demulsifier was higher for the resin alkoxylate which was about a 53% difference compared to the modified polyol type.

3.2.2 Effect of Temperature

Temperature plays an important role in the destabilization of emulsions. Demulsification evaluation also was conducted at lower temperature of 35 °C to determine the demulsifier performance at lower process temperature, as per Fig. 7. The test could not be conducted for crude oil at API 27 since this crude oil contains a high vacuum residue of 26.2% and comprises high asphaltene and saturates until it solidifies at this low temperature. Referring to the results in Fig. 7., the demulsifier performance was decreased at 35 °C, especially for crude oil at API 37, which had a high wax content.

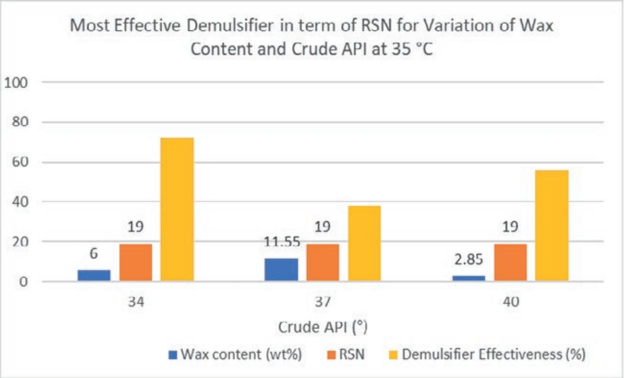


Figure 7. Most effective demulsifier based on the RSN for variation in crude oil API and wax content at 35 °C.

At low temperatures, especially below the wax appearance temperature (WAT), waxes precipitate and interact with water droplets, forming a physical network between the droplets (Freitas *et al.*, 2018). The formation of a network structure occurs by crystal aggregations through inter- and intramolecular non-covalent interactions in which wax concentration and crystal size affect the stabilization mechanism (Ghosh and Rousseau, 2011). This network can increase the emulsion stability (Visintin *et al.*, 2008). Low temperature conditions hinder the collision of droplets thus increasing the oil viscosity. This increases the strength of the stabilizing agents at the droplets, thus providing low chances of settling. Despite this, demulsifiers at RSN 19 continue to work with high efficiency even at low temperatures, which implies the robustness of these demulsifiers.

3.2.3 Effect of Asphaltene

As mentioned in the introduction, asphaltene content and solid content stabilized the emulsion (Zaki *et al.*, 2000). These two parameters have been studied in detail regarding their demulsification, by varying both components in the synthetic crude oil. SARA analysis of the Vacuum Residue shows the asphaltene content was 6%. This equated to the asphaltene content in the original synthetic crude oil being 1.6% (26.2/100*6%) in heavy crude oil of API 27, and 0.18% (3/100*6%) in the light crude oil, API 40.

Fig. 8 describes the demulsifier performance of each individual RSN upon varying the asphaltene content in the synthetic crude oil of the lowest and highest crude oil API. From the figure, the demulsifier performance reduced when the asphaltene content increased for both low and high crude oil API. (Zaki *et al.*, 2000) illustrat-

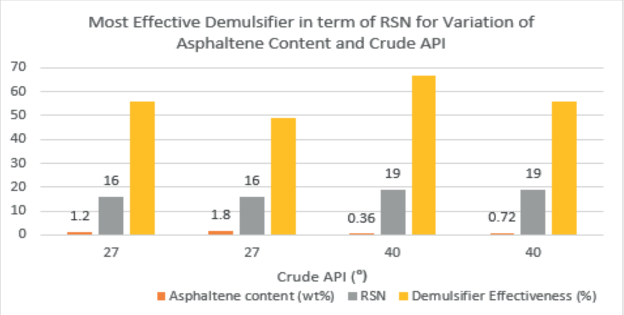


Figure 8. Most effective demulsifier based on the RSN for variation in crude oil API and asphaltene content.

ed that the higher the concentration of asphaltene, the higher the emulsion stability, which caused the demulsifier performance to reduce. Due to the large molecular weight of asphaltene, it forms a steric barrier to coalescence between two approaching water droplets which is considered the important factor in emulsion stabilization.

For a heavy crude oil of API 27, demulsifiers with RSN 16 work best for all asphaltene content between 1.2% and 1.8%, while for a light crude oil of API 40, demulsifiers with RSN 19 work best for all asphaltene content between 0.36% and 0.72%. Surfactant species that are available in the crude oil, such as asphaltenes and resins results in a HLD > 0. HLD is a dimensionless hydrophilic–lipophilic deviation from a reference state. The usual technique to dehydrate the crude oil is to break the W/O emulsion by adding a hydrophilic demulsifier surfactant that migrates at the drop interface and combines with the natural surfactants to attain an exact HLD = 0 mixture formulation (Salager and Forgiarinni, 2012). Grenoble and Trabelsi, (2018) also supported this theory and mentioned that asphaltenes, which have a more lipophilic character, require a more hydrophilic demulsifier (oil soluble or less water soluble demulsifier) to shift the hydrophilic lipophilic deviation (HLD) towards zero. The optimum condition for demulsification is when the HLD is 0. Both references support the result that a lower RSN (less water soluble) demulsifier works better than a demulsifier with high RSN in resolving the emulsion for a crude oil with high asphaltene content. To promote good destabilization at the interfacial phase, the demulsifier must competitively adsorb at the interface, remove, and break up the asphaltenic aggregates and reduce the interfacial tension between the hydrocarbon aqueous phases and hence facilitate the droplet coalescence kinetics (Salager and Forgiarinni, 2012).

3.2.4 Effect of Solid Content

Evaluation was continued to observe the demulsification effect when solid content was varied in the mixture of synthetic crude oil and water. To study the solid content effect to the emulsion stabilization, 0.1 and 0.2 wt% of Aerosil R974, a silica particle was mixed into the mixture of crude and water using a mechanical shaker. Aerosil R974, is a moderate hydrophobic type which tend to stabilize water-in-oil emulsions (Perino *et al.*, 2013). This type of silica particle, with a contact angle of 143.7° helps water droplets disperse in oil phases, resulting in stabilization of water-in-oil emulsions (Wu *et al.*, 2020).

Table 5 illustrates the percentage of working demulsifier at different solid amounts for both crude oil APIs. For crude oil API 27, because it had the highest amount of asphaltene at 1.6%, the combination of this asphaltene and solid caused the emulsion to become very stable, thus the percentage of working demulsifier was very low at about 16% compared to the high API crude oil that is easier to treat, and in which 63% of demulsifiers were still working to resolve the emulsion. Small particles strongly enhance water-crude oil emulsion stability when interactions with asphaltenes promote particle adsorption at the oil–water interface (Sullivan and Kilpatrick, 2002). The higher emulsion stability observed in the presence of hydrophobic particles results from the addition of severel effects: the tendency to form a structure in the oil dispersed phase and the influence of the attached particles at the interface (Perino *et al.*, 2013). Due to this tighter emulsion, the demulsifier to resolve the emulsion is limited, especially for low API crude oil of API 27.

Table 5. Percentage of working demulsifier for both solid contents and different crude oil APIs.

Crude Oil API (°)	Solid content (wt%)	Working Demulsifier (%)
27	0.1	31
27	0.2	16
40	0.1	63
40	0.2	38

Fig. 9 presents the results of the best demulsifier RSN when solid effect is the main factor in stabilizing the emulsion for the lowest and highest API crude oils. The results indicate that the demulsifier with RSN 19 worked best for all solid content except for the light crude oil of API 40%, which need a higher water soluble demulsifier, which is a demulsifier of RSN 21, to resolve the emulsion at the higher solid content of 0.2 wt%.

With respect to the different demulsifier chemistries, the chart in Fig. 10 illustrates the comparison between the modified polyol and resin alkoxylate demulsifiers

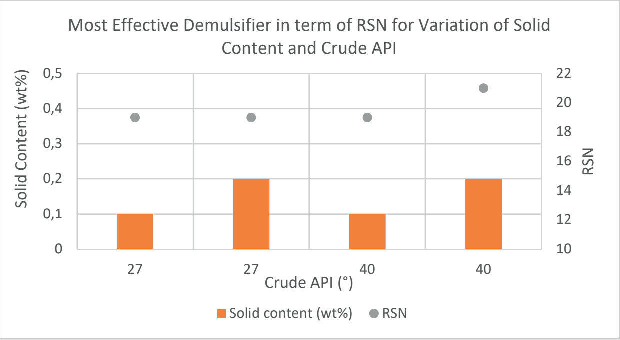


Figure 9. Most effective demulsifier based on the RSN for variation in crude oil API and solid content.

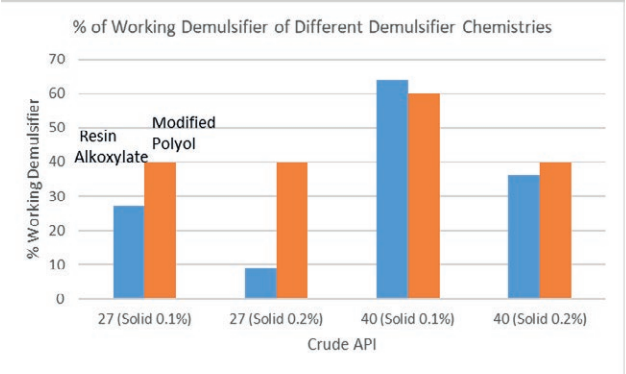


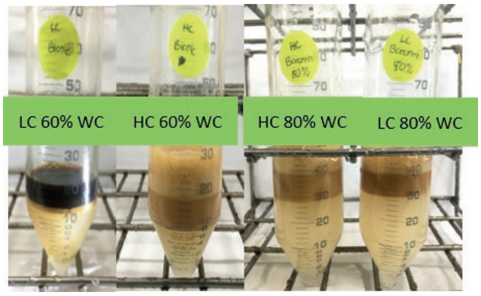
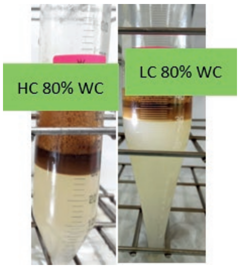
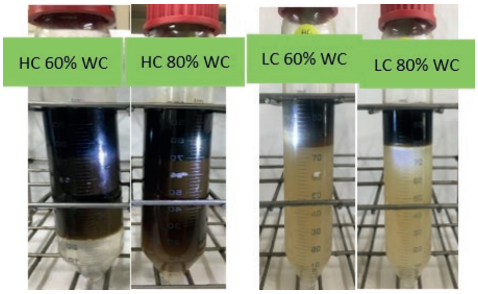
Figure 10. Percentage of working demulsifier of different demulsifier chemistries with the variation in solid content.

with the presence of solids in the synthetic crude oil emulsion. For heavy crude oil, modified polyol demulsifiers are good for resolving the emulsion with the presence of solids but for light crude oil, the performance of both demulsifier chemistries is comparable. In addition, polyol demulsifiers are claimed to work effectively in resolving bituminous emulsions in Canada. This bituminous hydrocarbon is known to be very viscous or even non flowable under reservoir conditions, thus it produces highly stable emulsions which are made even more stable by the usual presence of clays (LaBerge and McCoy, 1982).

3.3 *Emulsion Tendency Test (EOR Emulsion)*

The effect of amphoteric EOR surfactant concentration on the emulsion separation was studied with the concentrations of 250 ppm and 750 ppm for Field A CEOR application. For Field B EWAG and Field D EWAG application, the EWAG surfactant concentrations were 1000 ppm and 2700 ppm. For EWAG surfactant, it comprises of a mixture of amphoteric and anionic type of surfactant. Table 6 presents the EOR induced emulsion due to EWAG surfactant foam and CEOR surfactant chemical. HC is defined as High Surfactant Concentration and LC is Low Surfactant Concentration.

Table 6. Emulsion behavior of EOR induced emulsion.

No	Field	Emulsion Behavior
1	Field B EWAG	 Field B EWAG emulsion at 60% and 80% water cut for low and high surfactant concentrations
2	Field D EWAG	 Field D EWAG emulsion at 80% water cut for low and high surfactant concentrations.
3	Field A CEOR	 Field A CEOR emulsion at 60% and 80% water cut for low and high surfactant concentrations.

The results showed a general increase in emulsion volume at the high surfactant concentration. For the Field B EWAG case, for the high surfactant concentration, the emulsion was worst at 60% water cut in which the emulsion is about 40% compared to the 80% water cut in which the emulsion is about 25%; however, the foam produced was higher for the 80% water cut. Chen *et al.* showed that foam stability decreased when oil saturation increased (Chen *et al.*, 2020). However, for emulsions, the emulsion stability increases as the oil saturation rises. In another study, it was observed that as the water cut increased, the tendency of emulsion formation was reduced for foam assisted CO_2 WAG applications (Borhan *et al.*, 2014). These results support the findings of the Field B EWAG emulsion tendency test for the high EWAG surfactant concentration case. For the Field D EWAG case, the test was only conducted at the 80% water cut as that was the current water cut of that field. The emulsion was quite comparable between the low and high surfactant concentration except that it produced a higher foam height compared to the low surfactant concentration.

For the emulsion induced by the CEOR application of injecting amphoteric surfactant in Field A, it seems that the emulsion was worse for the 60% water cut compared to 80% water cut. At this water cut, the emulsion behavior can be either the oil-in-water or water-in-oil type (Borhan *et al.*, 2014). However, due to the nature of this CEOR amphoteric surfactant, which is a less water-soluble type of surfactant, it tends to produce a water-in-oil emulsion which is why a higher volume of crude oil is needed to produce a more stable emulsion. Furthermore, from the observation the higher CEOR surfactant concentration produced a more severe emulsion than the lower CEOR surfactant concentration. Nguyen *et al.*, (2012) showed that the EOR surfactant decreased the size of oil droplets, increased the surface charge of oil droplets and increased the film elasticity, thus making the oil–water separation more difficult, which was depicted in a CEOR emulsion tendency test.

3.4 Demulsification Test (EOR Emulsion)

A demulsification system was then formulated to address the emulsion formed by this EOR application. A demulsifier in the range 20 ppm to 100 ppm was used for treating the Field A CEOR application, and a 1000 ppm to 3000 ppm demulsifier concentration was used to treat the EWAG emulsion. This demulsifier can be further optimized as this screening is only referring to a single base demulsifier without combining with other demulsifiers or solvents, thus becoming a formulation. Table 7 describes the recommended demulsifier RSN for each EOR demulsification case with respect to the different fields, water cuts and surfactant type and concentration breakthrough.

The EOR demulsification is mostly impacted by the EOR surfactant properties and its concentration thus the EOR demulsification guideline was developed based on the EOR surfactant being the causative factor in EOR emulsion stability. For the Field D EWAG application, the effective demulsifiers had an RSN of 11 to 16, which was a lower RSN than the high RSN demulsifiers used for resolving non-EOR emulsions. The EWAG Surfactant E was highly water soluble which means it is highly hydrophilic thus it tends to produce an oil-in-water emulsion. This emulsion needs an oil soluble or less water-soluble demulsifier with a low RSN to resolve the emulsion. For the Field B EWAG application, the workable demulsifier RSN range was larger, being from 11 to 17 (low to medium RSN range) even though they were using a similar EWAG surfactant. Field B crude oil which is lighter than the Field D waxy crude oil may make the workable demulsifier RSN range bigger compared to Field D. At 80% water cut, the emulsion was more severe and the workable RSNs were between 16 and 17 only.

For Field A CEOR application, generally the effective demulsifiers had the RSN from 17 to 21. Properties of the CEOR Surfactant S which is less water-soluble (less hydrophilic) than foam surfactant, tends to produce the water-in-oil emulsion. This emulsion needs a highly water-soluble demulsifier that has a high RSN to resolve the emulsion. In one study, decreasing the extent of the interfacial tension acted on by the water solubility demulsifiers was bigger than the oil solubility demulsifiers for the surfactant polymer flooding application. With the increase in the demulsifier concentration for these demulsifiers, the interfacial tension decreased, and the dewatering rate increased (Yimei, 2014). (Zhang *et al.*, 2006) revealed that a non-ionic water-soluble mixed demulsifier was used successfully to treat the produced liquid from ASP flooding. The demulsifier increased the zeta potential and Interfacial Tension (IFT) and reduced the water content from 30.5 to 7.6%, at a 50 mg/kg dose. This demulsifier also managed to reduce the oil concentration in the water phase from 1623 mg/l to 530 mg/l which was about a 67% reduction.

Fig. 11 illustrates the comparison of the demulsifier performances between the resin alkoxylate and the modified polyol for EOR demulsification. The performance was comparable between the two demulsifier groups for

Table 7. EOR demulsification result.

Field	Process Temperature (°C)	Water Cut (%)	Surfactant Type	Surfactant Breakthrough (wt%)	Workable RSN
Field A	65	60	CEOR Surfactant	0.075	19 and 20
				0.025	17 to 21
		80		0.075	19 to 21
				0.025	17 and 20
Field B	40	60	EWAG Foam Surfactant	0.27	11 to 16
				0.09	11 to 17
		80		0.27	16 to 17
				0.09	16 to 17
Field D	55	80		0.27	11 to 16
				0.09	11 to 16

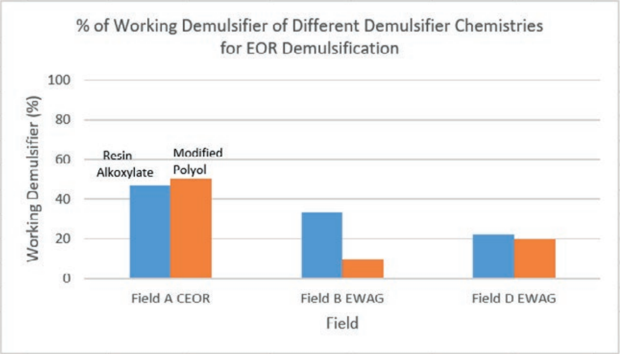


Figure 11. Percentage (%) of working demulsifier based on different demulsifier chemistries for EOR demulsification.

all three EOR applications except for the Field B EWAG demulsification where the resin alkoxylate demulsifier worked better than the modified polyol. The results also showed that not many demulsifiers effectively resolved the EWAG emulsion compared to the CEOR emulsion, as the effect of foam really increased the emulsion severity.

3.5. *Demulsifier Selection from Demulsification Guideline*

Based on the demulsification database that was developed earlier, the demulsifier selection guideline is summarized as below:

1. For a non-EOR emulsion, generally the best demulsifier ranges that work for all API crude oil are high, which is between 19 to 21.
2. The demulsifier with RSN 19 works for wax content 6% and below.
3. For a higher wax content, the demulsifier RSN needs to be higher, which is 21, for the demulsifier to work.
4. The demulsifier with RSN 19 works best at low process temperature of 35 °C.
5. For heavy crude oil, demulsifiers with RSN 16 work best for all asphaltene content between 1.2% to 1.8%; while for light crude oil, demulsifiers with RSN 19 work best for all asphaltene content between 0.36% to 0.72%.
6. On the solid effect, for heavy crude oil, demulsifiers of RSN 19 performed the best in resolving the emulsion at all solid content. For light crude oil, demulsifiers worked at RSN 19 for solid content of lesser than 0.2%. For higher solid content of more than 0.2%, they need a higher water soluble demulsifier which is demulsifiers of RSN 21 to resolve the emulsion.
7. For Field B EWAG application, demulsifier with RSN 16 and 17 work best and for Field D EWAG application, demulsifier with RSN 11 and 16 work best in resolving the EWAG emulsion.
8. For Field A CEOR application, the effective demulsifiers have an RSN from 17 to 21.

Table 8. Demulsifier blind test result.

No	Crude Oil	Crude Oil Properties				Demulsifier Properties	No. of Working Demulsifier of Similar RSN	Matching Rate (%)
		API	Wax (%)	Solid (%)	Asph (%)	RSN		
1	D1	34	13	0.29	1.19	21	2 out of 3	66
2	G2	46	6	0.2	1.2	21	1 out of 2	50
3	B3	39	2.7	0.14	0.1	19	2 out of 2	100
4	B4	35	4.3	0.12	0.1	19	2 out of 2	100
5	B5	37	3	0.1	0.04	19	2 out of 2	100
6	D6	31	4.7	0.1	0.53	19	2 out of 2	100
7	B7	44	2	0.01	1.78	19	2 out of 2	100
8	S8	36	4.8	0.09	0.09	19	2 out of 2	100
9	T9	24	6.9	0.08	2.19	19	2 out of 2	100
10	T10	23	1.3	0.06	1.25	19	2 out of 2	100
11	T11	25	3.3	0.09	2	19	2 out of 2	100
12	T12	26	1.3	0.04	3.6	19	2 out of 2	100
13	D13	33	25	0.4	0.1	19	2 out of 2	100
14	B14	41	4	0.2	0.1	19	2 out of 2	100
15	S15	19	2.1	0.17	1.25	16	1 out of 1	100

3.6 *Demulsifier Blind Test*

A blind test was conducted to test the demulsifier recommended by the demulsifier selection guideline with the actual crude oil. The most important parameters when applying the selection guideline are asphaltene content, wax content, solid content and API gravity, in which the crude oil properties are presented in Table 8. For the blind test, 15 crude oil samples from 5 fields were tested with base demulsifiers, in which their RSN was matched with their crude oil property data. The results of the blind test are depicted in Table 7 and some of the bottle test images are illustrated in Fig. 12.

For B3 crude oil, based on the crude oil properties data in Table 7, it was a high-API type of crude oil, which is close to 40°. The wax content was quite low, about 2.7%. Based on this data, since the wax content is lesser than 6%, the demulsifiers chosen should be RSN 19. In terms of the solid's relationship, B3 crude oil had a solid content of 0.14% which was less than 0.2%, and based on this, RSN 19 also worked best. For D1 crude oil, it was a bit waxy, and the solid content was also higher than B3 crude oil. Because the wax content was 13% and the solid content was 0.29%, base demulsifiers from the RSN 21 group were chosen for testing. In addition to this, the blind test results in Table 8 show that almost recommended demulsifiers worked efficiently in resolving the

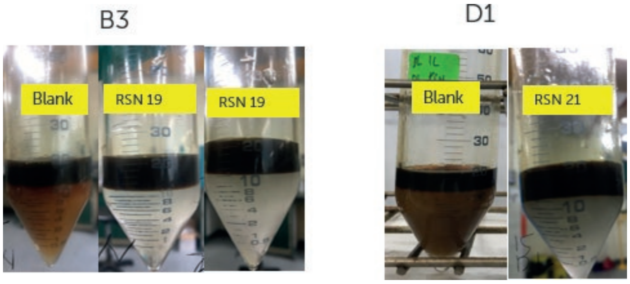


Figure 12. Blind test image of B3 and D1 crudes before and after addition of base demulsifier.

emulsion except for D1 and G2 crude oils. This led to a high matching rate of 86.7% based on the number of working demulsifiers between the guideline output and the experimental lab results.

4. CONCLUSION

This paper establishes a demulsifier selection guideline in resolving W/O emulsions based on the relationship of demulsifier properties with the crude oil characteristics. Based on the bottle test completion for all the test matrices, the demulsifier selection guideline was developed and then validated with the blind test in resolving the emulsion from the actual crude oil. The high matching rate of 86.7% between the selection guideline outputs versus laboratory test proved that good agreement was established between the demulsifier properties and the crude oil characteristics.

Abbreviation

RSN	Relative Solubility Number
EOR	Enhanced Oil Recovery
CEOR	Chemical Enhanced Oil Recovery
EWAG	Enhanced Water Alternate Gas
W/O	Water-in-Oil
O/W	Oil-in-Water
HLB	Hydrophilic–Lipophilic Balance
HLD	Hydrophilic–Lipophilic Deviation
SARA	Saturate Aromatic Resin Asphaltene
ASP	Alkaline Surfactant Polymer
API	American Petroleum Institute
HC	High Surfactant Concentration
LC	Low Surfactant Concentration
IFT	Interfacial Tension
TBP	True Boiling Point

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Research Article

A Role for Bose-Einstein Condensation in Astrophysics

Barry W. Ninham[1], Iver Brevik[2], Oleksandr I. Malyi[3], Mathias Boström[3,]*

[1] *Department of Materials Physics, Research School of Physics, Australian National University, Canberra, Australia*
[2] *Department of Energy and Process Engineering, Norwegian University of Science and Technology, NO-7491 Trondheim, Norway*
[3] *Centre of Excellence ENSEMBLE³ Sp. z o. o., Wolczynska Str. 133, 01-919, Warsaw, Poland*
E-mail addresses: Barry.Ninham@anu.edu.au; iver.h.brevik@gmail.com; oleksandr.malyi@ensemble3.eu; Mathias.Bostrom@ensemble3.eu
*Corresponding author.

Abstract. We revive a 60-year-old idea that might explain a remarkable new observation of a periodic low-frequency radio emission from a source at galactic distances (GLEAM-X J162759.5-523504.3). It derives from the observation that a high-density high-temperature charged boson plasma is a superconducting superfluid with a Meissner effect.

Keywords: Bose-Einstein condensate, Charged Bose gas, astrophysical chemistry.

INTRODUCTION

Sporadic forays over the years have explored the possibility that the physics of Bose-Einstein condensation ought to play some role in Astrophysics, e.g. [1,2]. Many of the particles involved in stellar evolution are bosons, i.e. have zero or integer spin. Bose-Einstein condensation is a fundamental macroscopic manifestation of quantum physics. It would seem remiss of the Creator not to have employed the phenomenon somewhere in building the Universe. Especially is this so since Fermi-Dirac and Classical Statistical Mechanics do figure largely. A suggestion of a role for Bose-Einstein condensation was made 60 years ago when quasars were first observed [1], and forgotten. Later attempts failed because they considered superconductivity and Bose condensation as classical low-temperature phenomena like that which occurs for electrons in metals. But the phenomena are not limited and exist for very high-temperature high-density charged particles [1].

We here revive that 60-year-old idea and suggest it might explain a recent extraordinary observation.

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THE PHENOMENON

Hurley-Walker *et al.* [3] recently reported an unusually slow periodic low-frequency radio emission from a source at galactic distances (GLEAM-X J162759.5-523504.3) with a pulse period of 18.18 minutes. One clue to its origin is that high linear polarization has been shown to be characteristic of a source with strongly ordered magnetic fields [4-6]. The observations are unlike emissions characteristic of stars, white dwarfs, white binaries, or exoplanets. Furthermore, the 0.5-light-second upper limit on the object's size and estimated brightness temperature of 10^{16} K led Hurley-Walker *et al.* [3] to propose that a radiation source is a compact object with a rotational origin.

THE IDEA

With that in mind, we give reasons to consider if Bose-Einstein condensation [1] might have something to do the phenomenon:

(i) Stable nuclei in stellar interiors have zero or integer spin. Nuclei of higher and higher atomic numbers built up during the evolution of stars. They are charged bosons.
(ii) A dense charged high-temperature boson plasma becomes nearly perfect as density increases (i.e., the Coulomb collective interactions become so weak that they can be ignored, and we can work with the perfect gas approximation).
(iii) It can undergo Bose-Einstein condensation to a superfluid state.
(iv) A conducting superfluid is a superconductor. A rotating superconducting superfluid has a Meissner effect. That is, it expels the magnetic field generated by rotation.
(v) Such a magnetic field would be trapped in the lower-density surface region. This process continues as the star collapses and its rotation speeds up.
(vi) Massive synchrotron radiation follows that dissipates this increasing build-up of energy.

The assumptions i-vi were originally made 60 years ago to explain the newly discovered quasars. Schafroth [8], Blatt [9], and Butler [10] had shown earlier that an ideal charged Bose gas below the critical point for superfluidity is a superconductor (see also Refs. [7,8-17]). These theories [7-17] call on electron pairing to generate charged bosons that then lead to Bose condensation and superconductivity *at very low temperatures.* Our situation is quite different. The stellar objects involve real boson nuclei of even spin. The high-density, high-temperature plasmas are close to ideal.

We recall the process of nucleosynthesis in stellar interiors [18-21]. The theory explains how nuclear reactions convert lighter elements into heavier ones through the fusion of atomic nuclei. As the star evolves, the fuel elements involve successive steps, with H, He, C, O, Ne, Si, Fe, and U providing increasingly heavier energy sources that drive the stellar evolution to completion [18]. We need to estimate the critical temperatures and core densities for Bose condensation for stars with different fuel elements to check that they can have a Boson core region.

CALCULATIONS

Consider an assembly of ions of even spin, mass *M and charge Ze*, in a background electron gas. Under extreme high-density and high-temperature conditions, the system is expected to behave like a mixture of ideal gases. That can be achieved by ensuring that the average energy of Coulomb interactions between two ions is small compared to their kinetic energy. At densities approaching the critical value for Bose-Einstein condensation of ions, i.e., when their chemical potential approaches zero, the mean energy, per particle of the ideal Bose gas is approximately equal to *kT*. The average distance between the particles is then [1]

$$\mathrm{r} \approx 2\sqrt[3]{3\mathrm{M}/[4\pi\rho]} \approx \lambda = h/(Mv) = h/\sqrt{2\ \mathrm{M\,kT}}, \tag{1}$$

where λ is the de Broglie wave length of an ion of mass *M* and kinetic energy ~*kT* (taken in Eq (1) equal to $Mv^2/2$). The condition that the actual gas be nearly ideal is [1]

$$\frac{2Z^2e^2}{r} \ll \mathrm{kT}. \tag{2}$$

Hence, taking the requirement Eq. (2) with Eq. (1), the critical expressions for temperatures, density, and particle separation can be estimated to be of the order

$$T_C \sim \frac{8MZ^4e^4}{h^2k} \tag{3}$$

$$\rho_C \sim \frac{384}{\pi}\frac{M^4Z^6e^6}{h^6} \sim \frac{6}{8\pi}\frac{Mk^3}{Z^6e^6}T_C^3, \tag{4}$$

$$\mathrm{r}_C \sim \frac{h^2}{4MZ^2e^2} \sim \frac{2Z^2e^2}{kT_C}. \tag{5}$$

The numerical values are summarized in Table 1. We expect that highly charged nuclei will be “dressed” by an inhomogeneous adsorbed relativistic electron cloud (mesons in another guise): just as for charged micelles or highly charged ions in electrolyte solutions. In that case, “bound” counterions are typically 80-90% of the bare charge. The effective charge is 10-20% of the actual charge. Without recognising such screening, estimated critical parameters for the separation of heavy ions become unphysical and ridiculous. In Table 1, we take two extreme estimates to bound these uncertainties: the unscreened Z and Z=1. To illustrate our point, we present also the critical temperatures with 10% and 20% effective charges in Table 2. For Uranium, from Table 2, the estimated critical temperatures are 10^{14} K<T_c<10^{15} K. These bounds are similar in magnitude to the observed brightness temperature of 10^{16} K discussed by Hurley-Walker *et al.* [3].

Table 1. The critical temperatures and mass densities for different fuel elements in the core of a Boson star are derived from Equations (3)-(5). Since we did not include screening we present two different estimates (a) based on setting Z=1 (columns 2 and 3) and (b) using Z from column 1 (columns 4 and 5). Here $h = 6.626\times10^{-27}$ erg s, $k = 1.381\times10^{-16}$ erg/K, $e = 4.803\times10^{-10}$ esu, and we estimate the mass as $M = A\times1.66\times10^{-24}$ g (Atomic number × proton mass).

Fuel element [A,Z]	T_C (Z=1) [K]	ρ_C (Z=1) [g/cm^3]	T_C (Z) [K]	ρ_C (Z) [g/cm^3]
He [4,2]	4.7×10^8	3.5×10^{10}	8×10^9	2×10^{12}
C [12,6]	1.4×10^9	2.9×10^{12}	2×10^{12}	1×10^{17}
O [16,8]	1.8×10^9	9.0×10^{12}	8×10^{12}	2×10^{18}
Ne [20,10]	2.3×10^9	2.2×10^{13}	2×10^{13}	2×10^{19}
Si [28,14]	3.2×10^9	8.5×10^{13}	1×10^{14}	6×10^{20}
Fe [56,26]	6.6×10^9	1.3×10^{15}	3×10^{15}	4×10^{23}
U [238,92]	2.8×10^{10}	4.4×10^{17}	2×10^{18}	3×10^{29}

Table 2. The critical temperatures for different fuel elements in the core of a Boson star are derived from Equations (3)-(5). Estimates (a) based on setting $Z\to Z\times0.1$ (column 2) and $Z\to Z\times0.2$ (column 3). Constants used are same as in Table 1.

Fuel element [A,Z]	T_C (Z→Z×0.1) [K]	T_C (Z→Z×0.2) [K]
He [4,2]	8×10^5	1×10^7
C [12,6]	2×10^8	3×10^9
O [16,8]	8×10^8	1×10^{10}
Ne [20,10]	2×10^9	4×10^{10}
Si [28,14]	1×10^{10}	2×10^{11}
Fe [56,26]	3×10^{11}	5×10^{12}
U [238,92]	2×10^{14}	3×10^{15}

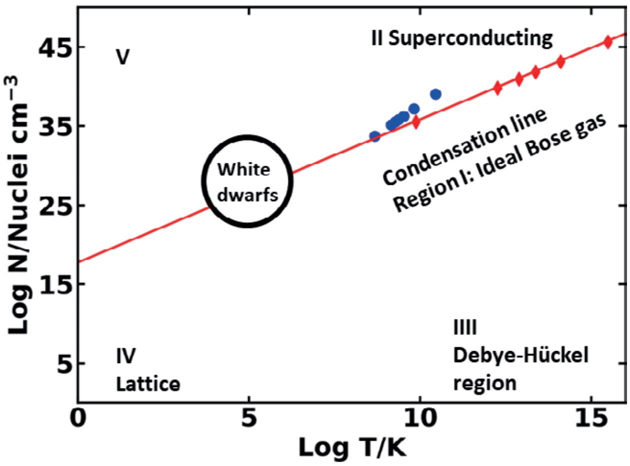

Figure 1. Number density (*N*) of stable nuclei vs. temperature phase diagram for the charged Bose gas. The condensation line shown use Eq. (4) and the data from Table 1. Adapted from Figure 1 in Ref. [1]. The data points from the unscreened model (Z from Table 1) are shown as red symbols while the results corresponding to Z=1 model are shown as blue symbols. We indicate schematically a region relevant for white dwarfs (large black circle) (from Figure 1 in Ref. [1]).

With even the lowest densities *N(He)*, the accompanying electron gas is highly relativistic and degenerate. We intend to go beyond these simple estimates using a screened intervening plasma including both magnetic and dielectric susceptibilities. Notably, the core temperatures for the seven ages of a 20M_o star discussed by Trimble are T = 1.9×10^8 K for a star with Helium as fuel element and T = 3.7×10^9 K for a star with Silicon as fuel element [18]. These numbers are in surprisingly good agreement with our estimates based on using Z=1 in Table 1.

In region I, near the condensation line, $\rho \sim \frac{6}{8\pi}\frac{Mk^3}{Z^6e^6}T^3$, the system is nearly an ideal Bose gas. Above the condensation line in region II (high density, high temperature), a rotating gas should become superconducting, Region III corresponds to the classical Debye-Hückel (high temperature, low density) region, and in region IV conditions are favourable for the formation of a lattice (low temperature, low densities). Region V (low temperature, high density), exhibits an energy gap (c.f. eq. (7)), where the quasi-particle elementary excitation energy has the form [1,12,13]

$$\varepsilon(p) = \sqrt{\left(\frac{p^2}{2m}\right)^2 + \left(\hbar\omega_p\right)^2}, \qquad (7)$$

where ω_p is the classical plasma frequency.

A DIVERSION

With Bose Einstein condensation in stellar systems, further unanticipated complications may occur. As they contract under the influence of gravitational forces, their core densities and temperatures will increase, leading to charged Boson core regions with increasingly heavy fuel elements. Available nuclear mass models show that not all numbers of proton-neutron combinations would be stable. For each state there is a minimum and a maximum number of neutrons and protons that are stable: a phenomenon known as the neutron and proton drip line [22]. The nuclear mass models demonstrated that certain ensembles of protons and neutrons are inherently unstable. That is, the ground-state configurations of such species are energetically unstable to the emission of a constituent nucleon [22]. The matter is still open.

Even the established sign of nucleon-nucleon interactions which can be used for plausible models of Bose condensation with neutron pairing [2] has been questioned. The data dating back to Seaborg's work from which that conclusion was reached has never been questioned. See references in [23,24]. Be that as it may, the possibility that Bose condensation and consequent magnetic events of even quarks and other exotic objects in the cores of neutron stars has seriously been broached [25]. Returning to our main theme, Hurley-Walker *et al.* [3] speculated that their observations might be due to a compact rotating magnetar. However magnetars are made of neutrons, that is fermions. Our considerations apply to bosons. Our propositions might then be appropriate rather to the early stages of the collapse of one of a pair of rotating massive binary stars. This would be consistent with the very low frequency of the pulses.

CONCLUSIONS

Quantum coherent Bose-Einstein condensation is a general property of matter with particles of even spin. Therefore, it might reasonably be expected to play a role in astrophysics one way or another, just as Fermi-Dirac statistics does in the theory of white dwarf and neutron stars. Attempts to invoke Bose condensation and superconductivity are few [1-2]. The present proposal is unlike the original low temperature theories of superconductivity [10-11, 14-17]. It is concerned with a phenomenon that occurs with charge bosons at high temperature and high density [1]. The charged ideal Bose gas is superfluid below its critical point [1,12]**.** And a rotating superfluid has a Meissner effect [8-10] with consequent, expulsion and buildup of large magnetic effects. The observed linearly polarized ultra-long period low-frequency radio emission is known to be related to magnetic fields [5-7]. The Bose-Einstein condensation could be the origin of the magnetic fields and the phenomenon, not previously observed, might be of wider occurrence, as anticipated in [25] A. Mann, "The strange hearts of neutron stars", *Nature* **579**, 20-22 (2020).

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Feature Article

Professors Trost and Sheldon's Promotion of Catalytic Technologies, Atom Economy, and the E-Factor Metrics in Synthetic Organic Chemistry and the Fine Chemical and Pharmaceutical Industries, to Speed the Early Evolution of "Green Chemistry"

Mark A. Murphy, Ph.D., J.D.

UVLAW Patents LLC, 171 China Creek Rd., Blowing Rock North Carolina 28605
E-mail: uvlawpatents@gmail.com

Abstract. The Academic chemical literature (and much current teaching to University Students) still often describes "Green Chemistry," as having originated in the late 1990s from the United States EPA, the "12 Principles of Green Chemistry", and/or Academia. But all of the "12 Principles" had already been in "un-enunciated" Industrial practice and had produced many commercialized examples of environmentally favorable chemical products and processes in major segments of Industry, long before the 1990s. This article briefly reviews the early 1990s publications of Professor Barry Trost and Roger Sheldon that spread awareness of the importance of catalysis to the evolving "Green Chemical" concepts of "Atom Economy", the "E-Factor" metrics, and into Academic "Green Chemistry" research. Trost and Sheldon's publications admitted that catalysis and "Atom Economy" had been in practice in the commodity chemicals industry for decades, but encouraged more use of those techniques and concepts in the Fine Chemical and Pharmaceutical industry segments, and into Academic research and teaching of organic chemistry, years before the words "Green Chemistry" or the "12 Principles" came into literature use.

Keywords: Green Chemistry, green engineering, history, atom economy, E-Factor, environmental quotient, catalysis, interdisciplinary research, evolution, industry.

1. INTRODUCTION

For the past 25 years, two questionable "narratives" about the origins of "Green Chemistry" have widely propagated in the Academic and Governmental literature, and in the trade and popular press, to the effect that 1) "Green Chemistry originated in the 1990s from the efforts of the US Government, US EPA and/or Academia," and 2) "Green Chemistry" should be "guided" by the '12 Principles' published by Anastas and Warner in 1998."[1,2,3] Over the last several years, this author (who conceived the BHC Ibuprofen Process that won one the earliest Presidential Green Chemistry Awards) has argued to the contrary, and previously documented that "Green Chemistry" was in fact a narrow subset of, and evolved from and renamed, the much earlier and much broader interdisciplinary "Pollution Prevention" efforts, mostly from Industry, during the 1970s and 1980s.[4,5,6]

Separately, the Academic literature has long attributed the "Green Chemistry Principle" of "Atom Economy"[7] to Professor Barry Trost of Stanford University. The Academic literature has also often attributed the "Environmental Factor" (typically called the "E-Factor") and/or "Environmental Quotient" metrics of Green Chemistry to a series of 1990s publications authored by Professor Roger Sheldon. Both men emphasized the importance of the use of catalysis as a technical tool to achieve improved environmental performance in the chemical industries.

Both Trost and Sheldon certainly inspired many subsequent applications of catalysis, to achieve many new examples of good Atom Economy and E-Factors in the fine chemical and pharmaceutical industry segments. But in little noticed early statements, both Trost and Sheldon admitted that use of catalysis, which had been in widespread use in the commodity chemicals industry for many prior decades, had produced many examples of already commercialized commodity chemical processes that were already in fact "Atom Economical," and had excellent E-Factors, decades earlier than the 1990s.

This article will focus on and briefly review early 1990s publications by Professors Trost and Sheldon that described the use of catalysis as a tool, to promote the introduction of the "Atom Economy", "E-Factor", and "Environmental Quotient" concepts into the Academic literature, research, and teaching. Trost's and Sheldon's articles also suggested and/or promoted new applications of catalysis to improve environmental performance in the Fine Chemical and Pharmaceutical industry segments, where the environmental performance had historically been much worse than in the commodity chemical industry.

Sheldon often praised one of the earliest examples of use of the Atom Efficiency and E-Factor concepts in the Fine Chemical / Pharmaceuticals industries, the BHC Ibuprofen process, that was conceived and developed in the mid-1980s and commercialized in 1992. This author, who conceived the BHC Ibuprofen Process in 1984, will add historical perspective and commentary, to further demonstrate that the origins of "Green Chemistry" were actually a result of long-term, very broad and complex interdisciplinary and evolutionary processes that had their beginnings in Industrial practice decades earlier than the 1990s.

Academic "Green Chemistry" recently appears to be evolving back toward a much broader interdisciplinary approach, a "paradigm change" this author supports.

2. PROFESSOR BARRY TROST'S "ATOM ECONOMY" – "A SEARCH FOR SYNTHETIC EFFICIENCY"

Professor Barry Trost, currently an Emeritus Professor of Chemistry at Stanford University[8], has been very frequently cited in the Academic literature as originating and/or promoting the concept of "Atom Economy", which is now considered the second of the "12 Principles of Green Chemistry" (after "Pollution Prevention"). Trost published many papers in the 1970s and 1980s illustrating the uses of transition metal complexes for coupling organic molecules, but the first Trost paper explicitly describing the "Atom Economy" concept was published in *SCIENCE* in 1991[9], and was titled "The Atom Economy – A Search for Synthetic Efficiency." The abstract of Trost's paper read as follows:

> Efficient synthetic methods required to assemble complex molecular arrays include reactions that are both selective (chemo-, regio-, diastereo-, and enantio-) and **economical in atom count (maximum number of atoms of reactants appearing in the products**). Methods that involve simply combining two or more building blocks with any other reactant needed only catalytically constitute the highest degree of atom economy. Transition metal-catalyzed

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[1] See Anastas, PT., and Warner, J. C., (1998)

[2] See Cann, M.C. and Connelly, M.E. (2000)

[3] See Anastas, P.T. and Beach, E.S., (2009)

[4] Murphy, M.A., (2020a)

[5] Murphy, M.A., (2021)

[6] Murphy, M.A.,(2018)

[7] The graphical abstract for this article, graphically illustrating "Atom Economy", was copied in June 2023 from a Wikipedia article on "Atom Economy available at https://en.wikipedia.org/wiki/Atom_economy , attributed there to a Wikipedia author Astrid 91, and used herein under a Creative Commons CC0 License.

[8] Professor Trost obtained a PhD in Chemistry at MIT in 1965 and moved directly to the University of Wisconsin-Madison, where he became a Villas Professor of Chemistry and remained until his move in 1987 to become a Tamaki Professor of Chemistry at Stanford University. This author (as a graduate student) took a single semester's course in synthetic organic chemistry from Professor Trost at Madison in 1978, and attended many Organic Chemistry seminars where Professor Trost spoke or was present, an experience he will always remember and value.

[9] See Trost, B.M., (1991)

> methods that are both selective and economical for formation of cyclic structures, of great interest for biological purposes, represent an important starting point for this long-term goal. **The limited availability of raw materials, combined with environmental concerns, require the highlighting of these goals**. (Bolding added)

In his second paragraph, Trost stated that:

> In the quest for selectivity, a second feature of efficiency is frequently overlooked – how much of the reactants end up in the product, a feature we might refer to as atom economy … An alternative process that is both selective and atom economical remains a challenge. The ideal reaction would incorporate all of the atoms of the reactants. Major benefits that derive from such processes include more effective use of limited raw materials and decreased emissions and waste disposal… The ability of transition metal complexes to activate organic molecules makes them attractive prospects for developing catalytic processes with high atom economy. **This concept is already embodied in important industrial processes such as Ziegler-Natta polymerization (5) and hydroformylation (6).** However, little or no attention has been focused on developing such methods for the synthesis of complex molecular architecture or for intramolecular processes. (Bolding added).

Then, with little additional commentary on the "theory" of Atom Economy, Trost's 1991 paper described many examples wherein "All of the reactions involve simple summation of the reacting partners to form products, and any additional reagents are used only in catalytic quantities to serve as true catalysts."

In a 1995 follow-up paper in *Angewante Chemie*[10] (entitled "Atom Economy – A Challenge for Organic Synthesis: Homogeneous Catalysis Leads the Way"), Trost stated in his Graphical Abstract that "If all atoms of the starting materials are found in the product and only catalytic amounts of other reagents are needed, a reaction may be defined as ideal. A promising route to this ideal state is approached by the use of transition metal complexes as catalysts for addition and isomerization reactions."

In the body of his full 1995 paper, Trost first re-iterated some of the concepts from the 1991 paper, but also stated that:

> …The ideal chemical reaction is also just a simple addition (either inter-or intramolecular) in which any other reactant is required only in catalytic amounts.
> **The producers of commodity chemicals have recognized the importance of these issues**…. 'Newer' processes represented by hydroformylation,[2] Ziegler-Natta Polymerization,[3] and hydrocyanation[4] are spectacular illustrations of how practical and important processes that possess these characteristics are**. On the other hand, such issues have not been emphasized for production of smaller volume chemicals**. Clearly, a high priority goal of any chemical production is an environmentally benign design.
> **With the increasing sophistication of the types of substances that we must produce to meet society's needs, this task in quite daunting**. (Bolding added)

In the rest of the 1995 paper, Trost went on to describe many examples from his laboratories of the use of transition metal catalyzed cross-coupling reactions in the synthesis of complex organic molecules.

In 1998, Professor Trost was awarded one of the EPA / ACS's earliest "Presidential Green Chemistry Challenge" awards[11], for "The Development of the Concept of Atom Economy". The first paragraph of the Award description states:

> Professor Trost developed the concept of atom economy: chemical reactions that do not waste atoms. Professor Trost's concept of atom economy includes reducing the use of nonrenewable resources, minimizing the amount of waste, and reducing the number of steps used to synthesize chemicals. **Atom economy is one of the fundamental cornerstones of green chemistry. This concept is widely used by those who are working to improve the efficiency of chemical reactions**. (Bolding added)

In the second paragraph, the 1997 Presidential Green Chemistry Award document stated:

> **Economics generally dictates the feasibility of processes that are "practical". A criterion that traditionally has not been explicitly recognized relates to the total quantity of raw materials required for the process compared to the quantity of product produced or, simply put, "how much of what you put into your pot ends up in your product."** In considering the question of what constitutes synthetic efficiency, Professor Barry M. Trost has explicitly enunciated a new set of criteria by which chemical processes should be evaluated. (Bolding added).

In the 4th paragraph, in discussing the general acceptance of the need for selectivity in chemical processes, the Green Chemistry Award commented:

> How much of the reactants end up in the product (i.e., atom economy) traditionally has been ignored. When Professor Trost's first paper on atom economy appeared in

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[10] See Trost, B.M., (1995)

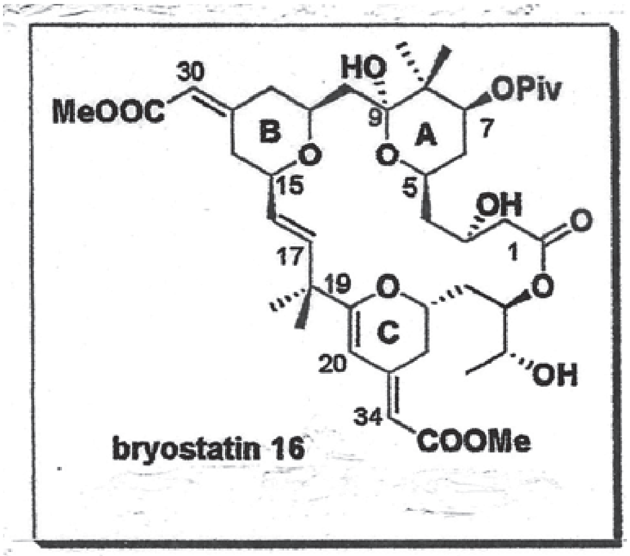
[11] See https://www.epa.gov/sites/default/files/2016-10/documents/award_recipients_1996_2016.pdf , page 96.

> the literature, the idea generally was not adopted by either academia or industry. **Many in industry, however, were practicing this concept without explicitly enunciating it. Others in industry did not consider the concept because it did not appear to have any economic consequence. Today, all of the chemical industry explicitly acknowledges the importance of atom economy**. (Bolding added)

It is important to recognize that prior to the 1990s, while many chemists (especially in Academia) were unaware of or uninterested in the "Atom Economy" and "waste minimization" concepts, both Professor Trost and the 1998 Presidential Green Chemistry Award acknowledged that the concepts of Atom Economy and waste minimization had been previously practiced in the commodity chemical Industry. A much fuller history of the early Industrial evolution of the use of catalysis to produce good Atom Economy and waste minimization will be the focus of another paper in preparation.

Professor Trost then lead the introduction of those concepts into the synthesis of complex organic molecules. For example, in 2002 Professor Trost published a review article in *Accounts of Chemical Research*[12], that described many uses of transition metal complexes (especially Ruthenium complexes) for conducting Atom Economical reactions in the context of the synthesis of complex organic molecules.

One of Trost's most spectacular subsequent examples was published in 2008 in *NATURE*[13], entitled "Total Synthesis of Bryostatin 16 via Atom Economical and Chemoselective Approaches." Bryostatins are complex natural products (see the structure drawing below) with potent anti-cancer activity but have extremely limited availability from natural sources. Trost and co-worker's total synthesis strategy for Bryostatin did employ numerous stoichiometric reagents and reactions traditionally used in synthetic organic chemistry, but also used new key steps employing homogeneous Palladium, Ruthenium, and Gold catalysts, and very substantially minimized the number of steps and stoichiometric reagents used in the prior synthetic schemes for Bryostatins. Trost's synthetic strategy also provided many opportunities for modifications (for example of the Pivalate derivative is shown in the previous column figure) in order to allow preparation of a much wider variety of Bryostatin derivatives / analogs than had been available previously.



3. PROFESSOR ROGER SHELDON'S "E-FACTOR" AND "ENVIRONMENTAL QUOTIENT" METRICS FOR GREEN CHEMISTRY

Professor Roger A. Sheldon's contributions to the evolution of "Green Chemistry" were early, many and varied. Sheldon obtained a PhD in chemistry in 1967, worked at Shell Laboratories in Amsterdam for 10 years, then spent 10 years as Vice President for R&D in Fine Chemicals at DSM Andeno. In 1991 he moved to the Delft University of Technology as a Professor of Chemistry, until 2015, when he moved again to the University of Witwatersrand as a Distinguished Professor of Chemistry.

While still working in Industry in the 1980s, Sheldon published several papers on applications of catalytic oxidations in fine chemical manufacture. For example, in 1987[14], Sheldon commented that "There is an increasing trend towards the use of catalytic methods in fine chemicals manufacture. This is largely a result of two effects: the need for cleaner, more efficient technologies due to increasing environmental constraints, and the forward integration of bulk chemical producers who are familiar with catalytic processes." Sheldon's comment was entirely consistent with this author's experiences at Celanese during the 1980s, because during the 1980s Celanese was actively investigating a variety of new technical approaches to fine chemicals and bulk pharmaceuticals involving catalytic methods[6].

Sheldon's first major literature contribution to "Green Chemistry"[15] occurred very shortly after his

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[12] See Trost, B.M., (2002)

[13] See Trost, B.M., Dong, G., (2008), "Total Synthesis of Bryostatin 16 Via Atom Economical and Chemoselective Approaches"

[14] Sheldon, R.A., (1987), "Catalytic Oxidation and Fine Chemicals"

[15] The term "Green Chemistry" was coined at the EPA by Paul Anastas in 1991, and first used publicly at an ACS Conference in 1993, then that

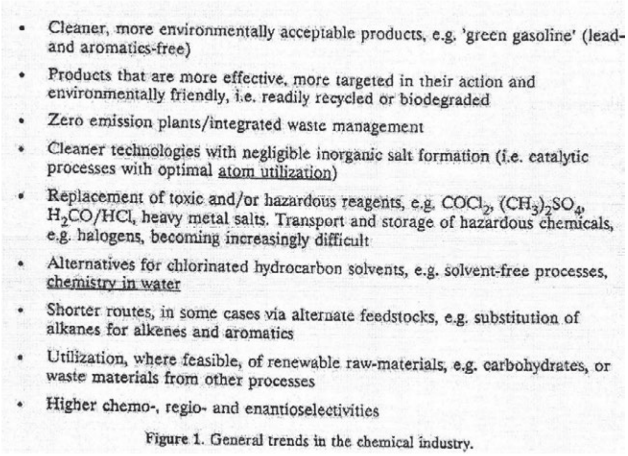
move into Academia, in the published proceedings of an interdisciplinary March 1992 Symposium at Texas A&M, focused on waste minimization in the chemical industry. Sheldon's 1992a paper was entitled "Catalysis, The Atom Utilization Concept, and Waste Minimization."[16] Only one other chemist was a speaker at the conference, most of the speakers were engineers. A monograph of papers from that interdisciplinary conference was published in November 1992, and the introduction to the book stated:

> The subject of this conference reflects the interest that has developed in academic institutions and industry for technological solutions to environmental contamination by industrial wastes. Progress is most likely with strategies that minimize waste production from industrial processes. Clearly the key to the protection and preservation of the environment will be through R&D that optimizes chemical processes to minimize or eliminate waste streams.

Sheldon's 1992a Texas A&M paper received little attention and few literature citations in the Academic literature, but in view of several important contributions by Sheldon that first appeared in that paper, this paper will reproduce below some important quotes and Figures from Sheldon's 1992a paper. Sheldon's Abstract stated:

> Following the advent of the petrochemicals industry in the 1920s, catalysis was widely applied in the manufacture of bulk chemicals. Traditionally environmentally unacceptable processes have largely been replaced by cleaner catalytic technologies. Fine chemicals, in contrast, have remained largely the domain the synthetic organic chemist who has generally clung to the use of stoichiometric methods.
>
> But times are rapidly changing. Increasingly stringent environmental requirements are making the use of classical stoichiometric methods prohibitive. Consequently, there is a general trend towards substitution of such antiquated technologies by cleaner catalytic methods that do not generate large amounts of inorganic salts.
>
> A useful concept for evaluating the environmental acceptability of various processes for producing a particular substance is atom utilization. The latter is defined as the ratio of the molecular weight of the desired product to the sum of all the materials (excluding solvents) used."

In his Introduction, Sheldon further stated:



- Cleaner, more environmentally acceptable products, e.g. 'green gasoline' (lead- and aromatics-free)
- Products that are more effective, more targeted in their action and environmentally friendly, i.e. readily recycled or biodegraded
- Zero emission plants/integrated waste management
- Cleaner technologies with negligible inorganic salt formation (i.e. catalytic processes with optimal atom utilization)
- Replacement of toxic and/or hazardous reagents, e.g. $COCl_2$, $(CH_3)_2SO_4$, H_2CO/HCl, heavy metal salts. Transport and storage of hazardous chemicals, e.g. halogens, becoming increasingly difficult
- Alternatives for chlorinated hydrocarbon solvents, e.g. solvent-free processes, chemistry in water
- Shorter routes, in some cases via alternate feedstocks, e.g. substitution of alkanes for alkenes and aromatics
- Utilization, where feasible, of renewable raw-materials, e.g. carbohydrates, or waste materials from other processes
- Higher chemo-, regio- and enantioselectivities

Figure 1. General trends in the chemical industry.

Figure 1. From Sheldon 1992a.

> After an induction period of a few decades, we now appear to be in the age of "environmentality". This is reflected both in the general trends in society as a whole, and in the chemical industry in particular. (see Figure 1).... Indeed, **integrated waste management and zero emission plants are the catch-words in the chemical corridors of power these days**. (Bolding added)

Sheldon's Figure 1 is shown above.

Readers inspecting Sheldon's Figure 1 should recognize that this was analysis and commentary from a highly informed 20-year Industrial veteran, regarding the status and trends in Chemical Industry in the early 1990s. This author, who was a 7-year veteran of the Chemical Industry in 1990, agrees with Sheldon's description of the status of industry at that time, especially in view of the already widespread popularity and prevalence of the "Pollution Prevention" efforts in Chemical Industry during the 1980s.[4,5]

Readers should also notice that there is very considerable overlap between the "General trends in the chemical industry" described by Sheldon's Figure 1 and the "12 Principles of Green Chemistry" that were only published six years later, in 1998.[1] Sheldon's Figure 1 also supports this author's previous documentation that each of the individual "12 Principles of Green Chemistry" were already in commercial practice in Chemical Industry, and also used in combinations, long before 1998.[4]

Later in his Texas A&M paper, Sheldon supported his Figure 1 "trends" by noting that "In the bulk chemical industry classically environmentally unacceptable processes have largely (but not completely) been supplanted with cleaner catalytic alternatives. In particular, catalytic oxidation and carbonylation are widely used for the conversion of petrochemical feedstocks to industrial

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terminology rose steeply in popularity in the Academic literature (and replaced the prior "Pollution Prevention" terminology) after the beginning of grants for Academic research by the NSF/ACS, and the initiation of the EPA / ACS Presidential Green Chemistry Challenge Awards in 1996.[4,5]

[16] See Sheldon, R.A. (1992a). Sheldon's text, Figures, and Tables from that paper reproduced in this paper are used herein with the permission of the current copyright holder, Springer Nature, see References.

Table 1. From Sheldon 1992a.

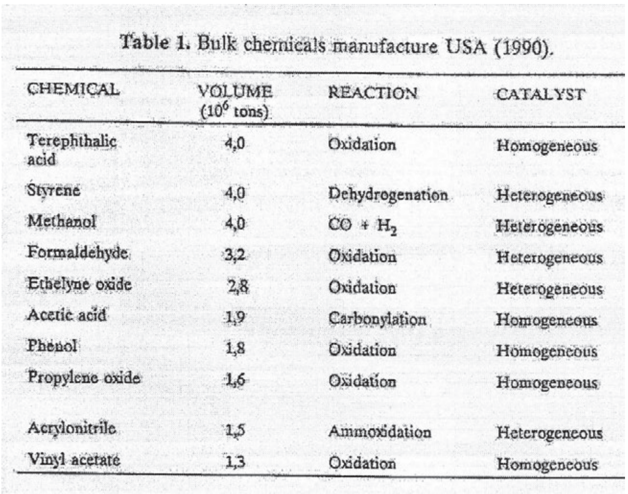

Table 1. Bulk chemicals manufacture USA (1990).

CHEMICAL	VOLUME (10^6 tons)	REACTION	CATALYST
Terephthalic acid	4,0	Oxidation	Homogeneous
Styrene	4,0	Dehydrogenation	Heterogeneous
Methanol	4,0	$CO + H_2$	Heterogeneous
Formaldehyde	3,2	Oxidation	Heterogeneous
Ethelyne oxide	2,8	Oxidation	Heterogeneous
Acetic acid	1,9	Carbonylation	Homogeneous
Phenol	1,8	Oxidation	Homogeneous
Propylene oxide	1,6	Oxidation	Homogeneous
Acrylonitrile	1,5	Ammoxidation	Heterogeneous
Vinyl acetate	1,3	Oxidation	Homogeneous

chemicals." Sheldon then provided his Table 1 of examples, also reproduced above. Additional examples of other such existing large volume chemical processes will soon be described in more detail this author's manuscript currently in preparation.

But Sheldon also noted that in smaller volume segments of the chemical industry (Fine Chemicals and Pharmaceuticals) the environmental performance was much worse, at least as measured in terms of the estimated ratio of the kg of waste products produced per kg of desired product. See Sheldon's Table 2, reproduced below.

This "Sheldon" ratio, "kg of waste to kg of desired product", was originally intended as a much broader metric for the Real-World waste / environmental performance of actual commercialized processes, considered as a commercialized final whole, as compared to Trost's concept of an "Atom Economy" measure of a theoretical 100% efficiency of a hypothetical chemical equation on paper, while contemplating future chemical reactions.[17]

Table 2. From Sheldon 1992a. Byproduct formation in chemicals production.

Industry Segment	Product Tonnage	Kg byproduct / Kg product
Oil Refining	10^6–10^8	ca. 0.1
Bulk Chemicals	10^4–10^6	<1–5
Fine Chemicals	10^2–10^4	5–>50
Pharmaceuticals	10–10^3	25–>100

Initially in this 1992 paper, and more prominently in his later papers, Sheldon named this ratio of wastes to desired product (in a Real-World functioning process) the "E-factor." This "E-Factor" has subsequently become a widely known and routine chemical metric, adopted and used by many others for evaluating the "Greenness" of actual industrial chemical processes.

But in 1992 Sheldon also publicly pointed out that the nature of and/or the toxicity or dangers from the waste also needed to be evaluated. Sheldon accordingly formulated an "equation" to incorporate the E-Factor" and also an "Unfriendliness Quotient" as well, to evaluate "Environmental Acceptability" as shown below.

Environmental =	**E**	**x**	**Q**
Acceptability	"Environmental factor" (kg waste / kg product)	x	"Unfriendliness Quotient"

Sheldon then commented that "For example, if innocuous salts such as NaCl or Na_2SO_4 were arbitrarily given an unfriendliness factor of 1, then chromium salts could be assigned a factor of say 100, and toxic metals e.g. Pb, Cd a 1000. Obviously, these figures are debatable and will vary from one company or production unit to another, being partly dependent on the ability to recycle a particular stream."

This author agrees that assigning numerically precise and non-subjective "Q" values is extremely difficult. But this author also agrees that "unfriendliness" should be carefully contemplated by scientists and engineers at the same time they evaluate the "E-Factor," as they imagine future processes and products, as well as later for the final commercial processes, even if "unfriendliness" can't be rigorously defined mathematically.

Professor Sheldon, after having emphasized the importance of catalysis to already existing industrial processes, then turned toward a historical explanation for the good environmental performance of the oil refining and commodity chemical industries, as compared to much worse environmental performance of the fine chemical and pharmaceutical industry segments. In a discussion of "Development of Organic Synthesis and Catalysis." Professor Sheldon stated:

> Another reason why catalysis has not been widely applied in the fine chemical industry is the more or less separate development of organic chemistry and catalysis (See Fig-

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[17] This author was coached that as much of the starting materials as possible be incorporated into the product by his Celanese supervisor, Pr. Adolfo Aguiló, in 1983. Aguiló advocated the concept be used when imagining new chemical reactions and products, as well as used to evaluate a final process. I had no impression that Aguiló believed these concepts to be either his, or new, but only an established part of practice in the commodity chemicals industry. In another manuscript currently under preparation, an explicit example from the 1970's literature illustrating the use of the "E-Factor" concept will be described.

> ure 8) since the time of Berzelius, who coined both terms, in 1807 and 1835, respectively.

See Sheldon's Figure 8 reproduced below. Sheldon commented that;

> In the late nineteenth and early twentieth century catalysis developed largely as a subdiscipline of physical chemistry. Following the advent of the petrochemicals industry, catalysis was widely applied in oil refining and bulk chemicals manufacture. Industrial organic chemistry on the other hand, really began with Perkin's serendipitous synthesis of aniline purple (mauveine) in 1856….The present-day fine chemicals and pharmaceuticals industries developed largely as spinoffs of this activity.

A few paragraphs later, Sheldon added that:

> Fine chemical manufacture has, to this day, remained primarily the domain of the synthetic organic chemist who, generally speaking, clings to the use of stoichiometric methods… Indeed, the fine chemicals industry, with its roots in coal-tar chemistry, is rampant with classical stoichiometric technologies that generate large quantities of inorganic salts. Examples include sulfonation, nitration, halogenation, diazotization, Friedel Crafts acylations, and stoichiometric oxidations and reductions…Many of these technologies are ripe for substitution by catalytic low-salt technologies.

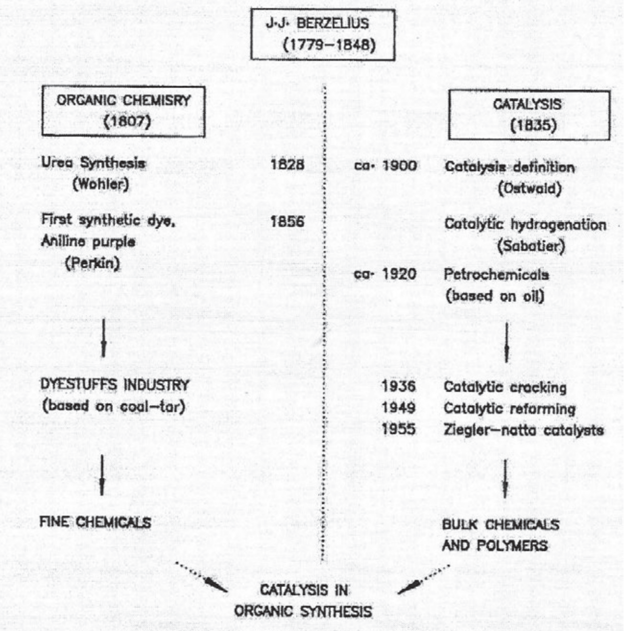

Figure 8. Development of catalysis and organic synthesis.

Figure 8. From Sheldon 1992a.

In subsequent paragraphs, Sheldon highlighted the BHC Ibuprofen Process (as he also did again in many of his subsequent papers) as an already existing example of the applications of catalysis and Atom Economy and the E-Factor in the Fine Chemical / Pharmaceutical industries. This author was the person who initially conceived the BHC Ibuprofen Process in 1984. That process was developed by a multi-disciplinary team at Celanese at Corpus Christi Texas, and then commercialized by BHC in Bishop Texas in 1992.[6] This author will review Sheldon's 1992 description of the BHC Ibuprofen Process, then add some comments below.

Sheldon's 1992 Texas A&M paper first discussed "Ibuprofen Manufacture" in terms of Ibuprofen's relatively high production volumes (for a Fine Chemical / Pharmaceutical), and how sales of the prescription drug converted to "generic" status in many countries after Boot's compound patent[18] expired. Then Sheldon commented regarding his Figure 14, reproduced on the next page:

> Two routes for the production of ibuprofen are compared in Figure 14. Both routes proceed via a common intermediate, p-isobutylacetophenone. The classic route, used by the Boots company (the discoverers of ibuprofen) involves a further five steps, relatively low atom utilization, and substantial inorganic salt formation.
> The elegant alternative, developed by Hoechst Celanese [*] involves only two (catalytic) steps from the common intermediate, 100% atom utilization, and negligible salt formation.

In 1992a Sheldon had broadly mentioned solvent waste and toxicity issues in his Figure 1 but did not directly comment on solvent usage / waste issues for any of the steps of the Boots process. But Sheldon[19] and many others have since explicitly recognized that solvents were and still are the major source of waste and/or pollution in many processes for producing pharmaceuticals.

Sheldon mentioned the similarity of the acylation steps of both synthetic routes shown in Figure 14, which both react iso-butylbenzene with acetic anhydride to produce p-isobutyl-acetophenone. The Boots acetylation reaction used a traditional batch process, solvents, and at least stoichiometric quantities of $AlCl_3$ as a co-reagent for the acetylation reaction, which resulted in the stoichiometric quantities of Aluminum wastes, also produced a mole of acetic acid waste, though its solvent waste production was not publicly known.

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[18] See U.S. Patent #3,385,886 to Nicholson and Adams, issued May 28, 1968, claiming priority to a British patent application first filed February 2, 1961. Nicholson was a chemist and Adams was a pharmacist.

[19] See Sheldon 1996, and Sheldon 2020, and several of his other articles.

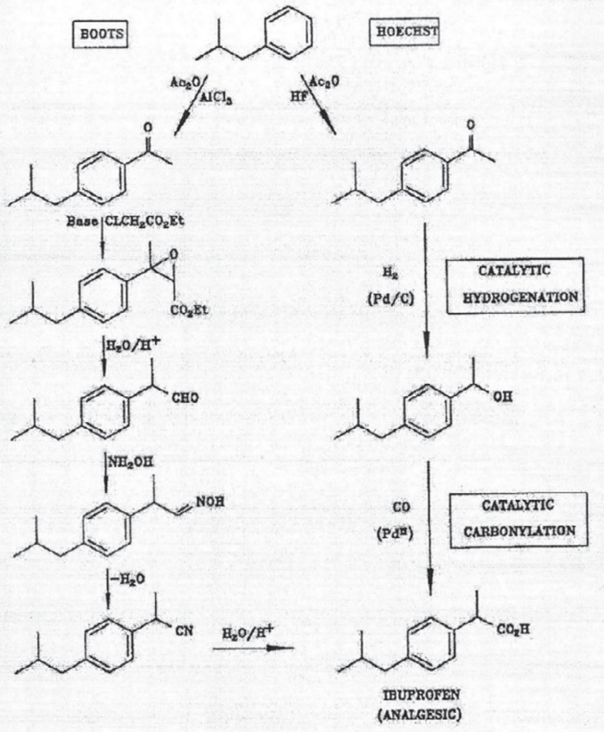

Figure 14. Two routes to ibuprofen.

Figure 14. From Sheldon 1992a.

In contrast, the BHC acetylation step[20] used HF as a liquid catalyst, in a continuous two-phase countercurrent and organic solvent-free process, which very efficiently carries out the acylation reaction, and also very efficiently recycles the corrosive and toxic HF and minimizes the HF inventory required. Because of the relatively high production volumes needed, the sophisticated engineering and high capital cost of the BHC custom continuous process was economically and environmentally justified. But had the volume of desired product been a good deal lower, a batch process might have been selected for economic reasons. Finally, the mole of stoichiometric acetic acid waste from the acylation step of the BHC Process is recovered, but the acetic acid "waste" is inexpensive, relatively non-toxic, bio-degradable, and could have been reasonably waste treated biologically at plant sites unsuited for reclaiming the acetic acid.

Because the p-isobutyl-acetophenone is a low-melting liquid, the BHC hydrogenation of the acetophenone was and is a solventless, but otherwise is a conventional, low pressure batch hydrogenation over Raney nickel, to produce the racemic liquid 1-phenylethanol required for the 3d carbonylation step. The hydrogenation step is perfectly atom economical in theory, and gives very good real yields, so can be viewed as being highly "Environmentally Acceptable". Many such hydrogenations of ketones to alcohols had been previously known. However, had either the starting acetophenone or the 1-phenylethanol been substantially higher melting substances, or had it been necessary to produce only one enantiomer of the 1-phenylethanol (or ibuprofen), a different and more difficult reduction strategy and/or reaction scheme would very likely have been required, both for the hydrogenation and/or subsequent carbonylation steps, unless a final optical resolution step was added that could have "wasted" 50% of the final product.

In his 1992a Texas A&M paper, Sheldon did not comment directly on the final carbonylation step, i.e. the carbonylation of (4'-isobutyl-)1-phenyl ethanol to give racemic ibuprofen. But Sheldon remedied that omission in his subsequent 1992b *Chemistry & Industry* paper, which stated:

> This example is a striking illustration of the benefits to be gained by catalytic thinking….the fact that the **key** carbonylation step bears a striking resemblance to the modern technology for acetic acid manufacture is no mere coincidence." (Bolding added)

Sheldon also commented in 1992b that "Catalytic conversions, on the other hand, are generally more direct: the acetic acid and ibuprofen syntheses via catalytic carbonylation are illustrations of such brevity." Sheldon, (unlike many subsequent Academic commentators who mostly ignored the carbonylation step in favor of praising the HF acylation step, and failed to cite either the Celanese patent or name the authors) actually understood the BHC Ibuprofen Invention, and that the carbonylation step was both the most patentably novel and strategically key step in the BHC scheme.

This author will now add some brief comments about that final strategic "key" carbonylation step. The primary Celanese technical disclosures were published in U.S. Patent # 4,981,995, issued to Elango, Murphy, Smith, Davenport, Mott, Zey (all chemists) and Moss (an engineer), and later assigned to Hoechst Celanese. U.S. Patent # 5,166,418, and a European Patent Application EP 0 337 803 published in 1989 named Hendricks, Mott and Zey as inventors. This author also described some of the other non-technical influences and events preceding and during the conception and development of the BHC Ibuprofen Process in Murphy (2018).

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[20] See U.S. Patent # 5,068,448 to Lindley, Curtis, Ryan, de la Garza, Hilton, and Kenneson, "Process for the Production of 4'-Isobutylacetophenone", assigned to Hoechst Celanese Corporation.

Dr. Veraderaj Elango carried out the early exploratory laboratory work on all three steps, and discovered the combination of palladium, triphenylphosphine, and aqueous HCl as catalyst for the key carbonylation step (initially in the presence of solvents, at modest pressures of carbon monoxide) that looked very promising and highly "atom economical"[21]. Mott and Zey then developed an organic-solventless two-phase version of the batch carbonylation reaction, in which the 1st phase is a molten combination of the 1-(4'-isobutyl)-phenyl ethanol, palladium, and triphenylphosphine, and the 2nd phase is aqueous HCl, then the two phase are strongly mixed together under carbon monoxide to produce the final racemic ibuprofen with good rates and in very good yield. In EP 0 337 803 Mott and Zey disclosed a method for efficiently separating active chloro-palladium / triphenylphosphine catalyst complexes from the ibuprofen product, and recycling them into the next carbonylation cycle. Joel Hendricks (an engineer) and Mott (a chemist) also discovered that including some ibuprofen with the starting materials substantially increases the reaction rates and selectivities, see U.S. Patent # 5,166,418. In his 2010 paper, Sheldon estimated that the carbonylation reaction proceeded to 99% conversion, 96% selectivity to racemic ibuprofen, at a catalyst turnover frequency of 375 per hr. A team of chemists, engineers, technicians, and operators managed by Dr. Larry O. Wheeler piloted the process at Corpus Christi and built and commercialized the process at Bishop Texas in 1992.

One early publication that described the BHC Process was a February 8, 1993 article in *Chemical & Engineering News*, titled "Custom Chemicals", which stated that "Environmental issues are the engines that drive the fortunes of the custom chemical manufacturing industry today." The article discussed the many technical, economic, and regulatory difficulties the chemical manufacturers were encountering while addressing the environmental issues, and featured a version of Sheldon's Figure 14 describing the BHC Process as one prominent example of a solution to the problems.

The BHC Ibuprofen Process then won Chemical Engineering Magazine's bi-annual Kirkpatrick Award for "Pioneering Chemical Engineering Innovation" in December 1993. The opening three sentences of the article stated: "Increasing the efficiency of a process is an ongoing directive in chemical process industries (CPI). Minimizing its impact on the environment is another. Traditional bulk-pharmaceutical manufacturing could use some help on both counts," then went on to describe the BHC Ibuprofen Process.

Another later example of a prominent publication that praised the BHC Ibuprofen Process was Cann & Connelly's 2000 ACS-supported book intended for students, "*Real-World Cases in Green Chemistry*". The book devoted a chapter to the BHC Ibuprofen Process example, as an example of the importance of catalysis and Atom Economy. It stated that the overall BHC Ibuprofen Process had a theoretical "Atom Economy" of 77% but noted that the lost mass / atoms attributable to the acetic acid produced in the first acylation step "is recycled", implying that the Real-World Atom Economy and Environmental Acceptability of the BHC Ibuprofen Process was very high. In Real-World practice the yields and efficiencies of each of the steps are in fact all very high, so that viewed together as a whole, the BHC Ibuprofen Process was a good deal unexpectedly better than the prior Boots process, and much better than just "the sum of the parts".

In the first moments and days of conception, this author clearly understood that there was potential for such good future outcomes, but there were many uncertainties. It took the further contributions and teamwork of the many subsequent Celanese chemists, engineers, management, and business-people, as well as a joint venture with Boots, to turn that potential into a commercial Reality that actually improved the Environment.

4. PROFESSOR SHELDON'S CONCEPT OF "CATALYTIC RETROSYNTHESIS"

Later in his 1992 Texas A&M paper Sheldon introduced into the Academic literature his concept of "Catalytic Retrosynthesis". Sheldon stated:

> The example of ibuprofen perfectly illustrates the benefits to be gained by paying attention to the atom utilization in different routes and for being catalysis-minded. Indeed, organic chemists should be urged to integrate these aspects into their retro-synthetic thinking. Thus in planning an organic synthesis, a 'catalytic retrosynthesis' could be constructed, identifying catalytic pathways to the desired product… Such a catalytic retrosynthesis for ibuprofen is shown in Figure 16.

Sheldon's Figure 16 "catalytic retrosynthetic" analysis of Ibuprofen is reproduced below. Retrosynthetic analysis was of course a standard part of traditional synthetic organic chemistry strategies, originated by E.J. Corey of Harvard University in the 1960s, a concept for which Corey won the Nobel Prize in 1990.

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[21] The words "atom economy" had not yet been coined at that time (in the mid-1980s), but the workers at Celanese (and likely many other industrial chemists of those times) were very familiar with the concept that as much of the weight of the starting materials as possible should be incorporated into the product.

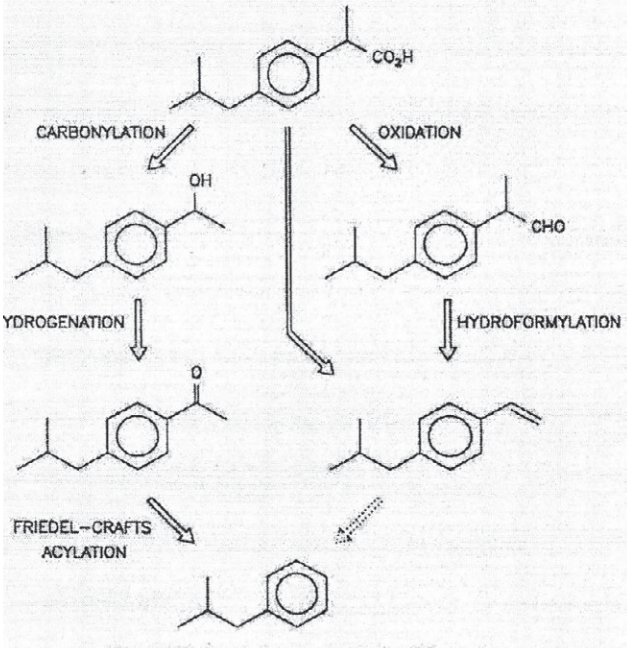

Figure 16. Catalytic retrosynthesis of ibuprofen.

Figure 16. From Sheldon 1992a.

This author did in fact, in May of 1984, consider both sides of the retro-synthetic analysis of racemic ibuprofen illustrated by Sheldon's Figure 16, and also intentionally used catalytic reactions, (as previously described in detail in Murphy (2018).[22] In 1984 I was working in a small Celanese team that was making major improvements in commercial rhodium-catalyzed methanol carbonylation technology.[23] I attended the 10th Annual meeting of the Organic Reactions Catalysis Society in Williamsburg Virginia in May 1984, where Professor John Stille of Colorado State University gave a talk on attempts (with modest results) to hydroformylate styrene asymmetrically.[24] Stille briefly showed a slide of structures of several known "profen" drugs, including Ibuprofen, that could be a target for a "hydroformylation" synthetic strategy. In my conference hotel room that night, I conducted a retrosynthetic analysis of Ibuprofen (and several other "profen" drugs whose structures Stille had revealed [6]) and considered both branches of the retrosynthetic analysis illustrated by Sheldon's Figure 16. I did not know that first night which of the "profen" drugs Stille had shown would have to be single enantiomers, or which ones would have credible / viable commercial markets.

I concluded quickly on that night that the "hydroformylation" strategy shown (for ibuprofen) along the right of Sheldon's Figure 16 was too long, uncertain, and incomplete to be especially attractive for Celanese, though I did not totally discount it.

Because I was actively working on methanol carbonylation, it seemed obvious to consider the "carbonylation" strategy illustrated on the left of Sheldon's Figure16. The synthetic scheme would have looked much more difficult had a single enantiomer of the Ibuprofen been required. Fortunately, it turned out (after I got home to Celanese) that only racemic Ibuprofen was needed. I shared my ideas for the "carbonylation" synthetic scheme with a separate Celanese research group in Corpus Christi exploring new routes to Fine Chemicals and Pharmaceuticals. Veraderaj Elango, who worked in that group, later found the Pd / PPh_3 / HCl catalyst combination that very efficiently carried out the key carbonylation step, to yield the racemic Ibuprofen, in good rates and yields.

Looking backwards another step, my intuition that night in Williamsburg was that a ketone hydrogenation to produce a racemic benzylic alcohol was reasonably likely to succeed in good yields, as many examples of such ketone hydrogenations were known.

Looking backward another step, I had reasonable initial confidence that a Friedel-crafts acylation of isobutyl-benzene to produce the needed acetophenone could succeed, something the literature (including the Boots patents) rapidly confirmed when I got home. But I did not know that night what volume of ibuprofen production would be needed, and whether or not it could justify an anticipated high capital cost to build a custom commercial plant to handle the dangerous and corrosive HF, and thereby avoid the use of $AlCl_3$ in the acylation step. That question was only answered a good deal later at the end of development, by the team of Celanese engineers who did the economic / market estimates and process design work.

Overall, the three-step BHC synthetic strategy produced by the "catalytic retro-synthetic analysis" seemed to have uncertain but very interesting potential "Quality"[4,25]. But a GREAT deal of inter-disciplinary teamwork was needed to resolve the initial uncertainties.

As commercialized in 1992, the BHC Ibuprofen Process directly illustrated six of the "12 Principles of Green Chemistry" (only published years later); 1) prevention of waste rather than treatment or cleanup, 2)

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[22] This author never considered (until years later) the combination of the two well-known techniques of catalysis and retro-synthetic analysis to constitute a new "Principle", a proposition this author still considers debatable.

[23] See Smith et.al, (1987).

[24] See Stille, J.K. (1985).

[25] See Murphy (2020b)

catalysis, 3) Atom Economy, 4) minimization of solvents, 5) energy efficiency, and 6) avoidance of protecting groups). Two more of the "12 Principles" had been used by Nicholson and Adams at Boots in the 1960s, during the discovery of Ibuprofen (designing safer chemicals and designing for degradation). It violated two of the "12 Principles", (less hazardous chemical synthesis and inherently safer chemistry), primarily because of the use of HF in the acylation step, but use of HF was much later determined to be both environmentally and economically superior to the use of stoichiometric quantities of $AlCl_3$ in the original Boots acylation step. The last two of the later published "12 Principles of Green Chemistry" (use of renewable feedstocks and "real time analysis to prevent pollution") were irrelevant to the BHC Ibuprofen process.

Looking back from a different perspective, there were indeed many benefits from a retro-synthetic analysis for Ibuprofen, using catalytic reactions. It "automatically" routed the analysis toward shorter, and highly atom efficient routes that avoided waste / pollution production and protecting groups, and toward raw material and energy efficiency.

Ibuprofen was a relatively simple target molecule for a pharmaceutical, but many uncertainties remained after the retro-synthetic analysis in the earliest moments and days of conception. Again, the teamwork of many people from many disciplines was required to address and overcome the uncertainties and turn the initial conception into a commercial reality that actually "Prevented Pollution". Many pharmaceuticals are more complex molecules than Ibuprofen, and therefore require more complex analysis, and Real-World compromises and teamwork, from the many subsequent scientists, engineers, and businesspeople required to turn original ideas into commercial realities.

In the remainder of his 1992 Texas A&M article, and in many of his subsequent articles over the following years (See appended Reference List for citations to many of Sheldon's subsequent publications), Sheldon described and/or predicted many applications and examples of the uses of catalysis in the fine chemical and pharmaceutical industries, to achieve waste and pollution reduction.

In Sheldon's later papers he also repeatedly discussed the importance of considering positive economic outcomes to the Real-World development and commercialization of environmentally superior commercial processes. Improved economic performance was a very important but far too often unrecognized driver of what was termed "Pollution Prevention" in Industry in the 1980s.[4,5]

Recently, Sheldon, Bode, and Akakios summarized thirty years of the subsequent evolution and application of concepts related to Green Chemistry metrics (Sheldon et. al. (2022)). Sheldon noted that "The ideal E-factor is zero conforming to the first principle of green chemistry: 'It is better to prevent waste than to treat or clean up waste after it is formed.'" Sheldon also later noted "An important driver for the widespread introduction of green chemistry in chemicals manufacture was always waste prevention at source [4], not only for its environmental benefits but also for its economic competitiveness through efficient and cost-effective use of raw materials."

Sheldon noted the E-Factor calculations have subsequently undergone some evolution, broadening, and refinements since his earliest paper 30 years ago, to explicitly include solvent losses and water utilization. Sheldon now defines the E-Factor as "the actual amount of waste, defined as 'everything but the desired product' produced per kg of product," but somewhat later remarked that:

> …current thinking is to calculate E-factors both with and without water [8,9]. This has led to the use of simple Efactors (sEF), that disregard solvents and water in early route scouting, and complete E-factors (cEF) that include solvents and water with no recycling [5]. The true commercial E factor will fall between the sEF and cEF, and can be calculated when reliable data for recycling and solvent losses are known.

This author agrees with Sheldon that "simple" E-factors which do not initially address solvent issues can be useful during the conception and exploratory scouting stages of a Real-World commercial project. At the stage of conception and early scouting experiments in the Ibuprofen project, we were uncertain if the basic catalytic chemistry would function adequately, so we initially and consciously but temporarily ignored the solvent issues (as being totally unpredictable until the basic chemistry and promising catalysts had been demonstrated). Consideration of solvents and/or process water questions was delayed until development began, and then it turned out then that solvents were unnecessary during the synthetic chemistry, but necessary during the separation of the expensive Pd catalyst from the ibuprofen product, and final purification of the ibuprofen!

Sheldon also noted in 2022 that "The pharmaceutical industry accepted the challenge and has spent the last 2-3 decades cleaning up their manufacturing operations[3]. However, in the intervening years APIs have become increasingly complicated molecules, compared with 40 years ago, thus requiring longer syntheses for their production." One of many new sources of information and tools, to address such large challenges, can be found on the website of the ACS Pharmaceutical Roundtable.[26] Trost's Bryostatin total synthesis provided a wonderful example of such challenges, and the use of homogeneous catalysts to shorten very long and complex total synthesis schemes in order to make them practical, and simultaneously improve the final E-Factor and environmental impacts as well.

5. CHANGE, EVOLUTION, AND THE FUTURE OF "GREEN CHEMISTRY"

Some larger perspectives are needed, about the scope and purposes of "Green Chemistry". Having a "Green Chemistry" idea, or following a set of "Principles", or even running a few experiments in the lab is only a beginning, toward a much larger goal and/or purpose.

In this author's opinion and experience, the primary goal and/or purpose of "Pollution Prevention / Green Chemistry" is not to try to discover or make a new "Science". In this author's opinion and experience, the goal and/or purpose of "Green Chemistry" has always been to use already known "Science", Engineering, and Technology to try to make new and improved Real-World processes and products, for the needs of the Real-World and its people, also while preventing the formation of waste and pollutants, so as do less damage to the natural World and its environment and ecology. Fortunately, a good deal of new "Science" has developed along the way.

Addressing that broader but primary goal, and transforming that goal into Real-World reality, has always required consideration of, and contributions from other "Sciences" outside Chemistry, including Biology, Ecology, Engineering, Economics, Business, and even Politics and Policy. For example, pharmaceutical research has always been interdisciplinary, with chemists making molecules for biological testing for activity, toxicity, etc., all for the use of doctors and patients. With the growing use of the techniques of modern biotechnology, to make antibody drugs and RNA vaccines, the pharmaceutical industry trend is now toward the increasing importance of biology, and also the engineering techniques necessary for Real-World production of such biotechnology drugs. Interdisciplinarity is now increasingly important.

Furthermore, the efforts of Trost and Sheldon as described above were only a limited (and very "Chemistry focused") part of the much earlier, broader, international, and interdisciplinary efforts at "Pollution Prevention" that developed in Industry in the 1970s and 1980s.[4,5] Those much broader "Pollution Prevention" efforts were a "paradigm change" that embraced everything from the mining of minerals, oil drilling and refining, to end use issues including toxicity, formulations, packaging, coatings, recycling, disposal, and degradability. Many industrial chemists were involved in the "Pollution Prevention" efforts of the 1970s and 1980s, but few Academic chemists became involved in such efforts until the 1990s.

Professors Barry Trost and Roger Sheldon were among the earliest "chemical" Academics to become involved. Sheldon brought a wealth of knowledge about and experience in the Chemical Industry with him when he moved to Academia in 1991.

Sheldon's Tables 1 & 2, and Figure 8 recognized some of those prior developments in industry, over the prior decades. Sheldon recognized that those developments contrasted with, and in some ways conflicted with, the different goals and techniques that had evolved in traditional synthetic organic chemistry, a "Field" largely dominated by Academic perspectives, goals, and the peer reviewed Scientific literature. But with the growth of research in both organometallic chemistry and homogeneous catalysis in both Industry and Academia in the 1960s and 1970s, the two previously largely separate fields of synthetic organic chemistry and catalysis began to merge, as Sheldon's Figure 8 correctly suggested.

Both Trost and Sheldon then made substantial contributions to the early evolution of methods for more cleanly synthesizing and manufacturing fine chemicals and pharmaceuticals in the early 1990s, years before the words "Green Chemistry" were used in public, or the "12 Principles of Green Chemistry" were published in 1998. Their later contributions are also indisputable, as are the later contributions by many other Scientists, from many "disciplines", in both industry and in Academia.

Unfortunately, with the publication of the "12 Principles of Green Chemistry" in 1998, too much of the Academic and government "worlds" began to narrow the focus toward chemistry only, while largely ignoring the much earlier and much broader interdisciplinary approaches that had produced many environmentally favorable commercial processes in the 1970s and 1980s. In this unfortunate "paradigm change" many Academics began to conduct research and teach students based on an inaccurate "narrative" that "Green Chemistry" had originated at the EPA, and could be "guided" by the wildly incomplete and highly Academic perspectives of the "12 Principles".

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[26] See the ACS Pharmaceutical Roundtable website, at https://www.acsgcipr.org/

This author has a very different perspective on, and has published (see Murphy 2020a), a very different interpretation of the history of the origins and emergence of "Green Chemistry", namely that:

> …Real-World Industrial "Green Chemistry" emerged as a holistic final outcome from an extremely varied and complex set of parallel evolutionary "random tinkering" sub-processes that began about the time of World War II, and that evolutionary process accelerated in the 1970s … That overall evolutionary process was the product of very complex interactions of very many internal and external events, carried out by many human investigators from multiple disciplines and countries, who were individually driven by many different goals, motivations, influences and input factors, including customer / societal needs and desires, economics, the environment, the legal / statutory / regulatory pressures, as well as the constantly evolving state of the underlying sciences of Chemistry, Biology, and Engineering, over decades. Many of the resulting individual inventions were also the direct product of individual human creativity, thought, and logic, as aided by intercommunications between the investigators, as well as the constraints of the laws of Nature, local circumstances, and elements of chance.[4]

This author believes that such an evolutionary and multi-disciplinary view of the history of "Green Chemistry" can have many implications for the directions "Green Chemistry" should go in the future. Fortunately, in the last ten years or so, some prominent "Green" Academic practitioners (including Professor Anastas) and their approaches seem to be broadening and evolving again, toward interdisciplinarity, "Sustainability", and "Circular" technologies and economics.[27] This author very much approves of and supports returning toward such broader interdisciplinary contributions and perspectives in the future.

Moving back toward such interdisciplinary and teamwork-based approaches is quite a "paradigm change". Deep knowledge, experience, and "expertise" in each of the relevant sub-disciplines is still required, but is clearly not enough. The interdisciplinary subject matter is far too Vast and/or infinite for any one person to understand completely, and a good deal of unpredictability is built into such Vastly complex evolutionary processes. Yet interdisciplinary teams can address and solve many very complex Real-World problems, by focusing on the scope of the specific Real-World problem they are attempting to address, and using interdisciplinary teamwork and iterative, evolutionary approaches.[28]

Lastly, this author is concerned that over the last 25 years hundreds of thousands of university students have been taught that the "12 Principles of Green Chemistry" were the primary cause of the much of the environmental progress of the last 25 years. Those narratives neglect the primary early role that Industry played, and have left hundreds of thousands of students with a false belief that the US government and Academia were primarily responsible for the "Green" progress that has been achieved. They also propagate a very questionable belief that top-down "command and control" legal/political governmental mandates were a primary cause the progress over the last 25 years, and neglect consideration of inherently interdisciplinary evolutionary developments that were actually responsible for much of the progress.

While such oversimplified narratives may be difficult to avoid when introducing K-12 and undergraduate students to Science, this author believes such narratives are somewhat destructive to the understanding and futures of Science and Engineering graduate students preparing to go out into a profoundly interdisciplinary and evolutionary Real-World. This author believes graduate students interested in inherently interdisciplinary fields such as "Green Chemistry" and "Green Engineering" should be exposed to and consider evolutionary and interdisciplinary perspectives about Science, and their relationships to the extremely complex external and evolutionary technical, social, and legal phenomena that are ubiquitous in the Real-World. This author believes such graduate students should be allowed to participate in interdisciplinary graduate coursework and/or seminars addressing environmental problems and solutions. This author is heartened by the indications that both "Green" R&D in general, and Science and Engineering education, seem to be evolving back toward such interdisciplinary approaches, and that these developments may represent another new "paradigm change" in Academic Education.

Mark A. Murphy Ph.D., J.D. is a retired industrial chemist and patent attorney, writing "Pro-Bono." He thanks his many prior colleagues from Science, Engineering, and Law, and the authors of the references cited herein, and his wife Mary Bertini Bickers (a woman of many very unusual talents in her own right) for her many forms of support. The opinions stated in this article are solely those of the author and were not induced or financially supported in any way by any other person, business, or legal entity.

Sheldon's Figure 1, Table 1, Table 2, Figure 8, and the several text passages quoted herein from Sheldon 1992a are being reproduced in this article with the permission of Springer Nature, current owner of Plenum Press's original copyrights.

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[27] See for example Mulvihill et.al. (2011), Iles and Mulvihill (2012), Constable (2021), and Ncube et.al. (2023).

[28] See Murphy (2020b).

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Feature Article

The Italian Neo-Idealists and Federigo Enriques The Dispute Between Benedetto Croce and Federigo Enriques: a Defeat for Enriques?

Luca Nicotra*

Editor in charge of «ArteScienza», of the «Bulletin of Philosophy of Human Sciences» and of the «Periodic of Mathematics». Engineer and science journalist
E-mail: luca.nicotra1949@gmail.com.

Abstract. The controversy that between 1908 and 1912 saw Benedetto Croce and Giovanni Gentile opposed on one side and Federigo Enriques on the other did not actually have a conclusive episode, but its end was perceived, for its results on culture, on society and teaching in Italy, as a "defeat" of Enriques. A more careful examination of the events and of the historical context in which it took place seems, however, to clearly demonstrate that we can speak not of a personal defeat of the great mathematician from Livorno, but rather of a defeat of the commendable attempts at cultural and social modernization of Italy in an international perspective, of which Enriques was not the only actor but certainly the most exposed. Such intentions were crushed by the myopic provincial conservatism of Italian neo-idealism, favored by the fascist regime, concerned only with affirming in the world an alleged autarkic national cultural superiority, based on the traditional literary-humanistic culture, ignoring the progress of the new technical-scientific thought, due to its nature instead placed in an international context.

Keywords: Federigo Enriques, Benedetto Croce, Giovani Gentile, Italian idealism, dispute between Croce and Enriques.

1. FEDERIGO ENRIQUES: AN INTELLECTUAL IN ALL AREAS

Federigo Enriques was one of the leading figures in the cultural panorama, not only in Italy but also in Europe, in the first half of the 20th century. Mathematician, philosopher and historian of science, he wrote works in each of these fields which – as Guido Castelnuovo[1] said – «would alone be enough to fill and illustrate the entire life of a scientist». Although it is not possible to separate the three directions mentioned by Castelnuovo in the intellectual activity of Enriques, it is possible to distinguish them into three periods, in each of which one or the other of the three directions prevailed: 1893-1906 (mathematics), 1906-1922 (philosophy) and 1922-1946 (history of science). In reality Federigo Enriques was not only a mathematician, philosopher and

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[1] Castelnuovo (1947).

historian of science, as recalled by his brother-in-law Guido Castelnuovo, in his commemoration held at the Accademia Nazionale dei Lincei on 11 January 1947. Due to the extraordinary variety of his cultural interests – of which will be explained later – Enriques was an all-round intellectual, and in particular one of the most notable references for overcoming the barriers between the "two cultures".

Abramo Giulio Umberto Federigo Enriques – this is his full name – was born on the 5th of January 1871 in Livorno from Giacomo Enriques, of Jewish origins with Portuguese descent, and Matilde Coriat, born in Tunisia and bilingual (Italian and French). In 1882 he and his family moved from Livorno to Pisa, where Federigo attended secondary school. In 1887 he finished high school and enrolled at the University of Pisa, also attending the highly prestigious Scuola Normale Superiore, where he was taught by Enrico Betti (1823-1892), Ulisse Dini (1845-1918), Luigi Bianchi (1856-1928), Vito Volterra (1860-1940) and Riccardo De Paolis (1854-1892), the leading Italian mathematicians of the time.

Even before graduating, in 1890 he published his first academic scientific memoir: *Alcune proprietà dei fasci di omografie negli spazi lineari ad n dimensioni* (*Some properties of homograph bundles in linear spaces with n dimensions*).[2] But Federigo Enriques' first (non-academic) publication dates back to 1885, when he was just 14 years old: *Table of perfect integer squares and cubes contained in 100000* (Pisa: Nistri, 1885), a 10 page file in 16-ths.

In the summer of 1891, at the age of twenty, he graduated in mathematics with De Paolis, defending a thesis entitled *Alcune proprietà metriche dei complessi di rette ed in particolare di quelli simmetrici rispetto ad assi* (*Some metric properties of complexes of lines and in particular of those symmetric with respect to axes*), published four years later.[3]

In November 1892, after a few months spent in Pisa, he arrived in Rome to continue the specialization course in algebraic geometry held by Luigi Cremona who, with his "birational transformations",[4] he had effectively introduced in Italy that new line of research, already promoted by Corrado Segre. On this occasion, in Rome he got acquainted with Guido Castelnuovo, who, together with Corrado Segre and Luigi Cremona, was the leading representative of the Italian school of algebraic geometry, of which Enriques himself would later join as the main protagonist. Subsequently he spent a few months of 1893 in Turin, completing his specialization course with Segre. During the period of the specialization course in Rome, Enriques published various academic works[5] which earned him in 1894 the position of teaching Projective Geometry at the University of Bologna. The first important results of his studies in algebraic geometry were the article *Ricerche di geometria sulle superficie algebriche* (*Geometry research on algebraic surfaces*)[6] of 1893 and his university textbooks *Lezioni di Geometria Descrittiva* (*Lesson of Descriptive Geometry*)[7] and *Lezioni di Geometria Proiettiva* (*Projective Geometry Lessons*)[8] published the following year. In 1896, at the age of 25, he was appointed full professor of Projective and Descriptive Geometry at the University of Bologna. In 1903 the first edition of a highly successful series of mathematics textbooks for upper secondary schools, which were adopted throughout Italy until the 1970s, was published with the title *Ementi di geometria* (*Elements of geometry*), written with Ugo Amaldi. In 1906 he published the volume *Problemi della Scienza* (*Problems of Science*),[9] which, due to its contents, can be considered twinned with the famous books by Henry Poincaré: *La science et l'hypothèse* (1902), *La valeur de la science* (1905) and *Science et methode* (1908). The book, written with material taken from previous articles by Enriques, contains his scientific philosophy, his psychological approach to the principles of geometry and anticipates Albert Einstein's views on the concepts of time, space, motion, force. In the same year he founded the "Società Italiana di Filosofia" (Italian Philosophical Society – SFI) in Bologna and chaired it until 1913. The following year, in 1907, he founded the «*Rivista di Scienza*» (*Journal of Science*), which would then take on the name «*Scientia*» in 1910. In 1908 he participated in the III International Congress of Philosophy in Heidelberg and there he received the task of organizing and presiding over the IV Congress to be held in Bologna in 1911. In 1912 he published *Scienza e razionalismo* (*Science and*

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[2] Enriques (1890).

[3] Enriques (1895).

[4] Cremonian transformations generalize homographies, as, for example, in the plane straight lines no longer change into straight lines but into curves of a higher order. They are called "birational transformations" because to any point of the initial space they associate another point of the transformed space whose coordinates are rational functions of those of the starting point.

[5] In 1892: *Le omografie cicliche negli spazi ad n dimensioni; Le omografie armoniche negli spazi lineari ad n dimensioni.* Nel 1893: *Sui gruppi continui di trasformazioni cremoniane nel piano; Sopra un gruppo continuo di trasformazioni di Jonquières nel piano; Una questione sulla linearità dei sistemi di curve appartenenti ad una superficie algebrica; Sui sistemi lineari di superficie algebriche le cui intersezioni variabili sono curve iperellittiche; Sugli spazi pluritangenti delle varietàcubiche generali appartenenti allo spazio a quattro dimensioni; Ricerche di geometria sulle superficie algebriche; Le superficie con infinite trasformazioni proiettive in se stesse.*

[6] Enriques (1893).

[7] Enriques (1894a).

[8] Enriques (1894b).

[9] Enriques (1906).

rationalism),[10] the book that contains more than any other the philosophical thought of Enriques, in which current philosophical views are compared with ancient ones. In the years from 1912 to 1914, the second edition in two volumes of the *Questioni riguardanti le matematiche elementari* (*Questions concerning elementary mathematics*)[11] was published, written together with other distinguished Italian mathematicians, which constitutes his major work dedicated to the teaching of mathematics. As President of the National Association of University Professors, in the years 1913-1915 he formulated a reform project for the Italian university, which however was not approved. In 1919 he was elected President of the "Mathesis Society" (founded in 1895), a position he held until 1932. In 1921 he assumed and maintained the direction of the «*Periodico di Matematiche*» (*Mathematical Periodical*) until 1938, being removed due to the racial laws. He will take over the direction from the fall of fascism until the year of his death, 1946. The following year, in 1922, he moved from Bologna to Rome, where he became full professor first of Higher Mathematics and then of Higher Geometry at the University "La Sapienza". In the same year his book *Per la storia della logica* (*For the history of logic*)[12] was published and the following year he founded the "National Institute for the History of Physical and Mathematical Sciences" in Rome, within which the "School of the history of sciences" was created. In 1923 the first volume of *Gli Elementi d'Euclide e la critica antica e moderna* (*Euclid's Elements and ancient and modern criticism*)[13] was published, the first Italian critical edition of Euclid's work, written with other collaborators. It will be completed in 1935 with the fourth volume. In 1925 he was appointed director of the Mathematical Section of the "Enciclopedia Italiana" by Giovanni Gentile, a position he would hold until 1937. In 1932 the first volume of the *Storia del pensiero scientifico* (*History of Scientific Thought*),[14] written with Giorgio de Santillana, dedicated to Antiquity, was published. The work remained unfinished, but in 1937 the *Compendio di storia del pensiero scientifico* (*Compendium of the history of scientific thought*)[15] was published (with Giorgio de Santillana), which contained the periods not included in the previous work. In 1934, in Paris, his book *Signification de l'histoire de la pensée scientifique*[16] was published, in which Enriques reaffirmed the theoretical value of science. Following the introduction of the racial laws also in Italy, in 1938 he was removed from university teaching and relieved of all public offices. However, he continued to have relations with France, where in 1941, in Paris, his book *Causalité et déterminisme dans la philosophie et l'histoire des sciences* was published, which contains a critical examination of the problem of determinism. With the fall of fascism, in 1944, he finally returned to teaching at the University of Rome, until his death following a heart attack on 14 June 1946 in Rome.

2. A CONTROVERSY WITH MULTIPLE INTERPRETATIONS

The controversy between Federigo Enriques and the major representatives of Italian neo-idealism, Benedetto Croce and Giovanni Gentile, began in 1908, reached its climax in 1911 and ended up being exhausted without a well-defined solution in 1912. There was, therefore, no document or an event that can be considered as the final "battle" that with its outcome has somehow decreed the winner and the loser. «However, Croce's authority had the practical effect of making a large part of the philosophical and cultural circles line up on positions that were hostile to Enriques, so that the end of the controversy was commonly perceived as a ''defeat'' of the Enriques».[17]

There are many questions that, after more than a century, it is legitimate to ask today about the meaning and outcome of that "clash". It was really only an unfortunate "academic controversy" or rather a real "conspiracy" concocted by Croce and Gentile to eliminate their most formidable opponent from the Italian cultural scene and, with him, everything that was linked to his efforts of renewal and cultural and social modernization of Italy at the beginning of the 20th century? How much "personal" and how much "academic" was the controversy which, in any case, took on an official public dimension? If we want to give the sense of a "personal" defeat to that story, was Federigo Enriques really the only defeated? Weren't there other scientists and philosophers who shared his same aspirations for cultural renewal in Italy and the idea of a scientific philosophy that would bring science and philosophy closer together? And if, on the other hand, we want to see it in impersonal terms, it was only the scientific world that capitulated under the conceit and arrogance of a so-called superior culture or, rather, it was not the defeat of

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[10] Enriques (1912).

[11] Enriques (1912, 1914). In 1927 the third edition in 4 volumes was published. The first edition had come out in 1900 with the title *Questioni rigardanti la geometria elementare* (*Questions concerning elementary geometry*).

[12] Enriques (1922).

[13] The second, third and fourth volumes were published in 1930, 1932 and 1935.

[14] Enriques (1932).

[15] Enriques (1937).

[16] Enriques (1934).

[17] Israel (1993).

the aspiration to modernity, into which Italy could enter on the threshold of the new century like other more advanced European nations?

To try to give an answer to these questions, as objective as possible, in the sense of coherent with the facts that can be established, it is necessary to analyze the multiple meanings assumed by that clash: between provincial conservatism and international modernism; between a secular traditional literary-humanistic culture (which erroneously included philosophy too) and a scientific culture with its new scientific philosophy; between neo-idealism and positivism/neo-Kantism; between different ways of conceiving society; between the personal aspirations of the contending parties for the philosophical and cultural hegemony in Italy.

All these facets of the controversy saw Enriques as protagonists in the forefront, on the one hand, and Gentile and Croce, on the other, these however with often overlooked but in reality, substantial differences, above all in their personal different consideration of science.

Furthermore, it should be noted that Enriques was not the only protagonist of that controversy, which in reality, in a more latent and discrete form, had already begun much earlier, through the work of a large group of other prominent personalities of science and in particular of Italian mathematics of the second half of the nineteenth century. Enriques, however, was undoubtedly the major champion of that clash, assuming the most exposed position to the attacks of neo-idealist philosophers. If, therefore, we want to speak of personal defeat, the only defeated was not Enriques but, with him, also all the Italian mathematicians, physicists, chemists, naturalists and philosophers who, albeit in different ways, shared his aspirations of cultural and social renewal of post-Risorgimento Italy and the beginning of the 20th century.

From the brief outlines that follow, two characteristics emerge, essential for better understanding both the meaning of the clash between Enriques and Croce-Gentile and the consequences, normally attributed to its outcome, on the difficulties of a solid affirmation of scientific culture in Italy: the connotation of Italian science at the end of the 19th century and at the beginning of the 20th century, on the one hand, and the strong presence of Italian scientists in leading government positions until the rise of fascism, on the other, a phenomenon which would disappear in the following years until nowadays.

.3. SCIENCE IN ITALY BETWEEN THE 19TH CENTURY AND THE EARLY 20TH CENTURY

To understand the cultural background of Federigo Enriques, and the same controversy that saw him engaged against the Italian neo-idealists, it is useful to look at the Italian scientific context over the period from the mid-nineteenth century to the early twentieth century. From the following pages emerges a picture of Italian science which, in the years between the 19th and 20th centuries, places it in the first places internationally, with some interesting characteristic features. This primacy of Italian science at an international level, which also extends to national political life, strengthens in Federigo Enriques the conviction of being able to assign to science, also in Italy, a leading place alongside literary-humanistic culture.

A first characteristic of Italian scientific community of that time was the desire to enter an international context, which at the time was essentially identified with the European one.[18] This aspiration is part of the modernization process that had already affected the most industrialized and technologically advanced countries of Europe. The modernization of society also involves scientific research, which requires being informed of the most advanced research conducted in other Countries.[19] So modernization and internationalism are two inseparable faces of the science of that time. International competition led Italian science to reach top positions, engaging it in frontier research which gave fundamental results in mathematics, physics and chemistry.

3.1 The first Italian scientific community

The conscience of a national scientific community, in Italy, can be traced back to the creation of the "Union of Italian Scientists", wanted by the zoologist Carlo Luciano Bonaparte, (son of Luciano, younger brother of Napoleon I) and by Vincenzo Antinori, Giovanni Battista Amici, Gaetano Giorgini, Paolo Savi and Maurizio Bufalini. However, its main promoter was Prince Carlo Luciano Bonaparte, who, animated by nationalist fervor, convinced the Grand Duke of Tuscany Leopold II to promote the first meeting of Italian scientists in Pisa from 1 to 15 October 1839, hosting scholarly memoirs in six sections: Physics, Chemistry and Mathematical Sciences; Geology, Mineralogy and Geography; Plant Botany and Physiology; Comparative Zoology and Anatomy; Medicine; Agronomy; Technology. The choice of Pisa seems the most suitable, both due to the fact that

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[18] The United States of America at that time had not yet conquered the international cultural leadership that has characterized them from the end of the Second World War to the present day.

[19] In particular «in the years of Enriques the culture of a philosophical-scientific-historical orientation was more significant in France and Germany than in England. Enriques was very attached to France and Germany» (Lombardo Radice, 1982).

it is located in Tuscany, where Leopold II is known for his scientific interests, and due to the fact that it was the birthplace of Galileo Galilei, universally recognized as the father of modern science. The meetings were first held on an annual basis until 1847, each meeting being made up of several meetings held on different days over a period of 15 days. Subsequently they resumed in unified Italy in 1861 in Florence with an extraordinary edition in 1862 in Siena (X meeting) and in 1873 in Rome (XI meeting). They finished with the last one of 1875 in Palermo (XII meeting), on the occasion of which the regulation of the "Italian Society for the Progress of Sciences" (SIPS) was approved, which therefore is to be considered the continuation of the "Union of Italian Scientists". Already in these meetings it is possible to glimpse the spirit of international openness that will increasingly characterize the activities of Italian scientific community. Indeed, some famous foreign scientists were also invited to the meetings, among which the names of William Herschel and Charles Babbage stand out, and the proceedings of the meetings were sent to the most important foreign scientific institutions.

3.2 Mathematics

In the first half of the 19th century, mathematics, both in teaching and in research, had suffered a long period of decline in Italy compared to the rest of Europe. But after the proclamation of the Kingdom of Italy, thanks to the work of many Risorgimento and post-Risorgimento mathematicians, the situation changed radically, starting a golden age of Italian mathematics. The most prominent mathematicians of this period are Enrico Betti (1823-1892), Francesco Brioschi (1824-1897), Giuseppe Battaglini (1826-1894), Felice Casorati (1835-1892), Luigi Cremona (1830-1903) and Eugenio Beltrami (1836-1900). These mathematicians also actively participate in the events of our Risorgimento.[20] However, despite being "patriots", they did not choose blind nationalism, but worked to give the mathematical research of the unified Italy an international connotation, establishing ties with the rest of Europe. Battaglini's students were several illustrious specialists in algebraic geometry: Enrico D'Ovidio, Riccardo De Paolis, Ettore Caporali, Domenico Montesano, as well as the algebraists Alfredo Capelli and Giovanni Frattini. In 1858 Betti, Brioschi and Casorati visited the universities of Göttingen, Berlin and Paris. On November 29, 1863 Brioschi, with his student engineer Giuseppe Colombo, founded the Royal Higher Technical Institute in Milan (which will later take on the name Polytechnic), taking analogous German institutions as a model. Bernhard Riemann, invited to teach at the "Scuola Normale Superiore" in Pisa, rejected the proposal for health reasons, but remained in Italy from 1863 to 1866, the year in which he died in Selasca, on Lake Maggiore, on 20 July. Those years were therefore an unrepeatable occasion for fruitful exchanges of ideas between the great German mathematician and Pisan mathematicians. The work of Betti, Brioschi, Casorati, Cremona and Beltrami gives extraordinary results , not only for their research but also for the formation of new generations of brilliant mathematicians, who bring Italian mathematics to the highest international peaks in the period from 1880 to First World War with: Ulisse Dini (1845-1918), Cesare Arzelà (1847-1912), Salvatore Pincherle (1853-1936), Gregorio Ricci Curbastro (1853-1925), Giuseppe Veronese (1854-1917), Luigi Bianchi (1856-1928), Giuseppe Peano (1858-1932), Ernesto Cesàro (1859-1906), Vito Volterra (1860-1940), Corrado Segre (1863-1924), Guido Castelnuovo (1865-1952), Federigo Enriques (1871 -1946), Tullio Levi-Civita (1873-1941), Guido Fubini (1879-1943), Francesco Severi (1879-1961), Leonida Tonelli (1885-1946), Guido Ascoli (1887-1957). The fame of these mathematicians was international, so much so that Felix Klein, for his great *Enzyklopädie der mathematischen Wissenschaften* (*Encyclopaedia of Mathematical Sciences*), entrusted the drafting of many entries to Italian mathematicians, including Salvatore Pincherle, Luigi Berzolari, Orazio Tedone and Federigo Enriques. In 1907 Klein asked the latter to draft the article *Prinzipien der Geometrie*, dedicated to the principles of geometry, which would turn out to be a real monograph on the subject. Algebraic geometry, due to the preponderant contribution of Italian mathematicians (and Enriques will be one of its fathers together with Corrado Segre, Luigi Cremona, Guido Castelnuovo and Francesco Severi) will be known in Germany as l'*Italienische Geometrie*, the Italian geometry. There are also international awards. In 1907 Federigo Enriques and Francesco Severi received the Bordin prize from the Academie des Sciences in Paris. In 1909, the same prize was awarded to Giuseppe Bagnera (1865-1927) and Michele de Franchis (1875-1946) for their work on the classification of elliptical surfaces. The philosopher and logical-mathematician Bertrand Russell defines Peano as «the great master in the art of formal reasoning» (Russell, 1970, p. 74) and Henry Poincaré, in the French newspaper «*Le Temps*», refers to the "Palermo Mathematical Circle" as to the largest mathematical organization in the world. And he has every reason to affirm it: out of 924 members, 618 are foreigners, that is almost 70%! On the pro-

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[20] Bottazzini, Nastasi, (2013).

posal of Vito Volterra, the IV International Congress of Mathematics was held in Rome from 6 to 11 April 1908. There were 700 participants in the congress. Italy is present with the highest number (213), followed by Germany (174), France (92) and Austria-Hungary (74). Volterra, in his inaugural speech, confirms the international character of science, which also informs the Italian one.

3.3 Physics

Pietro Blaserna, Antonio Pacinotti, Damiano Macaluso, Galileo Ferraris, Augusto Righi, Orso Mario Corbino, Domenico Pacini, Antonino Lo Surdo and Guglielmo Marconi were the leading figures in Italian physics from the mid-19th century to the beginning of the 20th century.[21] Physics, until about 1870, was essentially conceived as Galileo intended it: an experimental science, in which mathematics was reserved an auxiliary and instrumental function, a means of expressing quantitatively relationships between the physical quantities object of the experiment. Language and heuristic tool, then. But in the last thirty years of the nineteenth century, experimental physics was joined by the mathematical physics of Betti, Volterra and other physicist-mathematicians and engineers, such as Luigi Federico Menabrea and Alberto Castigliano, whose research converged into the rising Building Science. Only in 1926 Orso Mario Corbino explained very clearly the need to introduce theoretical physics, in addition to mathematical physics, to re-establish the lost contact between mathematical physicists and experimental physicists: he will introduce the first chair of theoretical physics in Italy, held by Enrico Fermi. The first-degree thesis in theoretical physics is that of the homonymous son of the philosopher Giovanni Gentile, Giovanni Gentile Jr (1906-1942), achieved in Pisa in 1927. The differences of methodological approach in the research of mathematical physics and theoretical physics[22] also explain the different professional connotations of the authors: mathematicians the authors of mathematical physics research and physicists the authors of theoretical physics research. But in the period considered here, prior to the famous dispute between Enriques and the neo-idealist philosophers, which began in 1908, theoretical physics does not existed as a separate discipline, being identified with mathematical physics. This explains why many mathematicians of that time were also physicists.

In 1844 Carlo Matteucci and Raffaele Piria founded the journal «*Il Cimento, giornale di fisica, chimica e storia naturale*» (*The Cimento, journal of physics, chemistry and natural history*) in Pisa, which in 1855 became «*Il Nuovo Cimento, giornale di fisica, chimica e storia naturale*» (*The New Cimento, journal of physics, chemistry and natural history*), often abbreviated to «*Il Nuovo Cimento,*». Forty-two years later, in 1897, it became the official press organ of the "Italian Physics Society" and one of the most authoritative and famous physics journals.

The first great reformer of Italian physics is Pietro Blaserna (1836-1918), who graduated in physics with honors at the age of 21 from the University of Vienna and then assistant to Henri-Victor Regnault at the University of Paris, where he dealt with theory gas kinetics. In 1862 – at the age of just 26 – he was called to fill the chair of Experimental Physics first at the Institute of Higher Studies in Florence and then, the following year, at the University of Palermo. In 1872 he went to Rome to hold the chair of Experimental Physics. Blaserna radically reformed the teaching of physics by introducing the institution of the "practical school", i.e., the physics laboratory. Furthermore, in 1881, on the model of the most advanced European university centres, Blaserna established a more modern physics institute in via Panisperna in Rome. In this same institute, a few decades later, Enrico Fermi's famous Roman physics school was born. Blaserna's research spans various fields of physics: properties of real gases, study of the ionization of air, thermodynamics, optics, geophysics, electrotechnics, acoustics, musical physics.

Antonio Pacinotti (1841-1912) has remained known in the history of science for the conception of the famous ring that bears his name, which is none other than the first rudimentary realization of the direct current electric dynamo, the first dynamic machine generating electricity.[23] As he himself recounts, he had the idea one evening during the Second Italian War of

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[21] Giuliani (1996, 2013).

[22] The works in mathematical physics and theoretical physics are characterized by a strong presence of mathematics, but with a different use of it. Mathematical physics works place the main interest in solving the mathematical problem faced and the comparison between mathematics and experience is not generally foreseen. The physical aspects of the problems addressed influence only the choice of the starting postulates, limiting their generality. Their goal is not so much the acquisition of new physical results but that of obtaining a rigorous formalization of already existing physical theories, following a hypothetical-deductive approach. On the contrary, in theoretical physics works, the role of mathematics is auxiliary and instrumental, being used as a language and tool to quantitatively express relationships between physical quantities and to formalize the physical theory, which remains, however, the true object of the research. Theoretical physics works involve the comparison with the experiment and are often themselves generated by seeking an interpretation to previous experimental results. Furthermore, theoretical physics research does not always follow a rigorous hypothetical-deductive method.

[23] Previously, the only way to generate electricity was the electro-chemical static one of the electric cells or batteries.

Independence in 1859 in which he participated as a volunteer sergeant, and it was published for the first time in the June 1864 issue of «*Il Nuovo Cimento*», in a paper entitled *Descrizione di una macchinetta elettromagnetica* (*Description of an electromagnetic machine*). Unfortunately, as with other discoveries made by Italians, even that of the direct current electric dynamo was plagiarized by foreigners. The paternity of the invention of the dynamo was publicly acknowledged to Pacinotti by Galileo Ferraris but never in France. The official priority of the invention of the direct current electric dynamo was recognized to him long after his death, at the Chicago Universal Exposition of 1933 and in 1934 at the Congress of Electrotechnical Scientists, on the occasion of the 75th anniversary of his conception.

In 1900, there were just 71 physicists in Italian universities, making up a scientific community that was too small and poorly equipped to deal with the new experimental discoveries and new ideas of the decade 1895-1905. However, original research works were also recorded in this period, such as, for example, those on magneto-optical effects. In 1885, the engineer Galileo Ferraris (1847–1897) discovered the principle of the rotating magnetic field, which is the foundation of the alternating current electric motor. In 1898 Damiano Macaluso (1845-1932) and Orso Mario Corbino (1876-1937), experimenting on vapors of alkali metals, discovered that the Faraday effect takes on particular characteristics when the wavelength of light approaches that of the absorption lines of the atoms constituting the vapour: the Macaluso-Corbino effect is still today the object of experimental and theoretical study. Corbino also studied the *Hall effect* in bismuth discs, in which a circular symmetry is maintained: the original radial current, produced by a potential difference applied between the center and the periphery of the disc, is partially transformed into circular current by the magnetic field applied perpendicular to the disk. This line of research intertwines with that of mathematical physics of which Vito Volterra is the greatest representative, thus constituting a real Italian tradition of research.[24]

A leading position in Italian physics of this period is held by Antonio Garbasso (1871-1933). His research concerns primarily, since the time of his degree in physics at the University of Turin, electromagnetism and its relationship with optics and in a more advanced age also spectroscopy. After graduation, he followed master classes with Heinrich Rudolf Hertz at the University of Bonn and with Hermann von Helmholtz and Emil Aschkinass at the University of Berlin. He carried out studies and research on X-rays, just discovered by Wilhelm Conrad Röntgen in 1895. Winner of two competitions for the chair of mathematical physics and experimental physics, he chose the latter, teaching experimental physics at the famous "Istituto di Studi Superiori, Pratici e di Perfezionamento" in Florence,[25] succeeding the illustrious mathematician and physicist Antonio Roiti (1843- 1921).[26] In Arcetri Garbasso created the Italian school of cosmic ray physics (Arcetri school), which conquers leading international positions in this line of research thanks to Enrico Persico (1900-1969), Giorgio Abetti (1882-1982) and the students of Garbasso (Antonino Lo Surdo, Rita Brunetti, Giuseppe Occhialini, Bruno Rossi, Franco Rasetti, Francesco Rodolico, Vasco Ronchi, Gilberto Bernardini, Daria Bocciarelli, Lorenzo Emo Capodilista). Garbasso also actively devoted himself to politics as a senator of the Kingdom of Italy from 1924 to 1933 and mayor of Florence from 1920 to 1928 with some brief interruptions. He adhered to the fascist regime but not to the Gentile reform which penalized scientific teaching.

In 1908 Blaserna called to Rome the Sicilian physicist Orso Mario Corbino, professor of Experimental Physics at the University of Palermo, to hold the chair of Complementary Physics. Corbino will continue Blaserna's work of reforming Italian scientific research, leading it to deal with frontier research of that time. Ten years later, in 1918, Corbino will hold the chair of Experimental Physics at the Royal Physical Institute left vacant by the death of Pietro Blaserna and will also replace him in the direction of the Institute. Corbino, in Sicily, had dedicated himself to cutting-edge research in the field of "modern physics" and wanted to transform the Physics Institute in via Panisperna into a center of excellence at the European level, which it will later become with the "ragazzi di Fermi" (Fermi's boys). Corbino is a scientist in the modern sense of the term. His activity is not limited to pure research, but also involves applied research, the industrial world, and politics.

In 1909 the Nobel Prize for Physics was jointly awarded to Guglielmo Marconi (1874-1937) and Karl F. Raun (1850-1918) in recognition of their contribution to the development of wireless telegraphy. It is the first Nobel awarded to an Italian scientist.[27]

The researches of the Italian physicists Antonino Lo Surdo (1880-1949) and Domenico Pacini (1878-1934) were

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[24] Nicotra (2021a).

[25] Which will later become the University of Florence.

[26] The precarious economic conditions of the young Vito Volterra would have forced him to abandon his studies, if he hadn't been helped by Roiti, who offered him a position as preparatory assistant at the "Institute of Advanced, Practical and Improvement Studies" in Florence in 1877 (Nicotra, 2021a).

[27] For the background of this Nobel, see Bischi (2017).

the basis for the research works that will yield the Nobel Prize for Physics respectively to Johannes Stark (1874-1957) in 1919 and to Victor F. Hess (1883-1964) in 1936.

Vito Volterra[28] he is undoubtedly the undisputed leader of the Italian scientific community in the second half of the 19th century and the first decades of the following 20th, until his isolation by fascism after 1926. His contributions to mathematics and physics are so numerous and known at international level to be called by the US newspapers "Mister Italian Science". The public and academic offices of Volterra are numerous and at an international level. His specialty was mathematical physics, but his interests ranged well beyond scientific ones, generously embracing humanistic and historical culture in particular, thus giving a shining demonstration of how false the separation between the so-called two cultures is, the humanities and science. He was also a tireless scientific organizer. Volterra was co-founder and first president of the "Italian Physical Society" in 1897 and does not missed an opportunity to relate Italy with the most qualified international scientific circles, through the exchange of researchers between the scientific communities of different countries, showing an incredible modernity of views on science policy. In 1900 Volterra was called by Blaserna to teach Mathematical Physics at the Royal Institute of Physics of the "La Sapienza" University of Rome, in via Panisperna. We owe him and Orso Mario Corbino the creation of the famous physics school in via Panisperna, which will be led by Enrico Fermi, of whom Volterra followed the first steps of the scientific career by giving him a scholarship from the Rockefeller Foundation in 1924 at the institute directed by Paul Ehrenfest in Leiden. In 1917 he created the "Inventions and Research Office". In February 1919 the "International Research Council" was established, of which Volterra was appointed a member. In the same year Volterra wanted to replicate the international scientific initiatives on a national level, proposing the establishment of the "National Research Council" (CNR), which should have incorporated various already existing research bodies: the "Inventions and Research Office", the "Committee for the Chemical Industries and the Aeronautical Institute". The project was approved by the Orlando government, but due to bureaucratic difficulties the activity of the CNR began five years later, in 1924, with Volterra as its first president.

Certainly, his example must have had a strong influence on the education of Enriques, who was his pupil in Pisa. Many characteristics of Volterra can be found in Enriques: versatility, the unified conception of culture, the passionate commitment to organizing events and scientific institutes of great prestige.

3.4 Chemistry

It is the chemistry of the late nineteenth century that demonstrates, even before the physics of the early twentieth century, that the world at a microscopic level is not characterized by continuity but by discontinuity. In 1912, Max Planck himself, who twelve years earlier had discovered the "elementary quantum of action" and therefore discontinuity in physics, wrote:

> Physical forces, gravity, electric and magnetic attractions or repulsions, cohesion, act continuously; the chemical forces, on the contrary, according to quanta. This law should be connected with that which permits masses in physics to act on one another in any quantity, whereas in chemistry they can act only in sharply defined, discontinuously variable proportions.

Italian chemistry is represented in this period by two illustrious names, Stanislao Cannizzaro and Giacomo Ciamician, and by another equally illustrious who preceded them: Amedeo Avogadro. All three have made fundamental contributions to this science.

In 1811 Avogadro (1776-1856) proposed the famous law that today bears his name: *Equal volumes of gaseous substances, at equal temperature and pressure, contain an equal number of molecules*. Avogadro gave the molecule the role, followed today, of the fundamental unit of chemistry. For Avogadro, reactions are exchanges between molecules. He gave a simple explanation of the relationship between the microscopic and macroscopic world, or between molecules and volumes, providing, among other things, a very simple way to determine the molecular weight. His ideas, however, were too ahead of their time. They clashed with those of the powerful Swedish chemist Jöns Jacob Berzelius, who disputed Avogadro's idea according to which the organic-biological world and the inorganic world are made of the same matter and obey the same physical laws. Furthermore, Berzelius and others contested Avogadro for some anomalies in the application of his law.

We had to wait at least half a century, 1860, before Avogadro's brilliant ideas were accepted by the scientific community, thanks to another great Italian chemist: Stanislao Cannizzaro (1826-1910) from Palermo, a student of the great Calabrian chemist Raffaele Piria (1814-1865), professor at the University of Pisa, considered the founder of modern chemistry in Italy. Cannizzaro accepted August Kekulé's invitation to participate in the

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[28] Nicotra (2021a).

congress of chemists from all over Europe in Karlsruhe, Germany, between 3 and 5 September 1860, during which he once again proposed Avogadro's clear distinction between atom and molecule. On the last day of the Congress, a note of his on atomic weights, written in 1858 and published in the *Sunto di un corso di filosofia chimica* (*Summary of a course in chemical philosophy*), was distributed, a synthesis work of his lessons as professor of chemistry in Genoa. In this note, Cannizzaro explicitly refers to Avogadro's Law of 1811. Cannizzaro's report received the full support of another congressman, the chemist Dmitrij Ivanovich Mendeleev, and thanks to his clarity of exposition, Congress officially accepted Avogadro's hypotheses. Cannizzaro demonstrated very clearly the falsity of the objections posed by Berzelius and others against Avogadro's law: the anomalies they detect in its application are only apparent, because they are due to dissociations of a thermal type. Cannizzaro demonstrated that in every compound every different chemical element is present with at least one atom and finally that molecules, despite being compound entities, have their own specific chemical identity and therefore are the constituent units of matter from a chemical point of view. It was a great international affirmation of Italian chemistry. Harold Hartley will write:

> The Karlsruhe Conference, thanks to the presence of Cannizzaro, was destined to have a decisive influence on the progress of chemical theory and to be a milestone in its history.

Thanks to the new approach of Avogadro and Cannizzaro, chemistry, just like physics, can apply mathematics and chemists can write the formulas of molecules with great precision and ease. Cannizzaro himself, thanks to these new instruments, was able to measure the exact atomic weight of 21 different chemical elements.

Emanuele Paternò (1847-1935),[29] a pupil of Stanislao Cannizzaro, became a professor of chemistry at the University of Turin at the age of just 24 and in 1872 he succeeded Cannizzaro in the same chair at the University of Palermo, later also becoming its Rector from 1886 to 1890. In 1871 he founded the «*Gazzetta Chimica Italiana*» *(Italian Chemical Journal*). His main research concerns photochemistry, in particular the action of light on organic molecules. In 1909, together with George Büchi, he discovered the Paternò-Büchi reaction. Freemason, he held important political offices for many years: mayor of Palermo from 1890 to 1892, senator of the Kingdom of Italy from 1890 to 1935 and Vice President of the Senate from 1904 to 1919, as well as numerous high parliamentary offices.

Raffaello Nasini (1854-1931),[30] after graduating, trained as a chemist in the Roman laboratory of Stanislao Cannizzaro and in the laboratory of Hans Heinrich Landolt in Berlin. Professor of General Chemistry first at the University of Padua and then of Pisa, he devoted himself to research on gases, on the theory of solutions, on electrolytic dissociation and then on electrochemistry, of which he launched the first university course in Padua in 1900, probably the first in all of Italy. After the discovery of argon by Lord Rayleigh and William Ramsay in 1894, he developed a particular interest in terrestrial gaseous emanations which will also lead him to be interested in radioactivity. Nasini's research activity spans various and different fields of chemistry with interdisciplinary results: organic, general, inorganic chemistry, physical chemistry and also industrial chemistry. In the latter field, his studied on the boraciferous fumaroles of Larderello are noteworthy,

Giacomo Ciamician (1857-1922), graduated from the Justus Liebig-Universität of Gießen in Germany, trained as a chemist at the school of Stanislao Cannizzaro in Rome. On 11 September 1912, invited by his American colleagues to the VIII International Congress of Applied Chemistry, he proposed photochemistry as a future research direction for chemistry. On 27 September of the same year, in «*Science*», he published his report: *La fotochimica dell'avvenire* (*The photochemistry of the future*). The proposal of the Trieste chemist was revolutionary for those times: fossil solar energy (alluding to fossil coal) was not the only energy source of solar origin useful for the development of civilization. We can learn from plant photosynthesis, using light to carry out a low-temperature chain reaction, thus creating a low-cost industrial photochemistry: an artificial photochemistry, of which Ciamician is considered the founder. A research program that already in 1903, he had begun to implement with a chemical device capable of capturing solar energy and transforming it efficiently. He had spoken about it in a speech given at the University of Bologna on November 7, 1903.

Mario Betti (1875-1942),[31] who succeeded Giacomo Ciamician in 1923 at the University of Bologna, made contributions in organic, naturalistic and hydrological chemistry. In particular, he carried out original studies on organic bases, on the optical antipode doubling of many compounds and on spontaneous oxidation reactions. The general synthesis reaction of heterocyclic derivatives devised by him is known as the "Betti reac-

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[29] De Condé Paternò di Sessa M., Paternò di Sessa O. (2018).

[30] Macchioni (2019).

[31] Naso (2017).

tion". He has carried out studies on the relationship between the chemical structure and the rotary power of the elements and on the qualities of mineral and thermal waters. From 1939 until his death (1942) he was senator of the Kingdom of Italy.

Original contributions on the study of ternary and quaternary metal alloys and on heterogeneous catalysis are owed to Nicola Parravano (1883 – 1938),[32] a pupil of Stanislao Cannizzaro and Emanuele Paternò.

3.5 Engineering

Many Italian engineers of this period are responsible for the birth of the Building Science, a set of different disciplines of a physical, mathematical and experimental nature: analytical mechanics, theory of elasticity, continuum mechanics, science of materials.

The Casati law of 13 November 1859 on public education unifies, in the rising Kingdom of Italy, the training of engineers and architects with the establishment of the Engineering Application Schools, separating their studies from those of mathematics, following the model French from the Ecole Polytechnique. Thus, were born the School of Applications for Engineers of Turin in 1860 and the Royal Higher Technical Institute of Milan in 1863. Other pre-existing institutions would follow their example, such as the School of Applications of Bridges and Roads existing in Naples since 1811, the School of Pontifical Engineers in Rome since 1817. Furthermore, new Engineering Application Schools were born in Palermo in 1866 and in Genoa in 1870 and still others in Bologna, Padua, Pisa, Turin. Luigi Federico Menabrea (1809-1896), considered one of the greatest Italian scientists of the 19th century, taught at the School of Application Engineering in Turin, having left significant contributions in the field of continuum mechanics and building science. He is also the author of the first scientific work on computer science: *Notions sur la machine analytique de Charles Babbage* published in French in 1842. Menabrea was the first to give a formulation of structural analysis based on the principle of virtual jobs, becoming a forerunner in the introduction of energetic principles in continuum mechanics. His theorem of minimum of the elastic potential energy of a deformable body, enunciated in 1858, is well known in the building science.

At the same School of Engineering Application in Turin, Giovanni Curioni (1831-1887) would teach from 1865, author of the mighty 6-volume treatise, *L'arte di fabbricare* (*The art of manufacturing*), which also contains a course on topography. Numerous memoirs on the science of construction assured him international fame.

To the engineer Eugenio Barsanti[33](1821-1864) we owe the conception and construction of the first internal combustion engine, an idea of his matured in 1841: illustrating to his students at the Collegio San Michele in Volterra, where he taught mathematics and physics, an experiment on the explosion of a incendiary mixture of air and hydrogen, he had the idea of using the rapid expansion of the mixture to raise a piston. In 1851 Barsanti met the engineer Felice Matteucci (1808-1887) with whom he would collaborate for the rest of his life, building various models of internal combustion engines. The two engineers presented the invention of the internal combustion engine on 5 June 1853 at the Accademia dei Georgofili in Florence and, in 1854, obtained the patent in England with the title *Obtaining Motive Power by the explosion of Gases.*

The engineer Quintino Sella (1827-1884) is, together with Luigi Federico Menabrea and Giuseppe Colombo, one of the scientist figures who most have a strong presence in post-Risorgimento Italian politics. Repeatedly Minister of Finance in 1862, in 1864-1865 and in 1869-1873, he contributed to the work of transformation and enhancement of Rome not only as the capital of Italy but also as a European scientific centre. His expertise as an engineer in the mining field earned him various public positions in the sector and his studies in mineralogy various international awards as a scientist. In 1855 he designed and built a machine, the "electromagnetic sorter", based on the principle of electromagnets, to separate magnetite from cupriferous pyrite, obtaining the patent, which was awarded a gold medal at the Universal Exhibition in London in 1862.

The engineer Giuseppe Colombo (1836-1921) was one of the first professors at the Royal Technical Institute of Milan, becoming in 1865 holder of the chair of Mechanics and Industrial Engineering, that he would hold until 1911. In 1897, after Brioschi, he became the second rector of the Milan Polytechnic. He was also a passionate scientific communicator, much appreciated by an audience of all social classes, collaborator and then director of the technical magazine «*L'industriale*», published from 1871 to 1877. Elected a member of parliament in 1886, he was appointed minister of Finance in 1891, Treasury Minister in 1896, first Vice President and then President of the Chamber of Deputies from 1899 to 1900, finally senator of the Kingdom of Italy in 1900. Giuseppe Colombo also possessed a brilliant and courageous entrepreneurial spirit: he understood the

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[32] Fontani, Salvi (2015).

[33] His real name was Nicolò. Eugene is the name he took as a priest in the Scolopi order.

application potential of Edison's dynamos to produce electric lighting and electricity in distributable form, as were gas and water. He asked for and obtained from Edison the exclusive right for Italy to use his method. With John William Lieb, a technician of the Edison Company, under his guidance, on June 28, 1883, in Milan, next to the Duomo, in a building built on the site of a former theater in via Santa Radegonda, he inaugurated the first power plant of the Continental Europe. His most famous writings certainly remain his numerous technical manuals, in particular the *Manuale dell'Ingegnere Civile ed Industriale* (*Manual of the Civil and Industrial Engineer*) (more familiarly known as " *il Colombo*") whose first edition, from the publisher friend Ulrico Hoepli of Milan, dates back to 1877. It will remain for decades, with numerous reissues and updates, the practical guide of generations of engineers, still on the market today.

A place of honor in the construction of the theory of elasticity, to which many mathematical engineers-physicists of that time made fundamental contributions, is undoubtedly occupied by Carlo Alberto Castigliano (1847-1884), a pupil of Curioni. Born into a family of humble origins, during his studies he had to face economic difficulties due to the loss of his father and then also of his stepfather, who had married his mother who was widowed for the second time. In 1871 Castigliano obtained a degree in pure mathematics and in 1873 a degree in civil engineering, discussing the thesis *Intorno ai sistemi elastici. Dissertazione* (*On elastic systems. Dissertation*), published in Turin in the same year. It contains the proof of the principle of elasticity or theorem of minimum work stated, but not proved, by Menabrea in 1858:

> Let us consider an elastic system made up of parts subject to torsion, bending or transversal sliding, and of rods jointed to those parts and to each other: I say that if this system is subjected to the action of external forces so that it deforms, the tensions of the rods after deformation are those which minimize the expression of the molecular work of the system, taking into account the equations that exist between these tensions, and assuming constant the directions of the rods and of the external forces.

This theorem proved Menabrea's principle in more general terms and will be known later as Primo Teorema di Menabrea (or "Menabrea's First Theorem"). This was the object of dispute between Menabrea and Castigliano, who accused Menabrea of plagiarism having not explicitly acknowledged his work. Indeed, in 1875, Menabrea, in another attempt to prove his principle of minimum energy, made use of Castigliano's demonstration, which he simply quoted in a footnote. Another result that made Castigliano famous all over the world is another theorem at the foundation of the theory of elasticity, the theorem of derivatives of work, known as *Castigliano's Theorem*,[34] used for calculating the displacements of a structure and therefore its stiffness with a test load. Once the elastic deformation energy has been calculated with the beam theory, it is sufficient to calculate its partial derivatives with respect to the applied forces to obtain the displacement. Finally, stiffness is the ratio between the applied force and the displacement it causes. Castigliano was appointed a member of the Accademia Nazionale dei Lincei and of the Academy of Sciences of Turin and in 1861 received the title of count. His results on the theory of elasticity, published in various works, were published in French in Turin by the publisher Negro in 1880, in the work *Théorie de l'équilibre des systèmes élastiques et ses applications*. This work, more than any other, made him known throughout the world. Castigliano owes many works of application of the theory of elasticity to engineering, and also the invention of an instrument, the multiplier micrometer, to measure the deformations produced by loads in metal constructions, which was very widespread in railway operations.

Camillo Guidi (1853-1941), who succeeded Curioni in 1882, was responsible for the text *Lezioni di Scienza delle Costruzioni* (*Lessons on the Building Science*) with an axiomatic-deductive approach, which was taken up and perfected by Eng. Gustavo Colonnetti (1886-1968) who took over from him the chair of Building Science in 1928. His book *Principi di statica dei solidi elastici* (*Principles of statics of elastic solids*) dated 1916 was later republished under the title *Scienza delle Costruzioni* (*Building science*) by Einaudi in 1941, remaining a classic for the teaching of that discipline until the seventies of the twentieth century.

3.6 Politics

Another characteristic aspect of Italian science of the period between the 19th and 20th centuries is the political and, in Italy of the Risorgimento, also military commitment by numerous Italian scientists, a phenom-

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[34] The Author formulated it as follows: «… the displacement (or rotation) of an elastic solid element is defined by the partial derivative of the deformation work, expressed as a function of the external forces (or moments), performed with respect to one of these forces that is applied to the element considered at the point and in the direction of the desired displacement". In more modern terms: «For a body whose behavior is part of the 1st order theory, with fixed constraints, not subject to temperature variations, the generalized displacement, relative to a generalized force Pi due to all the forces acting on the body, is given by the partial derivative of the elastic potential energy with respect to the same force Pi » (Cartapati, Gallo Curcio, Piccarreta, 1972, chap. IX).

enon almost completely absent in the political reality of of Italy today.[35]

The Italian scientific community of mathematicians, physicists, chemists and naturalists of the last decades of the nineteenth century and the first decades of the following, on the wave of nineteenth-century positivism, was firmly convinced that science could play a leading role in cultural social and economic development of Italy. The presence of many great Italian scientists in active politics with key governmental positions, bears witness to this. The following became Prime Ministers: the doctor Luigi Carlo Farini and the engineer Luigi Federico Menabrea (three times). The engineer Giuseppe Colombo was President of the Chamber of Deputies. The chemist Emanuele Paternò was Vice President of the Senate from 1904 to 1919. The following became ministers: the engineers Luigi Federico Menabrea, Quintino Sella and Giuseppe Colombo, the mathematician Luigi Cremona, the physiologist Carlo Matteucci and the physicist Orso Mario Corbino. The mathematicians Francesco Brioschi and Enrico Betti were undersecretaries. The following deputies or senators were elected: the mathematicians Ottaviano Fabrizio Mossotti, Francesco Brioschi, Enrico Betti, Luigi Cremona; the physicists Orso Mario Corbino, Giovanni Cantoni, Augusto Righi, Antonio Pacinotti, Galileo Ferraris, Antonio Garbasso; the chemists Emanuele Paternò (senator from 1890 to 1935), Mario Betti, Raffaele Piria, Stanislao Cannizzaro; the physiologists Carlo Matteucci, Jacob Moleschott, Giulio Bizzozero, Camillo Golgi.

4. THE BATTLE OF NEOIDEALISM AGAINST 19TH CENTURY POSITIVISM

On the philosophical level, the main reason for the dispute opened by the Italian neo-idealists against Enriques was the erroneous (or wanted?) identification of Enriques' philosophy with nineteenth-century positivism, opposed by neo-idealism. Enriques, from a young age, strongly and clearly appealed to positivism, but later his criticisms of positivism made him deviate from it clearly, as he himself declared. However, his criticisms were not fully understood by the Italian neo-idealists and his philosophy was superficially branded as positivist. It is therefore appropriate, to understand how much that dispute was animated by other real reasons, to recall the fundamental points of positivist thought and Enriques' reasons for dissent from it.

4.1 Characteristics of positivism

Positivism was a philosophical movement that was essentially the result of the Industrial Revolution of the first half of the 19th century and of the rising capitalism of the most industrialized European countries: England, France and Germany. It was founded on the exaltation of scientific and technological progress. Its name derives from the Latin *positum*, the past participle of the verb *ponere*: "that which is placed", that which is founded, that which has its basis in the reality of concrete facts. The founding thought of positivism was expressed by the French philosopher Auguste Comte (1798-1857) in the famous *Discours sur l'esprit positif* (1844) in five points, summarized as follows (Comte, 1985, pp. 47-48): the opposition of real to chimerical; the opposition of the useful to the useless; the opposition of certainty to indecision; the opposition of the precise to the vague; the opposition of the word "positive" to the word "negative", the opposition of organizing to destroying the new modern philosophy.

4.2 The value of science for positivism and for Enriques

Like positivism, Enriques gave science a primary place in the theory of knowledge. On the other hand, the points of divergence between the positivist thought and the philosophical thought of Enriques on the value of science are various and substantial.

The first major point of divergence is the purely utilitarian value of science for positivism,[36] while for Enriques it is above all fully theoretical and only subordinately utilitarian.

For positivism, science has absolute value, since its conquests are definitive and fully true; for Enriques, on the other hand, science has only a relative value because it is always approximate, never concluded, being in a continuous evolution and improvement:

> … science is a process of successive approximations which indefinitely prolongs its roots in the unconscious inductions of common life, and pushes its branches ever higher, touching on an ever wider, more certain and more precise knowledge.[37]

and because his purchases imply other previous ones:

> Science as well as approximate is also relative. This implies that the meaning of a scientific fact must be subordinated at all times to all the knowledge acquired. Pre-

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[35] Bottazzini and Nastasi (2013); Nicotra (2021b).

[36] As for neo-idealism.

[37] Enriques (1912, pp. 20,21).

> cisely because everything is relative, it is not permissible to take any fact or principle as an isolated one, nor to establish an absolute hierarchy of knowledge which places a primitive knowledge independent of the development of knowledge considered as a whole.[38]

A consequence of the relative nature of science is Enriques' criticism of the absolute classification of the sciences enunciated by the positivists Auguste Comte and Antoine Augustin Cournot, founded instead on the conviction of the absolute value of scientific knowledge.

Furthermore, Enriques contested positivism for limiting itself to explaining the "how" without seeking the "why" of a phenomenon:

> … hypotheses and imaginative representations lead beyond positive science. In this respect the causal explanation implies something more than the simple answer to the question of "how a certain phenomenon occurs". Science goes beyond this explanation when it tries to explain the "why."[39]

Positivism identifies the "brute fact" with the "scientific fact", attributing a scientific value to experimental or observational data. Comte stated that science must be made up only of ideas, hypotheses and theories that do not go beyond the reality of directly available data, thus affirming the absolute objectivity of the brute fact.

For Enriques, on the other hand, "brute facts" (experimental or observational data) have no meaning in themselves but receive it from the ideas according to which they are interpreted, ordered and correlated, thus becoming "scientific facts":

> But this doctrine [positivism], taken literally, would remove all value from science, reducing it to a simple collection of recipes. Because even what we rightly call "facts" receive their meaning precisely from the ideas according to which they are interpreted. […] A fact is never the brute encounter of certain sensible data, but the connection of several data of a certain order, dominated by an idea: its affirmation always implies recognizing objective and subjective data, separable up to a certain point, but never in an absolute sense.[40]

It is in this passage from the "brute fact" to the "scientific fact" that the construction of scientific knowledge consists of:

> Whoever intends to understand the differences between the brute fact in the vulgar sense of the word, and the scientific fact, first of all sees in the latter a much clearer conditional character. […] So a scientific fact grows, so to speak, from a multitude of brute facts contained in it; it gains in generality as it sums up new, more extensive relationships in itself.[41]

Enriques' distinction between brute facts and scientific facts is in perfect agreement with Poincaré's thought:

> We cannot be satisfied with pure and simple experience. No, this is impossible; it would be tantamount to completely disregarding the true character of science. The scientist must order; science is made with facts, as a house is made with stones; but a heap of facts is as little a science as a pile of stones is a house.[42]

From his own words the collocation of the philosophical-scientific thought of Enriques in the field of that experimental rationalism expressly mentioned by him is clear:

> But on the other hand, we can see how every observation and every experience has scientific value only insofar as it is based on a reasoning; otherwise he is reduced to waiting for nature to be kind enough to instruct us, answering by chance questions that we don't know how to ask or interpret.[43]

It is that physical-mathematical method of investigation which Galileo and Newton assumed as a paradigm for the birth of modern science, founded on the symbiosis between experiment and mathematics, which had – it must be pointed out – a brilliant precursor in Leonardo da Vinci:

> I believe that instead of defining what the soul is, which is something that cannot be seen, it is much better to study those things that can be known through experience, since only experience does not fail. And where one of the mathematical sciences cannot be applied, one cannot be certain.[44]

Enriques' highly interdisciplinary mentality and the particular place he has always assigned to psychology widen the domain of ideas according to which raw facts must be interpreted, ordered and correlated so that they become new acquisitions of science:

> The study of science, conceived as a "fact", must be aided by the teachings of History and the results of Psychology.[45]

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[38] There.

[39] Enriques (1945, p.107).

[40] Enriques (1936 b).

[41] Enriques (1906, pp.101, 102).

[42] Poincaré (1950, pp. 137-138).

[43] Enriques (1906, p. 126).

[44] Leonardo da Vinci (Codice Atlantico a 119 v).

[45] Enriques (1906, p. 79).

Even more explicitly, Enriques mentions the role of psychology in the genesis of scientific theories:

> Now in this second aspect, scientific theory appears to us as a psychological development, which proceeds in a properly inductive sense, that is, it draws new hypotheses from new associations, and from the verification of these it rises to more extensive and more precise associations and hypotheses. [46]

For positivism, reality is the experimental or observational datum itself, while for Enriques, reality is not identified with the experimental datum, but with what remains invariant in its mathematical representation:

> …the knowledge of a real always implies the coordination of conveniently associated data. In other words, reality is not a pure datum but something constructed thanks to the coordinating rational activity.[47]

This identification of reality with the invariance of its mathematical representation will be found several years later in Paul Dirac, for whom the Renaissance motto «*pulchritudo splendor veritatis*» was valid, i.e., the identification of the beauty of a mathematical formula with its truth. But why does beauty for Dirac lead to truth? The answer is simple: an equation, for Dirac, is beautiful if it contains invariants and invariance guarantees truth: therefore, beauty leads to truth.

5. THE SCIENTIFIC PHILOSOPHY OF FEDERIGO ENRIQUES

We have seen previously what results of primary importance and what international connotation reached Italian science in the second half of the nineteenth century and in the first years of the new century. Enriques had fallen into that international climate of cultural and social modernization which had science and scientists as its driving force and among these, first and foremost, Volterra. Enriques was perhaps the Italian mathematician closest to the multifaceted scientific and cultural personality of the latter, of whom he had been a pupil. Unlike Volterra, however, he never exposed himself politically and instead, unlike his Master, he cultivated strong philosophical interests. Like Volterra, he had exceptional qualities as an indefatigable cultural organizer and firmly held the idea of interdisciplinarity, as a corrective to the cultural isolation produced by the excesses of specializations. Furthermore, like Volterra, he rejected a clear distinction between pure and applied mathematics and demonstrated a remarkable ability to weave broad and intense cultural relationships with scientists and philosophers from all over Europe: France, Germany, United Kingdom, Belgium, Russia, Sweden. He had a privileged relationship with France,[48] due both to the fact that French was his second mother tongue (being Federigo's mother of French-speaking origins) and to the particular consonance of his philosophical and scientific thought with that of many French scientists and philosophers. The foreigners with whom he had cultural exchanges form a long list of prominent figures in the scientific and philosophical fields.[49] Evidence of these contacts can be found in the copious correspondence that Enriques maintained with his brother-in-law and collaborator Guido Castelnuovo, between 1894 and 1905.[50]

Many of his works were written directly in French and published in France before being translated and published in Italy. From 1895 to 1946 (the year of his death) as many as 56 works by Enriques were published in French, and he was also awarded various important positions in France, such as that of corresponding member of the "Académie des Sciences morale et politiques" and that of director of the series "*Philosophie et histoire de la pensée scientifique*" in the series "*Actualités scientifiques et industrielles*" of the publisher Herman of Paris.[51]

Federigo Enriques did not recognize the *status* of an autonomous discipline to philosophy, as he considered it a synthesis of critical observations on the sciences, referring to the thought of the pre-Socratic philosophers. He criticized the use of the term philosophy as «… a noun rather than an adjective (philosophical activity or spirit)».[52] For this reason it makes no sense to speak of a philosophical system of Enriques, but rather of his cultural program based on philosophy understood as a critical synthesis of the various sciences, a positive gnoseology, a philosophy of knowledge understood as the construction of a system of disciplines in which science

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[46] Enriques (1906, p. 150).

[47] Enriques (1912).

[48] Nastasi T. (2012).

[49] Henri Poincaré, Emile Picard, Pierre Hum- bert, Emile Borel, Paul Emile Appell, Jacques Hadamard, Paul Painlevé, Xavier Léon, Emile Meyerson, Héléne Metzger, Henri Berr, André Laland, Henri Bergson, Léon Brunschvicg, Louis Couturat, Edouard Le Roy, Lucien Lévy-Bruhl, Alexandre Koyré, Georges Sarton, Charles Singer, Wilhelm Ostwald, Max Noether, Felix Klein, Ernst Mach, Albert Einstein, Otto Neurath, Franz Brentano, Gösta Mittag-Leffler, Oscar Zarisky.

[50] Bottazzini, Conte, Gario (1996).

[51] Enriques published in this series a series of six volumes, which came out between 1936 and 1939, some of which (such as, for example, Les Ioniens…) in collaboration with Giorgio de Santillana. In 1936: *Les Ioniens et la nature des choses; Le problèmes de la matière: Pythagoriciens et Eléates; Les derniers "Physiologues" de la Grèce*. In 1937: *Le problème de la connaissance; Empirisme et rationalisme grecs; Platon and Aristote;* In 1939: *Mathématiques et astronomie de la période hellénique.*

[52] Enriques (1912, pp. 235-236).

(particularly mathematics), philosophy, history, didactics and educational sciences interact organically in the formation of knowledge. A more concise definition of scientific philosophy can be: unification of knowledge on a scientific basis, with the history of science and the philosophy of science in a central position.

Although not constituted in a philosophical system, it is possible to speak of a philosophical thought of Enriques, characterized by the composition of different antitheses in new syntheses:

1. Reason-Experience in experimental rationalism;
2. Rationalism-Historicism in historical rationalism;
3. Intuition-Logic united in a single active process;
4. Induction-Deduction united in the single inductive-deductive process.

Enriques' scientific philosophy was conceived as a philosophical approach of the scientists themselves to science, and consequently brought together philosophy and science in the same scientist, as at the dawn of philosophical thought.

The idea of a scientific philosophy conceived instead as a collaboration between scientists and philosophers must have been widespread enough perhaps even before the publication of the philosophical writings of Enriques, if already in 1906 the Unione Tipografico Editrice di Torino (UTET) published a large volume of 868 pages, titled *Saggio di Filosofia Scientifica (Pandynamismo) Libri Tre (Physis-Psyche-Ethos)* signed by Roberto Gaetani D'Aragona. In the "Introduction" the Author clearly indicates the meaning he intends to give to Scientific Philosophy:

> The function of Philosophy, as we have just said, is to coordinate, select, synthesize the products of the individual sciences for a high rational, economic, biological purpose, whereas that of the individual sciences consists in coordinating, selecting, synthesizing in short and comprehensive formulas the results of sensuous experience in order to know the causal link between a group of observed facts. But Philosophy has not always been understood in this way, the individual sciences have not always been distinguished from it. […] it is also true that [man] has confused the proper function of Philosophy with that of the individual sciences. Indeed, not even today does everyone agree on the goal that Philosophy must set itself, on its limits, on its method; just as there is no agreement on the proper function of each special science.[53]

D'Aragona dwells extensively on the interdisciplinarity that at the time involved scientists of various disciplines (physicists, chemists, physiologists, mathematicians, etc.) and formulates a clear definition of Scientific Philosophy, as it was understood at the time:

> … the philosophers will bring together the results obtained by all the technical scientists, and, working on this collected, elaborated, selected, coordinated material, they will create a new synthesis, they will build the Scientific Philosophy, which will be the true, the healthy, and not the fantastic, convoluted, empty Philosophy, based on nothing. […] Philosophy will be the heart of the scientific organism, the technical sciences, the single organs.[54]

The idea of Enriques' Scientific Philosophy can also be found in the famous *Wiener Kreis* (*Vienna Circle*),[55] founded in Vienna in 1922 by the German physicist and philosopher Moritz Schlick, murdered in 1936 by the Nazis. The Wiener Kreis was a philosophical and cultural club which brought together many prominent philosophers and scientists of the time.[56] In this circle Schlick founded a new philosophical direction, known by the names of logical positivism or neo-positivism or physicalism, which spread throughout the rest of Europe and in the Anglo-Saxon Countries. For his studies in the history of science, for his adherence to the project of a unitary encyclopaedia of science and for his conception of the new "scientific philosophy", Enriques figures, in the *Manifesto of the Club*[57], a reference thinker alongside Henri Poincaré, Hermann Ludwig Ferdinand von Helmholtz, Bernhard Riemann, Ernst Mach, Pierre-Maurice Duhem, Giuseppe Peano, Ludwig Boltzmann and Albert Einstein.

In fact, the philosophical-scientific approach of the Vienna Circle, expressed in its *Manifesto*[58] written by Hans Hahn, Rudolf Carnap and Otto Neurath, in 1929 with the title *Wissenschaftliche Weltauffassung* (*Scientific Conception of the world*), contains all the salient features of Enrique's thought: the unitary conception of sci-

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[53] D'Aragona (1906, pp.3,4).

[54] D'Aragona (1906, p. 5)

[55] Initially named "Verein Ernst Mach" (Ernst Mach Company) by Hans Hahn in honor of Ernst Mach.

[56] Ernst Mach, Rudolf Carnap, Otto Neurath, Philipp Frank, Friedrich Waismann, Hans Hahn, Gustav Bergmann, Carl Menger, Herbert Feigl, Viktor Kraft, Ludwig von Bertalanffy, Hans Reichenbach, Kurt Gödel, Carl Hempel, Alfred Tarski, Willard Van Orman Quine, Alfred Julius Ayer, Arne Naess. Ludwig Wittgenstein and Karl Popper did not physically attend the Circle but maintained cultural relations with it.

[57] https://www.phil.cmu.edu/projects/carnap/editorial/latex_pdf/1929-5.pdf

[58] H.Hahn, L.Carnap, O.Neurath, *Wissenschaftliche Weltauffassung. Der Wiener Kreis* (*The scientific conception of the world. The Vienna Circle*) dedicated to Moritz Schlick was published in the first international conference of the Circle held in Prague in 1929. In Italian: H.Hahn, L.Carnap, O.Neurath, *La concezione scientifica del mondo* (1979), edited by A. Pasquinelli Bari: Laterza.

ence, scientific research as a collective work, the denial of an autonomous existence of philosophy as a discipline in itself, the intelligibility of scientific knowledge, the project of a scientific philosophy.[59]

6. THE CLASH FOR THE PHILOSOPHICAL AND CULTURAL HEGEMONY IN ITALY

Enriques' philosophical thought could not be appreciated by Gentile and Croce, not because of his presumed adherence to nineteenth-century positivism, as they contested and in reality denied by Enriques himself, but because it profoundly undermined the cultural leadership of their philosophy.

Federigo Enriques was not only a great mathematician, a philosopher and a historian of science but also a great teacher, a passionate cultural organizer, an innovative reformer of culture: in short, an all-round intellectual of great stature. It is essential to underline this versatility of his figure as an intellectual, because it is closely connected with his cultural ideal of synthesis of the different sciences and more generally of the different "knowledge", in the spirit of the unity of culture which he contrasted with the centrifugal tendencies of the various "particularisms", as he called specializations. A cultural ideal opposite to that of Croce and Gentile, for whom it was "vain hope" to believe that the analytic and synthetic tendencies could coexist in a single philosophical perspective.

The international connotation of the scientists' work was not very welcome to fascism, to which Gentile adhered. As Pietro Blaserna said in his introduction to the collective volume *Cinquanta anni di storia italiana* (*Fifty years of Italian history)*, published on the occasion of the first fiftieth anniversary of the unification of Italy, it «flies like an eagle and knows neither limitations nor frontiers, nor customs tariffs and differentials». This absence of «frontiers» certainly could not have pleased fascism, which in fact always exerted a control action on the activities of Italian scientists, contributing to the dismemberment of Fermi's group of physicists.[60] The emigration of almost all the "boys of via Panisperna" was influenced not only by the racial laws of 1938 but also by the usual reasons for the lack of funds destined for research, which became very strong with the death of Corbino and Marconi, their "patrons", both passed away in 1937. In contrast to this international connotation of Italian scientific community, also aimed at pursuing a modernization and progress of Italian society, we find instead the culture of the neo-idealism of Croce and Gentile characterized by a provincial attachment to the cultural traditions of our country, strongly biased towards the literary-humanistic disciplines.[61]

Furthermore, his affirmed and acclaimed versatility placed Enriques, in the eyes of the two greatest Italian philosophers of the time, as a formidable opponent in the conquest of cultural hegemony in Italy, unlike other men of science of great fame and prestige, such as Giuseppe Peano , Giovanni Vailati and Vito Volterra, but much more "confined" in their respective scientific programs and, therefore, considered harmless by Croce and Gentile,[62] since culture in Italy is traditionally only humanistic:

> Croce and Gentile are not worried by those "two or three modest and withdrawn logicians who cultivated an Eng-

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[59] «The scientific conception of the world is characterized not only by peculiar theses but, rather, by the basic orientation, by the perspective, by the direction of research. It has as its goal the unification of science. Its intention is to connect and coordinate the acquisitions of individual researchers in the various scientific fields. From this program, derives the emphasis on collective work, on intersubjectivity, as well as the search for a global system of concepts. Accuracy and clarity are pursued, dark distances and impenetrable depths rejected. In science there is no "depth"; everywhere is the surface: all experience constitutes an intricate network, sometimes inscrutable and often only partially intelligible. Everything is accessible to man and man is the measure of all things. In this there is an affinity with the sophists, not with the Platonists; with the Epicureans, not with the Pythagoreans; with all advocates of the mundane or the earthly.

The scientific conception of the world knows no insoluble riddles. Clarification of traditional philosophical questions leads, in part, to unmasking them as pseudo-problems; in part, to convert them into empirical questions, subject, therefore, to the judgment of experimental science. Precisely this clarification of questions and statements constitutes the task of philosophical activity, which, however, does not tend to establish specific "philosophical" statements. The method of this clarification is that of logical analysis» (Hahn, Carnap, Neurath, 1979, pp.74,75).

[60] Franco Rasetti (1901-2001) emigrated to Canada in 1939, where he taught at the Laval University of Québec; Emilio Segrè (1905-1989) in 1938 was at the University of California, "Berkeley". In that same year, the enactment of the fascist racial laws forced him to stay there for the rest of his life; Since 1936, the year in which he went to Paris to carry out studies with Irène Curie and Frédéric Joliot, on the collisions of neutrons with protons and on the electromagnetic transitions between isomers, Bruno Pontecorvo never returned to Italy, living and working in various foreign countries (USA , United Kingdom, Finland and finally USSR); Enrico Fermi (1901-1954) after receiving the Nobel Prize, at the end of 1938, moved directly to the USA with his wife of Jewish origins, and remained there until his death.

[61] Lombardo Radice (1982).

[62] Vailati, who could have been a potential opponent in the conquest of philosophical hegemony in Italy, died in 1909. Peano was now on the threshold of retirement and his philosophical interests were limited to formal logic understood as an integral part of mathematics. While Volterra firmly shared – together with others such as Enrico Betti, Ulisse Dini, Luigi Bianchi, Giuseppe Peano and Enriques – the aversion and concern for the separation between humanistic studies and mathematics, however, he devoted a large part of his activity to the applications of science aimed at socio-economic progress of Italy.

> lish garden next to their house".[63]

The «two or three modest and withdrawn logicians» are Peano, Vailati and Volterra in the allusive words of Giovanni Papini, quoted above. Enriques, then, combined with his cultural versatility an extraordinary ability to organize events and cultural institutes of the highest order, which reflected the absence of boundaries of specialization in his fervor for unitary culture.

Enriques' main opponents in the battle for philosophical and cultural hegemony in Italy were certainly Giovanni Gentile and Benedetto Croce, but the style, intensity and results of the controversies that characterized that battle were very different for the two greatest Italian philosophers. Therefore, it is convenient to treat Enriques' relations with Gentile and with Croce separately.

Furthermore, the controversy that saw them as protagonists for the philosophical and cultural hegemony in Italy included different aspects: on the surface they only seem to be ideological differences, but behind the scenes clear personal jealousies emerge on the part of the two idealist philosophers, who took the form of a real "conspiracy" against Enriques.

6.1. Enriques and Gentile

A useful source for forming an idea of the evolution of the personal relationships between Enriques and Gentile are the 24 letters sent by the Livorno mathematician to the Sicilian philosopher in the period from 14 June 1907 to April 1942.[64]

Gentile's criticisms of Enriques always remained within the orthodox limits of ideological differences, expressed in articles, without ever bordering on indecorous denigration, as instead happened with Croce. There was always a relationship of mutual esteem between the two, despite the "difference of views", which strengthened after 1923 to the point of assuming the connotation of a true friendship, which can be explained by Gentile's undisputed intellectual honesty which allowed him to recognize other people's commendable goals, beyond differences of views, both in the cultural and political fields.[65] The heading of the letters mentioned reflects and confirms this evolution of the interpersonal relationships between Enriques and Gentile, passing from the « Distinguished Colleague», of the letters from 14 June 1907 to 12 June 1910, to the «Dear Minister», of 23 December 1922 and 15 April 1923, to «Dear Gentile», of the letters between 20 December 1924 and 8 December 1940, ending with a «Dearest Friend» in the letter of April 1942, written by Enriques to share with Gentile his «affectionate participation» in the «immense pain» for the loss of his son, the theoretical physicist Giovanni Gentile junior, known as Giovannino. Gentile's attitude towards science changed radically after the First World War, probably due to the influence of both his pupil Ugo Spirito and his sons Gaetano (doctor) and Giovannino (theoretical physicist). Science had fully entered the Gentile family, as transpired, in 1935, from Giovanni Gentile's own words:

> Which [Italian scientists] have therefore opened the doors of their Congresses to philosophy. And it is to be hoped that the philosophers will abandon their tradition of their special Congresses.[66]

The controversy between Enriques and the Italian neoidealists began in 1908 with Giovanni Gentile, following his severe criticism of Enriques' volume *Problemi della scienza* (*Problems of science*) (1906), which appeared in «*La Critica*» (1908, VI, pp. 130-146), in which the Sicilian philosopher denied Enriques' scientific philosophy the value of a true philosophy, «oscillating between philosophy, never achieved, and the particular science hardly philosophized, with I don't know what advantage of the scientific spirit». Gentile rejects Enriques' conception of a science that is never complete and always perfectible, which he attributes to the incorrect identification between the history of knowledge and knowledge: «The progressive correction of knowledge is the history of knowledge», while knowledge is a "vision of the eternal" since the "formal theory of knowing" is out of time. Furthermore, Gentile disputes the unitary recomposition capacity of individual scientific acquisitions, which is the heart of the spirit of the scientific philosophy advocated by Enriques thanks to the «substitution […] of social work for individual efforts». He considers it a contradiction and a «vain hope»:

> What is this All of the enthusiasts of the new scientific philosophy? […] The contradiction […] between the analytic tendency and the synthetic tendency, which today fatally oppose each other in the mind of every scientist, is a true contradiction, and more profound than Enriques thought because it is basically the fundamental contradiction of thought.[67]

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[63] Guerraggio, Nastasi (1993, p. 58).

[64] Guerraggio, Nastasi (1993).

[65] During the Republic of Salò, when, on 21 November 1943, he was nominated by Mussolini as president of the Italian Academy transferred from Rome to Florence, Gentile proposed to the Duce the appointment of academics, including non-fascists.

[66] Guerraggio, Nastasi (1993, p.68).

[67] «*La Critica*», a. VI 1908, pp. 130-146; also in Paolo Casini, *Federigo Enriques e i filosofi neoidealisti.*

The denial that the analytic and synthetic tendencies of science can coexist in a single philosophical perspective, in the new scientific philosophy, leads Gentile to harshly criticize also the validity of the «*Rivista di scienza*» (*Journal of Science*) founded by Enriques the year before, in 1907, with the engineer-philosopher Eugenio Rignano, the chemist Giuseppe Bruni and the doctors Antonio Dionisi and Andrea Giardina:

> A magazine which discusses, in the same issue, the electromagnetism of the universe, mediumship, the relationship between chemistry and biology, the need for light that plants have, consciousness, the Austrian economic school, the main laws of sociology , of the origins of religious celibacy, of the reform of the teaching of elementary mathematics, etc., in my opinion, can only encourage scientific amateurism, of which I don't know how much science can benefit.[68]

An accusation, that of "scientific amateurism", which clashes with the plethora of excellent names of the collaborators of the Journal. Among the Italians: Vito Volterra, Giuseppe Peano, Guido Castelnuovo, Giovanni Vailati, Orso Mario Corbino, Enrico Fermi, Edoardo Amaldi, Camillo Golgi, Gino Loria, Ludovico Geymonat. Among the foreigners: Bertrand Russell, Ernest Rutherford, Sigmund Freud, Henri Poincaré, Emile Picard, Albert Einstein, Arthur Eddington, Werner Heisenberg, Rudolph Carnap, Otto Neurath, Ernst Mach, Hans Driesch, Pierre Janet, Jules Tannery.

Gentile, however – as Enriques challenged him in 1909 in the preface to the second edition of the *Problemi della Scienza* (*Problems of Science*) – dwells only on chapter III ("The problems of logic") of the book, criticizing Enriques' empirical reduction of logic to psychology. Gentile ignores the remaining chapters IV, V, and VI dedicated to geometry and mechanics, not having the preparation to understand their content, as he himself confessed in a letter to Croce:

> Tomorrow, I hope to write the review of Enriques, which is a book that I don't know which way to take, not to say too badly with the fear of not having understood, through my fault, what good there may be.[69]

Enriques replies to Gentile's criticism, without however quoting it, in the "Preface to the second edition" of *Problems of Science* (1909), claiming the originality of his research in the gnoseological theme:

> But most of the more superficial critics, among the philosophers who have examined my work, have believed they could limit themselves to the first two chapters, and have not seen at all the new solution to the problems of Kantian criticism developed in the subsequent ones.

The following year, in 1910, Enriques polemically tackled the Hegelian dialectic in the article *La metafisica di Hegel considerata da un punto di vista scientifico* (*Hegel's metaphysics considered from a scientific point of view*),[70] published in the «*Rivista di Filosofia*» (*Journal of Philosophy*)[71] in which he qualified Hegel «as a great fantasy and a *pauvre intellect*» while recognizing in him «an extraordinary imagination, poetic genius, coherence of sentimental inspiration».

Hegel's style, continues Enriques, «... already reveals to us a fundamental aspect of the Hegelian psyche which is adverse to scientific thought». Enriques defined the Hegelian dialectic as an «interesting psychological document, or a tissue of empty verbal associations of formalism», making fun of some obvious "horrors" of the Hegelian dialectic: the absurd a priori deduction of the law of gravitation; the definition of light as a pure ideality, which is particularized in the star and recovers its universality in the sun; the dialectical figure who assimilates the obligatory trajectory of the moon to the "rigidity" of the concept and the free trajectory of comets to the "dissolution" of the same logical entity; the magnet seen as a syllogism, where the poles are joined in the middle term.

Croce reads Enriques' article on Hegel and urges Gentile to reply:

> You will have seen Enriques's nonsense on Hegel's Metaphysics, published in the place of honor in the "Revue de métaphysique". It is also full of insolences against the Hegelians. If you want to dedicate a review or a small variety (but short: 3 or 4 pages at the most) go ahead and send it to me soon.[72]

But he adds in the subsequent letter to Gentile dated February 3, 1910:

> do not accentuate too much the polemic against his person and against his Society.[73]

Gentile follows Croce's "advice" by writing the article *Scherzi innocenti intorno alla metafisica hegeliana*

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[68] «*La Critica*», a. VI 1908, p. 130-146; also in Guerraggio, Nastasi (1993, p. 59).

[69] Letter dated Palermo, July 26, 1908, in Giannantoni (1974, p. 253).

[70] Enriques (1910).

[71] Immediately afterwards translated into French: *La métaphysique de Hegel considérée d'un point de vue scientifique* in the review «*Revue de métaphysique et de morale*», 1910, VIII, pp. 1-24).

[72] Croce A.(1981).

[73] Croce A.(1981, pp. 368-370).

(*Innocent jokes around Hegelian metaphysics*) in «*La Critica*», reacting harshly to those that:

> they seem insolent and they are not. They are the only way in which Professor Enriques is capable of expressing his quite dispassionate historical judgment about the value of Hegelianism considered from his point of view: they are the forthright, naively accepted, written and published expression of what Professor Enriques feels, reading the Hegelian Encyclopedia.[74]

This is the only occasion in which Gentile crosses the ideological terrain of contrast, indulging in hostile personal appreciations:

> Let's say it frankly: Prof. Enriques demonstrates in a thousand ways the most commendable practical zeal for the increase of philosophical studies in Italy, and has even come to create the name, if not yet the reality, of an Italian Philosophical Society. But shouldn't he also do something to his own advantage, endeavoring to educate himself mentally and form a clear concept of the present state of philosophy, conscientiously studying its history? [75]

6.2. Enriques and Croce

Even Benedetto Croce with regard to the «*Rivista di Scienza*» expresses, in «*La Critica*», a negative judgment on its multidisciplinarity:

> There is and cannot be anything in common except the material unit of the periodical, a unit which is not that advantage (when it is an advantage) that one can believe: because it can also be a damage, and a serious one.

The controversy became more bitter with the subsequent intervention by Benedetto Croce in his interview given to Guido De Ruggiero in "*Il Giornale d'Italia*" on April 16, 1911, immediately after the IV International Congress of Philosophy in Bologna:

> … willing professor Enriques, who with zeal but little preparation dabbles in philosophy" […] "and takes on the burdens of the philosophers' congresses, as meritorious as mine would be meritorious and disinterested, if I organized mathematics congresses.

His resentment at the intrusion of the mathematician Enriques into his field of study, philosophy, which he believes should be cultivated only by professional philosophers, is evident in Croce's words.

Croce, unlike Gentile, denies any cognitive value to science, considered a set of "pseudo-concepts" (abstractions derived from empirical data) as opposed to the "pure concepts" of philosophy (specific cognitive forms of reality as a *continuum* of infinite individuations), recognizing them only as a practical utility. Position, therefore, in stark contrast to that of Enriques.

The controversy soon degenerates into personal attacks by Croce against science:

> Scientific knowledge is not true knowledge, but devices of a practical order. The related concepts are pseudo-concepts, suited to tiny minds not to the universal minds of idealist philosophers.
> Men of science […] are the embodiment of mental barbarism, deriving from the substitution of schemes for concepts, of piles of information for the philosophical-historical organism.[76]

On the contemporary discoveries and conceptual arrangements of Frege, Peano and Russell, Croce expresses himself as follows:

> The new devices [of mathematical logic] are to be recommended, if anything, to traveling salesmen [so that] they persuade customers and merchants of the usefulness of the new commodity and buy it […] their philosophical nullity remains […] fully proven.[77]

And against Enriques:

> With the procedures of prof. Enriques one can, at most, when one is lucky […], drag along a crowd of the ignorant […] nothing more treacherous than the crowds of the ignorant […] like nothing more faithful and persistent than the little chosen ones who, feeling joined by truths, they know they have the present and the future for themselves.[78]

As Giorgio Israel states, the polemic «continued with decreasing intensity until 1912 without definite conclusions. However, Croce's authority had the practical effect of making a large part of the philosophical and cultural circles line up on positions hostile to the E., for which the end of the controversy was commonly perceived as a "defeat" of the E. ».[79]

Croce does not even spare Francesco Severi, who had criticized the intolerance of idealism, admonishing him in a poisonous way:

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[74] Gentile (1910).
[75] Gentile (1910, p.145).

[76] Croce B. (1908).
[77] Croce B. (1909).
[78] Therein.
[79] Israel, (1993).

> To the prof. Severi who is a man of study I would like to address a prayer; and it is not to risk discussing concepts that belong to a field foreign to him, and to enter in which I don't know if he has the inclination (everyone has their own inclinations), but he certainly doesn't have the preparation.[80]

7. THE CONSPIRACY OF CROCE AND GENTILE

It has been said previously that the presence, in the "controversy" between Croce, Gentile and Enriques, of a strong personal component raises the suspicion of a real "conspiracy" concocted by the two philosophers, to eliminate from the Italian cultural scene their most fearsome opponent. The correspondence between Croce and Gentile seems to corroborate this further reading of the clash.

Gentile's scientific lack of preparation confessed to Croce, in preparing to write in «La Critica» the review, warmly supported by Croce, of the *Problems of science*, suggests that more than the intellectual need for an "honest" critique of the book by Enriques has guided the pen of Gentile the will of a personal attack instigated by Croce. A clash probably matured from certain jealousies shared with his friend Croce, which arose from the alternation, within the space of only two years of important events which constituted many dangerous signs of encroachment by Enriques in the field where Croce and Gentile felt undisputed protagonists. In 1906 the "mathematician" Enriques had created the "Italian Philosophical Society" and made his debut in the philosophical field with the *Problems of science*. The following year, in 1907, he had founded «*Journal of Science*» and organized the 2nd congress of the "Italian Philosophical Society" in Parma, in which Enriques, with his inaugural speech *Il rinascimento filosofico nelle scienza contemporanea e il valore della scienza* (*The philosophical renaissance in contemporary science and the value of science*)[81] underlines the importance of the debate that logicians, physicists and mathematicians have opened or intend to start with philosophers. Finally, in 1908, at the III International Congress of Philosophy, Enriques was invited to participate as President of the Italian Philosophical Society, receiving the task of organizing the 1911 IV International Congress in Bologna.

Enriques always made himself very available for a serious and constructive dialogue with Gentile and Croce, despite the declared strong ideological differences, showing on several occasions his willingness to involve them in all his initiatives of a philosophical nature. But he always received, in response, attitudes of total closure and hostility.

In a letter dated June 14, 1907, Enriques explicitly invites his "colleague" Gentile to participate in the 2nd Congress of the Italian Philosophical Society (SFI), to be held in September in Parma, in conjunction with the Congress of the Italian Society for the Progress of Sciences:

> Distinguished Colleague,
> … Now it would be desirable for our meeting to be attended largely by the most valiant philosophers. […] The purpose of this letter is precisely to ask you to come to the Congress and to bring you some communication, eg. on the new Hegelian movement in Italy or on any other theme you prefer.
> I will add that I would also gladly invite Croce; but I am held back by the doubt that my question does not please him, since he is a stranger to our Society.[82]

But Gentile refused Enriques' invitation, as can be seen from the subsequent letter dated 15 July written to Gentile from Riccione, where Enriques was on holiday. In the same letter, Enriques' willingness to establish a wider collaboration with Gentile also clearly appears, which concerned both the management of the SFI itself and the participation in the III International Congress of Philosophy scheduled for the following year, in 1908, in Heidelberg:

> Dear Colleague,
> … I am very sorry that you cannot intervene also because I was counting on consulting with you on many issues that concern our social action [that of the SFI], and on what we can do to prepare for the next congress in Heidelberg.[83]

Furthermore, Enriques tries to involve Gentile in the project of a series of philosophical texts to be produced with the Sandron publishing house:

> With Sandron we are in principle in agreement for a collection of works under the title: Library of the Italian Philosophical Society. Now we need to think about putting this into action by presenting respectable names to the public. Please think about it too. We are very grateful to you for the report on German philosophical societies which we await with keen interest. Have me, dear Colleague, cordially with the highest esteem
> Yours F. Enriques.[84]

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[80] Croce B. (1914).

[81] Enriques (1908).

[82] Guerraggio, Nastasi (1993, p. 143).

[83] Guerraggio, Nastasi (1993, p. 144).

[84] There.

In a letter dated February 1910, Gentile expresses to Croce all his disagreement with Enriques' role as "protagonist" in the organization of the IV International Congress of Philosophy to be held in Bologna the following year:

> Dearest Benedetto, I have rethought the matter of the Philosophical Congress of Bologna; and I am convinced that we must absolutely resign from the Organizing Committee, if prof. Enriquez does not recognize the advisability of leaving the main position which he has taken on himself, and he does not defer to the whole Committee, or at least to the first nucleus of it, as designated by the Heidelberg congress, and of which, if I am not mistaken, you too take part in the deliberation on the ways and methods of organizing the Congress, reserving for yourself only the part that the Committee itself will assign to you, naturally considering your special condition of being in Bologna.[85]

In the same letter, Gentile's jealousy and resentment for the notoriety evidently enjoyed by Enriques as an all-round intellectual, therefore not only as a mathematician, but also as a philosopher and, not negligibly important, as a cultural organizer are clearly expressed:

> If the newspapers must continue to talk and gossip about the Congress as a personal work of prof. Enriquez; [86][…] if the prof. Enriquez must present himself to the Congress as the most competent representative of the Italian studies of Logic and General Philosophy, and then speak at the inauguration as the President of the Italian Philosophical Society; I do not agree. […] and, in any case, I believe that this role, which it seems to me that they are arrogating, of head boy does not benefit him or the Italian studies.[87]

8. THE LEGACY OF THE "DEFEAT" OF ENRIQUES

When speaking of the consequences of Croce's philosophy on events in Italy, I think we must distinguish three aspects: Croce's anti-scientism, the failure of Enriques' cultural program, the difficulties of affirming scientific culture in Italy with the consequent delay of its industrial development compared to other countries.

8.1 Croce's anti-scientism

Opinions on Croce's anti-scientism are very different: those who, like Giulio Giorello, affirm it without any doubts and those who, like Corrado Ocone and Giuseppe Giordano instead consider it a false reading of Croce's thought.[88]

On Croce's anti-scientism, his expressions of contempt for mathematics, science and scientists themselves are unequivocal and numerous. It is only a sleight of hand, of which certain philosophers are masters, wanting to overturn them and disguise them with the usual empty whirlwinds of meaningless words. Giulio Giorello, in his dialogue with Corrado Ocone on 19 November 2012 *È vero che Croce odiava la scienza?* (*It is true that Croce hated science?*) published by Reset,[89] quotes a passage from Croce's work *La storia come pensiero e come azione* (*History as thought and as action*), where the philosopher from Pescasseroli says that science performs its "useful office" certainly not when it «makes abstractions, builds classes, establishes relationships between classes called laws, mathematical formula and the like. All of these are works of approach aimed at saving acquired knowledge and procuring new ones, but they are not the act of knowing». And what else is the act of knowing? I agree perfectly with Giorello when he observes:

> I would like to know what this act of knowing is for the scholar from Pescasseroli! In 1938 we are now far from Newton; in 1900 Planck introduced the first quantum hypothesis, in 1905 Einstein revived quantum theory, reshaped statistical mechanics and laid the foundations of relativity; in 1915-16 general relativity was born; quantum physics went on with Bohr and his model of the atom to the formulations of what will be called quantum mechanics in the strict sense. The science is this: calculus, general topology, algebraic topology, functional analysis, differential geometry, etc.
> Where is the act of knowing if not in mathematics? It is significant that at the very beginning of the 1930s Paul Dirac insisted that mathematics surpasses the empirical information of the world and defines the new objects which will then be explored and controlled in the laboratory.[90]

An attempt to redeem Croce's anti-scientism was made by Giuseppe Giordano,[91] who drew attention to a 1940 work by Croce, *Il carattere della filosofia moderna* (*The Character of Modern Philosophy*), republished in 1991, in which the philosopher recognized science as a human product , having its own history and therefore its own author:

> Not unlike poetry, a scientific theory is born from a dark background, almost a glimmer that gradually grows in

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[85] Guerraggio, Nastasi (1993, pp. 60-61).

[86] This is the (incorrect) spelling of the original.

[87] Guerraggio, Nastasi (1993, pp. 60-61).

[88] Giorello, Ocone (2012); Giordano (2016).

[89] Giorello, Ocone (2012).

[90] Therein.

[91] Giordano (2016).

> strength and creates clarity, or like a very lively lightning that cuts through the darkness and then seems to get lost and requires long tension and patience waiting for it to return and for the clear light to remain still. Sometimes this process lasts chronologically for a long time, and of the great works of science as of those of art we can say equally what has been said sometimes of one or the other, which are youthful thoughts implemented in manhood. [92]

In the same work Croce, very clearly, recognizes the same genius in the scientist that instead Kant considered the exclusive gift of the artist:

> But one is not a Newton without a gift of genius equally generous from nature as the one it bestowed on the poet.[93]

The thought that Croce expresses in his 1940 volume is unfortunately too late to correct the widespread idea of his anti-scientism. However, it is very interesting, because it overshadows the same historicism that belonged to Enriques, with which he instead argued at the beginning of the twentieth century.

8.2 The failure of Enriques' cultural program

Many words have been spent on the question of the outcome of the controversy between Enriques and Croce-Gentile, hypothesizing very different scenarios.

However, one fact seems certain, from what we have been able to reconstruct of those events: Enriques was left substantially alone in that battle.

Yet, in 1908, there were still leading scientific personalities who, with their authority, could have teamed up with Enriques. Among the mathematicians, the aforementioned Ulisse Dini, Cesare Arzelà, Salvatore Pincherle, Gregorio Ricci Curbastro, Giuseppe Veronese, Luigi Bianchi, Giuseppe Peano, Corrado Segre, Guido Fubini, Leonida Tonelli, Guido Ascoli and Guido Castelnuovo himself, Enriques' brother-in-law. Only Severi and Volterra had the audacity to enter into conflict with Croce, denouncing the intolerance of his philosophy towards science. Among the physicists, Damiano Macaluso and the influential Orso Mario Corbino, Pietro Blaserna, Antonio Pacinotti, Guglielmo Marconi, Domenico Pacini, Antonino Lo Surdo were still alive. In short, there was an Italian scientific community of the highest order, internationally established, which could have intervened in favor of Enriques. Why didn't this happen? There was probably an incapacity of our scientific community to know how to face Croce's dialectic on a philosophical and cultural level with equal vis-à-vis. Only Enriques could oppose it, but while Croce had a multitude of supporters on his side, Enriques was essentially alone.

A first cause of the failure of Enriques' cultural project, centered on the collaboration between philosophers and scientists, or rather on the application of the scientific method to philosophy, with the birth of scientific philosophy, is certainly the bitter dispute between Enriques and the Italian neo-idealists, whose it was said. But Ludovico Geymonat adds two more to it.

One is Enriques' misunderstanding of the importance that modern mathematical logic and mathematical formalism were increasingly assuming, which according to Geymonat transpires from the same work *Per la storia della logica* (*For the history of logic,* 1922) and which manifested itself openly in the contrasts with Giuseppe Peano:[94]

> Unfortunately, there were many mathematicians in those years, in Italy and not only in Italy, who viewed research in logic with strong suspicion; but it was certainly particularly serious that this attitude was also shared by a scholar like Enriques who did not want to be and was not a pure technician of science. It ended up by throwing a considerable discredit, among "pure mathematicians", towards mathematicians who also dealt with other problems (logical, historical or philosophical). […] the aforementioned closure with regard to logic has notably weakened the position taken in favor of rationalism, the claim to defend, in our century, the rights of reason without basing this defense on full recognition of the merits acquired in this field by the most refined logical-formal research. However, it is certain that the serious gap did not contribute to making the criticisms raised by the two authors in question effective (or at least immediately effective) [alluding to Enriques and the French epistemologist Gaston Bachelard] against the intrusive idealistic, spiritualistic, irrationalists.[95]

The other reason for the failure of Enriques' program is, according to Geymonat, its psychological orientation (common to Bachelard) clearly expressed in his work *Il significato della storia del pensiero scientifico* (*The Meaning of the History of Scientific Thought*, 1936) where:

> We read that the task incumbent upon it is to enucleate the genesis of scientific ideas, of the great changes they underwent, of the "natural errors" and of the "nonsenses" which even the greatest scientists incurred. It is a study that demonstrates to us the coexistence of both the rational and the empirical factor in cognitive processes, and therefore the irreducibility of science to only one of

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[92] Matrogregori (1991).

[93] Therein.

[94] Who also saw Vito Volterra on Enriques' side.

[95] Geymonat (1976, vol. VII, pp .690-691).

> them.[96]

Geymonat's hypotheses are certainly plausible and apparently very restrictive. Indeed, however, the lack of a united front on the part of the scientists and philosophers who were on their side must have constituted an element of weakness against the much more solid and united opposing front of the neo-idealists.

I believe another hypothesis on the failure of Enriques' cultural program could be, more generally, the incomprehension of Enriques' philosophical thought by the entire Italian cultural *establishment* of the first half of the twentieth century. A clear manifestation of that hiatus between humanistic culture and scientific culture which, a few decades later, would be stigmatized by the English physicist-writer Sir Charles Peirce Snow in his famous lecture *The Two Cultures*, held at the University of Cambridge on 7 May 1959 and then republished, with some additions, in the small volume of the same title in 1963.

There was probably a lack of preparation on the broader cultural level, on the part of the basic Italian scientific community (the secondary school science teachers), unlike those who instead gravitate in the humanistic field. For a long time, the third pages of newspapers were always dedicated to topics of a literary, philosophical (but not philosophy of science) and artistic nature, rarely to scientific topics and when this happened it was only with reference to sensational practical applications of scientific discoveries. I think Richard Feynman has nailed this problem right by writing:

> And I believe that science has remained a marginal phenomenon because we scientists are waiting for someone to ask us questions or invite us to explain Einstein's theory to people who don't even understand Newtonian mechanics, while nobody ever invites us to attack miraculous healings nor does he ask us what the science of astrology thinks today. I think we should mostly write in newspapers.[97]

Furthermore, the lesser ability, compared to the Risorgimento and post-Risorgimento past, to "combine scientific research and civil commitment" should not be underestimated.

> But, after the war, it was the philosophers, first with Croce and then with Gentile, who settled in the Palazzo della Minerva where mathematicians had been at home for decades as well as in parliamentary halls. With the isolated exception of Volterra […] the mathematical community no longer has a voice in the political institutions of a country that had seen them among the protagonists for so many decades.[98]

Even the influence of the Catholic Church, traditionally not prodigal towards science, has certainly held back the spread of a scientific mentality and culture in Italy, where its presence is greatest. It should be kept in mind that in post-Risorgimento Italy laicism and anticlericalism were much stronger than at the beginning of the twentieth century.

In a more realistic vision that takes into account the real complexity of human events, probably all the scenarios mentioned above should be taken into consideration, without excluding anyone.

8.3 The influence of Croce on the scientific and industrial development of Italy

As for the difficulties of affirming scientific culture in Italy, I believe that they are not to be attributed only to Crocianism and the infamous Gentile Reform, although they had a considerable weight. Giorello says:

> Italy would be scientifically backward due to the fault of Benedetto Croce: this is a historiographical myth that even an anti-Crociano like Geymonat has repeatedly contested and which was the subject of the issue 4/2012 of Il Mulino by an intervention by Alessandra Tarquini. Italy's backwardness in the scientific field is the result of bad choices by politicians on the one hand and of cultural resistance and the inability of the scientists themselves to communicate on the other and which are therefore independent of Croce's idealism. At the cultural level, if anything, there are other forces that could be attributed to the scientific delay, see for example the nefarious influence of the Church on some aspects of bioethical research.[99]

Opinions on this issue are also very varied and conflicting.

Particularly curious is the opinion of the physicist Carlo Bernardini, who attributes the difficulties of development of scientific culture in Italy to none other than our own language, penalized compared to English, in the ability to communicate science.[100] And to think that modern science was born in Italy with the beautiful vernacular of Galilei!

Returning, however, to the topic already treated by Bottazzini and Nastasi (2013) of an insufficient presence of men of science in political and social life compared to

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[96] Geymonat (1976, vol. VII, p. 691).

[97] Feynman (2002, pp. 121-122).

[98] Bottazzini, Nastasi (2013, p. 416).

[99] Giorello, Ocone (2012).

[100] Bernardini, De Mauro (2003).

the Risorgimento era, I like to close these pages with the thought of Gaspare Polizzi, which I fully share:

> But even in our republican Italy the presence of mathematicians, and more generally of scientists, in the public and political scene will no longer be as consistent as in the nineteenth century, and above all science will no longer be seen as a decisive orientation for cultural and productive development of the country. And this is perhaps one of the underlying problems that do not allow Italy to return to being a great nation of culture and science.[101]

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Historical Article

Enzo Ferroni (1921-2007): the History of an Eclectic Chemist

Luigi Dei

Dipartimento di Chimica "Ugo Schiff", Università degli Studi di Firenze, via della Lastruccia, 13, 50019 Sesto Fiorentino (FI), Italy
Email: luigi.dei@unifi.it, URL: https://www.unifi.it/p-doc2-0-0-A-3f2a3d2b34282a.html

Abstract. Enzo Ferroni (Florence, 25 March 1921 – 9 April 2007) was an Italian chemist, full professor in physical chemistry at the University of Florence, where he served as Rector from 1976 to 1979, a renowned international scientist who initiated a new branch of chemistry, that applied to cultural heritage conservation. The history of his scientific and academic life offers a particular interest in a half-century cross-section of the history of chemistry in Italy and the entire world. In particular, Ferroni developed the colloids, surface, and interface chemistry in Italy immediately after the Second World War in a country where it was almost non-existent, sensing the extraordinary potential of this branch of chemistry in the fields of basic and applied research. This paper aims to reconstruct the history of this eclectic chemist starting from his pioneering studies in Italy on colloids, surfaces, and interfaces that, after the Second World War, came to be widely popular within the international scientific literature following three milestones represented by the studies of the Nobel laureates in chemistry, Richard A. Zsigmondy (1925), Theodor Svedberg (1926), and Irving Langmuir (1932). Enzo Ferroni's far-sighted and visionary ideas concerning the investigation of these systems and others with biological implications by the nascent resonance spectroscopies and surface diffraction techniques were recognised and underlined as the revolutionary approach by ever more sophisticated instrumentations that were to characterise chemistry research to this day. The consecration of the extraordinary potential and peculiarities of colloids, surfaces, and interfaces would come to fruition in 1991 with the Nobel laureate in physics Pierre-Gilles de Gennes, who finally discovered that "the methods developed to study ordinary phenomena in simple systems can be generalised to more complex states of matter, especially liquid crystals, and polymers" (official motivation of the Prize), recognising soft matter as a peculiar form of matter in the condensed phase. These pioneering frontiers in the newly established soft matter field can be considered Ferroni's last message in the bottle to young researchers facing the twenty-first century. The eclecticism of this chemist emerged from two other compelling aspects that are illustrated in this article: the chemistry for cultural heritage that Ferroni conceived, pushed by the dramatic damages suffered by the works of art after the Florence flood in 1966, and his strong vision about the equal dignity of basic and applied research, that led him to establish fruitful relationships with industries aimed to enhance technological fallouts, as the research by the Nobel laureates in chemistry (1963) Giulio Natta and Karl Ziegler had clearly shown.

Keywords: history of 20th-century chemistry, colloids, surfaces and interfaces, chemistry for cultural heritage conservation, fundamental and applied research, soft matter.

1. INTRODUCTION

From the vantage point of the second fifth of the 21st century we have the possibility to look at the history of science of the second half of the 20th century with the eyes of the science historian, considering that all the discoveries made after the end of the Second World War until the beginning of the new century can be considered as sufficiently sedimented to re-evaluate them in a historical perspective.[1] The advance of science and technology in every field during such period was tremendous, and the people devoted to its progress have exponentially increased. Every discipline underwent an extraordinary multiplication of specialisations; simultaneously, science and technology had the need to be increasingly more multi- and inter-disciplinary. Moreover, science and technology started to create bridges towards human and social sciences in a sort of total globalisation of knowledge. In this frame, many scientists in every part of the world substantially increased their cooperation and research groups in different countries developed the various topics of each discipline, creating centres of excellence able to attract young scholars interested in the progress of science and technology. In this context, Italy was a noteworthy case since it emerged from twenty years of darkness characterised by the totalitarian fascist regime with all the consequences for the freedom of research and teaching.

Until the end of the Second World War the biggest advances in science were mainly prerogative of the United States of America, Germany, and United Kingdom: as an example, Italy had earned only two Nobel prizes in physics (Enrico Fermi, 1938; Guglielmo Marconi, 1919) and one in medicine or physiology (Camillo Golgi, 1906), whereas three great writers received the Nobel Prize in literature (Giosuè Carducci, 1906; Grazia Deledda, 1926; Luigi Pirandello, 1934).[2] Chemistry had lived through a less prosperous period with respect to the glorious 19th century, where the giants Amedeo Avogadro[3] (Turin, 1776-1856), Stanislao Cannizzaro[4] (Palermo, 1826 – Rome, 1910), and Raffaele Piria[5] (Scilla, 1814 – Turin 1865) had dominated the world scenario.[6] Indeed, some important chemists worked in Italy in the first half of the 20th century: among them we can include Giacomo Ciamician[7] (Trieste, 1857 – Bologna, 1922), Nicola Parravano[8] (Fontana Liri, 1883 – Fiuggi, 1938), Emanuele Paternò[9] (Palermo, 1847 – 1935), Raffaello Nasini[10] (Siena, 1854 – Rome, 1931), and Mario Betti (1875 – 1942),[11] but nobody succeeded in gaining the same great renown as the Italian school of physics: the first Nobel Prize in chemistry – still the only one – will arrive in 1963 with Giulio Natta (Porto Maurizio, 1903 – Bergamo, 1979).[2] Due to the proximity of the second half of the 20th century with our times, apart from the Nobel laureate Giulio Natta,[12] the literature is quite scarce about chemists who have lived and worked in this period: as examples, we recognize interesting papers on Giovanni Battista Bonino (Genoa, 1899 – 1985)[13], Massimo Simonetta (Pella, 1920 – Milan, 1986),[14] Adolfo Quilico (Milan, 1902 – 1982),[8] Giovanni Canneri (Montelupo Fiorentino, 1897 – Florence, 1964),[7,8] Lamberto Malatesta (Milan, 1912 – 2007),[15] Piero Pino (Trieste, 1921 – Milan, 1989),[16] Eolo Scrocco (Tivoli, 1916 – Rome, 2012).[17]

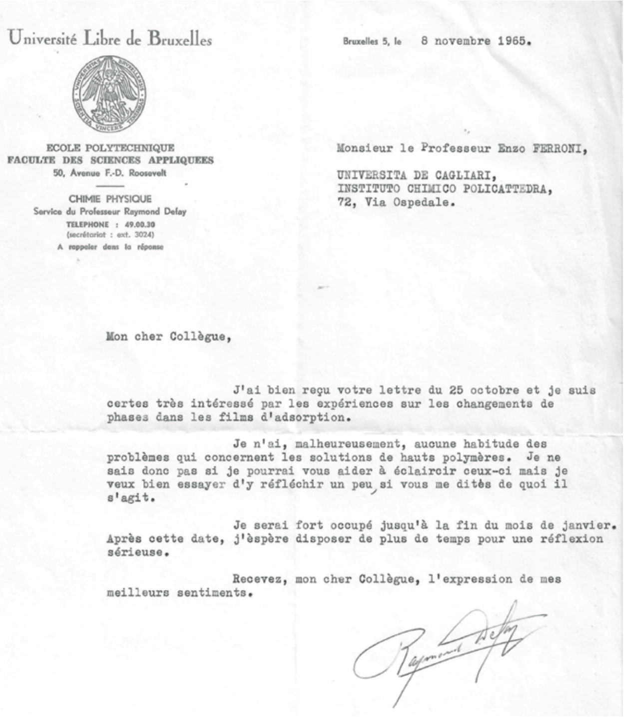
Since the present paper aims to report and discuss the work of the academic chemist Enzo Ferroni (Florence, 1921 – 2007), it seemed worthwhile to frame the scenario where he carried out most of his scientific activity, that is, the University of Florence. After the end of the Second World War, chemistry in Italy presented six main branches: analytical, industrial, inorganic, organic, pharmaceutical, and physical; inside each of these broad sub-disciplines, there were some specialisations within which, during the following decades, some important centres of excellence developed. At the University of Florence, inorganic chemistry took the path of coordination chemistry thanks to work initiated by Luigi Sacconi (Santa Croce sull'Arno, 1911 – Florence, 1992).[18] As far as organic chemistry is concerned, the path set by Angelo Angeli (Tarcento, 1864 – Florence, 1931)[8,19] and Adolfo Quilico (Milan, 1902 – 1982)[8,19] who moved to the Politecnico di Milan in 1943, was followed by Giovanni Speroni (Florence, 1910 – 1984).[8,19] Analytical chemistry was led by the already mentioned Giovanni Canneri. In contrast, pharmaceutical chemistry had two key scientists, Sergio Berlingozzi (Montevarchi, 1890 – Fiesole, 1957) and Mario Torquato Passerini (Casellina e Torri, now Scandicci, 1891 – Florence, 1962).[8,19] Industrial chemistry started to develop precisely in the period subject of the present study thanks to the work of Franco Piacenti (Florence, 1927 – 2002).[20] The chair of physical chemistry, the discipline that Enzo Ferroni selected for his chemistry master's degree thesis, was held by Giorgio Piccardi (Florence, 1895 – Riccione, 1972), a significant Italian scientist, though for some aspects quite controversial.[21] Enzo Ferroni defended his chemistry master's thesis (from now on, it will be used for this title the verb to graduate) in 1945 *magnum cum laude*, under the supervision of Giorgio Piccardi. The title of his work was "*Recent advances and opinions on chemical kinetics*" .[23] Starting from this first research, Enzo Ferroni began a long academic career that allowed him to open many new research fields in physical chemistry that the time will reveal being characterised by the strong impact on the history of chemistry.

This paper aims to reconstruct the milestones of the academic life of this scientist, individuating the five topics which demonstrate the remarkable visionary capacity of this man to open new horizons in his field of research, creating research paths that nowadays appear normal and foregone but that at the time of Ferroni's work were completely uncharted and for which it was impossible to foresee the success they would have. By initially looking at his pioneering studies on colloids, surfaces, and interfaces, the present study is devoted to following how Ferroni sensed the importance of the nascent resonance spectroscopies and surface diffraction techniques, the fruitful relationship between chemistry and cultural heritage conservation, the new frontiers in soft matter, and the strategic role played by applied chemistry, technology, and industry. Finally, the study aims to show that some of the most current topics in chemistry, such as supramolecular chemistry, self-assembly, nanoscopic world, nanomaterial chemistry, scientific diagnostics in cultural heritage conservation, and soft matter, were already outlined in the studies and research Enzo Ferroni designed and carried out.

2. THE BEGINNING: COLLOIDS, SURFACES, AND INTERFACES

Ferroni started his research activity at the beginning of the second half of the 20th century: indeed, his first two articles[23, 24] clearly showed the direction he wanted to pursue, i.e., physical chemistry of colloids, surfaces, and interfaces. One of these systems' most peculiar physical properties is surface tension, which became the first topic on which Ferroni focused his attention and desire to deepen his knowledge. Ferroni intuitively knew that the works by three Nobel laureates in the chemistry of the last decades, namely, Richard A. Zsigmondy (1925), Theodor Svedberg (1926), and Irving Langmuir (1932)[2] could be fundamental milestones and the basis for a new branch of physical chemistry in Italy. In particular, he read with great curiosity and interest Langmuir's papers,[25-53] from which the crucial and peculiar role of the solid-liquid, solid-gas, solid-vacuum, and liquid-gas interfaces emerged, indicating that surface chemistry was fundamental in determining the physicochemical mechanisms of a vast multitude of phenomena.

At the beginning of his research career, Ferroni was attracted by the liquid-gas interface. His attention was focused on measuring the surface tension of many liquid systems in static or dynamic conditions.[54-58] These first studies were also the result of the interaction with the group of Raymond Defay (Anderlecht, 1897 – Brussels, 1987)[59] and Ilya Prigogine (Moscow, 1917 – Brussels, 2003)[60] at the Université Libre de Bruxelles with whom Ferroni had collaborations, even spending time at their laboratories in Brussels. Indeed, during these years, Ferroni's scientific activity converged with the studies of these two great scientists, as proved by the subject of some of their publications[61-66] focused on surface tensions of many different liquid systems. Moreover, the proof of these relationships is given by correspondence dated some years later, also denoting a friendship, from which we report, in Figures 1 and 2, two letters (from Raymond Defay to Ferroni and from Ferroni to Maria Prokopowicz Prigogine, the second wife of Ilya Prigogine) coming from Ferroni's Archive.[67,68] The research on the liquid-gas (air) interface was immediately extended to the bulk of the liquid that contained surfactants to investigate critical micellar concentration,[69,70]



Université Libre de Bruxelles

ECOLE POLYTECHNIQUE
FACULTE DES SCIENCES APPLIQUEES
50, Avenue F.-D. Roosevelt

CHIMIE PHYSIQUE
Service du Professeur Raymond Defay
TELEPHONE : 49.00.30
(secrétariat : ext. 3024)
A rappeler dans la réponse

Bruxelles 5, le 8 novembre 1965.

Monsieur le Professeur Enzo FERRONI,

UNIVERSITA DE CAGLIARI,
INSTITUTO CHIMICO POLICATTEDRA,
72, Via Ospedale.

Mon cher Collègue,

J'ai bien reçu votre lettre du 25 octobre et je suis certes très intéressé par les expériences sur les changements de phases dans les films d'adsorption.

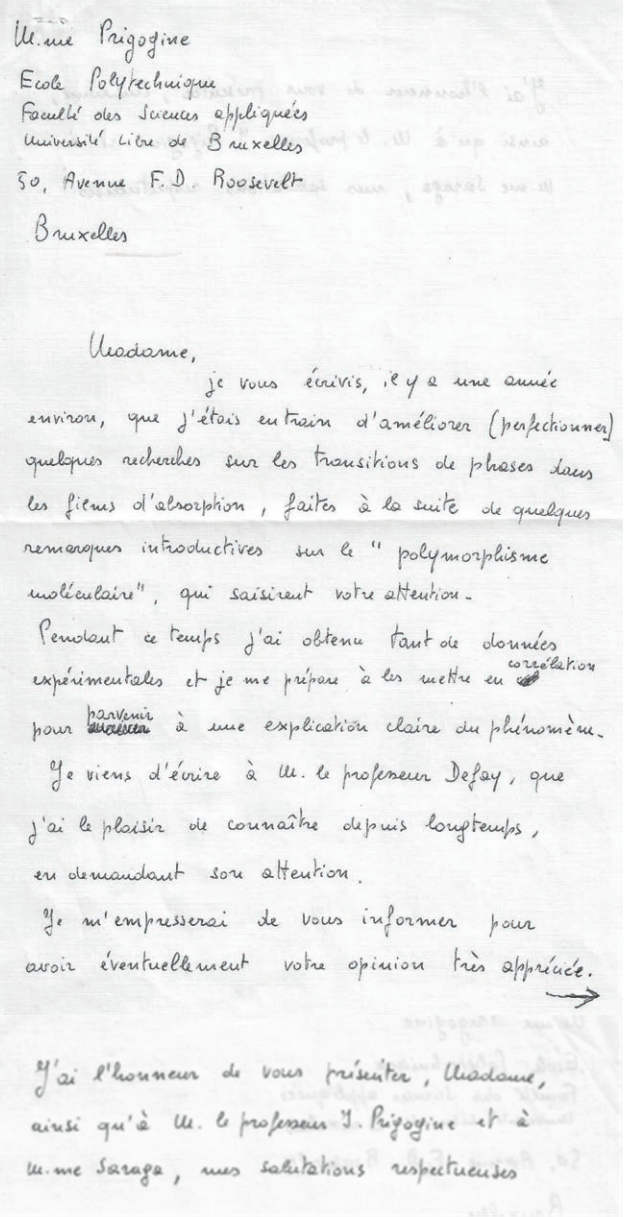
Je n'ai, malheureusement, aucune habitude des problèmes qui concernent les solutions de hauts polymères. Je ne sais donc pas si je pourrai vous aider à éclaircir ceux-ci mais je veux bien essayer d'y réfléchir un peu, si vous me ditès de quoi il s'agit.

Je serai fort occupé jusqu'à la fin du mois de janvier. Après cette date, j'èspère disposer de plus de temps pour une réflexion sérieuse.

Recevez, mon cher Collègue, l'expression de mes meilleurs sentiments.

Raymond Defay

Figure 1. Letter by Raymond Defay, Université Libre de Bruxelles, to Enzo Ferroni dated 8 November 1965. "*My dear Colleague, I received your letter dated 25 October, and I am surely interested in your experiments on phase transitions in adsorption films. Unfortunately, I have no experience dealing with high molecular weight polymers in solution. Therefore, I am not certain I will be able to elucidate your doubts, but I am happy to try and ponder on it if you state exactly the precise question. I will be quite occupied with many commitments until the end of January. After this date, I hope to have enough time for a deep and serious reflection. Please accept, my dear Colleague, my best regards, yours sincerely, Raymond Defay*". (Translation by the author).



M.me Prigogine
Ecole Polytechnique
Faculté des Sciences appliquées
Université Libre de Bruxelles
50, Avenue F. D. Roosevelt
Bruxelles

Madame,

je vous écrivis, il y a une année environ, que j'étois en train d'améliorer (perfectionner) quelques recherches sur les transitions de phases dans les films d'absorption, faites à la suite de quelques remarques introductives sur le "polymorphisme moléculaire", qui saisirent votre attention.

Pendant ce temps j'ai obtenu tant de données expérimentales et je me prépare à les mettre en corrélation pour parvenir à une explication claire du phénomène.

Je viens d'écrire à M. le professeur Defay, que j'ai le plaisir de connaître depuis longtemps, en demandant son attention.

Je m'empresserai de vous informer pour avoir éventuellement votre opinion très appréciée.

→

J'ai l'honneur de vous présenter, Madame, ainsi qu'à M. le professeur I. Prigogine et à M.me Saraga, mes salutations respectueuses

Figure 2. Draft of a letter by Enzo Ferroni to Maria Prokopowicz Prigogine, the second wife of Ilya Prigogine. "*Dear Madame, I wrote you just one year ago that I was improving (fine-tuning) some research on phase transitions in adsorption films, carried out following some remarks about the "molecular polymorphism" that grabbed your attention. During this time, I have obtained several experimental results and I am going to put them in a good correlation frame to draw some concluding considerations able to explain this phenomenon clearly. I have just written to Professor Defay, whom I have known for a long time, asking for his comments and suggestions. I shall inform you without delay to ask for your much appreciated opinion if you would. Please accept, Madame, and extend my best regards to your husband, Professor I. Prigogine and M.me Saraga. Yours sincerely, Enzo Ferroni*". (Translation by the author).

polymerisation,[71,72] electrophoresis,[73] aggregation phenomena,[74,75] and equilibrium constants and complex formation.[76,77] Following the path traced by Langmuir, Ferroni continued his pioneering work for building a school of colloids, interfaces, and surfaces in Italy, extending his studies to monomolecular films at the liquid-gas interfaces but also starting to explore solid-gas and solid-solid interfaces. His attention was concentrated on polymorphisms at the interface,[78-81] mono- and multilayers of organic substances,[82,83] adsorption onto solid surfaces,[84] solid → gas reactions,[85] and epitaxy.[86,87]

Ferroni's intense work resulted in a remarkable scientific impact in the physical chemistry of condensed phases following the research lines of two great schools, that of Irving Langmuir at General Electric Company Laboratories, Schenectady, USA, and of Raymond Defay and Ilya Prigogine at the Université Libre de Bruxelles, and allowed him to gain the chair – full professor in physical chemistry – at the University of Cagliari in 1961 presenting 85 scientific publications,[88] including three articles on the *Journal of Physical Chemistry*,[76] the *Journal of the American Chemical Society*,[84] and *Nature*.[79] In 1965, he succeeded in gaining the same chair at the University of Florence, Faculty of Mathematical, Physical, and Natural Sciences, where he remained until his retirement in 1996, becoming Emeritus the subsequent year. During the years spent at the University of Florence, he was Director of the Institute of Physical Chemistry (1965 – 1968), Dean of the Faculty of Mathematical, Physical, and Natural Sciences (1968 – 1971), Rector (1976 – 1979), and Head of the Chemistry Department (1983 – 1985).[89] From 1961 until the end of 1965, when he returned to the University of Florence, he continued his activity in Cagliari[90-99] cultivating his pupils Enzo Tiezzi (Siena, 1938 – 2010) and Gianfranco Rovida (Rome, 1939), who followed him at the University of Cagliari after getting their chemistry master's degree at the University of Florence in 1963 under the supervision of the young colleague Giulio G. G. T. Guarini (Forlì, 1932 – Florence, 2015). Another pupil of Ferroni's, older than Rovida and Tiezzi, was Gabriella Gabrielli (Cortona, 1930 – Florence, 2022), who had already published many papers with Ferroni.[55-57, 74-76, 79-81] To the same team, even though not his pupils, belonged Silvano Bordi, almost a peer of Ferroni's (Florence, 1922 – 1995) and Rolando Guidelli (Florence, 1938) who, taking inspiration from the school of large interface systems founded by Ferroni, would go on to develop the physical chemistry of surfaces and interfaces in electrochemistry.[89]

The path was then traced during the two decades 1950-1970, and the consecration and consolidation of the Italian school on colloids, interfaces, and surfaces founded by Ferroni came in 1993 (*vide infra*) with the foundation of the Italian Centre for Colloids and Surfaces (*Consorzio interuniversitario per lo sviluppo dei Sistemi a Grande Interfase*, CSGI) which is still active. Enzo Ferroni was its President from the foundation until his death in 2007; its director for over 25 years was Piero Baglioni (Florence, 1952), who graduated in chemistry under the supervision of Ferroni in 1977, with the dissertation "Membranes selectively permeable to gases". Baglioni succeeded in continuing the legacy and of his Maestro, leading the CSGI to become a Centre of Excellence highly regarded all over the world.[99]

3. THE ADVENT OF RESONANCE SPECTROSCOPIES AND SURFACE DIFFRACTION TECHNIQUES

When Ferroni returned to his hometown, he found a group of young scientists, partly pupils of his, partly of other colleagues at the University of Florence: the first group included the already mentioned Gabrielli, Guarini, Rovida, and Tiezzi; in the second one he found Bordi and Guidelli; and finally in the third Giorgio Taddei (Florence, 1935 – 2019), Mario Pio Marzocchi (Arezzo, 1935). A few years later, Giacomo Martini (Pistoia, 1943 – Quarrata, 2012), another chemist, albeit not one of his pupils, joined Ferroni's team. As soon as he got back to the University of Florence on 15 December 1965, Ferroni took over the direction of the Institute of Physical Chemistry[88, 89] and, strengthened by his experience at the University of Cagliari where he held the first chair in Italy of physical chemistry of colloids and interfaces in the academic year 1963-1964,[88] put together a group of scientists devoted to the physical chemistry of colloids, surfaces, and interfaces.

He had already constituted the first seed during 1950-1961, writing some papers with Gabrielli and directing his pupil Guarini to investigate solid interfaces. Still, on his return to Florence at the end of 1965, he had his second great visionary idea, partly generated by a fortuitous case (*vide infra*), sowing the seed for a novel approach to the physical chemistry of large interface systems by exploiting the unique potentialities of the nascent resonance spectroscopies and surface diffraction instrumental techniques. Indeed, Ferroni had already perceived the importance of the spectroscopic approach when he published two papers with Marzocchi[100, 101] studying halogen-amine interactions by infrared spectroscopy, but he had not yet in mind, immediately after the graduation of Tiezzi and Rovida, what topics could represent some new research lines in the field of colloids and surfaces. The fortuitous case originated the research line dealing with Nuclear Magnetic Resonance (NMR) and Electron Paramagnetic and Spin Resonance (EPR/ESR) spectroscopies, while the second idea was associated with the subject of surface diffraction techniques. Tiezzi and Rovida, after graduating in chemistry in 1963, became Ferroni's assistants at the University of Cagliari where they remained until 1965 – Tiezzi – and 1966 – Rovida –, and participated with him in the 20th International IUPAC Congress in Chemistry held in Moscow on 12 – 18 July 1965. Figure 3 shows Ferroni and Tiezzi at the Congress discussing with the Russian chemist and physicist Boris Vladimorovič Derjagin (1902 – 1994), one of the world's most prominent scientists in the field of colloids and surfaces.

Figure 3. Photo taken during a coffee break at the International IUPAC Congress of Chemistry, Moscow, 12-18 July 1965: from left to right Enzo Ferroni, Enzo Tiezzi, and Boris Vladimorovič Derjagin.

But Ferroni was also always eager to hire promising young researchers besides his pupils and consequently, when back to Florence, selected Leo Burlamacchi (Viareggio, 1933), a 1960 graduate from the University of Pisa, to work as a pioneer in the field of EPR/ESR. Indeed, Burlamacchi, as a graduate worked some years in the industry, and in 1965 he attended the laboratories at the National Council of Research, Institute on Microwaves in Florence, founded and directed by the distinguished physicist Nello Carrara (Florence, 1900 – 1993).[102] In these laboratories, two instruments were built for EPR/ESR and NMR measurements. Still, nobody used them since no chemists – the principal users of such apparatuses for physicochemical characterisation – were present there at that time. Therefore, Burlamacchi had been involved in scientific investigations using these two emerging techniques. Ferroni, consulted by Director Carrara, immediately found a fellowship for Burlamacchi, entrusting him with opening new research frontiers. He suggested creating a couple of young researchers – Burlamacchi and his pupil Tiezzi – to introduce EPR/ESR and NMR techniques to the Florence research group on colloids and surfaces. The first papers[103-107] showed that exploring these new frontiers of physicochemical research was possible. It is worth recalling that Tiezzi taught at the University of Cagliari[102] when Ferroni held the chair of physical chemistry there. Even after Ferroni's transfer to Florence in December 1965, Tiezzi continued his activity at the University of Cagliari. Ferroni himself suggested to Enzo Tiezzi to spend one year in the United States to deepen his knowledge of resonance techniques: indeed, during 1966 and 1967, Tiezzi worked in the laboratories of the University of Washington in St. Louis, Department of Physics under the supervision of Samuel I. Weissman (1912 – 2007) with a Fulbright scholarship, developing the use of electron spin resonance, and then as Post-Doctoral Research Associate, at the Department of Botany and Centre for the Biology of Natural Systems of the same University under the supervision of Barry Commoner (1917 – 2012), further refining his skills in the field of magnetic resonance spectroscopies. In particular, Tiezzi started to explore the possibility of using resonance spectroscopies in biology and medicine.[102,108] Tiezzi would always be deeply grateful to Ferroni, stating several times that he considered Ferroni his mentor since the academic year 1957-1958 when he attended his lectures on Fundamentals of Chemistry 2nd course at the University of Florence.[102] When Tiezzi returned to Florence, he was ready to carry out fundamental research using ESR/EPR and NMR spectroscopies collaborating with Burlamacchi and, from 1967, with the young Martini (see above).[109-114] After the Florence flood, in 1967, Ferroni obtained funds to buy the EPR/ESR instrument from Varian that was placed at the Institute of Physical Chemistry of the University of Florence in the city centre, via Gino Capponi, 7-9. Tiezzi would become a full professor in physical chemistry at the University of Siena in 1979 and one of the most distinguished scientists in the world developing, the first in Italy, the concept of sustainability together with other scientists from across the globe. Burlamacchi became a full professor in 1980 at the same University of Cagliari that twenty years before had welcomed Ferroni.

This research line was pursued for many years with the contribution of other people, among which the already mentioned Baglioni, Maurizio Romanelli (Florence, 1943) and Maria Francesca Ottaviani (Florence, 1951; later Sandra Ristori (Florence, 1960) also joined the team. The research was developed in collaboration with Larry Kevan (1938 – 2002) at the Chemistry Department of the University of Houston. Many papers were published over several years, finally extending their scope to large interface systems, as it was in Ferroni's mind.[115-139] It is worth mentioning that Ferroni appeared only a few times as co-author of these studies of which he was a staunch supporter: we recognise in this behaviour both a commendable generosity and a habit of mind diametrically opposed to what one might imagine in the common sense of the university barony, and intellectual honesty, since Ferroni was aware that he had no skills in resonance techniques when he suggested to Burlamacchi to start his adventure with EPR/ESR and to Tiezzi with NMR. The fortuitous case allowed Ferroni to meet Nello Carrara and Leo Burlamacchi and to create the conditions for the subsequent development of resonance techniques in the Florence colloids and surfaces group headed by Ferroni.

The second route associated with his visionary idea to apply new instrumental techniques to colloids and surfaces studies dealt with surface diffraction techniques. Ferroni set the goal to understand atomic and molecular mechanisms at the basis of gas adsorptions on well-characterised surfaces, namely {hkl} metal monocrystal faces. To realise this objective Ferroni encouraged his pupil Rovida to spend some months in Paris at Trillat's Laboratories (*vide infra*) to ascertain whether the technique of Reflection of High Energy Electron Diffraction (RHEED) under grazing incidence was able to reach the goal or not. Rovida's trials did not produce reliable results. Indeed, Ferroni was fascinated by the concept of understanding atomic and molecular mechanisms at the basis of gas adsorptions onto solid surfaces. When he was back at the University of Florence, Ferroni had the opportunity to read a brochure illustrating that, thanks to the ultra-high-vacuum instrumentation supplied by Varian Associates, it had become possible to build instrumentations able to collect reproducible and well-interpretable Low Energy Electron Diffraction (LEED) patterns. Ferroni was impressed by the brochure's content, which illustrated this innovative technique's impressive power to study all the phenomena at the solid-vacuum interface, especially to deepen the gas adsorption mechanisms onto well-characterised solid surfaces, namely well-defined crystallographic faces. The future Nobel Prize in chemistry (2007) Gerhard Ertl (Stuttgart, 1936) was involved in these studies, and two years later he published a ground-breaking article that opened vast horizons for surface science studies.[140] Ferroni grasped the opportunity and gave Rovida the brochure asking his opinion about the new LEED instrumentation. The answer was positive and a new and fascinating challenge started. Ferroni obtained funds to order the LEED apparatus, which arrived in the autumn of 1966. Still, it had to remain at the customs offices for several months due to the Florence flood (*vide infra*) that had damaged the Institute of Physical Chemistry of the University. Finally, during the spring of 1967, the LEED instrument arrived, was installed, and in a short time, the first two articles on surface studies by LEED from the University of Florence Institute of Physical Chemistry were published.[141, 142] Once again, the path was open thanks to a scientist who constantly desired to see farther, to guide his pupils, but simultaneously leave them free to unleash their talents and abilities without undue pressure or need for complacency and flattery towards him. In the following years, the group that welcomed Ermanno Zanazzi, Marco Torrini, Ugo Bardi and Andrea Atrei gradually came to be headed by Rovida and published many important papers,[143-157] establishing international cooperations, among which the most meaningful was that with Gabor A. Somorjai (1935), University of California, Berkeley.[158, 159]

4. FLORENCE FLOOD (1966): CHEMISTRY AND CULTURAL HERITAGE CONSERVATION

As it is well known[160] the dramatic event of the Florence flood on 4 November 1966, caused a great echo across the world, mainly because of the extensive damages suffered by the exceptional concentration of cultural heritage present in the city. This echo is well condensed in the book *Dark Water* by Robert Clarke: "*There is Florence and there is Firenze. Firenze is the city where the citizens of the capital of Tuscany live and work. Florence is the place where the rest of us come to look*." [160] Ferroni had been back in Florence for just a year and he was immediately involved with all his other colleagues in rescuing damaged instrumentations, books, documents, chemicals, laboratory glassware from the Chemistry Institutes (see Figure 4) in the centre of the city where the Arno's water reached ca. 1 m of height. After the emergency of the first few days, it appeared clear that the damage to the works of art was vast, especially for the wall paintings that could not be removed. Ferroni understood that a scientific approach was essential to help in solving the myriad of problems that conservators and cultural heritage officials encountered. During those frantic days Ferroni was able to invent two different methodologies and simultaneously inaugurate a new epoch for conservation and restoration, the scientific approach and the continued and constant integration between art history, conservation, science and specifically chemistry.[161]

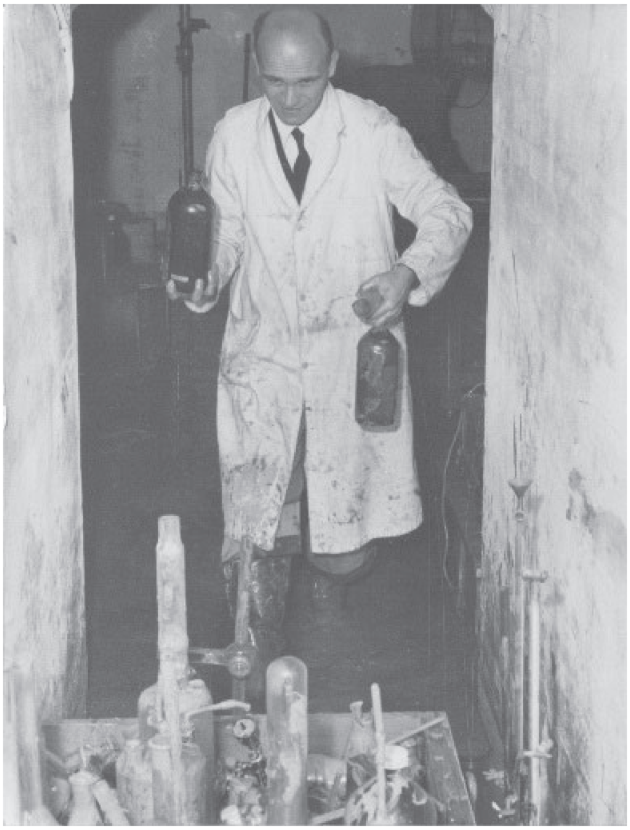


Figure 4. Enzo Ferroni rescuing some laboratory glassware from the cellars of the Chemical Institutes of the University of Florence some days after November 4, 1966.

The first dramatic emergency came from the rapid deterioration of the fresco *L'ultima cena* (*The last supper*) by Taddeo Gaddi (ca. 1300 – 1366) in the Refectory of Santa Croce Basilica. After the waters receded the consequent salt efflorescence due to nitrates was rapidly causing the colour to fall off the wall. This masterpiece was literally vanishing before the anxious eyes of the experts. The only solution was to urgently detach the fresco from the wall and transfer it onto another suitable support. Unfortunately, the detachment was made impossible due to the very high nitrates concentration into the water impregnating the porous structure of the wall. This high ionic force inhibited the sol → gel transition of the animal glue solutions used to impregnate both the paint surface and the canvases onto which, after the gelation of the animal glue, the painting layers would have had adhered allowing the detachment of a few microns of pictorial mortar. The situation was desperate; each day that went by, the coloured powder was found at the feet of the fresco. Ferroni remembered some of his studies[96, 162] where he had demonstrated that tributyl-phosphate

(TBP), an organic compound almost insoluble in water (only 6 g/L at 20 °C)[163] and with very low surface tension (27.79 mN/m at 20 °C),[163] forms monomolecular films onto nitrates water solution with an average molecular area depending on the cations, due to the formation of the different complexes at the water-air interface. He thought that wetting the wall surface with TBP would lead to monomolecular films spread onto the aqueous nitrate solution layers, which adhered to the solid particles of both the mortar and the pigments, besides filling the wall pores. In a way, he prefigured that in this manner, the whole exposed surface of the first layers of the wall would become highly hydrophobic due to TBP, forming a sort of impermeable film that would prevent the migration of the ions coming from the nitrates into the animal glue solution, which therefore would be able to gel and allow the subsequent detachment.[164, 165] The various experts were very sceptical about this hypothesis, and Ferroni replied as Isaac Newton: "*hypotheses non fingo*, please try!" The trial was carried out by the restorer Dino Dini on a small portion of a less famous fresco by Jacopo Ligozzi (ca. 1547 – 1627) and the result was astonishing: the glue set, and the small portion could be easily detached. The whole fresco by Gaddi was then subjected to the same treatment, detached, and repositioned in the same place onto appropriate support. It is still there in good health: it was an actual rescue rather than a restoration or conservation intervention. Without this most significant and brilliant idea by the chemist Ferroni, we would not be able to admire this wonderful work of art now.

The second critical question about wall painting damage was the worsening of the degradation by a process called sulphatisation.[166] The transformation of the binding $CaCO_3$, formed by the setting of lime, into gypsum ($CaSO_4 \cdot 2H_2O$) resulted in a severe deterioration of the painted surface with formation of white patinas, crusts, powdering, and other dangerous pathologies that compromised both the reading and the stability of the pictorial surface: it was evident that the flood had visibly accelerated this phenomenon. Again, Ferroni activated his brilliant and eclectic mind and proposed to re-convert gypsum into $CaCO_3$ by using ammonium carbonate followed by a barium hydroxide treatment. To ascertain whether this chemical approach was effective in recovering a readable and compact painting surface, Ferroni remembered both his time at the CNRS Laboratoire de Diffraction des Rayons X at Bellevue in France and the correspondence[167] with its Director Jean Jacques Trillat (Paris, 1899 – Versailles, 1987). Trillat was a very distinguished scientist with expertise in colloids and interfaces. In 1956 he authored a fundamental book[168] and precursor of the studies that would be developed in Italy by Ferroni, such as those on molecular layers of fatty substances on metals.[169] Reflecting on these memories, Ferroni and co-workers measured the reconversion of gypsum to $CaCO_3$ using ammonium carbonate and subsequent barium hydroxide treatment by X-Rays Diffraction (XRD) using an apparatus invented by Trillat and reconstructed at the Institute of Physical Chemistry of the University of Florence.[170] The results were extremely encouraging since the XRD patterns were in agreement with a total reconversion (see Figure 5). The successive application on the wall painting *San Domenico in adorazione del crocifisso* (*St. Dominic in adoration of the crucifix*) by Beato Angelico (ca. 1395 – 1455) at the San Marco Convent in Florence showed excellent results, not only in terms of reconversion but also in firmly consolidating the painting surface and the thin layers of mortar (*intonaco*) underneath.[171] During the subsequent years and up to the present day, this technique became the legacy of wall painting conservators worldwide. It was named the Ferroni-Dini method after the chemist inventor and the conservator who devised and applied the procedure.[172-178]

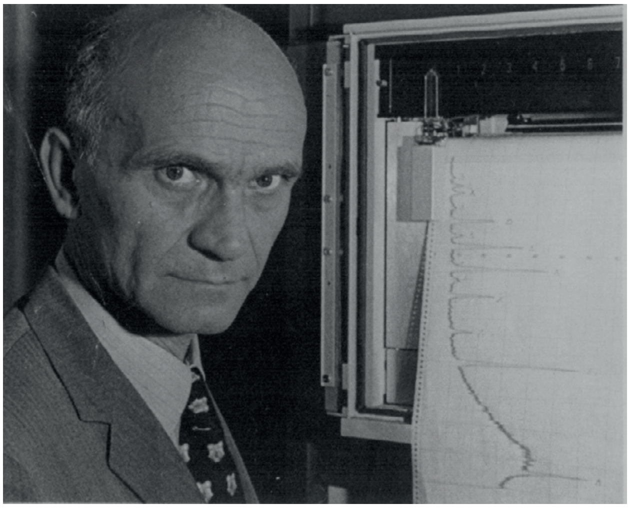


Figure 5. Enzo Ferroni close to a flow chart recorder during the collection of XRD to ascertain the mechanism of the frescoes' sulphatisation and the reconversion to calcium carbonate thanks to the treatment with ammonium carbonate followed by barium hydroxide, the so-called Ferroni-Dini method.

Ferroni's passion for connecting science and art continued throughout his life, and several other studies testified to the outstanding contribution this chemist made to the world of cultural heritage conservation: autogenous lime-based grouts[179-181] and oil-in-water microemulsions[182-185] used for the conservation of wall paintings by Masaccio (1401 – 1428) in the Brancacci

Chapel[164, 165, 186-188] in Florence, the role of the deliquescent salts[189, 190] for the deterioration of the wall paintings of *La leggenda della vera croce* (*The legend of the true cross*) by Piero della Francesca (ca. 1412 – 1492) in the San Francesco Basilica in Arezzo,[191] the chemical stability of some pigments[192] or solvents[193] used for cleaning pictorial surfaces, until his last intuition about a possible role of nanoscience and nanotechnology[194-199] for a revolutionary approach to conservation and restoration. Ferroni had been convinced ever since that the studies dealing with the physical chemistry of colloids and interfaces with potential applications for cultural heritage conservation had to be considered on par with traditional physicochemical papers. Towards the end of his long career, he received a prestigious award when the Journal named after the scientist that was Ferroni's inspiration, Irving Langmuir, decided to dedicate the cover of its 26th issue of 1999, published on 1 December to a photo illustrating the damage done by salt efflorescence in wall paintings. The image was the damaged face of Christ in *The last supper* by Taddeo Gaddi, which Ferroni had rescued about thirty years before. The article[200] was penned, among others, by two of Ferroni's pupils, Piero Baglioni and the author of the present article. Subsequently, many renowned international journals accepted papers on the physical chemistry of colloids and interfaces devoted to bringing a contribution to the improvement of cultural heritage conservation and sometimes dedicating again their covers[201]: Enzo Ferroni's challenge was definitively won at the beginning of the 21st century, as testified by various papers[201-208] that received critical reviews .[209-220]

5. NEW FRONTIERS IN SOFT MATTER

As previously written, at the beginning of the 1990s, the physical chemistry of colloids and interfaces was well cultivated at the Department of Chemistry of the University of Florence into which, in 1983, the Institute of Physical Chemistry was merged. There were at least six sub-groups that germinated from the seeds sown by Ferroni: the teams of monolayers and Langmuir-Blodgett films (Gabrielli with her pupil Gabriella Caminati, Florence, 1960), surface diffraction techniques (Rovida), ESR/EPR (Martini), solid-state reactions and solid-gas interfaces (Guarini), scattering techniques (Baglioni), and electrified interfaces (Guidelli). Moreover, in almost all the Universities in Italy, there were scientists actively working on these topics and the discipline that forty years before was almost inexistent in Italy was in excellent health. During the second part of the 1970s and the entire 1980s, Ferroni pointed his attention to monomolecular films constituted of polymers.[221-231] This interest had been certainly inspired by his previous relationship with the Nobel laureate Giulio Natta[167] and by the Flory-Huggins theory[232-234] for polymer solutions. Indeed, one of the articles Ferroni published in these years directly involved Huggins[221]. The results of a study on the bi-dimensional state conformation of poly β-benzyl-L-aspartate were compared precisely with Huggins' theory.

Ferroni's interest in surface properties of polymers was also stimulated by reading the studies by de Gennes: the future Nobel laureate in physics (1991) considered the physical chemistry of polymers at the interface and their interactions with surfactants as one of the most advanced topics in the physics of the condensed phases.[235-241] The year after winning the Nobel Prize, de Gennes published a short survey on *Science* entitled *Soft Matter*:[242] a new era for physics, chemistry, and physical chemistry was born, and Ferroni would have been pleased to have preconised, some forty years before, that this branch of science had the characteristics to play a fundamental role. In his article,[242] de Gennes explained the peculiarities of this soft matter, often called complex fluids, and he introduced the two main characteristics: complexity and flexibility. He then investigated the various systems that can be considered as belonging to this fourth state of the matter: polymers, surfactants, monolayers, bilayers and multilayers, cell membranes, liquid crystals, micelles, vesicles, and liposomes. This opened a staggering multitude of theoretical and applicative studies in many fields, such as biology and medicine, materials science, technology, and electronics, among others.

Ferroni thought that the times were ripe to launch the institution of a National Centre for Colloids and Interfaces. On 4 May 1993, a new Government was constituted with Prime Minister Carlo Azeglio Ciampi (Livorno, 1920 – Rome, 2016), the future President of the Italian Republic, and the chemist and industrialist Umberto Colombo (Livorno, 1927 – Rome, 2006) was appointed as the Minister for the university and scientific research. Colombo immediately saw the strategic importance of Ferroni's proposal regarding the institution of a National Centre on Colloids and Surfaces, and at the end of 1993, the *Consorzio interuniversitario per lo sviluppo dei Sistemi a Grande Interfase*, CSGI – as was called the National Centre for Colloids and Surfaces – was born under the supervision and control of the Italian Ministry for university and scientific research. Ferroni was appointed President, and his pupil Baglioni, Director.

6. APPLIED CHEMISTRY, TECHNOLOGY, AND INDUSTRY

The first mention in the *Chemical Abstract* of Enzo Ferroni as an author is relative to an Italian patent[243] deposited on 27 February 1948 aimed to formulate a thermosetting powder. The young researcher who had carried out a chemistry master's degree thesis on theoretical considerations of chemical kinetics,[22] immediately demonstrated to be interested in aspects dealing with applied chemistry, technology, and industry. Indeed, this feeling and approach would continue throughout his long career and life: Ferroni profoundly understood the deep meaning of IUPAC (*International Union of Pure and Applied Chemistry*), that, as its name implies, focused on the union of pure and applied chemistry.

Among the various aspects of his applied research, we selected four emblematic instances of his approach. First, we thought it significant to recall the ten years of correspondence between Ferroni and Natta from 1958 until 1968, as recently studied by Laura Colli.[167] The interaction between them was intense and found its significant moment just one year after the awarding of the Nobel Prize to Natta: they published a paper in cooperation that linked the two domains of study these scientists had carried out in the last years, that is polymers for Natta and surface adsorbed films for Ferroni.[244]

The second significant contribution was generated by the extended partnership with the Italian entity SnamProgetti operating in the field of fuels and energy. Ferroni was convinced that the idea of SnamProgetti to build a coal pipeline, apparently, a utopian mirage, could actually be pursued since large interface systems as coal-water stable dispersions would be able to generate slurries with suitable fluidity to flow into the pipeline and simultaneously burn at the end of the pipeline without separating the coal from the water. Thanks to some *ad hoc* surfactants Ferroni and co-workers developed stable suspensions of fine powdery coal in water containing up to 70% coal by weight, which was above the threshold required to be burnt without eliminating water.[245, 246] These suspensions are called slurries, and they were heavily investigated[247-249] discovering their viscosity behaviour as non-Newtonian fluids with memory. Ferroni had the idea to involve his friend and colleague, the mathematician Mario Primicerio (Rome, 1932), in the study: the mathematical analysis succeeded in calculating the exact length (security distance) of the pipeline between two contiguous pumping stations to avoid coal sedimentation and stoppage.[250, 251]

Another interesting connection with the industry to find applications of large interface systems has already been mentioned in section 4. dedicated to chemistry applied to cultural heritage conservation. Both autogenous lime-based grouts and oil-in-water microemulsions created during the conservation workshop of the Masaccio, Masolino, and Filippo Lippi wall paintings in the Brancacci Chapel were developed in cooperation with the national industry Syremont S.p.A. whose President at the time was a friend of Ferroni's, Paolo L. Parrini.[179-184]

Figure 6. During the workshop "Energy and industry, financial aspects, technological Innovations: the experience in the textile sector at Prato" held in Prato on 28 November 1980: Enzo Ferroni is the fourth from the left seated at the organisers' table.

Finally, there was the long and fruitful cooperation with yet another industrial sector, Tecnotessile of Prato, founded in 1972 and still actively operating in the field of new technologies applied in the textile industry. Ferroni was designated as President of this Technology Centre right from its inception in 1972. In 1980 he was still collaborating with the textile industry district in Prato (see Figure 6).

The cooperation was mainly dedicated to developing large interface systems able to improve textile production. Ferroni was convinced that soft matter could offer many fruitful opportunities to the textile industry, but at that time, the textile industry was not ready to develop strong synergies with academic research. And again, in this case as well, Ferroni could see ahead of him: at the beginning of the 21st century, some papers from researchers of the CSGI were published, and Ferroni was lucky enough to see them.[252-256] The last of his ideas we will mention is that of UV radiation-absorbing fabrics using nanotechnology; it was again a brilliant idea, but Ferroni was not able to read the paper: it was published online on 30 October 2007, six and half months after the eclectic chemist had passed away.[257]

7. CONCLUSIONS

The scientific activity of Enzo Ferroni, critically revisited and investigated in the present study, allowed us to individuate the main original, novel, and creative ideas developed by this scientist, who operated mainly in the second half of the last century. It showed how he succeeded in creating a new physicochemical school in Italy on colloids, interfaces, and surfaces, a field that the future would reveal particularly worthy of being thoroughly investigated until the end of the 20th century when it became a sort of new state of the matter called "soft", after the studies by the 1991 Nobel laureate in physics Pierre-Gilles de Gennes.

Ferroni perceived this discipline's enormous potential, studying Irving Langmuir's work and deepening his knowledge and skills attending the laboratories led by Raymond Defay and Ilya Prigogine at the Université Libre de Bruxelles. His first visionary idea to develop a branch of physical chemistry, almost neglected in Italy until the end of the Second World War, was followed by his second extraordinary intuition of applying the new and budding resonance spectroscopies (NMR and EPR/ESR) to research, first in solution chemistry and successively to investigate large interface systems.

His eclecticism forcefully emerged in the aftermath of the Florence flood in 1966 when he understood that chemistry, and science and technology in general, could play a fundamental role first in solving the dramatic and urgent problems facing the damaged works of art and then inaugurating a new conception of conservation and restoration, with solid scientific bases and a continuous cross-exchange among different and complementary competencies to create what, in the following years, would become the field of scientific restoration and conservation of cultural heritage. All these merits were acknowledged in the obituary that appeared in *The Independent*.[258]

The consecration of his visionary ideas and intuition arrived in 1991 when Pierre-Gilles de Gennes was awarded the Nobel Prize in physics for having discovered that the methods developed for studying ordinary phenomena in simple systems can be generalised to more complex states of matter, especially liquid crystals, and polymers, individuating soft matter as a peculiar form of matter in the condensed phase. Some new topics, such as supramolecular chemistry, soft matter, self-assembly, nanoscience and nanotechnology, nanoscopic phases, and so on, surely have their root in the colloids and surfaces that Ferroni selected as his main interest for his long academic career.

The paper also showed Ferroni's eclecticism, considering his vision of the relationship between fundamental or basic research and applied chemistry, technology, and connection with industry. Ferroni was always convinced that all aspects of research possessed equal dignity, and the proof of this vision was the close relationship that Ferroni had with the Nobel laureate in chemistry Giulio Natta and the numerous applied studies he carried out having as Partners important companies in the energy, fuels, and textiles sectors.

Thanks to his long and fruitful work, Ferroni received numerous awards, among which we recall: the Gold Medal by the Italian Ministry of the Public Education (1967) as meritorious for school, culture, and art for "his generous collaboration offered for the preservation and recovery of the artistic and cultural heritage of Florence damaged by the flood of 4 November 1966"; the designation of *Grande Ufficiale dell'Ordine* (1977) by the President of the Italian Republic Giovanni Leone (Naples, 1908 – Rome, 2001); the granting of the title *Officier de l'Ordre National du Mérite* (1979) by the President of the French Republic Valéry Giscard d'Estaing (Coblenz, 1926 – Authon, 2020); the title of *Emeritus* in physical chemistry (1997) by the Italian Minister for the university and scientific research Luigi Berlinguer (Sassari, 1932).

The amazing variety of interests and subsequent content of his numerous studies and papers leads to conclude that for Enzo Ferroni, two different statements – the first by Leonardo da Vinci[259] and the second by Primo Levi[260] – can be used to summarise his multifaceted personality. Leonardo stated, "*study science first, and then follow the practice born from that science*" ("*studia prima la scienza, e poi seguita la pratica nata da essa scienza*")[259]. Levi wrote about his the following, speaking about his own chemistry, and we suggest the same is applicable to Ferroni's: "[a] *solitary chemistry, unarmed and on foot, at the measure of man, which with few exceptions has been mine: but it has also been the chemistry of the founders, who did not work in teams, but alone, surrounded by the indifference of their time, generally without profit, and who confronted matter without aids, with their brains and hands, reason and imagination*" ("*chimica solitaria, inerme e appiedata, a misura d'uomo, che con poche eccezioni è stata la mia: ma è stata anche la chimica dei fondatori, che non lavoravano in équipe ma soli, in mezzo all'indifferenza del loro tempo, per lo più senza guadagno, e affrontavano la materia senza aiuti, col cervello e con le mani, con la ragione e la fantasia*").[260] Ken Shulman, in his wonderful book on the Brancacci Chapel,[164] succeeded in masterfully condensing these two quotations in an exceptional sentence: "*Ferroni preferred to work alone, ruminating in his office in the early morning, applying his genially elastic mind until arriving at a solution*".[261]

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Historical Article

Dalton's Long Journey from Meteorology to the Chemical Atomic Theory

Pier Remigio Salvi

Dipartimento di Chimica "Ugo Schiff", Università di Firenze, via della Lastruccia 3, 50019 Sesto Fiorentino (FI), Italy
E-mail: piero.salvi@unifi.it

Abstract. The purpose of this paper is to review Dalton's contributions to science in various fields of research in relation to the first intimation of the chemical atomic theory. Early *"germs"* of his physical ideas may be found in the initial meteorological studies where water vapour is viewed as an *"elastic fluid sui generis"* diffused in the atmosphere and not as a species chemically combined with the other atmospheric gases. The next object of Dalton's attention was atmosphere itself. He discarded affinity between atmospheric gases as a possible cause of homogeneity and, making recourse to Newtonian *Principles*, considered the repulsive forces among particles. Experiments on the *"nitrous air test"* and on the diffusion and solubility of gases were instrumental to arrive at the chemical atomic theory. The slow, laborious, and persevering work of Dalton to get the first table of atomic weights is a fascinating piece of science which may be fully appreciated by referring to his laboratory notebook.

Keywords: history of chemistry, Dalton's atomic theory, elastic fluids, mixed gases, gas solubility in water, law of multiple proportions.

1. INTRODUCTION

There has been in the years continuing interest on the genesis of the Dalton's chemical atomic theory [1-20]. According to Thomson[1] Dalton told him in a meeting that occurred in August 1804 that he had come to the theory by speculating on the analyses of methane (*"carburetted hydrogen gas"*) and ethylene (*"olefiant gas"*) which indicate that for a given weight of carbon methane contained twice as much hydrogen as ethylene. This narrative cannot be trusted [4] given that the reported data were acquired in the summer of 1804, almost one year after the appearance, September 1803, of the first table of atomic weights in Dalton's notebook [4]. A second proposal[2] was advanced by William Henry, Dalton's closest friend, and his son, William Charles, Dalton's pupil. In conversation with them twenty-seven years after the event, Dalton stated he took inspiration for the atomic hypothesis thinking about the

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[1] see ref. [1], p. 289.

[2] see ref. [2], p. 63, 84-85.

importance of Richter's table of equivalents. This is an equally doubtful assertion since (i) it is generally accepted [4,8-10] that Dalton was not aware of Richter's work in 1803 and (ii) in the table of atomic weights no entry refers to acids and bases, the subject of Richter's studies [8]. The young Henry himself expressed uncertainty about the validity of this recollection[3]. A third account, coming from a Dalton lecture held at the Royal Institution in 1810, was provided by Roscoe and Harden [4], responsible for the precious discovery and publication of Dalton's laboratory notebooks[4]. They point to the fact that the theory arose from considerations on the physical properties of gases rather than from experiments on multiple proportions. Unfortunately, this version comes from beliefs about atomic sizes and weights that Dalton proposed in 1804 or 1805 [5,9], rather than 1803 as claimed [4]. All this considered, it has been acutely remarked that a great scientist is not necessarily a good historian [5]. Successively, two positions emerged [5,8,9]. Shortly, the first [5] focuses the attention on the experiments performed by Dalton in 1803 relative to the reaction of nitric oxide with oxygen while the second [8,9] strongly advocates that the theory was first conceived to explain the differences in water solubility of various gases and that only in a second time Dalton realized the importance of application to chemical processes. More recently, other studies appeared [10-17]. In one of them [10] the initial Dalton's recognition of the novelty and significance of the theory from the chemical point of view is on the contrary stressed. In another study of particular interest, the nitric oxide/oxygen crucial experiment has been reproduced [12] and Dalton's pioneering observation of oxygen combination with one or two volumes of nitric oxide has been confirmed. Dalton also tested the nitrous oxide/oxygen reaction by eudiometry [13]. Finally, the influence of London atomists, such as William and Bryan Higgins, on Dalton has been hypothesized and the concept of atomic sizes reexamined [14-16].

On the other hand, it may be worthwhile to review the evolution of Dalton's scientific studies from meteorology [21] to the physics of atmosphere [22,23] and to the first papers on the atomic theory [24,25] through a detailed analysis of his contributions to these fields, as it is proposed in this work. In summary, the paper is organized as follows. In the next Section meteorological observations such as pressure measurements of water vapour, are presented and the conclusion is reached, in disagreement with the leading view at his times, that steam is an *"elastic fluid"* not chemically combined with the other atmospheric components [21]. Then at the end of the 18th century Dalton became interested in the nature of the atmosphere. To explain the atmospheric homogeneity, the theory of mixed gases was elaborated, and the enunciation was made of the law of partial pressures. This is the subject of Section 3 [22,23]. Gas diffusion and solubility were two experiments in agreement with the theory [26-28]. The two papers introducing the chemical atomic theory are reviewed in Section 4 [24,25]. In the first [24], by applying the *"nitrous air test"* to oxygen detection in the atmosphere, Dalton discovered the law of multiple proportions. In the second [25], the solubility of a series of gases in water was investigated and discussed as a purely physical process. The big difficulty, not amenable to the physical origin, was that the solubility varies considerably from one gas to another. Dalton's concern about this effect brought him to meditate about chemical atomism and eventually to present the first table of atomic weights. In Section 5 the main ideas developed on this issue and the criteria on which the table is based, are described with the fundamental help of his laboratory notebook [4]. The Conclusions Section includes a few comments on the outgrowth of the atomic theory. It is hoped that our approach, though of limited historical viewpoint, will not be without interest for scholars curious about the birth of modern chemistry.

2. METEOROLOGICAL STUDIES

Dalton kept a constant interest in meteorology all along his life. In 1793 he published his first book, *Meteorological Observations and Essays*, the second edition appearing in 1834 [21]. The book, divided into two parts with appendixes, deals with various aspects of meteorology ranging from descriptive information on instruments such as barometers and thermometers, to data collection about atmospheric pressure and temperature and to reports on thunderstorms, winds, snow, and the like. Attention was also devoted to *Aurora Borealis* as a phenomenon related to the occurrence of magnetic matter in the atmosphere. Later, Faraday reported on *"atmospheric magnetism"* after his discovery of paramagnetic oxygen [29]. The second part of the book accounts for a few atmospheric processes; the sixth essay is concerned with evaporation, rain, and dew and shows *"germs"* of his physical ideas about vapour. Dalton states in the opening lines of the essay the two opposing views on vapour

> whether the vapour of water is ever chemically combined with all or any of the elastic fluids constituting the atmosphere *[i.e., the view of Lavoisier and French chemists]*, or

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[3] see ref. [2], p. 86.

[4] Dalton's laboratory notebooks were destroyed during the Second World War in a bombing over Manchester.

> it always exists therein as a fluid **sui generis**, diffused among the rest.[5]

and reports on pressure measurements of saturated water vapour at several temperatures in the range 80 – 212ºF (≈ 26 – 100ºC). The results were interpreted in agreement with the second hypothesis although he acknowledged that the observed behaviour with temperature could have also suggested the first choice,

> the fact that a quantity of common air of a given temperature, confined with water of the same temperature, will only imbibe *[dissolve]* a certain portion of the water, and that the portion increases with the temperature, seems characteristic of chemical affinity; but when the fact is properly examined, it will, I think, appear, that there is no necessity of inferring from it such affinity.[6]

There are comments on vapour saturation and condensation that are still valid. Suppose, he says, to reduce the pressure of 1 atm on vapour in equilibrium with water at 100ºC, to a smaller value, 1/10 atm. The new equilibrium temperature is t(ºC) < 100ºC, associated not only with the saturation pressure of 1/10 atm but also with the maximum vapour density at that temperature, called *"extreme density"* by Dalton. Then vapour, if mixed with dry air at t(ºC), will not condense until the pressure reaches 1/10 atm and the vapour density 1/10 that at normal ebullition (neglecting the weak dependence on temperature). Dalton concludes that *"there is no need to suppose a chemical attraction in the case"*.

The independence of the saturated vapour pressure on dry air addition is the second point of interest of the essay. The general, though not universal, view about water evaporation was in the opposite sense, i.e., it was argued that the water vapour is chemically combined with air and that only at the boiling temperature, 212ºF, and above the vapour takes the form of an elastic fluid, called steam [5]. The only contrary opinion was from Wallerius, which was able to evaporate water into a vacuum [18]. However, affinity remained a necessary factor for evaporation under open air, it was replied, since the pressure of the saturated vapour is much lower than one atmosphere at ordinary temperatures and then not sufficient to cause the escape from the liquid. In the appendix to the sixth essay, Dalton reports on pressure measurements at several temperatures on water placed into the vacuum of a barometer, confirming the values taken in the presence of air. Thus, vapour does not combine with air but rather

> the vapour of water (and probably of most other liquids) exists at all times in the atmosphere, and is capable of bearing any known degree of cold without a total condensation and the vapour so existing is one and the same thing with steam, or vapour of the temperature of 212ºF or upwards. The idea, therefore, that vapour cannot exist in the open atmosphere under the temperature of 212ºF unless chemically combined therewith, I consider as erroneous; it has taken its rise from a supposition, that air pressing upon vapour condenses vapour equally with vapour pressing upon vapour, a supposition we have no right to assume.[7]

Dalton concludes that *"the condensation of vapour exposed to common air does not in any manner depend upon the pressure of the air"*. It is fair to say that this statement is substantially, but not entirely, correct. In fact, as it may be seen in various physical chemistry textbooks [30-32] and educational papers [33], the pressure of saturated vapour in the presence of air increases with respect to that in a vacuum, the effect being related to the collisional pressing of nitrogen and oxygen molecules on the liquid inducing an additional transfer of water molecules in the gas phase [30,31]. The difference between pressures with and without air is significant only for added air at extremely high pressure while under the external pressure of 1 atm the two values are practically the same [33]. Summarizing, water vapour is viewed as an independent elastic fluid and evaporation is explained in mechanical terms without invoking a chemical combination of water with atmospheric gases. Maximum vapour pressure is associated with any given temperature, and water evaporates until this value is reached and no further.

3. THEORY OF MIXED GASES

The preliminary account of the theory was published in October 1801 [22] while the final expanded version is contained in the first of four *Experimental Essays*, read the same month, and printed one year later [23]. Dalton recalls that it was *"ascertained"* in the past that atmosphere behaves as *"a homogeneous fluid* [all its particles are of the same kind]" and that *"the elastic force of air was accurately as its density, in a given temperature* [i.e., at constant temperature the air pressure is proportional to density, as required by the Boyle law]". Being Dalton strongly influenced by Newtonian mechanics he was eager to explain the result on the basis of the Newton's *Mathematical Principles of Natural Philosophy* [34]. To this purpose, he takes inspiration from proposition 23,

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[5] Ref. [21], p. 125.

[6] Ref. [20], p. 128.

[7] Ref. [21], p. 188.

book 2 of the *Principles*

> If the density of a fluid composed of particles that are repelled from one another is as the compression, the centrifugal forces [or forces of repulsion] of the particles are inversely proportional to the distances between their centres. And conversely, particles that are repelled from one another by forces that are inversely proportional to the distances between the centres constitute an elastic fluid whose density is proportional to the compression.[8]

As to the nature of the elastic fluid, Newton added cautiously at the end of the scholium accompanying the proposition

> Whether elastic fluids consist of particles that repel one another is, however, a question of physics. We have mathematically demonstrated a property of fluids consisting of particles of this sort so as to provide natural philosophers with the means with which to treat that question.[9]

On the authority of Lavoisier, an elastic fluid was thought to be a combination of matter, or material principle, with caloric [18]. Dalton conceived [4] the *"ultimate atoms of bodies"* as *"those particles which in the gaseous state are surrounded by heat; or they are the centres or nuclei of the several small elastic globular particles"*[10]. Since the caloric around the particles was postulated to be self-repelling [36], a plausible argument is provided for the supposed repulsion, putting apart the prudent warning from Newton. Dalton recalls that *"the atmosphere is not a homogeneous fluid; it is constituted of several elastic fluids"*, in sharp contrast with a basic principle of Aristotelian physics. But for an atmosphere of this kind, the Newtonian proposition is still valid? The question led him to discuss two critical points: (a) whether particles of different fluids repel each other as it happens for particles of the same fluid, and (b) why from their mixing a homogeneous fluid is formed. Dalton answers by taking advantage of the static model of fluid particles, of Newtonian origin [18], i.e., particles in fixed positions each with respect to any other. In this model, the pressure is due only to the repulsion between particles [19]. On expanding at a given temperature the interparticle distance increases, the repulsion weakens, and the pressure upon any particle lowers. On increasing the temperature at constant volume, the repulsion between particles increases [36] and the pressure goes up.

According to Dalton, when two fluids A and B are mixed four types of *"affections* [interactions]*"* may be guessed

> 1. The particles of one elastic fluid may repel those of another with the same force as they repel those of their own kind.
> 2. The particles of one may repel those of another with forces greater or less than that exerted upon those of their own kind.
> 3. The particles of one may possess no repulsive (or attractive) power or be perfectly inelastic with regard to the particles of another; and consequently, the mutual action of such fluids, or the action of the particles of one fluid on those of the other, will be subject to the laws of inelastic bodies.
> 4. The particles of one may have a chemical affinity, or attraction, for those of another.[11]

Dalton considers the four cases and concludes that only the third is consistent with atmospheric homogeneity. Suppose, he says, that m *"measures* [volumes]*"* of A and n *"measures"* of B are enclosed in two boxes having a common wall, under atmospheric pressure at a given temperature. Removing the wall, the total volume will be in the first three cases ($n + m$). As to cases 1 and 2, if the two fluids have different *"specific gravities"*, the lightest would rise to the upper part of the vessel, due to the weaker gravitational attraction. The two fluids will separate in layers, forming what it may be called in our terms a two-phase fluid system. The pressure on any particle would be equal to one atmosphere. No two elastic fluids behave in this way [23]. On the contrary, since in the third case the repulsion between A and B particles is absent

> The two fluids, whatever their specific gravities may be, will immediately or in a short time, intimately diffused through each other, in such a manner that the density of each, considered abstractedly, will be uniform throughout; namely (calling the density of the compound, unity) that of A will be m/(n+m) and that of B = n/(n+m) … The pressure upon any one particle in this case will not be as the density of the compound, as before, but as the density of the particles of its own kind: that is, the pressure upon a particle of A will be equal [m/(n+m)]·30 inches of mercury; that upon a particle of B = [n/(n+m)]·30 inches; those pressures arising solely from particles of their own kind.[12]

The fourth case implies that after mixing *"a union of particles ensues"*. The product may be solid, liquid, or gaseous. For instance, *"when muriatic acid gas*

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[8] Ref. [34], p. 697. The proof of the direct theorem in an updated version may be found elsewhere [35].

[9] Ref. [34], p. 699.

[10] Ref. [4], p. 27.

[11] Ref. [23], p. 536.

[12] Ref. [22], p. 242-243.

[HCl] *and ammoniacal gas* [NH_3] *are mixed together in due proportion, a solid substance, muriate of ammonia* [NH_4Cl] *is formed, and the gases wholly disappear"*. When a gas is formed, the most probable effect is the volume reduction together with an increase of specific gravity and temperature, for instance *"when nitrous gas* [NO] *and oxygenous gas* [O_2] *are mixed in due proportion, the two unite and form a new elastic compound of greater specific gravity and consequently of less bulk, nitric acid gas* [NO_2]". No evidence of chemical affinity has been reported mixing O_2 with N_2 and therefore *"this hypothesis fails equally with the other two"*. As a result of these considerations the structures of single atmospheric gases and their mixture are illustrated in Fig. 1, where *"in the compound atmosphere the same arrangement is made of each kind of particles as in the simple; but the particles of different kinds do not arrange at regular distances from each other; because it is supposed they do not repel each other"*. A law is stated, which is now known as Dalton's law of partial pressures:

> When two elastic fluids, denoted by A and B, are mixed together, there is no mutual repulsion amongst their particles; that is, the particles of A do not repel those of B, as they do one another. Consequently, the pressure of whole weight upon any one particle arises solely from those of its own kind.[13]

On this basis Dalton makes remarkably advanced considerations. The four components of the atmosphere considered by Dalton (nitrogen, oxygen, water vapour and carbon dioxide) press on the surface of earth independently of each other so that the disappearance of any one of them does not affect the density and the pressure exerted by the others. Therefore, the definition of atmosphere by Lavoisier as *"a compound of all the fluids which are susceptible of vaporous or permanently elastic state in the usual temperature* [liquids, like water, undergoing evaporation or gases at ordinary temperatures], *and under the common pressure"*[14] can be accepted only if the last five words are omitted. Second, even if all atmospheric fluids were eliminated, except aqueous vapour, little effect would result on the water evaporation, the only important factor being the pressure of saturated vapour at the given temperature. This was a strong argument against the prevailing idea that water was in liquid form at room temperature because of the atmospheric pressure on its surface.

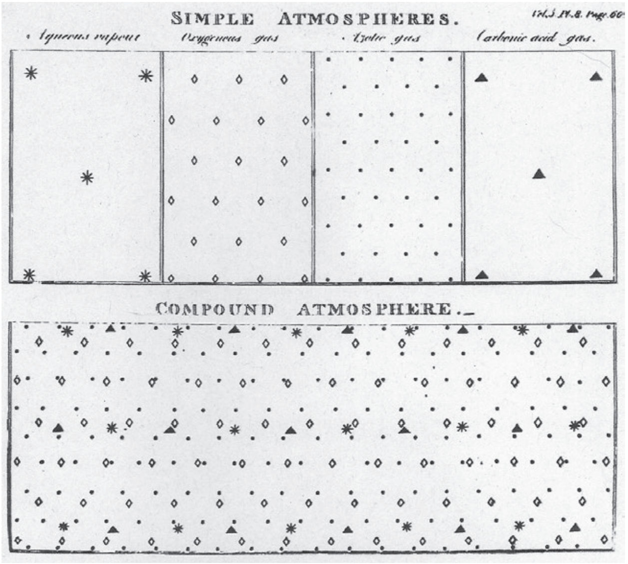

Figure 1. Dalton original plate [23] of simple (*"aqueous vapour, oxygenous, azotic, carbonic acid gases"*, upper) and mixed (*"compound"*, lower) atmospheres.

3.1 Studies on gas diffusion and solubility in water under pressure

Two experiments support the theory of mixed gases [37,38]. In the first [37] (read January 28th, 1803, published in 1805) the gas diffusion is investigated: two gases are enclosed in two phials connected by a narrow vertical tube with the heavier in the lower phial. Such a simple set-up was kept *"in the state of rest"* as much as possible and the capillary tube, ten inches long, was *"not instrumental in propagating an intermixture from a momentary commotion at the commencement of each Experiment"*. Although Priestley had already shown that elastic fluids of different specific gravities do not separate in layers, with the heaviest in the lowest place [39], he nevertheless hypothesized that *"if two kinds of air, of very different specific gravities, were put into the same vessel, with very great care, without the least agitation that might mix or blend them together, they might continue separate, as with the same care wine and water may be made to do"*[15]. Dalton was aware that the outcome of his experiment, *"which seems at first view but a trivial one, is of considerable importance; as from it we may obtain a striking trait, either of the agreement or disagreement of elastic and inelastic fluids in their mutual action on each other"*, i.e., may corroborate or not the theory of mixed gases. Obviously, in the long run, all pairs of gases mix uniformly, CO_2 (*"carbonic acid gas"*, lower phial) with

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[13] Ref. [23], p. 536.

[14] A. Lavoisier, *Traité de Chimie, 1789, i,* p. 31.

[15] cited in ref. [37], p. 260.

air, H_2, N_2 and NO (*"nitrous gas"*) and H_2 (upper phial) with air and O_2, thus establishing *"the remarkable fact that a lighter elastic fluid cannot rest upon a heavier"*.

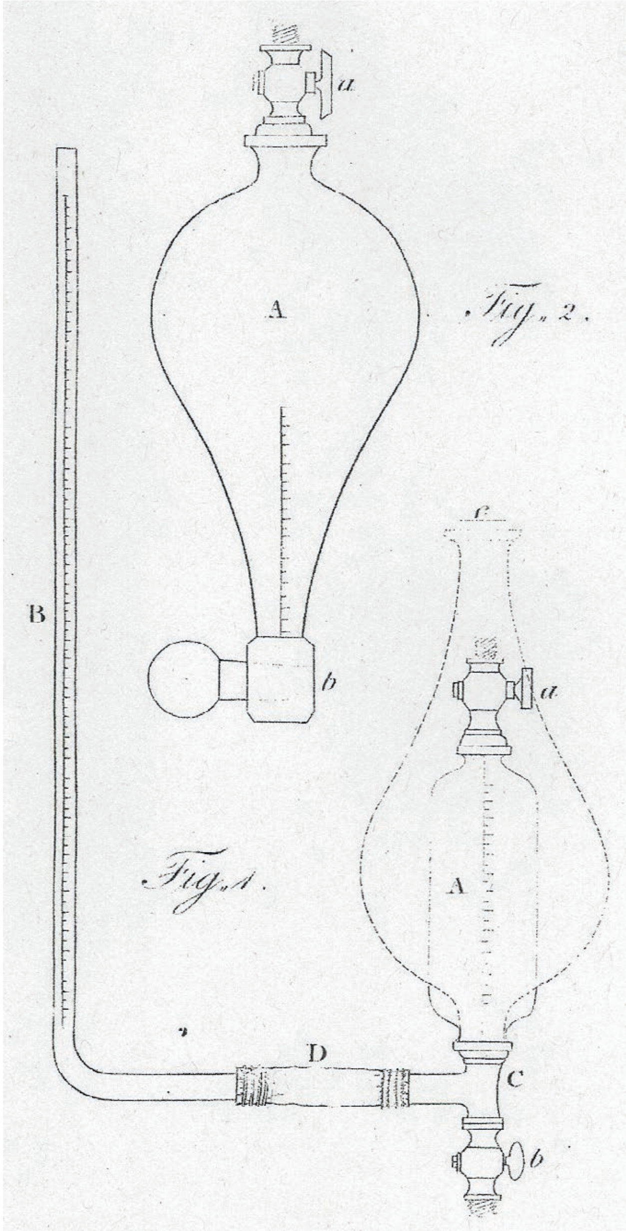

Figure 2. Solubility of gases in water: Henry's experimental apparatus for measurements under pressure from ref. [38]. The larger vessel A was used with *"less condensible gases"*.

The second experiment is concerned with gas dissolved in water under pressure. The study reports on what is now known as Henry's law [38]. It is in our opinion worth outlining the experimental apparatus, as an example of the chemical expertise of Dalton's times. As shown in Fig. 2, the two legs (A and B) of a syphon tube, A being a small, graduated bottle and B an ordinary glass tube open to the atmosphere, are filled with mercury up to the complete replenishment of A and rise at the corresponding level in B. A given quantity of water and a volume of gas may be poured into the bottle through the stopcock *a* when the stopcock *b* situated between the two legs is opened to allow mercury to run out. Then, with *a* closed the level of mercury in both legs is adjusted to the same height so that the gas is under atmospheric pressure. Let us suppose now to add mercury in B to form a column 76 cm higher than the A level. The gas inside the bottle is compressed to two atmospheres and its volume is found to be half that previously occupied. The bottle is vigorously agitated, the absorption of gas takes place and the level of mercury in the bottle rises. To reestablish the pressure difference between A and B it is necessary to add mercury in B: in these conditions, the gas pressure is again two atmospheres and the volume of gas absorbed by water is exactly equal to the mercury added in the last step. With this apparatus Henry determined the solubility of gases such as *"carbonic acid"*, *"sulphuretted hydrogen [H_2S]"*, *"nitrous oxide [N_2O]"*, *"oxygenous and azotic gases"* in water up to three atmospheres. The most significant result was that *"under equal circumstances of temperature water takes up in all cases the same volume of condensed gas as of gas under ordinary pressure"*. To exemplify, if a given quantity of water absorbs 10 ml of a gas at p = 1 atm, it will absorb 10 ml of the same gas at p = 2 atm. But the volume absorbed at p = 2 atm, if expanded to p = 1 atm, would be double that absorbed at p = 1 Atm, or in more general terms

> water takes up of gas condensed by one, two, or more additional atmospheres, a quantity which, ordinarily compressed, would be equal to twice, thrice, etc. the volume absorbed under the common pressure of the atmosphere.[16]

Then, the weight of the gas dissolved at p = 2 atm will be double that at 1 atm and the law takes the more familiar enunciation that the absorbed gas weight is proportional to the incumbent gas pressure [19]. Dalton realized that this behaviour could not be explained in terms of chemical combination of dissolved gas with water, given that the gas is kept in water only due to the gas pressure. This point is clearly attested by Henry in the Appendix [40] of the paper with the following words

> The theory which Mr. Dalton has suggested to me on this subject, and which appears to be confirmed by my experiments, is, that the absorption of gases by water is purely

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[16] Ref. [38], p. 42.

> a mechanical effect, and that its amount is exactly proportional to the density of the gas, considered abstractedly from any other gas with which it may accidentally be mixed.[17]

3.2 *Theory of mixed gases: historical perspective and limits*

After having reviewed the theory of mixed gases, we feel appropriate to refer shortly to the underlying topic, i.e., forces acting between *"ultimate particles"*, and specifically on the theory proposed by the mathematician and astronomer Roger Boscovich [41]. Then, we will make a few general comments on the Dalton theory. Let us start by saying that in the 18th century matter was considered to consist of discrete particles or *"corpuscles"* supposed to be stationary, namely motionless and not colliding [35]. The concept of potential energy was unknown, and the physical world was described in terms of mechanical forces between particles [35]. Of great interest for the originality of the model was the Boscovich theory of oscillatory force. At the planetary and interstellar scale, the gravitational force of attraction, depending on distance as $1/r^2$, dominates. As r recedes, the force is increasingly negative and particles accelerate when approaching each other but at sufficiently short distances, to account for the fact that matter cannot disappear into itself, particles must slow down and then, as r decreases, a repulsive force is supposed to emerge leading first to the inversion of the force from negative to positive and for $r\to 0$ to a repulsion force arbitrarily high. If these two forces were the only ones in action, a single homogeneous solid would result at equilibrium, i.e., at the inversion point. Boscovich assumed that between the two extremes, $r=0$ and $r\to\infty$, additional inversion points occur so that the force oscillates alternatively, depending on the experimental conditions [42]. For instance, the caloric fluid, capable of flowing in and out of all matter, was known to be self-repulsive and then responsible for the repulsion force suggested by the Boyle law. The point at which the gravitational and caloric forces are equal constitutes a second inversion point which determines the static equilibrium in gases. In summary, starting from exceedingly small distances the force oscillates from highly repulsive to attractive (in solids) to repulsive (in gases) and again to attractive at exceptionally large distances.

Going to the second point, it has been wisely noted [18] that the subject of mixed gases can be correctly treated only after admitting that the particles are in motion and not rigidly located at fixed positions. In the absence of the kinetic theory of gases[18] and not resorting to the thermodynamic notion of entropic increase to justify why elastic fluids of whatever density occupy all the available volume, Dalton ascribed to the supposed repulsion between particles the tendency of gases to expand in the whole space. Now we know that gaseous particles weakly attract each other, as it was established by the van der Waals equation for non-ideal gas, but only seventy years later. Thus, a gas must be rather regarded as composed of particles in motion exerting weak attraction forces on each other. All these considerations give evidence of the extraordinary degree of ingenuity of Dalton who, though lacking essential theoretical instruments, arrived at the law of partial pressures by taking only advantage of a bold *ad hoc* hypothesis, *"every gas is a vacuum to every other gas"*, as expressed concisely and brilliantly by Henry [44].

4. STEPPING INTO THE CHEMICAL ATOMIC THEORY

As already noted in the Introduction, the narratives concerning the origin of Dalton's atomic theory go back to Dalton himself [1,2,4]. In later years they were critically reviewed, and alternative explanations were proposed [5,8-10,12,13]. In this Section, we approach the atomic theory taking into consideration the two basic papers [24,25] upon which the theory is founded with the essential support of the Dalton laboratory notebook [4].

4.1 *Experimental enquiry into the proportion of the several gases or elastic fluids, constituting the atmosphere [24]*

The essay under heading was read at the meeting of the Literary and Philosophical Society of Manchester on November 12th, 1802; the publication was delayed until November 1805. Starting from the consideration, based on the theory of mixed gases, that the pressure of a fluid is the same as a single component or in a mixed state, depending only on density and temperature, Dalton determines (i) the pressure of each *"simple atmosphere"* in the *"compound atmosphere"* and then the volume percent of each gas, (ii) the weight percent in a given volume and (iii) the dependence of these properties upon the height above the earth's surface. The gases under examination are *"azotic, oxygenous, aqueous vapour, and carbonic*

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[17] Ref. [40], p. 274.

[18] It should be however recalled that the concept of particle motion was at the centre of the Bernoulli equation obtained in 1738 [43], $pV=(\frac{1}{3})nmv^2$, where p is the pressure defined as the force f, due to the collisions in unit time on the container wall, over its area A, n the number of particles, each of mass m and mean velocity v.

acid”, which were detected in any atmospheric region by means of the analytical methods known at his time.

Beginning with (i), the reactions for oxygen detection were carried out over water and *“if it should appear that by extracting the oxygenous gas from any mass of the atmospheric air, the whole was diminished* $^1/_5$ *in bulk, still being subject to a pressure of 30 inches of mercury* [one atmosphere]*; then it ought to be inferred that the oxygenous atmosphere presses the earth with a force of 6 inches of mercury”*[19]. The reagents were *“nitrous gas* [NO]*”*, *“liquid sulphuret of potash and lime* [water solutions of K_2S and CaS, the reaction being $[2HS^-+O_2\rightarrow 2S+2OH^-]$*”*, *“hydrogen gas* $[2H_2+O_2\rightarrow 2H_2O]$*”* and *“burning phosphorous* $[P_4+5O_2\rightarrow 2P_2O_5]$*”*. Dalton reports volumetric estimates of air reduction only for the first and third reaction, specifying that when all these reactions are conducted *“skilfully”* no difference between results occurs. For instance, by firing 60 *“measures”* of hydrogen with 100 of common air, the final volume is again 100 with complete oxygen disappearance. From these data he found that the oxygen volume is 21 *“measures”* and then the oxygen pressure 6.3 inches. We may suppose that the calculation was done along the following lines (in present-day notation)

$$\text{(a) } V_A+V_{O_2}=100 \quad \text{(b) } V_{H_2,r}+V_{H_2,unr}=60 \quad \text{(c) } \frac{V_{H_2,r}}{V_{O_2}}=1.85$$
$$\text{(d) } V_A+V_{H_2,unr}=100$$

where V_A is the volume of all gases in common air except oxygen and $V_{H_2,r}$, $V_{H_2,unr}$ the reacted and unreacted parts of the total hydrogen volume. The ratio (*c*) is the value measured by Dalton [24], 1.85, (the theoretical value 2 was unknown). Solving for V_{O_2} he obtained $V_{O_2}=21$.

The “nitrous air test”

Greater attention must be deserved to the oxygen detection with *NO*. After the discovery by Hales pouring nitric acid on Walton pyrites [45] the reaction was studied in detail by Priestley in 1772 [46]. Since then, many chemical investigators (including Dalton) used this reaction to estimate the purity or *“goodness”* of air. Priestley found that combining any kind of metals then known (except zinc) with *“spirit of nitre* [nitric acid]*”* an *“air”*, that he called *“nitrous air”*, evolved forming deep *“red fumes”* in the presence of common air. In actual terms the reaction is

$$\underset{\text{“nitrous air”}}{2NO}+O_2\rightarrow\underset{\text{“red fumes”}}{2NO_2}$$

and since NO_2 is easily dissolved in water (while *NO* is not) it follows that, if correctly chosen volumes of *NO* and O_2 are mixed over water, all gases disappear. Starting with common air Priestley always found a large amount of residual gas, which turned out to be the smallest when two volumes of common air were mixed with one of *NO*. In this case, the residue was about 1.8 volumes and the remarkably high contraction of 1.2 volumes corresponded to the volume of added *NO* plus 20%. The degree of volume reduction was then $\sim ^1/_3$. He noted with satisfaction that this contraction

> is peculiar to common air or air fit for respiration; and …. very nearly, if not exactly, in proportion to its fitness for this purpose; so that by this means the **goodness of air** may be distinguished much more accurately than it can be done by putting mice or other animals, to breathe in it … a most agreeable discovery to me.[20]

On the contrary, no reaction with *NO* was observed for air *“unfit for respiration”* such as fixed air (CO_2) or inflammable air (H_2) so that their *“goodness”* is zero. Intermediate degrees of reduction between zero (no reaction) to $\sim ^1/_3$ (reaction of 1 volume of *NO* and 2 volumes of common air) represent intermediate degrees of *“goodness”*. Priestley proudly stated that *“we are in possession of a prodigiously large scale* [i.e., $0\text{-}^1/_3$] *by which we may distinguish very small degrees of difference in the goodness of air”*.

Going now back to the Dalton paper, he found that the reacting volumes were strongly dependent on the experimental conditions. In fact, after preparing *“nitrous gas”* adding the water solution of nitric acid to copper or mercury (point 1), he says in the successive points

> 2. If 100 measures of common air be put to 36 of pure nitrous gas in a tube $^3/_{10}$ of an inch wide and 5 inches long, after a few minutes the whole will be reduced to 79 or 80 measures and exhibit no signs of either oxygenous or nitrous gas.
> 3. If 100 measures of common air be admitted to 72 of nitrous gas in a wide vessel over water, such as to form a thin stratum of air, and an immediate momentary agitation be used, there will, as before, be found 79 or 80 measures of pure azotic gas for a residuum.
> 4. If, in the last experiment, less than 72 measures of nitrous gas be used, there will be a residuum containing oxygenous gas; if more, then some residuary nitrous gas will be found.[21]

These data indicate that a given volume of oxygen (making part of the common air) reacts with another of

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[19] Ref. [24], p. 246.

[20] Ref. [46], p. 114, bold letters, our addition.

[21] Ref. [24], p. 249.

NO or its double. This implies the law of multiple proportions. The conclusion is expressed by Dalton with the following significant words

> These facts clearly point out the theory of the process: the elements of oxygen may combine with a certain portion of nitrous gas, or with twice that portion, but with no intermediate quantity. In the former case **nitric** acid [$2NO+O_2 \rightarrow 2NO_2$] is the result; in the latter **nitrous** acid [$4NO+O_2 \rightarrow 2N_2O_3$]: but as both these may be formed at the same time, one part of the oxygen going to one of nitrous gas, and another to two, the quantity of nitrous gas absorbed should be variable; from 36 to 72 per cent for common air…. In fact, all the gradation in quantity of nitrous gas from 36 to 72 may actually be observed with atmospheric air of the same purity; the wider the tube or vessel the mixture is made in, the quicker the combination is effected, and the more exposed to water, the greater is the quantity of **nitrous** acid and the less of **nitric** that is formed.[22]

There has been much debate among science historians about when Dalton obtained the results of points 2 and 3. These, if presented at the reading date, November 12th, 1802, would mean that the law of multiple proportions was discovered long before the proposal of the atomic theory (which is, as it is well known [4], September 6th, 1803). The Dalton notebook [4], from November 1802, the date of the earliest records on his laboratory activity, until the end of 1803, supports the idea that both the experimental results and the discussion were made at a time later than November 1802. For instance, Dalton writes, March 21st, 1803, *"Nitrous gas – 1.7 or 2.7 may be combined with oxygen, it is presumed"*[23]. Second, on April 1st, 1803, several experiments are listed on *"nitrous gas"* and common air in relation to the higher absorption of the reactant when the mixture is rapidly formed but the record ends with the doubtful question *"Query, is not nitrous air decomposed by the rapid mixture?"*. At that date, six months after November 1802, Dalton had not reached the well-defined conclusions expressed in the paper [4]. The discrepancy between presentation and publication has been explained [4] by the fact that Dalton, as Secretary of the Manchester Literary and Philosophical Society since 1800, had many opportunities to revise the work according to his latest findings. Further, the numbers quoted in points 2 and 3 of the paper were written in the notebook at an undetermined date between October 10th and November 13th, 1803, more than one month after the first appearance of the atomic weight table [4].

However, Dalton in some experiments before September 1803 had noticed a simple ratio for the volumes of *"nitrous gas"* reacting with a given volume of oxygen. The notebook reports, August 4th, 1803, that *"it appears, too, that a very rapid mixture of equal parts com. air and nitrous gas, gives 112 or 120 residuum. Consequently, that oxygen joins to nit. gas sometimes 1.7 to 1 and at other times 3.4 to 1* [the theoretical ratios, unknown to Dalton, for the formation of nitric and nitrous acid, are 2:1 and 4:1, respectively]*"*[24]. This extract paved the way for the proposal [5] that Dalton, pondering about the significance of the 2:1 ratio of the reacted *"nitrous gas"* under different conditions, made the bold generalization, going from the particular *NO* reaction to the law of multiple proportions and then to the chemical atomic theory, which would have appeared within one month. In other words, here the suggestion is that the atomic theory was derived from the law of multiple proportions [5]. This view has been subject in the following years to a strong criticism emphasizing the experimental difficulties to replicate these ratios even when the reaction was carried out with the updated instrumentation available to researchers more than one century later [7,8]. For instance, it has been pointed out that, out of many reaction trials personally performed, few of them gave a ratio reasonably approximating 3.4:1, the most difficult to replicate [8]. But, in contrast, a successful reconstruction of the experiment has been recently reported, where the narrow tube value, 1.7:1, has been confirmed and the 3.4:1 ratio justified observing that gas-phase and dissolved oxygen in the wide water vessel are involved when *NO* is in excess with respect to O_2 [12]. It has been added [12] that if the reaction is complete, i.e., in the presence of a sufficient amount of water, all excess *NO* is consumed and any NO/O_2 ratio greater than 2:1 may be obtained; then Dalton carried out the reaction optimizing the experimental conditions to achieve the desired result, as it is evident comparing the notebook entries of March 12th and August 4th. Thus, the plausible conclusion was that Dalton discovered the first example of the law of multiple proportions having already in mind the implications of the atomic theory [12].

For completeness, it remains to report on the other points discussed in the paper. The pressures of water

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[22] Ref. [24], p. 250.

[23] Ref. [4], p. 34. The two ratios, 1.7:1 and 2.7:1, are narrow tube and wide vessel values, respectively.

[24] Ref. [4], p. 38. A possible justification of the second ratio, 3.4:1, may be derived as follows. The three equations to be considered are (a) $V_A+V_{O_2}=100$; (b) $V_{NO,r}+V_{NO,unr}=100$; (c) $V_A+V_{NO,unr}=112$, where *A* denotes, as usual, all atmospheric gases except oxygen and $V_{NO,r}$ and $V_{NO,unr}$ are the reacting and excess volumes of *NO*. Taking from previous experiments as a reasonable approximation of the oxygen volume $V_{O_2}=20$ we have $V_{NO,unr}=32$; $V_{NO,r}=68$ and then $\frac{V_{NO,r}}{V_{O_2}}=3.4$. The same calculation with 120 residuum gives $\frac{V_{NO,r}}{V_{O_2}}=3$.

vapour and *"carbonic acid"* [CO_2] in the atmosphere were determined by means of the analytical methods known at that time. Dalton took advantage of the pressure diagram of saturated water vapour with temperature, already determined by himself and reported in *Meteorological Observations and Essays*. It was enough to measure the dewpoint temperature of the vapour: the pressure of this vapour in the atmosphere coincides with that of the saturated vapour at dewpoint temperature[25]. Then, Dalton analyzed the amount of CO_2 by adding *"lime-water"* [saturated water solution of $Ca(OH)_2$] to precipitate atmospheric CO_2 contained in a bottle with a capacity of *"102400 grains of rain water* [≈7L]*"*. He found that *"102400 grains measures of common air contain 70 of carbonic acid"*. Going to point (ii) of the paper, Dalton, using densities from Lavoisier and Kirwan (N_2 and CO_2), Davy (O_2) and himself (H_2O vapour), arrived at the gravimetric percent composition of the air from volumetric data. Pressure (in *"inches of mercury"*) and percent of each component resulted to be: *"azotic gas"* 23.36, 75.55%; *"oxygenous gas"* 6.18, 23.32%; *"aqueous vapour"* 0.44, 1.03%; *"carbonic acid gas"* 0.02, 0.10%. As to point (iii), it was found that at higher altitudes the atmospheric oxygen decreases with respect to the other gases but only slightly. From this Dalton concluded that *"at any ordinary heights the difference in the proportions will be scarcely if at all perceptible"*.

3.2 On the absorption of gases by water and other liquids [25]

This paper was read in front of a selected audience of nine members and friends at the meeting of the Literary and Philosophical Society of Manchester held on October 21st, 1803 and printed on the Manchester Memoirs of the Society in November 1805, following the paper of the previous subsection. The experiments on gas solubilities in water were prompted by Henry's studies in this field and represent a big part of Dalton's work in the last months of 1802, from January to March 1803 and in August of the same year [4]. Both men interpreted the results as being due to a mechanical, rather than to a chemical effect, arising only from the pressure of the absorbed gas and independent of the presence of any other gas [40]. Fifteen experiments, numbered as *"articles"* in the paper, are presented, the most significant being undoubtedly the second:

> If a quantity of water thus freed from air be agitated in any kind of gas, not chemically uniting with water, it will absorb its bulk of the gas [CO_2, H_2S, N_2O], or otherwise a part of it equal to some one of the following fractions, namely, $^1/_8$[C_2H_4], $^1/_{27}$[O_2, NO, CH_4], $^1/_{64}$[H_2, N_2, CO], &c. these being the cubes of the reciprocals of the natural numbers 1, 2, 3, &c. or $^1/_{1^3}$, $^1/_{2^3}$, $^1/_{3^3}$, $^1/_{4^3}$, &c. the same gas always being absorbed in the same proportion …: – It must be understood that the quantity of gas is to be measured at the pressure and temperature with which the impregnation *[saturation]* is effected."[26]

It has been noted [8] that Dalton often indulged in the search of simple mathematical relations even in the presence of experimental values affected by a large error such as those relative to solubility measurements of the period January – March 1803 [4]. The difficulties encountered in data acquisition are evident in this long paragraph of the paper:

> In my Experiments with the less absorbable gases, or those of the 2d, 3d, and 4th classes, I used a phial holding 2700 grains of water, having a very accurately ground-stopper; in those with the more absorbable of the first class, I used an Eudiometer tube properly graduated and of aperture so as to be covered with the end of a finger… *[which]* was applied to the end and the water within agitated; then removing the finger for a moment under water, an additional quantity of water entered, and the agitation was repeated till no more water would enter, when the quantity and quality of the residuary gas was examined. In fact, water could never be made to take its bulk of any gas by this procedure; but if it took $^9/_{10}$, or any other part, and the residuary gas was $^9/_{10}$ pure, then it was inferred that water would take its bulk of that gas. The principle was the same in using the phial; only a small quantity of the gas was admitted, and the agitation was longer.[27]

But by March 6th, 1803, he trusted data on hydrogen, nitrogen and oxygen [4] since *"it now appears more than probable that in all cases hydrogen and azotic gases in water have their particles 4 times the distance that they have incumbent* $=^1/_{64}$ *or 1.5625 per cent, and oxygen gas 3 times* $=^1/_{27}$ *density* =3.7 [per cent]*"*. To our opinion, much of the credit for the better-defined relation of solubilities to inverse cubes of natural numbers belongs to the more reliable Henry data [39], as Dalton fairly acknowledg-

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[25] Dalton had already given the definition of dewpoint in the following terms [47]:*"whatever quantity of aqueous vapour may exist in the atmosphere at any time, a certain temperature may be found, below which a portion of that vapour would unavoidably fall or be deposited in the form of rain or dew, but above which no such diminution could take place, chemical agency apart. This point may be called the* ***extreme temperature*** [i.e., dewpoint] *of vapour of that density. Whenever any body colder than the extreme temperature of the existing vapour is situated in the atmosphere, dew is deposited upon it"*.

[26] Ref. [25], p. 271.

[27] Ref. [25], p. 280.

es with these words: “*by the reciprocal communication* [between Dalton and Henry] *since, we have been enabled to bring the results of our Experiments to a near agreement; as the quantity he has given in his appendix to that paper nearly accord with those I have stated in the second article*”. On October 21st, 1803, Dalton had sound data for the three gases (and for “*carbonic acid*” and “*nitrous oxide* [N_2O]” [4,8]). The data relative to “*carburetted hydrogen*” and (probably) “*olefiant gas*” were obtained at a later date [4,8,18].

Dalton explains the solubility of gases in water in “*mechanical*” terms saying that “*all gases that enter into water and other liquids by means of pressure, and are wholly disengaged again by the removal of that pressure, are mechanically mixed with liquids, and not chemically combined with it*”[28]. As already outlined in the past Section, the gaseous particles were thought to form an array of hard-packed spheres repelling each other both in water and out of it; further, the gas was retained in water only by the pressure of particles of the same kind and “*water has no other influence in this respect than a mere vacuum*”. Dalton asks in the notebook [4]: “*is it not two atmospheres pressing one against the other?*” of which one is the “*atmosphere*” of the gas pressing on water and the other the hypothetical “*atmosphere*” of the dissolved gas. The two “*atmospheres*” have different densities and the ratio is given by the reciprocal of cubes of natural numbers. For instance, oxygen in water is less dense than out by $^{1}/_{3^3}={}^{1}/_{27}$; the same ratio for nitrogen is $^{1}/_{4^3}={}^{1}/_{64}$. Thus, the distance between adjacent dissolved particles is a multiple of the distance in the atmosphere, “*in oxygenous gas, &c. the distance is just three times as great within as without; and in azotic, &c. it is four times.*”[29] Some drawings are attached to the paper, to make more explicit Dalton's physical theory of gas absorption. In “*View of a Square Pile of Shot*”, Fig. 3, squares of packed spheres (white, water particles) are pressed by the upper sphere (black, a gas particle) and the pressure is distributed among the water particles, first on 4, then from 4 to 9, from 9 to 16, etc., until the next lower particle of absorbed gas is reached. Since in Fig. 3 the ratio of the distance between gas particles and between water particles is supposed to be 10:1 the final pressure is distributed among 100 water particles and “[since] *in the same stratum each square of 100* [has] *its incumbent particle of gas, the water below this stratum is uniformly pressed by the gas, and consequently has not its equilibrium disturbed by that pressure*”[30].

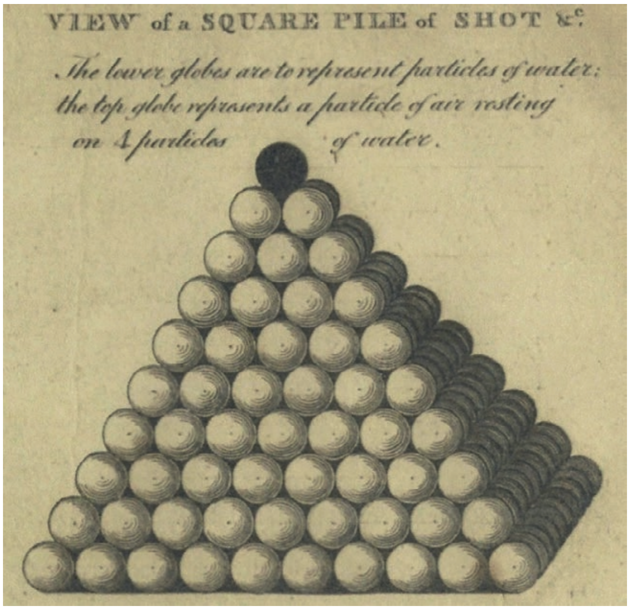

Figure 3. A particle of gas (black sphere) pressing particles of water (white spheres), from ref. [25].

In “*Profile View of Air in Water*”, Fig. 4, right, the oxygen dissolved in water is considered. Its pressure amounts to $^{1}/_{27}$ of the incumbent pressure and, as Dalton points out, this pressure is exerted on the container walls and on the gas above the water, not on water. At equilibrium, atmospheric oxygen presses the dissolved portion by the same pressure, $^{1}/_{27}$, and the remaining, $^{26}/_{27}$, is the pressure of the gas on the water's surface. There is repulsion between the two strata of oxygen just adjacent to this surface, though much smaller, $^{1}/_{27}$, than between particles in the atmosphere. Being the repulsion inversely proportional to the distance, this means that the two strata must be apart 27 times the distance of particles in the atmosphere. Applying the same line of reasoning to N_2 and H_2, the distance between the two strata increases to 64 times, as seen in Fig. 4, left.

In the concluding paragraph of the paper, the big difficulty arises in the application of the hard spheres model to the solubility data of gases. The model cannot explain the intriguing result of his (and Henry's) experiments: why different gases dissolve differently in water? It has been suggested [8] that Dalton answered this question by invoking the correlation between solubility and density data. On September 19th, 1803, the specific gravities of several gases (with respect to air) are reported in the laboratory notebook, including those of the first and last group of the table, i.e., hydrogen (0.077), nitrogen (0.966), “*carbonic acid* [CO_2]” (1.500), “*nitrous oxide* [N_2O]” (1.610). Taking into consideration only the gases

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[28] Ref. [25], p. 283.
[29] Ref. [25], p. 281.
[30] Ref. [25], p. 284.

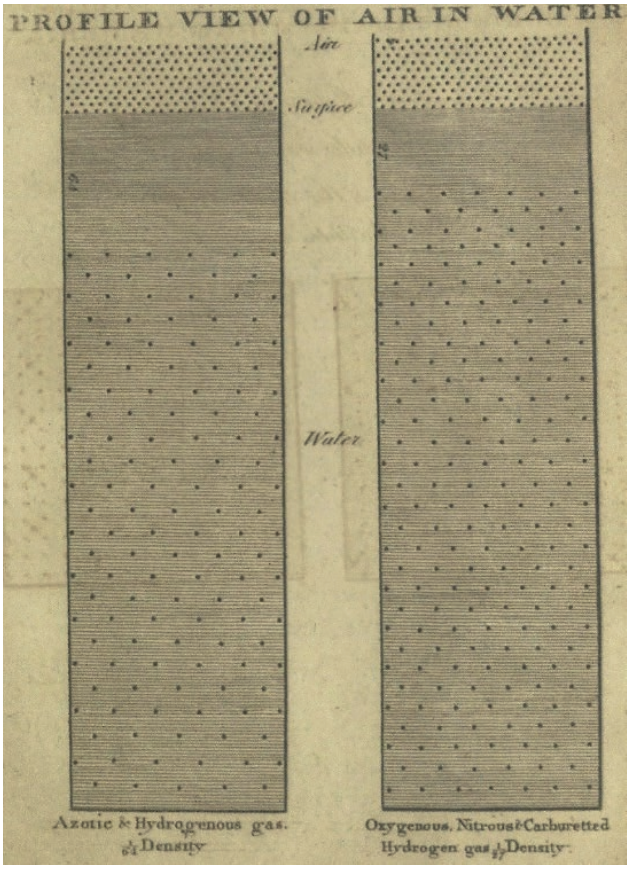
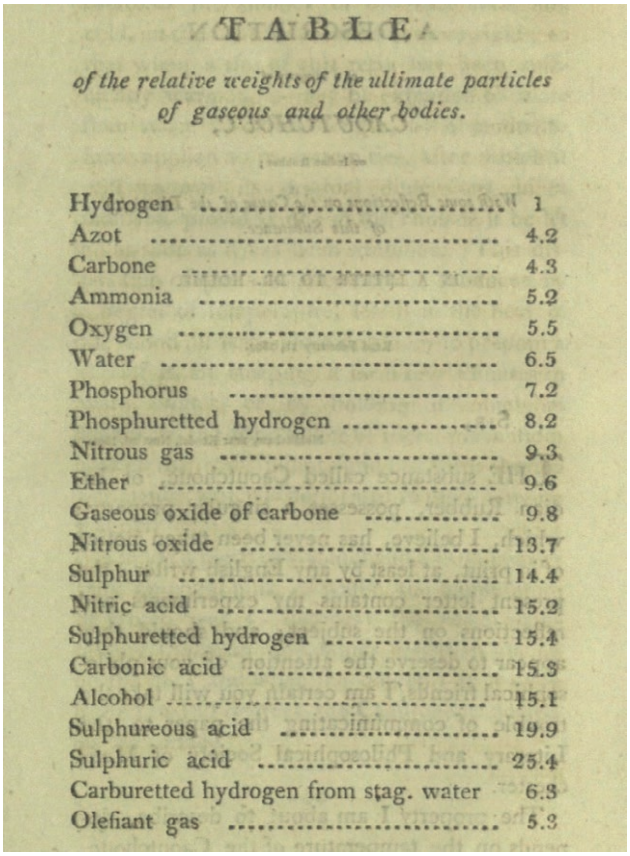


Figure 4. The gas profile along the vertical axis, from ref. [25]: left, N_2 and H_2; right, O_2, NO and CH_4.



TABLE

of the relative weights of the ultimate particles of gaseous and other bodies.

Hydrogen	1
Azot	4.2
Carbone	4.3
Ammonia	5.2
Oxygen	5.5
Water	6.5
Phosphorus	7.2
Phosphuretted hydrogen	8.2
Nitrous gas	9.3
Ether	9.6
Gaseous oxide of carbone	9.8
Nitrous oxide	13.7
Sulphur	14.4
Nitric acid	15.2
Sulphuretted hydrogen	15.4
Carbonic acid	15.3
Alcohol	15.1
Sulphureous acid	19.9
Sulphuric acid	25.4
Carburetted hydrogen from stag. water	6.3
Olefiant gas	5.3

Figure 5. The table of relative weights of *"ultimate particles"* of elements and compounds from ref. [25].

on which solubility data were known at the reading date, the indication is clear: elementary and low-density gases are scarcely soluble in water while compound and high-density gases are appreciably soluble. Given this premise, to the question *"why does water not admit its bulk of every kind of gas alike?"* Dalton was enabled to answer with great ingenuity (bolds are our additions) *"**the circumstance depends on the weight and number of the ultimate particles of the several gases**: Those whose particles are lightest and single being least absorbable and the others more according as they increase in weight and complexity"*[31]. Dalton had in mind **weight** and **complexity** of the *"ultimate particles"*, thus initiating the transition from a physical to a chemical atomic theory. The correlation of solubility with density led to a research project described in these terms *"An enquiry into the relative weights of the ultimate particles of bodies is a subject, as far as I know, entirely new: I have lately been prosecuting this enquiry with remarkable success."* Thus, the paper ends with the result of this enquiry, a long table (see Fig. 5) containing *"the relative weights of the ultimate particles of gaseous and other bodies"*. How this table was obtained by Dalton and on which criteria was based in order to get to the particles' weights is the subject of the next Section.

5. DALTON'S CHEMICAL ATOMISM

In his laboratory notebook, September 6th, 1803, Dalton wrote notes bound to become a milestone in the history of chemistry [4]. The earliest set of *"characters* [chemical symbols]*"* was drawn to represent the *"ultimate particles"* of the elements and to give an unequivocal description of their combination in a compound. In agreement with his idea of atoms, Dalton's *"characters"* are circles with a distinguishable inner part; the initial choice for hydrogen and oxygen (open and dotted circle, respectively) were interchanged in later tables. The original page 244, taken from ref. [4], is shown in Fig. 6.

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[31] Ref. [25], p. 286. In the footnote, Dalton adds: *"Subsequent experience renders this conjecture less probable"*.

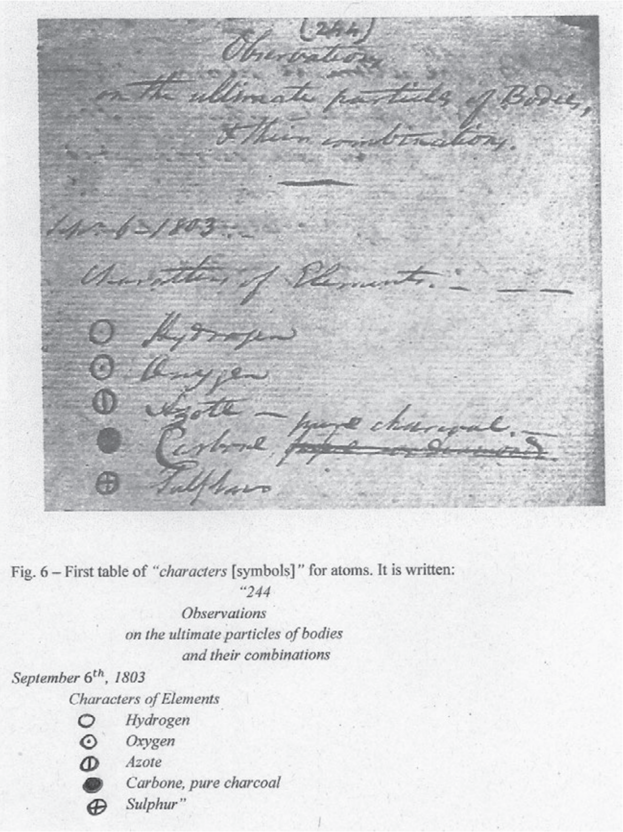

Fig. 6 – First table of *“characters* [symbols]*”* for atoms. It is written:

“244

Observations

on the ultimate particles of bodies

and their combinations

September 6^th^, 1803

Characters of Elements

○ *Hydrogen*

⊙ *Oxygen*

⦶ *Azote*

● *Carbone, pure charcoal*

⊕ *Sulphur”*

Figure 6.

Figure 7. The first table of the relative weights of elements and compounds from the original in ref. [4].

It is written on page 248:

“ *Ult. at.*	*Hydrogen* *1*	
-------	*Oxygen* *5.66*	
-------	*Azot* *4*	
-------	*Carbon (charcoal)*	*4.5*
-------	*Water* *6.66*	
-------	*Ammonia 5*	
-------	*Nitrous gas*	*9.66*
-------	*Nitrous oxide*	*13.66*
-------	*Nitric acid5.32*	
-------	*Sulphur* *17*	
-------	*Sulphureous acid*	*22.66*
-------	*Sulphuric acid*	*28.32*
-------	*Carbonic acid*	*15.8*
-------	*Oxide of carbone*	*10.2”*

Page 248, shown in Fig. 7, contains the first table of (relative) atomic weights, two years before that of Fig. 5. The numerical values could have been easily established from the relative gas densities if Dalton had been willing to accept what is now known as the Avogadro’s principle. For instance, from the densities reported in the notebook[32], the oxygen and nitrogen weights would have been found to be 14.6 and 12.5, respectively, that of hydrogen. But this hypothesis was rejected since the very first conception of the atomic theory with the following words

> Though it is probable that the specific gravities of different elastic fluids have some relation to that of the ultimate particles, yet it is certain that they are not the same thing; for the ult. part. of water or steam are certainly of greater specific gravity than those of oxygen, yet the last gas is heavier than steam.[33]

It is plain, Dalton says, that, if the *“ultimate particle”* of water is composed by those of oxygen and hydrogen, it must be heavier than that of oxygen. Then, being experimentally observed that the water vapour is less dense than oxygen, this necessarily means that in equal volumes fewer particles of water vapour are contained than of oxygen. This was not a unique example since from the same table (see footnote 32) it is seen

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[32] See ref. [4], p. 41.

[33] Ref. [4], p. 27. The rebuttal of Avogadro’s hypothesis was justified by Dalton also on a different basis in *A New System of Chemical Philosophy*, p. 71: *“It is evident the number of ultimate particles or molecules in a given weight or volume of one gas is not the same as in another: for, if equal measures of azotic and oxygenous gases were mixed, and could be instantly united chemically, they would form nearly two measures of nitrous gas, having the same weight as the two original measures; but the number of ultimate particle could at most be one half of that before the union. No two elastic fluids, probably, therefore, have the same number of particles, either in the same volume or the same weight”*. The apparently impeccable argument of Dalton runs as follows: starting from n *“ultimate particles”* of nitrogen and of oxygen in equal volumes V, *“nitrous gas”* is obtained in the volume $2V$. Since the particles of *“nitrous gas”* cannot be more than n, this means that $^n/_2$ particles of *“nitrous gas”* are in the volume V.

that ammonia, formed by nitrogen and hydrogen, is less dense than nitrogen, and carbon oxide, formed by oxygen and carbon, is equally less dense than oxygen. It would be difficult to avoid the conclusion that different numbers of particles were in the same volume of several gases [48].

Excluding the information from physical data, Dalton made use of chemical data for the derivation of atomic weights. In simple words, the question was: being known from the Lavoisier analysis that the oxygen weight content of water is 85% (and hydrogen 15%), is it possible to determine the weight of an oxygen atom (with respect to hydrogen)? The entries of Fig. 7 contain the Dalton answer not only for oxygen (5.66) but also for three other elements (nitrogen, carbon, and sulphur, 4, 4.5 and 17, respectively), however without any detailed explanation of the computational procedure to arrive at these values. It has been said [8,18] that all calculations, implicitly or explicitly, are based on the following principles: (i) matter is constituted of extremely minute particles (atoms), (ii) atoms are indivisible and cannot be created or destroyed, (iii) atoms of a given element are identical and have the same invariable weight, (iv) atoms of different elements have different weights, (v) the particle of a compound is formed by a fixed number of atoms of its component elements (law of definite proportions) and its weight is the sum of the weights of the constituent atoms, (vi) if more than one compound of two elements is known, the numbers of atoms of either element in the compound particle are in the ratio of whole (small) numbers (law of multiple proportions).

Given a binary compound of A and B composed of particles with n atoms of A and m of B, i.e., A_nB_m, and the weight percent, $(\%)_A$ and $(\%)_B$, in the compound, the atomic weight of B with respect to A, $\frac{p_B}{p_A}$, results $\frac{p_B}{p_A} = \frac{n}{m} \cdot \frac{(\%)_B}{(\%)_A}$. To determine $\frac{p_B}{p_A}$, it is then necessary to know not only the percent composition of each element in the compound but also the number of A and B atoms entering the particle. If this latter information is missing but it happens that only one compound of A and B is formed, Dalton adopted the *"rule of greatest simplicity"*; he reasonably assumed that the compound is AB, n=m=1, unless there is some reason to the contrary. The water particle was taken to be OH and therefore $\frac{p_O}{p_H} = \frac{0.85}{0.15}$=5.66. Being not known any other compound of nitrogen and hydrogen in addition to ammonia, which in an old Austin analysis was reported to be composed by about 80% nitrogen and 20% hydrogen, Dalton found $\frac{p_N}{p_H} = \frac{0.80}{0.20}$=4 with the ammonia particle expressed as NH. The atomic weight of carbon, $\frac{p_C}{p_H}$=4.5, was determined from the Lavoisier analysis of the *"carbonic acid"* gas, 72% oxygen and 28% carbon. Since two gases, *"carbonic acid"* and *"oxide of carbone"*, are composed by the same elements, carbon and oxygen, the specification of the *"ultimate particles"* requires an additional proviso. The extended version of the *"rule of greatest simplicity"* dictates that in this case one particle is CO and the other CO_2 or C_2O[34]. Dalton correctly opted for CO_2, as to *"carbonic acid"*, and for CO in the case of *"oxide of carbone"*, using probably as a clue the relative gas densities (see footnote 32). With this assignment he calculated $\frac{p_C}{p_H} \left(\frac{p_C}{p_O} \cdot \frac{2}{1}\right) \cdot \frac{p_O}{p_H} = \left(\frac{0.28}{0.72} \cdot 2\right) \cdot 5.66=4.4$ (in the table of Fig. 7 the entry is either a miscalculation or a "rounded off" value [4]). In the same table the reported weights of the *"ultimate atoms"* of the two gases are 15.8 (CO_2) and 10.2 (CO). As to the atom of sulphur, two sets of data were available for the *"sulphuric acid"* gas, one from Chenevix (61.5% sulphur; 38.5% oxygen) and the other from Thenard (56% sulphur; 44% oxygen). As for the pair CO/CO_2, the particles of *"sulphureous acid"* and *"sulphuric acid"*, not breaking with the *"rule of greatest simplicity"*, were taken to be (incorrectly) SO and SO_2. *"Sulphuric acid"* was assumed to be SO_2, the choice being presumably based again on the densities of the two gases (see footnote 32). The atomic weight of sulfur was calculated from the expression $\frac{p_S}{p_H} = \frac{p_S}{p_O} \cdot \frac{p_O}{p_H}$, which gives 18.1 and 14.4 depending on the set of data, averaged to 17. The weights of SO and SO_2 are 22.66 and 28.32 (see Fig. 7)[35].

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[34] Dalton in later years justified this rule starting from the Newtonian proposition 23 [49] with the following speculation about the atomic architecture of the AB_n particles: "*When an element A has affinity for another, B, I see no mechanical reason why it should not take as many atoms of B as are presented to it, and can possibly come into contact with it (which may probably be 12 in general), except so far as the repulsion of the atoms of B among themselves are more than a match for the attraction of an atom of A. Now this repulsion begins with 2 atoms of B to one of A, in which case the two atoms of B are diametrically opposed; it increases with 3 atoms of B to 1 of A, in which case the atoms of B are only 120° asunder; with 4 atoms of B it is still greater, as the distance is then only 90°; and so on in proportion to the number of atoms. It is evident then from these positions that, as far as powers of attraction and repulsion are concerned (and we know of no other in chemistry) … binary compounds must first be formed in the ordinary course of things, then ternary and so on, till the repulsion of the atoms of B … refuse to admit any more*".

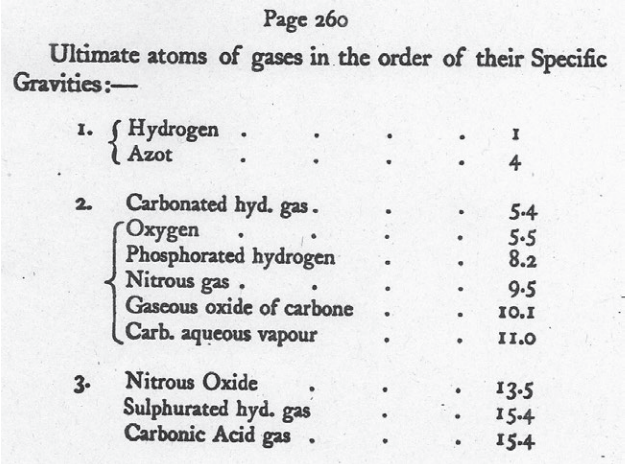
[35] It should be again stressed that the relative atomic weights could have been determined from the weight percent and the Avogadro principle. In fact, being in this hypothesis $m\frac{p_B}{p_A}=(\%)_B \cdot \frac{(np_A+mp_B)}{p_A}=(\%)_B \cdot \frac{\rho(A_nB_m)}{\rho(A)}$, the weight of B in A_nB_m results to be an integral multiple of $\frac{p_B}{p_A}$. Thus, analyzing a sufficiently large group of compounds of B and determining their densities $\rho(A_nB_m)$ (together with $\rho(A)$, the A density) at equal temperature and pressure, the smallest of these multiples corresponds very probably to m=1 and therefore identifies $\frac{p_B}{p_A}$. This proposal, which is substantially the Cannizzaro rule, was unfortunately advanced only sixty years later.

Table I. The composition of the three nitrogen oxides according to theoretical (Dalton) and experimental (Davy) results. The particle weight is expressed in units of the nitrogen weight (see ref. [4]); r is the ratio O(%)/N(%).

	Weight	Dalton results				Davy experimental results			
		N(%)	O(%)	r		N(%)	O(%)	r	
N_2O	2+1.42	58.5	41.5	0.71	0.5	63.3	36.7	0.58	0.46
NO	1+1.42	41.3	58.7	1.42	1	44.05	55.95	1.27	1
NO_2	1+2·1.42	26.0	74.0	2.84	2	29.5	70.5	2.39	1.88

The last three entries of the table refer to *"nitrous gas"*, *"nitrous oxide"* and *"nitric acid"*. According to the *"rule of greatest simplicity"* and given the relative gas densities (see footnote 32) they were formulated as NO, N_2O and NO_2. The assignment is correct for the first two gases. As to the third, since Dalton accepted the composition proposed by Lavoisier for nitric acid [18], the weight was calculated 4+2·5.66=15.32, corresponding to NO_2. In addition, since the atomic weight of an element does not vary from a compound to another, as a second point of interest in these gases Dalton observes that *"from the composition of water* [OH] *and ammonia* [NH] *we may deduce ult. at. azot 1 to oxygen 1.42* [i.e., $\frac{p_O}{p_N}=\frac{p_O}{p_H}\cdot\frac{p_H}{p_N}=\frac{5.66}{4}$=1.42]" so that the *"ult. atom of nit. gas* [NO] *should therefore weigh 2.42 azot* [i.e., p_{NO}=2.42p_N]"[36]. The law of equivalent proportions says that the ratio of the weight of oxygen to that of nitrogen in the three oxides is either equal to or a simple multiple or fraction of 1.42 (see Table I). This means that also the law of equivalent (or reciprocal) proportions is implied by the theory [18]. In occasion of the first lecture, December 22th, 1803, of a series of 20 at the Royal Institution in London Dalton received the experimental results of Davy on the three compounds, reported by Dalton in Table I [4].

Within approximately one month from September 6th Dalton (i) tested the theory regarding the dependence of the gaseous solubilities on the particle weight and (ii) presented a set of chemical formulae for an appreciable number of compounds. On September 19th, 1803, eleven gases were arranged in order of increasing weight and divided into three groups [4] (see Fig. 8). Hydrogen and nitrogen, having the least particle weights, are the least soluble gases in water. On the opposite, *"nitrous oxide* [N_2O]", *"sulphurated hyd. gas* [H_2S]" and *"carbonic acid gas"* with the highest particle weight are the most soluble gases. In the middle six gases of intermediate weights have intermediate solubilities. Once compared with the second *"article"* of the paper [18], the order results being nearly the same, except for CO.



Page 260

Ultimate atoms of gases in the order of their Specific Gravities:—

1.	Hydrogen	1
	Azot	4
2.	Carbonated hyd. gas	5.4
	Oxygen	5.5
	Phosphorated hydrogen	8.2
	Nitrous gas	9.5
	Gaseous oxide of carbone	10.1
	Carb. aqueous vapour	11.0
3.	Nitrous Oxide	13.5
	Sulphurated hyd. gas	15.4
	Carbonic Acid gas	15.4

Figure 8. The three groups of gaseous solubilities ordered according to the weight of the compound atom. The *"carbonated hyd. gas"* is ethylene, elsewhere called *"olefiant gas"*, while the *"carb. aqueous vapour"* was later shown by Dalton to be a mixture of CO and H_2.

The table of Fig. 8 was probably prepared to establish the correlation between solubilities and diameters of gaseous particles [8]. Dalton calculated this parameter (with respect to the diameter of a reference particle, in this case that of liquid water, see footnote 32) assuming that the gas is an ordered array of spherical particles. The attempt was obviously unsuccessful, and the negative result may have caused the appearance of the already cited footnote in the paper of 1805 [25] about the lower probability of the atomic *"conjecture"*.

On October 12th, 1803, a classified list of *"ultimate atoms"* of compounds appears in the notebook, reproduced in Fig. 9. The advantages of the Dalton approach to identify the compound are apparent, (i) each atom has its own symbol, (ii) the compound particle is represented by means of the symbols of the constituting elements and (iii) the number of times each atom is present in the compound particle is indicated by the symbol repetition. In Fig. 9 the phosphorus symbol is added to those of nitrogen, sulphur, hydrogen, and oxygen (the latter two are exchanged with respect to Fig. 6). Dalton distinguishes binary, ternary, etc. *"ultimate atoms"*, some of which have been already considered in the table of Fig. 7. Among binary particles, *"carbonated hydrogen gas* [i.e., *"olefiant gas"*, ethylene]" is formulated as CH, *"phosphorous acid"* as PO and *"phosphorated hydrogen* [posphine]" as PH. *"Ether"* is constituted by ternary particles C_2O. In analogy with *"sulphuric acid"*, the formula

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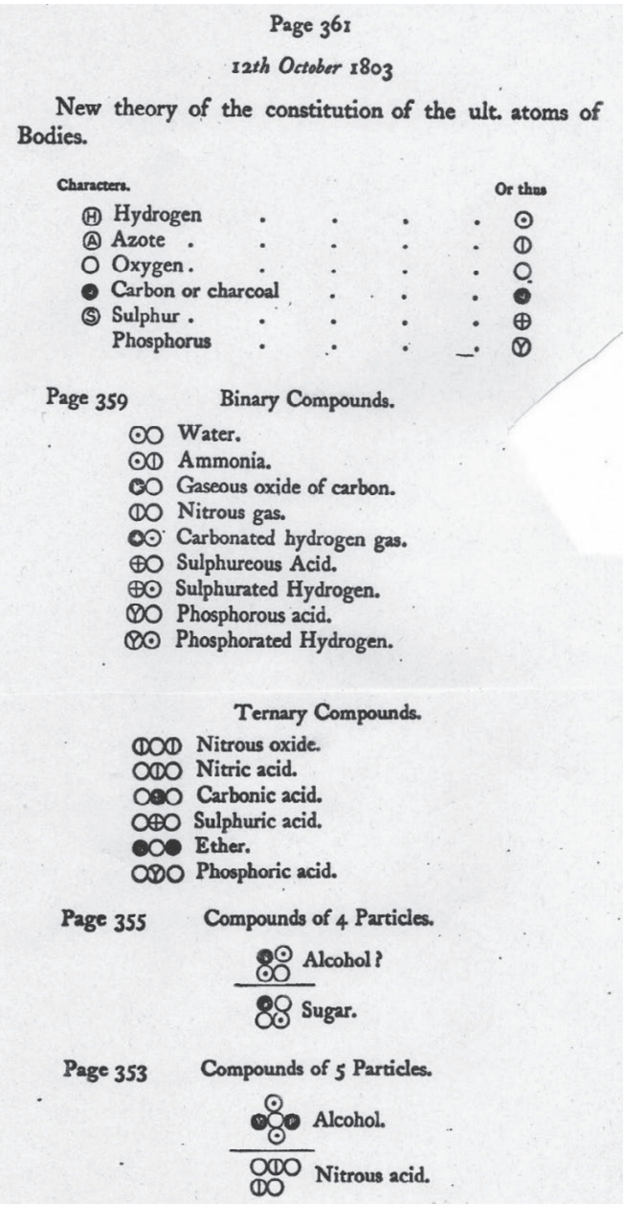
[36] Ref. [4], p. 28.



Page 361

12th October 1803

New theory of the constitution of the ult. atoms of Bodies.

Characters. Or thus

Hydrogen

Azote

Oxygen

Carbon or charcoal

Sulphur

Phosphorus

Page 359 Binary Compounds.

Water.

Ammonia.

Gaseous oxide of carbon.

Nitrous gas.

Carbonated hydrogen gas.

Sulphureous Acid.

Sulphurated Hydrogen.

Phosphorous acid.

Phosphorated Hydrogen.

Ternary Compounds.

Nitrous oxide.

Nitric acid.

Carbonic acid.

Sulphuric acid.

Ether.

Phosphoric acid.

Page 355 Compounds of 4 Particles.

Alcohol?

Sugar.

Page 353 Compounds of 5 Particles.

Alcohol.

Nitrous acid.

Figura 9. The constitution of some bi- and polyatomic particles according to the Dalton theory.

of “*phosphoric acid*” is PO_2.[37] Tetra- and penta-atomic particles are viewed as second-order compounds. Thus, alcohol is $CH+OH$, the combination of the hydrocarbon particle CH with water OH. Sugar is $CO+OH$, “*gaseous oxide of carbon* [CO]” and water OH. In “*nitrous acid* [N_2O_3]” the complicated ratio 2:3 is expressed as the combination of two particles, $NO+NO_2$ [18].

The notes contained in the Dalton’s notebook between September and October 1803 are the essence of the chemical atomic theory. The theoretical principles remained unchanged in all later publications [5,18]. Comparing now with the table of Fig. 5, the gases present in Fig. 7 and 9 appear in this table with compositions confirmed except in two cases. The “*ether*” particle is represented as C_2H in Fig. 5, not C_2O, with weight 2·4.3+1=9.6 and the particle of alcohol as C_2OH (not COH_2) with weight 2·4.3+5.5+1=15.1. But a new piece of information appears in Fig. 5 and comes from the “*carburetted hydrogen from stagn. water* [methane]” formulated as CH_2 with weight 4.32+2=6.3. As already noted, the relation between methane and ethylene (“*olefiant gas*”) was established almost one year after the proposal about the atomic theory. Dalton describes in his notebook, August 24th, 1804, the reaction of ethylene and methane with oxygen with volumetric details [4]

“*Olefiant gas* [ethylene]

Meas.	*Acid.*	*Oxy.*	*Dimin.*
100	*200*	*300*	*200*

Stagnant [methane]

100	*100*	*200*	*200*”[38]

which may be interpreted in modern terms as

$$C_2H_4+3O_2\rightarrow 2CO_2+2H_2O$$

$$CH_4+2O_2\rightarrow CO_2+2H_2O$$

Fixing the same number of carbon atoms for both compounds, i.e., the same volume of “*carbonic acid*” gas precipitated by “*water lime*”, for instance 100 “*measures*”, a little reflection on the volumetric data shows that the volumes of the reacting and products gases (in the same order given by Dalton) are in the ratio 50:100:150:100 for ethylene and 100:100:200:200 for methane. Thus, the final volumes in the fourth place are 1:2 and therefore the ratio of the hydrogen atoms in the particles of the two gases is 1:2. This means that the particle of “*carburetted hydrogen from stagn. water*” contains a number of hydrogen atoms double that in “*olefiant gas*”. The former was formulated as CH_2 and the latter as CH, a conclusion which stands as the first successful experimental verification of the atomic theory after one year of silence [8]. It was a result particularly impressive for Dalton to the point that he informed Thomson, who visited him August 27th, 1804, about the atomic theory referring spe-

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[37] The atomic weight of phosphorus, $^{p_P}/_{p_H}=7.2$, appears in the notes of September 19th, 1803 [4] and is calculated considering the Lavoisier data about “*phosphoric acid* [PO_2]”, 39.4% phosphorus and 60.6% oxygen, and assuming 5.5 as the atomic weight of oxygen.

[38] Ref. [4], p. 63.

cifically to these gases. This narrative, centered on the chemical development of the theory one year later with respect to the intimation, has been questioned and it was argued, on the contrary, that Dalton actively tested the implications of the incipient theory from the start and was eager to communicate his merits [10]. For instance, it has been noted [10] that the law of multiple proportions was already in operation in the table of Fig. 7 and considered as the rule by means of which the atom-to-atom association in the compound formation may occur. Examples are the weights of the *"ultimate atoms"* of the oxides of nitrogen, carbon and sulfur [10]. As to the diffusion of the theory, Dalton included the atomic theory as a small part of the subject matter in the lectures held at the Royal Institution on natural philosophy in the period December 1803 – January 1804, as evidenced by reported annotations [10]. In this occasion Dalton was introduced to Davy and not only was informed about nitrogen oxides but also, had the opportunity to present to Davy the atomic theory. Finally, on his return to Manchester Dalton gave on February lectures whose content is unfortunately not known but whose titles suggest that atomic theory was part of them [10].

6. CONCLUSIONS

In this paper, the attention is directed to the history of Dalton scientific interests from the studies in meteorology to the first intimation of the chemical atomic theory. The distinctive traits of his personality were great perseverance, self-reliance, and a laborious mind. He promoted vigorously the theory of mixed gases explaining atmospheric homogeneity in terms of repulsive forces acting among particles of the same kind rather than of affinity or chemical combination. Differing specific gravities of the particles would have caused the atmospheric gases to settle down in layers. To avoid this difficulty Dalton opted for the theory of mixed gases which would ultimately lead to the formulation of the atomic theory. But he had a peculiar aversion to the idea of a direct relation between specific gravities and particle weights. The statement was reiterated over the years saying that it is a *"confused idea … that the particles of elastic fluids are all of the same size"*[39].

Dalton's contributions to the atomic theory have been discussed at length [9,48]. There is no need to say that the idea dates back to the Greek (and earlier) philosophies and that interest in the atomic theory revived in the XVII century [7,17,19]. The following magnificent, perhaps unsurpassed, passage of Newton's *Opticks*, transcribed by Dalton's own hand in the notebook [4,48], is proof that atomistic ideas were diffused among the XVIII century scientists

> All these things being consider'd, it seems probable to me, that God in the Beginning form'd Matter in solid, massy, hard, impenetrable Particles, of such Sizes and Figures, and with such other Properties, and in such Proportion to Space, as most conduced to the End for which he form'd them; and that these primitive Particles being Solids, are incomparably harder than any porous Bodies compounded of them; even so very hard, as never to wear or break in pieces; no ordinary Power being able to divide what God himself made one in the first Creation. While the Particles continue entire, they may compose Bodies of one and the same Nature and Texture in all Ages: But should they wear away, or break in pieces, the Nature of Things depending on them, would be changed. Water and Earth, composed of old worn Particles and Fragments of Particles, would not be of the same Nature and Texture now, with Water and Earth composed of entire Particles in the Beginning. And therefore, that Nature may be lasting, the Changes of corporeal Things are to be placed only in the various Separations and new Associations and Motions of these permanent Particles; compound Bodies being apt to break, not in the midst of solid Particles, but where those Particles are laid together, and only touch in a few Points.

Thus, the striking advance of Dalton's theory may be synthesized in three points, (i) the emphasis on a single atomic property, the weight of the atom, singled out of the several properties of the *"ultimate particles"* envisioned by Newton, weight (*"massy"*), hardness (*"hard"*), size, shape (*"figures"*) [8], (ii) the calculation procedure for deriving atomic weights or, in other words, the rule of greatest simplicity [9,10], (iii) the symbolic representation of atoms and their combinations [4].

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Historical Article

The Mixed Blessings of Pragmatism. Jean-Baptiste Dumas and the (Al)chemical Quest for Metallic Transmutation

Leonardo Anatrini

Dipartimento di Lettere e Filosofia (DILEF) – Università degli Studi di Firenze, Via della Pergola, 60 – 50121, Italt
E-mail: leo.anatrini@gmail.com

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ORCID
LA: 0000-0001-9001-3240

Abstract. There were at least three prerequisites for the transmutability of metals to become once again a scientifically acceptable subject of research from the 1810s: new hypotheses concerning the mutual reducibility of certain elements, such as those of integer multiples and protyle put forward by the British chemist and physician William Prout; the experimental confirmation that chemical compounds with the same percentage composition could be substances with very different properties, i.e. the discovery of isomerism and allotropy; the comparison between metals and compound radicals of organic chemistry. This paper aims at illustrating how these premises were exploited by Jean-Baptiste Dumas, one of the leading French chemists of the 19th century, to reintroduce in the chemical discourse the alchemical topic of transmutation.

Keywords: transmutation, Jean-Baptiste Dumas, ammonium, Jöns Jacob Berzelius, Cyprien-Théodore Tiffereau.

INTRODUCTION

The experimentations of late 18th century, which helped to describe the regularity and reproducibility that characterised a wide range of chemical compositions and led, for example, to the enunciation of the law of definite proportions by Joseph-Louis Proust (1754 – 1826), were propaedeutic to the spread of a new idea of atomism. Besides, with a simple logical step, it was possible to deduce, from the regularities observed in chemical reactions, a necessary regularity in the composition of matter of a corpuscular nature. The atom originally theorised in Democritus' time (c. 460 – c. 370 BC), however, was the minimal entity of a uniform and continuous matter understood ontologically and not instrumentally, whose essentially identical parts differed only in size, form and motion. In such a system, chemical change was generated by alterations – occurring in a vacuum – in the ordering of atoms into *molecular* structures. Nevertheless, everything since the results produced by the chemical reform of Georg Ernst Stahl (1659 – 1734), suggested the existence of a whole range of elements characterised by exclusive qualities.

Stemming from the desire and need to quantify the ultimate units of matter for calculative purposes, aiming at a consequent mathematisation of chemistry, the atomic theory of John Dalton (1766 – 1844) was born. With it, the English scientist united quantitative speculations inspired by Democritus with a qualitatively categorised matter, overcoming the very limits beyond which Antoine Lavoisier (1743 – 1794) had relegated a purely philosophical investigation of Empedoclean descent. With an effort of hopeful pragmatism, Dalton's atom was no longer the omnipresent manifestation of matter, becoming instead the physical unit of measurement of Lavoisier's *substances simples*[1].

Although the acceptance of the physical reality of the Daltonian atom in the first half of the 19th century was certainly not extraordinarily widespread in France, the theorisations of the English scientist had emphasised the importance of the quantification guaranteed by the system of atomic weights in the elaboration of the categorisations and classifications necessary to establish the foundations of a science of chemical relationships, a prodrome to structural chemistry. And it was precisely in this field that in 1826 one of the fathers of organic chemistry, Jean-Baptiste Dumas (1800 – 1884), brought his research to the attention of the international scientific community[2]. By experimentally applying the hypothesis of Amedeo Avogadro (1776 – 1856)[3] – which he knew and studied through André-Marie Ampère (1775 – 1836)[4] -, he proposed new methods for determining the molecular weight of gases, obtained through volume density, succeeding in optimising and even correcting the data of Jöns Jacob Berzelius (1779 – 1848), who, with his calculation of the atomic weights of 45 different elements and the centesimal composition of some 2000 chemical compounds, is remembered as the greatest experimenter of the early 19th century[5]. In 1818, he was able to theorise a first set of atomic weights based on entirely experimental data[6], disproving the possibility of a total generalisation of the hypothesis developed in 1815 by the physician and chemist William Prout (1785 – 1850) aimed at illustrating the atomic weights of the elements as integer multiples of that of hydrogen[7]. Then, from 1826 onwards, Berzelius refounded his investigation – and in this context, the desire for revenge provoked by Dumas' essay must have played no small part – through the instrumental adoption of two innovations of particular importance for chemical research.

In 1819, chemist Pierre Louis Dulong (1785 – 1838) and physicist Alexis Thérèse Petit (1791 – 1820), succeeded in calculating the specific heat of 13 different elements (11 metals, tellurium and sulphur) and discovered their similar heat capacity (between 0.3675 and 0.3830, for O = 1 and H_2O having c = 1), i.e. the constant describing the product between the relative atomic weight of an element and its specific heat[8]. In the same year, the German Eilhard Mitscherlich (1794 – 1863), in the course of lengthy crystallographic experiments, put forward a hypothesis concerning the possibility that substances with similar chemical properties and crystalline form, called isomorphic by Berzelius himself, might have similar formulae[9].

BELIEVING IS SEEING: THE CONVICTIONS OF A SCIENTIST

Dumas desired to succeed in obtaining stable and experimentally consistent principles, and the opportunity that Avogadro's hypothesis offered was unrepeatable. However, from the time of his first major publication – as is also evident from his 1832 doctoral thesis – the young chemist had been grappling with a problem difficult to surmount, found in the measurement of the molecular volumes of the phosphorus contained in his trichloride (PCl_3) and the sulphur contained in hydrogen sulphide (H_2S)[10].

In the particular case of phosphorus and chlorine, by reacting one volume of the former with three volumes of the latter, Dumas could not explain how it was possible that, if Avogadro and Ampère had been right, not one but two volumes of phosphorus trichloride would be generated[11]. The cause of the problem lay in the widespread terminological confusion linked to the atomistic lexicon, which Dumas had declined from Ampère's, even going so far as to hypothesise the divisibility of the elementary molecules, although he did not realise the tetratomicity of liquid phosphorus and the diatomicity of chlorine in the gaseous state (and, more generally, not imagining that elements placed in reaction could give rise to *variations in atomicity*), finally resorting to expressions that were variously criticised, when not entirely oxymoronic, such as that of 'half-atom'[12]. Moreover, the values he calculated were based on Berzelius' 1818 atomic weights, which for phosphorus and chlorine were twice as high as they should have been. Thus, he would have expected a synthesis reaction of the type $P + 3Cl \rightarrow PCl_3$, whereas what he obtained was $P_4 + 6Cl_2 \rightarrow 4PCl_3$[13].

From 1828 onwards, Dumas endeavoured to adopt the Avogadrian criterion of the distinction between the physical particle and the chemical particle, constantly emphasising the material reality of the former and the purely instrumental dimension of the latter, with a methodology partly borrowed from the research of William Hyde Wollaston (1766 – 1828)[14]. This latter, in fact, decided to address the shortcomings caused by an ontologically understood atomism from a decidedly more pragmatic point of view, emphasising the priority of practical effects and purposes of chemical research. In a celebrated 1814 essay entitled *A Synoptic Scale of Chemical Equivalents*, he introduced a stable categorisation to define the minimum quantities required for elements to enter combinations forming compounds[15].

Dumas, however, was not satisfied with a utilitarian implementation of Wollaston's equivalents[16]. In fact, by the time his colleague Marc Antoine Gaudin (1804 – 1880), with his *Recherche sur la structure intime des corps inorganiques* (1833), had brought to the attention of the scientific community the importance of a stable nomenclature that provided a clear distinction between concepts such as 'molecule' and 'atom', especially in virtue of the increasingly encouraging results provided by research into atomic weights (regarding which Gaudin was the first to hypothesise the polyatomicity of certain elements), Dumas had become definitively convinced that the results of his experiments offered a clear refutation of Avogadro's hypothesis[17].

As has been persuasively illustrated by some scholars, at the basis of Dumas' rejection was surely the perception that atomism was little more than a faith and that, in the end, no experimentation would be able to account for the existence of ultimate physical entities[18]. Therefore, faced with the results of his experiments, rather than questioning the ontological value of what he probably considered to be non-essential abstractions, he chose, while recognising the instrumental usefulness of the system developed by Dalton, not to engage in theoretical elaborations concerning the physical dimension of ultimate entities. Conversely, he showed an increasing interest in another hypothesis, based on experimental data which, although variously manipulated and aiming at an even more general theorisation, were plausibly preferred as they could be used to investigate the relationships between the various elements without necessarily delving into lucubrations on the nature of matter. The hypothesis in question is that of the integer multiples of hydrogen elaborated by Prout, which Dumas no doubt became acquainted with thanks to the French edition of *An Attempt to Establish the First Principles of Chemistry by Experiment* (1825), by Dalton's pupil and first biographer, Thomas Thomson (1773 – 1852)[19]. Added to this, there were two other factors which plausibly, at a time before proper research on valence and stereochemistry, led Dumas to increasingly doubt the value of atomic theory.

In 1828, the German chemist Friedrich Wöhler (1800 – 1882) documented the first case of isomerism, unintentionally demonstrating the convertibility between organic and inorganic compounds. Trying to obtain ammonium cyanate (CH_4N_2O – an inorganic salt), he succeeded instead in synthesising urea ($CO(NH_2)_2$ – an organic compound contained in the urine of almost all tetrapod organisms) by reacting purely inorganic substances such as silver cyanide ($AgCN$) and ammonium chloride (NH_4Cl). This experience led to the formulation of the principle of isomerism, whereby substances with very different physical properties and chemical behaviour can have the same molecular mass and percentage composition[20]. Something similar was observed for elementary substances (at the time mainly in carbon and sulphur), thanks to the polymorphic nature of certain *corps simples*, describing phenomena to which Berzelius would give the name allotropy in 1841[21].

Convinced of the absolute precedence of experimental data in the elaboration of hypotheses otherwise judged arbitrary and aprioristic, Dumas, perhaps due to a lack of imagination and an excess of faith in the mathematisation of scientific research, abandoned the prophetic intuitions of Avogadro and Ampère in favour of data useful to quantify an illusion.

At this point, it would be as easy as it would be wrong to make Dumas a follower also of Prout's other famous hypothesis, enunciated for the first time one year after the hypothesis of integer multiples of hydrogen, as distinct from (though superimposable to) it, defining the hypothetical unity of matter as originating from a mysterious primordial element called protyle[22]. As already mentioned, the former became acquainted with the latter's work through the mediation of Thomson, who was as enchanted by the hypothesis of integer multiples as he was certainly annoyed – especially in virtue of the degree of probability he attributed to the Daltonian theory – by the possibility of discussing the unity of matter once again.

Dumas had shrewdly foreseen how the explanation of isomerism and the various phenomena of polymorphism, such as allotropy, passed through the investigation not only of the percentage composition of bodies but also of the structural arrangement of their constituents. However, in the absence of stable terminology and a clear distinction between atom and molecule, the constraint indicating the element as the limit of qualitative decomposability was lost. Thus, faced with the apparent superimposability and proportionality between the atomic weights of inorganic elements, it must have seemed natural to Dumas to ask himself whether it was not indeed possible to convert one species into another, to transmute matter. As if this were not enough, there was a whole tradition of studies revolving around the concept of transmutation of metals, which, within the elite of French scientific research came back to make its authority felt, as witnessed by one of Dumas' most famous works, the *Leçons sur la philosophie chimique*, published in 1837. Particularly interesting, and useful in clarifying how Dumas' alchemical knowledge came from a thoughtful as well as partial study of primary sources, is the attempted description in *chemical terms* of a supposed procedure for the production of the philosopher's stone, extracted from a work by the 15th-century English alchemist George Ripley (c. 1415 – 1490). Dumas adopted a hermeneutic oblivious of the philosophical and symbolic values of the chosen source, interpreting it in the light of his own chemical knowledge and using the visual and thermal variations described as his only compass, decoding the various entities as the signifiers of an allegory and coming to the conclusion that Ripley's philosopher's stone was nothing more than acetone (C_3H_6O), obtained by repeated distillations of lead diacetate – $Pb(CH_3COO)_2$[23].

It is curious to note, in such an attitude, the adoption of a mirror-image approach to written testimony by the scientists and those who were to become, in the second half of the century, the *new* alchemists. For if the latter could be accused of anti-scientific behaviour in their constant substitution of the experimental method for textual authority, to which they generally attributed far greater value, the former resorted to anti-historical methods, carefully selecting the only data useful for the elaboration of a tradition no less unreal than that on which the hermeticists based their hermeneutics.

Considering the inescapable precedence that Dumas attached to experimental data, it is difficult to imagine that he could have devoted himself to such a felt study of alchemical texts before his calculations of atomic weights caused him probabilistic doubts. The fact remains that the reasons that led him to establish the possibility of some link between the superposition and proportionality of the atomic weights of many metals and the concept of transmutation stemmed from his inability to interpret the data of his experiments while preserving Avogadro's hypothesis. To seek an answer in the millenary tradition that glorified a process that could perhaps resolve his doubts, represented the crystallisation of a human limit, which concealed an insatiable desire for knowledge and not necessarily adherence to any form of esoteric thought. And Dumas certainly believed he could overcome the incompatibility between chemistry and alchemy by quantifying the study of the latter, so as to extract data useful for his research. However, this was a dangerous process, especially from a value-based point of view. Alchemy had been brought into play in order to reach a truth that chemistry, although hypothetically, was not even managing to describe comprehensively. The implicit risk was that of attributing a similar if not overlapping gnoseological value to the two disciplines, placing alchemy, which had already long since arrived at the concept of transmutation, in a privileged position, thus establishing an epistemologically null but logically consistent and easily misunderstandable parallel between textual authority and scientific authoritativeness that were no longer clearly distinct. Not to mention that every alchemical theory rested on concepts of unity of matter that, in the face of possible scientific confirmation of transmutation, would have offered an opportunity for generalisation that would have been difficult to avoid.

In spite of his ideals, Dumas chose to believe in order to see. Nonetheless, he probably never fully realised how contingent the value of the data from his experimental research was on his personal interpretation of them. Furthermore, as mentioned, there was a third factor that led him to question the plausibility of the elemental nature of many of the simple substances in mineral chemistry, namely the possibility to put in relation metals and compound radicals of organic chemistry. This factor arose from the field of investigation in which he recorded some of his greatest successes, that of chemical substitutions.

By 1833, Dumas and his students had embarked on an intensive experimental campaign concerning the chlorination processes of organic compounds and by the following year, he had collected sufficient data concerning the action of chlorine on turpentine essence and ethanol (C_2H_5OH) to affirm the ability of the said element to replace hydrogen 'atom by atom' in these compounds, which nevertheless had almost identical chemical properties[24]. In doing so, he reinforced his belief that these properties depended more on the arrangement than on the nature of the particles.

In the eighth of the *Leçons*, Dumas' observations on the hypothetical transmutability of elements were based on three different principles: isomerism, allotropy and supposed direct proportionality observable according to the atomic weight of different elements (16 metals, tellurium and sulphur)[25]. These formulations and observations could describe the change of species produced by a transmutation but were not proof of the composite nature of metals. Hence the circumspection in the choice of words with which Dumas described the possibility and not the probability of a feat of alchemical memory. There was, however, at least one *sensata esperienza* that could have been used as evidence. Nevertheless, such evidence was carefully omitted in the *Leçons* (only a veiled allusion is made)[26] by virtue of the interpretability of the phenomenon on which this datum was based and the fact that, as the only useful experimental evidence, it certainly did not meet the criteria of exhaustiveness and rigour on which a theory should be based.

In 1808, Berzelius, together with his friend and future court physician Magnus Martin de Pontin (1781 – 1858), replicated the experiments that the previous year had led Humphry Davy (1778 – 1829) to the discovery of sodium and potassium, obtained from their hydroxides[27]. The two Swedes extended Davy's research to another substance that resembled the so-called caustic alkalis in chemical properties, i.e. ammonia (NH_3). By subjecting a negatively electrified quantity of mercury to electrolysis and placing it in contact with an aqueous ammonia solution, they produced a substance that had the appearance of an amalgam[28]. In this regard, the sentence at the end of the first part of Berzelius and de Pontin's account of their experiments is particularly interesting, in which the two scientists, apologising for the 'almost alchemical' tone of their lucubrations, observe how the phenomenon they investigated could have led to the 'decomposition of metals' and the discovery of the processes necessary to perform chrysopoeia, as already suspected by 'many chemists':

> And even if these discoveries do not bring us any closer to the goal [i.e. the transmutation of metals] so unsuccessfully pursued for so many centuries, they do at least give us a clearer idea of the decomposability of metals, making the possibility somewhat intelligible. We may be forgiven this almost alchemical argument; however, many chemists had already predicted […] that one day we would discover the composition of gold and devise the means to assemble its components[29].

So, how to explain such a phenomenon, considering that the composite nature of ammonia was well known?

When confronted with the work of his colleagues, Davy was enthusiastic and inclined to devise a classification of metals – described as hydrogenated compounds – at the basis of which, given its instability and discernible composite nature, was the hypothetical metallic element that together with mercury formed the amalgam, called *ammonium*:

> The more the properties of the amalgam obtained from ammonia are considered, the more extraordinary do they appear.
> Mercury by combination with about 1/12000 part of its weight of new matter, is rendered a solid, yet has its specific gravity diminished from 13.5 to less than 3, and it retains all its metallic characters; its colour, lustre, opacity, and conducting powers remaining unimpaired. It is scarcely possible to conceive that a substance which forms with mercury so perfect an amalgam, should not be metallic in its own nature; and on this idea to assist the discussion concerning it, it may be conveniently termed ammonium [30].

The Stahlian dream of a metallising phlogistic principle seemed within reach once again, especially in light of the fact that ammonia was composed of non-metallic elements [31]. From the study of the amalgam, the formula for *ammonium* was logically deduced, parallel to that of today's ammonium ion (although it should be specified that the amalgam is formed after the alkaline or electrolytic reduction of the cation NH_4^+ into the ammonium radical $NH_4^{\cdot}$).

Thus Berzelius, in the first edition of the second volume of his *Lärbok i kemien* (1812), did not hesitate to include *ammonium* in the list of elements that could be obtained from earths and alkalis, being all metals[32]. Moreover, it is in this book that can be found the first clear conceptual overlap between the radicals of organic chemistry and metals, observable in the title of the relevant chapter: «Alkaliernas och jordarternas metalliska radicaler» (*Metallic radicals of alkalis and earths*)[33].

The problem also interested some of the leading French scientists of the time. First Claude-Louis Berthollet (1748 – 1822), then Ampère[34] examined the potential of Berzelius and de Pontin's discovery. Anyway, the scientific community, faced with the impossibility of finding a solution, and building on the results of an increasing number of studies based on better-established concepts of element, atom and molecule, although remembering the *ammonium* amalgam phenomenon, ended up shelving it almost completely until the mid-20th century[35]. One of the few scientists who continued to take an interest in *ammonium* was exactly Dumas, who on three separate occasions while writing his *Traité de chimie* – one of the most important manuals dedicated to technical and industrial applications of chemical research of the period, the editing of which kept him busy for eighteen years, between 1828 and 1846 – dealt with Berzelius and de Pontin's discovery and what it might entail[36]. Seeking to establish a classification of metals on the basis of their respective chemical properties, after observing and describing the isomorphism of potassium, sodium, lithium, barium, strontium and calcium, he put forward a conjecture about the composite nature of metals (the highly speculative nature of which he himself affirmed), observing how, from the known data, it might be plausible to conclude that «ammonia is transformed into a metal when, to the three volumes of hydrogen it contains, a fourth is added»[37].

In the fifth volume (1835), on the other hand, building on the discoveries that led him to the substitution theory, attempting an initial classification of nitrogen and hydrogen compounds, Dumas identifies *ammonium* as a 'metal-like body', with a related discussion concerning the advantage that the identification of its oxide would represent. Firstly because, just as *ammonium* in the amalgam experiment was shown to be able to replace potassium, the hypothetical oxide would have confirmed the superposition of its chemical properties with those of sodium and potassium hydroxides. Second, because an entity such as *ammonium* oxide would have led to the assumption of «the existence of a large number of unknown combinations, which would replace all known hydrogenated compounds in the products they form by uniting with acids»[38]. This statement is only apparently obscure since after a few lines it becomes clear what Dumas is aiming at, namely extending his theory of ethers to inorganic chemistry.

Between 1827 and 1828, together with his colleague and pharmacist Félix-Polydore Boullay (1806 – 1835), Dumas had managed to enunciate the formula for the synthesis of ethers – $C_nH_{(2n+2)}O$ –, compounds formed, in the authors' words, from 'an acid combined with two volumes of ethylene – C_2H_4, called *oleophilic gas* – and one volume of water vapour'; a description elaborated by generalising to an entire class of compounds the values describing the components of diethyl ether, at the time known as *sulphuric ether* ($C_4H_{10}O$)[39]. But this generalisation, since supported by serious experimentation, had proven to be accurate, producing, as Charles Adolphe Wurtz (1817 – 1884) defined it forty years later in his history of chemistry, the first occasion on which:

> in organic chemistry a series of similar phenomena was grouped together by theory and […] the facts relating to the formation, composition and metamorphoses of an entire class of bodies were given a simple interpretation, using atomic formulae and equations[40].

In their account, Dumas and Boullay offer a term of comparison which, interpreted in the light of the mystery of *ammonium*, serves to clarify the curious digressions in the fifth volume of the *Traité*. The two had in fact described in an analogical key the function of ethylene in the formation of ethers with that of ammonia in the formation of ammonia salts, by virtue of the latter's ability to decompose diethyl ether[41].

The choice of comparative term stemmed from the observation of the properties of ammonia, which described capacities for the analysis of organic compounds and the synthesis of saline compounds in the presence of acids that overlapped and even exceeded those attributed to metal hydroxides used for the same purposes.

Years passed, and by the time Dumas wrote the next passage of the *Traité*, the constant comparison between *ammonium*, alkalis and earths had matured in him a definite conviction. Faced with the impossibility of isolating the fabled metal, obtaining its oxide would have provided solid proof not of the existence of a metallic phase of the radical $NH_4^{\cdot}$ (a concept unknown to the chemistry of the time), but of the composite nature of metals, since the properties of the new *element* would have fallen squarely within the casuistry described by the alkaline and alkaline-earth metals (as we have already seen with Berzelius):

> Nevertheless, this is the place to bring out a theory already proposed by Ampère, on the occasion of the peculiar combinations that have been described under the names of ammoniacal hydrides of mercury or potassium and mercury. According to Ampère, these compounds, which have so often been compared to alloys, contain a kind of metal made up of 2 parts nitrogen to 8 parts hydrogen[42]. There is nothing to prevent us from classifying such a compound alongside the metals when we already classify cyanogen alongside chlorine and other similar non-metallic bodies.
>
> If we assume this base, we would have the following series:
>
> Az^2 H^4 a chlorine-like substance found in amines.
> Az^2 H^6 ammonia.
> Az^2 H^8 a metal-like substance. Ammonium.
> Az^2 H^8 O ammonium protoxide.
> Az^2 H^8, Ch^2 ammonia hydrochlorate or rather ammonium chloride.
> Az^2 H^8 O, S O^3 ammonia sulphate or rather ammonium protoxide sulphate,
>
> and so on for the different ammonia salts known. With regard to the combination of anhydrous sulphuric acid, for example, and ammonia, it would necessarily be considered an amine.
>
> Here are the main advantages of this theory, as far as I can appreciate them.
>
> It explains the formation of the remarkable amalgams that first gave us the idea.
>
> It eliminates hydrochlorates, hydriodates and other similar ammonia salts, whose existence embarrasses the theory of chlorides, iodides, etc.
>
> It gives perfect simplicity to the formulae of double chlorides, double iodides and other similar compounds containing ammoniacal combinations, whereas in the other theory, these formulae are complicated and of an unusual form.
>
> It gives a good idea of the basic role of ammonia since it is no longer ammonia that plays the role of base, but an oxide produced by the union of ammonia and water. This oxide is therefore completely comparable to potash or soda.
>
> This better explains the isomorphism of ammoniacal salts with similar combinations of potassium or sodium; since,

> for example, ammonium replaces potassium everywhere, and ammonium oxide replaces potash.
> As for its disadvantages:
> It is based on the existence of a combination Az^2 H^8, which has not been isolated.
> And on the existence of an ammonium oxide, Az^2 H^8 O, which is completely unknown to us, although ammonia and water can produce it by combining and these two bodies have been brought together in circumstances most favourable to combination.
> It leads us to suppose the existence of a large number of unknown combinations, which would replace all the known hydrogenated compounds, in the products that these form by uniting with acids.
> It therefore forces us to admit a large number of hypothetical hydrogen carbides, playing the role of metals, which is possible, but difficult to admit without proof.
> Thus, as has already been pointed out, the theory of ethers and that of ammoniacal combinations are so closely linked that they will probably be decided by each other. Those who attribute the role of a base to the sulphuric ether will admit ammonium oxide; those who regard ammonia as a base must attribute the same role to carbonated hydrogen and its analogues. By showing that both theories are admissible, we have given a fair idea of the state of the question; by preferring the latter point of view, we have followed the general opinion.
> Chemists who have turned their attention to the philosophy of science have all been struck by the difficulties that the history of ammonia has given rise to, and have long sought to discover some metallic radical in it, in order to bring this body back into the great family of oxides. After the useless attempts made by Davy and Berzelius twenty years ago, they returned to the original idea of considering ammonia as a base in itself. This discussion, almost forgotten, has been rejuvenated by its connection with the ether theory.
> […]
> On the other hand, however, it is not an uncommon fact that ammonia is considered to be an alkaline base. It is a consequence of a principle that is no less extensive than the previous one, nor less worthy of attention. Is it not natural to admit, in fact, that hydrogen, by uniting with simple bodies, can sometimes constitute acids, sometimes bases, depending on whether its properties predominate or succumb in the presence of the antagonistic element?
> If the ammonium theory had been generally accepted, sulphuric ether and its analogues would have been given the role of base. Of all the known phenomena, only those relating to the theory of substitutions can be explained by a single hypothesis, the one accepted in this book […].
> Leaving aside these hypotheses, we shall confine ourselves here to the pure and simple expression of facts […]. We will therefore consider ammonia as a base in itself[43].

Before asserting the plausibility of a hypothesis, Dumas considered it necessary to produce empirical proof. Otherwise, claiming its veracity on a logical-consequential basis would have led beyond the limits of a scientifically provable analogical correspondence, trespassing into the domain of personal convictions to which one could arbitrarily attribute the function of principles. So much so that the problem of *ammonium* in the *Leçons*, a work with historical ambitions but with a strongly programmatic slant, is only hinted at transversally through recourse to the authority of certain 'illustrious chemists', Berzelius in the lead (and the only one to be quoted by name), who had «put forward conjectures such as to make the composite nature of nitrogen conceivable»[44]. Hence Dumas' progressive (and definitive) rejection of physical atomism, which he increasingly saw as a set of aleatory speculations about an invisible world, in favour of research with far greater classificatory potential, one that was devoted to the radicals of organic chemistry. On the strength of his successes in the elaboration of the substitution theory, in the same year of publication of the *Leçons*, he drafted, together with another great organic chemist of the time and long-time rival, Justus von Liebig (1803 – 1873), a programmatic article, a manifesto, with which the quest to finally bring order to the tumultuous sea of organic compounds was inaugurated, entitled *Note sur l'état actuel de la chimie organique*[45].

The historiography of chemistry has always emphasised how Dumas, at least from the early 1830s onwards, set atomism aside in favour of recourse to immediately measurable quantities such as equivalents, and that is true. However, the instrumental value of atomism was never denied by him, and in order to lend solid mathematical representability to his research, in the aftermath of the *Leçons* the scientist prepared an experimental investigation aimed once again at calculating the atomic weights of the principal agents of organic chemistry (carbon, hydrogen, oxygen and nitrogen). The results of this investigation, together with the theory of substitution and that of types, earned him the Copley Medal of the Royal Society in 1843. In the very definition of chemical type offered by Dumas, in fact, the recourse to atomistic concepts remained central, while to have been partially excluded was the concept of element, instrumentally necessary but *functionally replaced* by that of type[46].

As is well known, the idyll between Dumas and Liebig was very short-lived due to disagreements at a theoretical level[47]. Ironically, it was Liebig's theory of compound radicals[48] that provided the rationale for hypothesising the analogy that Dumas, in the absence of *ammonium* oxide, had refused to enunciate openly out of methodological rigour. One of the fathers of structural chemistry, Alexandre-Édouard Baudrimont (1806 – 1880), who in turn adopted at least in part Prout's integer multiples and protyle hypotheses, was the one who performed the feat. Epitomising his words, in inorganic chemistry, oxygen, chlorine and sulphur could be combined with a metal to produce compounds in which the latter played the role of a radical that, on the other hand, in organic chemistry never consisted of a single element. From the juxtaposition of the relevant data, Baudrimont concluded that metals not only could but plausibly should be *corps composés*:

> Just as a chemical element subjected to analysis turns out to consist only of its own matter, so it can only be produced with this same matter. Thus, in the present state of chemistry, nothing other than gold can be found in gold, and gold can only be made with gold. This is the limit of experience; the rest is mere conjecture or supposition. It is known, however, that alchemists claim to have made gold from bodies that were not gold, but these facts, although often presented with candour and with testimonies that leave little room for doubt, will only be accepted by science when proven experimentally.
>
> However, despite the deliberate obscurity that reigns in the writings of the alchemical philosophers, we can say with certainty that they did not produce gold by combinations, but by imprinting on the nature of the bodies a modification of the kind that gives rise to isomerism, under the influence of a catalytic agent. The bodies on which they worked were lead and mercury; their agent was the projection powder, an item that they produced with such slow and arduous labour.
>
> In addition to what the alchemists say, we also find the theoretical considerations of Prout, who believes that all bodies are constituted of the same matter, the disposition of which alone causes the differences that we observe in bodies considered simple […].
>
> Liebig's theory, at least in most if not all cases, establishes radicals that are entirely comparable to metals. The theory I have defended leads us to suspect that metals are compounds, and I believe this view to be as well-founded as that of Lavoisier, who thought that earths and alkalis could be metallic oxides. Let us hope that a new Davy will resolve this question. Hydrogen would be the link that binds the constituent parts of metals together. If this bond could be broken, they could undoubtedly take on new arrangements, and metallic transmutation would take place[49].

In a period during which Berzelius' electrochemical dualism was slowly being replaced by unitary theories also thanks to the discoveries of Michael Faraday (1791 – 1867) but immediately preceding the first studies on valence and the dawn of stereochemistry – yet still far from the refinement of nomenclature and atomistic conceptualisation brought about by Stanislao Cannizzaro (1826 – 1910) in the late 1850s -, the plausibility of hypotheses such as the transmutation of metals were hardly deniable.

SEEING IS BELIEVING: THE DREAMS OF AN INVENTOR

During one of the sessions devoted to chemistry at the 21st annual conference of the *British Association for the Advancement of Science*, held in Ipswich in July 1851, Michael Faraday returned to emphasise how many scholars (including himself) expected future developments that would restore a simpler view of matter to physical and chemical research. This attitude implied a strong desire to curb that multiplicative drift characterised by an increasingly crowded pool of chemical elements, still interpreted by more than one scholar in the mid-century as an illogical break from an organisation of the physical world of (albeit now distant) Democritean and Empedoclean ancestry. Galvanised by Faraday's words, Jean-Baptiste Dumas took the opportunity to present his own convictions concerning the plausibility of transmutation to an audience of scholars. Carefully avoiding the edge case of *ammonium*, Dumas resorted to the categorisation principles developed more than twenty years earlier by his German colleague Johann Wolfgang Döbereiner (1780 – 1849). This latter, after more than a decade of experimentation, had managed in 1829 to group fifteen elements into triads characterised by physical and chemical affinities, the middle term of which had an atomic weight equal to or close to the average of the sum of the atomic weights of the two extremes[50]. Such research, further developed after the middle of the century, sanctioned a turning point that in the following decade culminated, thanks to the work of Dmitrij Ivanovič Mendeleev (1834 – 1907), in a stable theorisation of the periodicity of the elements[51], while Dumas chose instead to resort to such organisational criteria for the purpose of revaluation. According to a rather obvious analogical process (and arguably influenced also by Baudrimont's lucubrations concerning the transmutability of matter), the French chemist saw in the triadic organisation of certain elements the possibility of deriving numerical ratios parallel to those of compound radicals. In doing so, his observations became part of a possible confirmation of Prout's integer multiples hypothesis, by which the elements that constituted triads in inorganic chemistry were characterised by an analogical relationship with the components of organic chemistry's homologous series[52]. Always well aware of the highly speculative nature of this kind of hypothesis, Dumas undertook further laboratory research before presenting them at the *Académie des Sciences* (where they ended up at the centre of a heated debate between 1858 and 1859)[53]. Thus, on the occasion of the conference, he chose not to submit any paper, as indicated by the fact that the related *Report* contains no contribution of his own, nor any mention of the matter by Faraday. The only valuable, detailed account of the affair was published anonymously in the 12 July 1851 issue of *The Athenaeum*, the leading English generalist weekly magazine devoted to art and literature as well as scientific news and dissemination. Taking into account the technical knowledge required to produce such an account, we can attribute it with a fair degree of certainty to the scientist and politician Lyon Playfair (1818 – 1898), at the time co-chairman of the committee of the *British Association*'s section dedicated to chemical research[54], as well as correspondent of *The Athenaeum*[55]:

> […] Dr. Faraday expressed an opinion that chemists had of late years viewed with regret the increase in the number of metals, and hoped that the day was not far distant when some of the metals would afford honour to chemists by new modes of investigation leading to their decomposition.
>
> […] Prof. Dumas gave many examples of groups of bodies, such as the alkalies, earths, &c., arranged in the order of their affinities. He called the attention in the Triad groups, to the intermediate body having most of its qualities intermediate with the properties of the extremes, and also that the atomic or combining number was also of the middle term, exactly half of the extremes added together; thus, sulphur 16, selenium 40, and tellurium 64. Half of the extremes give 40, the number for the middle term. Chlorine 35, bromine 80, and iodine 125. Or the alkalies, lithia, soda, and potassa, or earths, lime, strontia, and baryta, afford, with many others, examples of this coincidence; hence the suggestion, that in a series of bodies, if the extremes were known by some law, intermediate bodies might be discovered; and in the spirit of these remarks, if bodies are to be transformed or decomposed into others the suggestion of suspicion is thrown upon the possibility of intermediate body being composed of the extremes of the series, and transmutable changes thus hoped for. Prof. Dumas then showed that in the metals similar properties are found to those of non-metallic bodies; alluding to the possibility that metals that were similar in their relations, and which may be substituted one for the other in certain compounds, might also be found *transmutable* the one into the other. He then took up the inorganic bodies where substitutions took place which he stated much resembled the metals. After discussing groups in triads, Prof. Dumas alluded to the ideas of the ancients of the transmutation of metals and their desire to change lead into silver and mercury into gold; but these metals do not appear to have the requisite similar relations to render these changes possible. He then passed to the changes of other bodies, such as the transmutation of diamonds into black lead under the voltaic arc. After elaborate reasoning and offering many analogies from the stores of chemical analysis, Prof. Dumas expressed the idea that the law of the substitution of one body for another in groups of compounds might lead to the transformation of one group into another at will; and should endeavour to devise means to divide the molecules of one body of one of these groups into two parts, and also of a third body, and then unite them, and probably the intermediate body might be the result. In this way, if bodies of similar properties and often associated together were transmutable one into the other, then by changes portions of one might often, if not always, be associated with the other […].
>
> Dr. Faraday expressed his hope that Prof. Dumas was setting chemists in the right path; and although conversationally acquainted with the subject, yet he had been by no means prepared for the multitude of analogies pointed out[56].

At the time, Dumas could not have known that a young researcher, Cyprien-Théodore Tiffereau (1819 – 1909), had sent a memoir to the *Académie* in January of the same year entitled *Nouveau point de vue sous lequel nous devons envisager les métaux, basé sur un fait acquis à la science par l'expérimentation* (*A new way of looking at metals, based on a fact acquired by science through experimentation*), which stated that the theory of a metallising principle, openly borrowed from Stahl's thought, was one step away from experimental confirmation[57]. That young man, who by mid-century was already making a name for himself as an inventor and photographer, is today mainly remembered for his dream of succeeding in transmuting metals, which accompanied and haunted him for 60 years[58].

After a scientific education of which we know very little, Tiffereau, a native of a small village in the Vendée, worked as a chemical preparator at the *École Professionelle* in Nantes and in 1842 sailed to Mexico eager to further his studies on the terrains in which precious metals are found and the technologies used for their mining. As can be deduced from the numerous biographical passages in the contributions he published after his return to France[59], during the period between 1843 and 1845 he travelled extensively, producing a considerable amount of photographic evidence of his mining and chemical research, unfortunately lost today. It is, however, easy to see that his studies aimed at technological development in the field of photography were the occasion (if not even the pretext) to deepen chemical experimentation that was already tending towards the desire to confirm the transmutability of metals. In fact, it is impossible not to see clear points of contact between the methodologies employed at the time for the development of daguerreotypes and the particular transmuting procedures devised by Tiffereau, which, by then, retained only a vague memory of the alchemical tradition.

In 1846, he decided to settle semi-permanently in Guadalajara, where he earned a living as a photographer (which also allowed him to subsidise his chemical research). It was at this juncture that Tiffereau became convinced, thanks to an experiment that was successfully replicated twice more over the next year, that he had achieved the synthesis of artificial gold. After subjecting nitric acid (HNO_3) to the direct action of sunlight for a few days, he added filings of a copper-silver alloy, leaving everything exposed to the sun again until the partial dissolution of said alloy. The next step, consisting almost of a trivial parody of the alchemical *solve et coagula*, involved *cooking* the metals until the solvent evaporated, which was again added and evaporated until the solid residue, initially blackish in colour, became progressively lighter. Once a bright yellow metallic hue was reached, the assay confirmed the successful transmutation into gold:

> I reduced 10 grams of silver alloyed with copper to filings and projected them into a flask 2/3 full of pure 36 degree [Bè] nitric acid. At first, there was a lively release of nitrous gas. Shortly afterwards, as the reaction decreased in intensity, the release slowed down almost abruptly, becoming barely perceptible, but still uniform, until the end of the operation. On the other hand, the [portion of] filings not affected by the reaction seemed to increase slightly in volume. After 3 weeks, I boiled the liquor in the sun on my terrace. The nitrous vapours ceased to be released and the boiling, which continued until the compound was dry [i.e. until the evaporation of the liquor], showed me an opaque matter with a blackish tint, aggregated into a solid whole. I did not notice any saline deposits or impurities.
>
> I poured 36 degree [Bè] nitric acid over the residue thus obtained. I boiled it and proceeded to complete dryness. I obtained, as before, an agglomerate but whose black colour took on a greenish hue. Further treatments and subsequent boilings with concentrated acid provided me with a residue that was still agglomerated but whose colour gradually changed from greenish to yellowish. Finally, during the last boiling and drying phase, the matter, which had always been clustered until then, separated into a number of particles, clearly showing that it was filings that could easily be shattered with a hammer blow. These different particles were all golden yellow in colour[60].

This procedure, in all likelihood at least partly borrowed from alchemical readings that Tiffereau never explicitly quoted, was influenced by the traditional idea of accelerating the *ripening time* of metallic substances combined with a concept of photosensitivity attributed to metals and acidic materials that was nevertheless foreign to traditional literature (which spoke at most of the astrological circumstances favourable or adverse to the Great Work). Tiffereau's experiments recalled instead the photographic impression procedures regulated by precise exposure times, considering how the development of daguerreotypes took place through the direct action of light on silver plates. The extent of the alchemical contribution to the genesis of Tiffereau's transmutational hypotheses remains unknown to this day, so to trace them back to the cross-reading of precise alchemical texts would represent mere conjecture.

After the outbreak of the Mexican-American War (1846-48), Tiffereau was forced to leave the New World. Already planning an industrialisation process to put his incredible discovery to good use, he sailed from Tampico to Paris in early 1848, but once back home, he came up against an obstacle he would never be able to overcome. For unknown reasons, it was impossible for him to successfully replicate his Mexican experiences. In the period immediately following his return, Tiffereau nevertheless managed to consolidate his position by establishing himself as a photographer and inventor. Over the next twenty years, several devices of his own creation, such as hourglasses for calculating the exposure times of photosensitive materials used in photography, laboratory gasometers and hydraulic clocks, became very popular and earned him academic prizes and awards. So much so that his first contact with the *Académie des Sciences* came by way of a *pli cacheté* dated November 1850 in which he discussed the possibility of using special aerostatic devices to irrigate cultivated fields[61].

While Tiffereau was privately continuing his experiments in an attempt to carry out the transmutation once again, on 31 May 1852 he sent the *Académie* a sample of the artificial gold that had been transmuted in Guadalajara in 1846, together with a second missive, in which he stated that apart from himself, the only person made aware, on 23 June 1851, of the procedure successfully used in Mexico, was none other than Napoleon III (1808 – 1873), at the time *Président de la République*, who on that occasion granted the ambitious researcher financial support for his investigations[62]. When he felt ready to divulge his discovery, in June 1853 Tiffereau published a short memoir eloquently entitled *Les métaux ne sont pas des corps simples, mais bien des corps composés* (*Metals are not simple bodies, they are compound bodies*), of which he sent a copy to the *Académi*e clamouring for its judgement, plausibly ignoring the rule by which this institution refrained from commenting on scientific contributions already published in France. Surprisingly, it was nevertheless decided to summon him and so, on 17 October, Tiffereau presented the account of his Mexican experiences before the French scientific gotha, showing more samples of artificial gold. The aspiring transmuter must have realised early on that presenting a hypothesis partially based on the recovery of Stahl's phlogiston, considered for decades to be a pseudoscientific device, would not have been received as a wise or inspired choice. Thus, he reshaped his ideas about transmutation on more recent concepts, considered at least probable and shared by more chemists, from the comparison between the compound radicals of organic chemistry and metals dear to Baudrimont and Dumas to Prout's integer multiples hypothesis. The attempt at theoretical generalisation, constructed using language more in keeping with mid-century chemical research, thus revolved around the possibility that metals, defined as isomer compounds (in deference to what Dumas had suspected since his *Leçons sur la philosophie chimique*), whose unknown radical would consist of one or even more allotropic states of hydrogen (in homage to Prout's integer multiples), could be transmuted through oxidation processes regulated by the catalytic and fermentative action of nitrogen (with indirect reference to the phenomenon of *ammonium*). Metals were thus presented as oxyhydrides, the more inert and dense the more the amount of oxygen present in them increased, thus justifying the use of nitric acid, a known oxidising agent.

Bearing in mind the decades-long debate about the actual 'simplicity' of metals, it should come as no surprise that the *Académie* responded by setting up a commission of enquiry[63], chaired by the leading expert on the subject, Jean-Baptiste Dumas; his mentor Louis-Jacques Thénard (1777 – 1857), since the 1810s accustomed to studying related topics, as we have seen in the case of *ammonium*[64]; the most knowledgeable scholar of alchemical sources available to the institution, Michel-Eugène Chevreul (1786 – 1889), one of the founders of modern organic chemistry and a pioneer of fatty acid chemistry. On 7 November, the committee members informed Tiffereau that they would need more technical data to reach a judgement. In essence, they were asking him to reveal his experimental protocol. It took six months to formulate a reply, for a rather obvious reason. Realising the magnitude of the economic and financial repercussions that would result from the confirmation of his hypothesis and, consequently, the achievement of the technical reproducibility of transmutation, Tiffereau wished to protect himself as the inventor of the procedure. To this end, on 22 December he applied for a fifteen-year patent – registered by imperial decree on 10 February 1855 – «for transmuting metals into one another»[65].

The new memoir, which reached the members of the commission in May 1854, finally explained the terms and methods of the experiments conducted in Mexico between 1846 and 1847, also asking for the scientific community's help in unravelling the mystery behind the impossibility of reproducing transmutations on French soil. However, Tiffereau received no further response. During the same year, he sent three more papers to the *Académie*, after which, having obtained the patent, he broke his silence and collected the communications sent to the institute in 1853-54 in a booklet with another self-explanatory title: *Les métaux sont des corps composés* (*Metals are compound bodies*). The fifth of these communications (sent to the *Académie* on 16 October 1854) is of particular interest, as it testifies to the repetition of Tiffereau's experiments at the Imperial Mint under the direction of the essayer and prominent metallurgist Alexandre Irénée François Levol (1808 – 1876)[66]. The results, although ambiguous, were deemed conclusive and Tiffereau's request for further examinations was rejected[67]. Between the end of 1855 and 1858, he produced two more memoirs, but, faced with the indifference of the experts, he temporarily shelved the enterprise and concentrated on his career. He married and had four children, and when he retired to private life in 1884 after selling the now-famous photographic atelier located at 130 rue du Théâtre to one of his employees, he resumed his research into transmutation, updating his hypotheses in the light of the latest chemical discoveries.

CONCLUSIONS

It could be argued that it was Dumas himself who indirectly took up Tiffereau's baton. The former, in fact, having long since abandoned all hope of confirmation of Avogadro's principle but constantly searching for criteria of categorisation and ordering useful in chemical research, between 1857 and 1859 produced a series of contributions of extreme interest in fully understanding the reasons for the survival of speculations concerning the transmutability of matter in the chemical field[68].

First with a *Mémoire sur les équivalents des corps simples* (1857) and then with a *Note* on the same subject published the following year, Dumas, building on the successes achieved through the application of his substitutions and types theories, made explicit his strategy aimed at achieving two co-implicating aims. One was the validation of Prout's hypothesis of integer multiples for as many *corps simples* as possible. The other, representing a crucial step towards analogical generalisations informed more by speculations typical of magical thinking than by scientifically plausible inductive inferences, involved the demonstration of the existence, between elements belonging to the same family, of relationships analogous to those of the homologous series of organic chemistry (just like speculated during the Ipswich conference of 1851)[69]. Thus, Dumas implicitly repeated that comparison between radicals from organic chemistry and elements from inorganic chemistry that we found in Berzelius as the conceptual overlay that later evolved into a true hypothesis with Baudrimont.

Dumas, however, could not have known that in that same period his Italian colleague Stanislao Cannizzaro, with his *Sunto di un corso di filosofia chimica* (1858), was laying the foundations for one of the first turning points towards the acceptance of the physical reality of atoms. And it was Cannizzaro himself who emphasised first the methodological shortcomings of Dumas' hypotheses by reiterating what had been stated in his *Sunto*:

> Dumas has set out to resolve one of the most important and general questions of natural philosophy. However, to this end, it seems to me that one should compare not the quantities of bodies that are substituted, but the weights of their ultimate particles that always as wholes constitute their molecules, and [the weights] of their compounds, namely the atomic weights[70].

Regardless of Cannizzaro's remarks, the following year Dumas came to a definitive systematisation of his research into the *équivalents des corps simples*. In a long essay, characterised by philosophical digressions and almost prophetic accents, the scientist's arguments culminate in the hope of finally achieving the 'decomposition of the radicals of inorganic chemistry':

> It is no more necessary to teach chemists that bodies they cannot decompose do not decompose than it would be to teach them that compound bodies decompose; these are two truths of the same order.
>
> Chemists have taken their analysis as far as the power of the forces at their disposal or the energy of the reactions whose formulae they know.
>
> They have done even better, for by this analysis they have reduced all the natural bodies to certain metallic or non-metallic bodies, showing by indisputable common characteristics and by an energetic mutual affinity that they are all radicals of the same order.
>
> When, in this state of affairs, there appears to be a reason to doubt that these radicals are simple bodies and that chemistry has said its last word about them, is it necessary to repeat this series of perfectly established demonstrations which prove that it has not hitherto been possible to decompose them? I do not think so. The infinite manipulations of the laboratories of science and industry over the last century have left no clouds in people's minds on this subject. There is no question of going back to the past; what it has left us, everyone takes to be true and sufficiently proven. It is a question of looking to the future and seeing if we can go one step further. But it is a difficult step, the most difficult, in my opinion, that human science has ever attempted, and which requires something other than the use of heat or the application of ordinary electrical forces.
>
> Chemistry may be a new science, but chemical phenomena are as old as the world itself, and the radicals of inorganic chemistry that are to be subjected to further decomposition have been known to mankind for a long time. Their existence is revealed from the earliest historical times when their immutability is also revealed in a way […].
>
> Decomposing the radicals of inorganic chemistry would therefore be a more difficult task than the one Lavoisier had the pleasure of undertaking and accomplishing. For it would mean revealing not only new and unknown beings, as we discover from time to time, but beings of a new and unknown nature whose appearances and properties our minds cannot by any analogy imagine. This would mean taking the analysis of matter to a point that neither the most energetic natural forces nor the combinations and processes of the most powerful science have ever reached. It would mean harnessing forces that we are unaware of, or reactions that no one has imagined.
>
> It's one of those problems that human thought needs to ponder for centuries […][71].

Nowadays, we can safely assume that this essay represents one of the last academic contributions to that chemical research on metallic transmutation influenced by concepts, images and speculations of alchemical derivation. Moreover, when in 1888 Tiffereau returned to the question of how to replicate the Mexican transmutations of over forty years earlier, his interlocutor would no longer be Academia, but the elite of the Second Generation of French occultism[72]. Within the *fin de siècle* occultist milieu, constantly seeking an epistemologically impossible synthesis between science and esoteric beliefs, speculations on the unity of matter would know a new phase, aiming at a representation and study of matter understood as an epiphenomenon of ether, described in turn as the material and vital principle of the entire phenomenic reality[73].

By contributing to the acceptance of an atomism physically intended – which, however, in France would prevail only in the early 20th century[74] – Cannizzaro's reform, crowned by the endorsement of the greater part of the chemistry community gathered in Karlsruhe for its first international conference (3-5 September 1860)[75], in all likelihood also contributed to the demise of theoretical elaborations such as those of Dumas.

Just as alchemy did not meet its end with the birth of modern chemistry during the second half of the 18th century, it did not continue to exist, from then on, solely as an esoteric discipline governed by gnoseological paradigms irreconcilable with any modern idea of science. In this respect, the enquiry into the relationships between chemistry and alchemy during the 19th century offers an excellent chance to investigate in a more in-depth and impartial fashion not only debates on the nature and behaviour of matter on the one hand and esoteric conceptualisations on the other. Such an enquiry grants also the opportunity to analyse the set of biases, convictions and personal beliefs (often part of unconscious cognitive processes) that characterised the history of both disciplines during a period of epochal transformations. The case of Dumas dealt with on this occasion has been chosen both for its relevance and to illustrate how it does not represent a rare exception, but rather part of a large and multi-faceted chapter in the history of science and ideas still largely to be written.

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[28] J. J. Berzelius, M. M. de Pontin, *Economiska Annaler med Kongl. Maj:ts Nådigste Tillstånd utgisna af Kongl. Vetenskaps-Academien*, **1808**, *6* (May), pp. 110-130, *6* (June), pp. 113-118 (*maxime* pp. 122-130); see ref. 9 (Solov'ev, Kurinnoi), pp. 59-63; see ref. 6 (Melhado), pp. 203-210. The curious amalgam was independently discovered and similarly described during the same year by Thomas Johann Seebeck (1770 – 1831) and Johann Friedrich August Göttling (1753 – 1809); cf. T. J. Seebeck, *Journal der Chemie, Physik und Mineralogie*, **1808**, *5*, pp. 482-483; J. F. A. Göttling, *Elementarbuch der chemischen Experimentirkunst*, Bey H. Ch. W. Seidler, Jena, **1808-9** (2 vols.), I, pp. 247-249; J. R. Partington, *A History of Chemistry*, Macmillan, London, **1961-70** (4 vols.), IV, p. 48.

[29] See ref. 28 (Berzelius, de Pontin), p. 130.

[30] H. Davy, *The Collected Works of Sir Humphry Davy, Bart.* (Ed.: J. Davy), Smith, Elder and Co., Cornhill, London, **1839-40** (9 voll.), V, pp. 102-139 (*Electro-Chemical Researches on the Decomposition of the Earths* – 30 June **1808**): 130-131.

[31] R. Siegfried, *Chymia*, **1964**, *9*, pp. 117-124.

[32] See ref. 5 (Berzelius **1808-18**), II, pp. 48-65.

[33] Ivi, pp. v, 45-68.

[34] C.-L. Berthollet, *Nouveau bulletin des sciences, par la Société Philomathique de Paris*, **1808**, *1*, pp. 150-152; A.-M. Ampère, *Annales de chimie et de physique*, **1816**, *2*, pp. 5-32: 16. Joseph Louis Gay-Lussac (1778 1850) and Louis Jacques Thénard – Dumas' mentor – for some time were even inclined to believe in the existence of a phlogistic principle whereby metals would be hydrogenated compounds: J. L. Lussac, L. J. Thénard, *Annales de chimie, ou recueil de mémoires concernant la chimie et les arts qui en dépendent*, **1808**, *65*, pp. 325-326; Idd., ivi, **1808**, *66*, pp. 205-217; Idd., ivi, **1810**, *73*, pp. 197-214.

[35] M. Bernal, J. M. Harrie, S. W. Massey, *Monthly Notices of the Royal Astronomical Society*, **1954**, *114,2*, pp. 172-179; D. J. Stevenson, *Nature*, **1975**, *258,5532*, pp. 222-223; A. Baranski, W. Lu, *Electroanalytical Chemistry*, **1993**, *355,1/2*, pp. 205-207. The solution to the problem required knowledge that would not be within the reach of physicochemical research for several decades yet. Moreover, the reasons behind the behaviour of ammonium remain largely to be clarified, after stabilisation of the metallic phase of the compound. So far, it has only been theorised and plausibly believed to exist under particular conditions of temperature and pressure, such as those hypothetically detectable in the cores of planets like Uranus and Neptune.

[36] See ref. 12 (Dumas), II, pp. 39-44; III, pp. 634-637; V, pp. 691-692.

[37] Ivi, II, p. 43.

[38] Ivi, V, p. 692.

[39] See ref. 2 (Chaigneau), pp. 96-102; J.-B. Dumas, F.-P. Boullay, *Annales de chimie et de physique*, **1827**, *36*, pp. 294-310; Idd., ivi, **1828**, *37*, pp. 15-53; U. Klein, *Experiments, Models, Paper Tools: Cultures of Organic Chemistry in the Nineteenth Century*, Stanford University Press, Stanford, **2003**, pp. 118-129, 133-137.

[40] C.-A. Wurtz, *Histoire des doctrines chimiques depuis Lavoisier jusqu'à nos jours*, Librairie de L. Hachette et C^{ie}, Boulevard Saint-Germain, n° 77, Paris, **1869**, p. 77.

[41] See ref. 39 (Dumas, Boullay **1828**), pp. 36-37.

[42] See ref. 34 (Ampère).

[43] See ref. 12 (Dumas), V, pp. 690-694.

[44] See ref. 23 (Dumas), p. 267. In chronological order, the first of the 'illustrious chemists' Dumas was thinking of might have been Christoph Girtanner (1760 – 1800), who already prophesied an alchemical vengeance ushered by the decomposition of bodies deemed elementary, starting with nitrogen: "There is no refuted opinion to which we may not recur, and again examine. Philosophy acknowledges no authority which can proscribe it from admitting, or forbid it to examine. There are many other opinions, long ago refuted, to which we ought still to recur; for example, that of the transmutation of metals. What chemist at present will dare to deny the possibility of it? The change of one metal into another ought to appear less difficult than the conversion of the sweetest body (sugar) into the sourest (oxalic acid); than the change of the hardest body (the diamond) into the softest (carbonic acid gas); than the change of the most transparent (the diamond) into the most opake (charcoal). In the 19th century the transmutation of metals will be generally known and practised"; C. Girtanner, *The Philosophical Magazine*, **1800**, *6*, pp. 335-354: 353.

[45] J.-B. Dumas, J. von Liebig, *Comptes rendus de l'Académie des Sciences*, **1837**, *5*, pp. 567-572; see ref. 39 (Klein), pp. 161-163. T. H. Levitt, Elixir: *A Parisian Perfume House and the Quest for the Secret of Life*, Harvard University Press, Cambridge (MA), 2023, pp. 157-158.

[46] J.-B. Dumas, *Comptes rendus de l'Académie des Sciences*, **1840**, *10*, pp. 149-178: 158; Id., *Annales de chimie et de physique*, **1840**, *73*, pp. 73-100; Id., *Justus Liebigs Annalen der Chemie*, **1840**, *33*, pp. 259-300; see ref. 2 (Chaigneau), pp. 117-131; C. Gérard, *L'actualité chimique*, **2002**, *254*, pp. 38-46; see ref. 39 (Klein), pp. 188-202.

[47] See ref. 2 (Chaigneau), pp. 78-79; W. H. Brock, *Justus von Liebig: The Chemical Gatekeeper*, Cambridge University Press, Cambridge, **1997**, pp. 80-87; A. J. Rocke, *Nationalizing Science: Adolphe Wurtz and the Battle for French Chemistry*, The MIT Press, Cambridge (MA)-London, **2001**, pp. 94-95; J. Drulhon, *Jean-Baptiste Dumas (1800-1884). La vie d'un chimiste dans les allées de la science et du pouvoir*, Hermann, Paris, **2011**, pp. 84-87.

[48] J. von Liebig, *Annalen der Pharmacie*, 1838, *26,2*, pp. 113-189; E. I. Hjelt, *Sammlung chemischer und chemisch-technischer Vorträge*, **1908**, *12*, pp. 447-482 (or. ed. *Berzelius – Liebig – Dumas i deras förhållande till radikalteorin 1832-1840*, Edlundska bokhandeln, Helsingfors, **1903**). see ref. 47 (Brock), pp. 78-93.

[49] A.-É. Baudrimont, *Traité de chimie générale et expérimentale, avec les applications aux Arts, à la Médecine et à la Pharmacie*, chez J.-B. Baillière, Paris, **1844-46** (2 vols.), I, pp. 68-69, 275.

[50] J. W. Döbereiner, *Annalen der Physik und Chemie*, **1829**, *15*, pp. 301-307; E. Scerri, *The Periodic Table: Its Story and Its Significance*, Oxford University Press, Oxford-New York, **2020**^{2}, pp. 46-54.

[51] Id., *Foundations of Chemistry*, **2010**, *12,1*, pp. 69-83; see ref. 50 (Scerri), pp. 33-135. Id., *Foundations of Chemistry*, 2022, 24,2, pp. 285-300.

[52] L. Cerruti, in S. Cannizzaro, *Sunto di un corso di filosofia chimica* (Ed.: L. Cerruti), Sellerio, Palermo, **1991**, pp. 73-282: 185; L. Anatrini, M. Ciardi, *La scienza impossibile. Percorsi dell'alchimia in Francia tra Ottocento e Novecento*, Carocci, Roma, **2019**, p. 39-41, see ref. 50 (Scerri), p. 56.

[53] W. V. Farrar, *The British Journal for the History of Science*, **1965**, *2,4*, pp. 297-323: 305-306; see ref. 52 (Cerruti), pp. 185-190.

[54] *Report of the Twenty-first Meeting of the British Association for the Advancement of Science; held at Ipswich in July 1851*, John Murray, Albemarle Street, London, **1852**, p. xxi.

[55] L. A. Marchand, *The Athenaeum: A Mirror of Victorian Culture*, The University of North Carolina Press, Chapel Hill (NC), **1941**, p. 226.

[56] [L. Playfair], *The Athenaeum: Journal of Literature, Science, and the Fine Arts*, 12 July **1851**, *1237*, p. 750; see ref. 53 (Farrar), p. 304.

[57] This kind of papers, sent in the form of *pli cacheté* to be kept sealed, was used in disputes concerning discoveries and inventions, in order to establish precedence. The senders made use of them in particular, as in the case of Tiffereau, when they considered the results of their research not definitive, and therefore not disclosable. Thus, in most cases, as no dis-

pute arose, these papers remained secret and their content known only to the authors. The *Académie des Sciences*, since the early 1980s, has adopted a new policy whereby papers dating back at least one hundred years can be opened; É. Brian, C. Demeulenaere-Douyère, *Histoire et mémoire de l'Académie des sciences: guide des recherches*, Tec & Doc, Paris, **1996**, pp. 73-74. The contents of the memoir sent by Tiffereau on 6 January 1851 only became known on 9 June 1983; Archives de l'Académie des Sciences, *pli cacheté* 1070.

[58] Tiffereau is one of the very few protagonists of 19th century alchemical research on whose work a dedicated study has been conducted: L. M. Principe, *Alchemy and Chemistry. Breaking Up and Making Up (Again and Again)*, Smithsonian Libraries, Washington D.C., **2017**, pp. 24-53. For a detailed biographical profile of Tiffereau, see P. Virat, *Vaugirard-Grenelle: Bulletin de la Société Historique et Archéologique du XVe Arrondissement de Paris*, **2015**, *45*, pp. 47-58.

[59] C.-T. Tiffereau, *Les métaux sont des corps composés. Production artificielle de l'or* […], Imprimerie A. Quelquejeu, rue Gerbert, 10, Paris, **1888**, pp. 9-20, Id., *La science en face de la transmutation des métaux. Production chimique de l'or*, Imprimerie Billon, rue du Commerce, 47, Paris, **1906**, pp. 4-8.

[60] Id., *La transmutation des métaux. Les métaux sont des corps composés ainsi que les gaz, preuves incontestables basées sur des faits indéniables*, chez l'Auteur, Vaugirard; Imprimerie A. Quelquejeu, rue Gerbert, 10, Paris, **1900**, pp. 4-5. Of the numerous accounts of the experiment provided by Tiffereau, this is arguably the most detailed one.

[61] Archives de l'Académie des Sciences, *pli cacheté* 1052; C.-T. Tiffereau, *Nouveaux procédés d'irrigation, de desséchement et de drainage spécialement applicables à la grande et à la petite industrie agricole* […], Imprimerie de L. Martinet, rue Mignon, 2, Paris, **1854**.

[62] This other *pli* remained sealed until 1983, while the incredible annex containing the artificial gold sample was not opened until 2015 (related chemical analyses have yet to be conducted); see ref. 58 (Principe), pp. 28-33; Id., *L'actualité chimique*, **2017**, *424*, pp. 68-71: 70-71.

[63] *Comptes rendus de l'Académie des Sciences*, **1853**, *37*, p. 579.

[64] See ref. 34 (Gay-Lussac, Thénard).

[65] *Bulletin des lois de l'empire français. XIe série*, Imprimerie impériale, Paris, **1853-69** (34 voll.), V (**1855**), pp. 1161, 1178.

[66] J. C. Poggendorff, *Biographisch-literarisches Handwörterbuch zur Geschichte der exacten Wissenschaften* […], Verlag von Johann Ambrosius Barth, Leipzig, **1863** (2 vols.), I, col. 1442; F. Szabadváry, *History of Analytical Chemistry*, Pergamon, Oxford, **1966**, p. 274.

[67] C.-T. Tiffereau, *Les métaux sont des corps composés* […], Imprimerie d'Alfred Choisnet, rue de l'Église, 6 et 8, Vaugirard, **1855**, pp. 47-52. As carefully pointed out – see ref. 58 (Principe), p. 74 – the experimental protocol followed by Levol at the mint differed from the one originally developed by Tiffereau in Mexico. Unfortunately, the same goes with the only known reproduction conducted in more recent times; cf. A. Truman Schwartz, G. B. Kauffman, *Journal of Chemical Education*, **1976**, *53,3*, pp. 136-138, *53,4*, pp. 235-239: 238.

[68] J.-B. Dumas, *Comptes rendus de l'Académie des Sciences*, **1857**, *45*, pp. 709-731; Id., ivi, **1858**, *46*, pp. 951-953; *47*, pp. 1026-1034 ; Id., ivi, **1859**, *48*, pp. 139-142, 372-375; Id., *Annales de chimie et de physique*, **1859**, *55*, pp. 129-210.

[69] See ref. 2 (Chaigneau), pp. 178-183.

[70] S. Cannizzaro, *Nuovo Cimento*, **1858**, *8*, pp. 16-17: 16.

[71] See refs. 68 (Dumas **1859** *Annales*), pp. 207-209, 52 (Cerruti), pp. 188-189, and 52 (Anatrini, Ciardi), pp. 39-40.

[72] See ref. 58 (Principe), p. 51.

[73] See ref. 52 (Anatrini, Ciardi), pp. 117-118, 160-161. On the role of ether physics in late 19th-century chemical research and esoteric discourse, see *Conceptions of Ether. Studies in the History of Ether Theories, 1740-1900* (Eds.: G. N. Cantor, M. J. S. Hodge), Cambridge University Press, Cambridge, **1981**; H. Kragh, *Ambix*, **1989**, *36,2*, pp. 49-65; E. Asprem, *Aries. Journal for the Study of Western Esotericism*, **2011**, *11,2*, pp. 129-165.

[74] P. Colmant, *Revues des questions scientifiques*, **1972**, *33*, pp. 493-519; A. J. Rocke, *Chemical Atomism in Nineteenth Century*, Ohio State University Press, Columbus (OH), **1984**, pp. 321-326. C. Kounelis in *Communicating Chemistry: Textbooks and Their Audiences, 1789-1939* (Eds.: B. Bensaude-Vincent, A. Lundgren), Science History Publications, Canton (MA), 2000, pp. 207-231.

[75] See refs. 14 (Faershtein), pp. 342-343, 5 (Solov'ev), p. 151, and 52 (Cerruti), pp. 207-214; H. Hartley in *Studies in the History of Chemistry*, Clarendon Press, Oxford, **1971**, pp. 185-194; M. Ciardi, *Reazioni tricolori. Aspetti della chimica italiana nell'età del Risorgimento*, Franco Angeli, Milano, **2010**, pp. 182-183.

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ORCID
AK: 0000-0001-8572-7070

Historical Article

Animal Oil, Wound Balm, Prussian Blue, the Fire and Light *Principium* and the Philosophers' Stone Made from Phosphorus: on the 350th Birthday of the Chymist Johann Conrad Dippel (1673-1734)

Alexander Kraft

Kraft Consult, Am Graben 48, 15732 Eichwalde, Germany
E-mail: ak@kraftconsult.de

Abstract. On the basis of many newly found archival sources and a close study of his relevant books, the life story of the chymist Johann Conrad Dippel is re-described. The preparation of his most important chymical products, i.e. animal oil, wound balm, and Prussian blue, is described. His own chymical theory was build around a fire and light *principium*. For decades, Dippel tried to find a process for the preparation of the philosophers' stone. He was convinced that phosphorus was the right starting material for this. This article does not deal with his theological and philosophical views and undertakings or his medical practice, but is focused on Dippel the chymist.

Keywords: alchemy, chymistry, Prussian blue, phosphorus, philosophers' stone.

INTRODUCTION

On August 10, 1673, Johann Conrad Dippel was born at castle Frankenstein near Darmstadt in Hesse, Germany. Therefore, in 2023 we celebrate the 350th birthday of this fascinating personality. During his lifetime, Dippel, whose portrait is shown in Figure 1, was a well-known but highly controversial theologian, as well as a physician and chymist. Although born in Germany, he lived a transnational life with longer stays in the Netherlands, Denmark and Sweden.[1]

Today, Johann Conrad Dippel is mainly known as one of the two discoverers of the pigment Prussian blue in 1706 and as the alleged model for Mary Shelley's character Victor Frankenstein in her novel *Frankenstein or the new Prometheus* from 1818. [1] The latter speculation is based on Radu Florescu's (1925-2014) book *In Search of Frankenstein* from 1975. [2] But there are no

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[1] See the recent conference: Ein transnationales Leben: Bausteine zur Biographie von Johann Konrad Dippel (1673–1734) on 26.–27. January 2023 at Forschungszentrum Gotha of the University Erfurt, Germany, Organisation: Martin Mulsow (Erfurt/Gotha), Vera Faßhauer (Erfurt/Gotha).

Figure 1. Johann Conrad Dippel (1673-1734), radical Pietist theologian, physician and chymist. (source: Justus-Liebig-Universität Giessen).

sources that support Florescu's hypothesis. Quite the contrary, it has been shown convincingly that Florescu's speculation has no basis. [3]

The fact that very little is known about Dippel's activities as a chymist has certainly encouraged this kind of speculation, such as that of Radu Florescu or the even more ridiculous of the German journalist Walter Scheele. [4] But in the last 15 years, several new archival sources have been discovered or rediscovered which shed a new and much brighter light on Dippel's acitivities as a chymist. Among these archival sources from archives in Berlin, Frankfurt am Main, Hamburg, Bad Laasphe and Münster are many previously unknown letters written by Dippel, extensive notes of Dippel's young admirer Johann Christian Senckenberg (1707–1772) about talks he had with Dippel and last but not least several recipes concerning the preparation of the philosophers' stone which can be attributed directly or indirectly to Dippel. Together with a close reading of some of the books he published during his lifetime, a much more detailed picture of Dippel as a chymist emerges from the fog of unreliable internet sources which depict him as a mad scientist, [5,6] and creator of monsters who experimented with nitroglycerin and dead human bodies.

In the following chapters of this article I will present a short biography of Dippel the chymist, structured mainly according to the sources used.

DIPPEL'S BIOGRAPHY OF HIS FIRST 25 YEARS: 1673-1698

Johann Philipp Dippel (1636-1704), the local pastor, had registered the birth and baptism of his son Johann Conrad on August 10, 1673 in the church register of Nieder-Beerbach, [7] a village in the northern part of the Odenwald mountain range. According to this church book entry, the family had fled to nearby Frankenstein Castle (Figure 2) because of French soldiers ("Französische Völcker") who were active in the area. It was the far-reaching Franco-Dutch War (1672-1678), during which French troops also attacked allies of the Republic of the Netherlands on the territory of the German Empire, leading a French army into southern Hesse. Because he was sickly and frail, Johann Conrad Dippel was baptized just one hour after his birth. Johann Conrad's mother was Anna Eleonora Münchmeyer (*ca.* 1640-1710).

Before he went to Nieder-Beerbach as a pastor in 1672, Johann Conrad's father had been a teacher in Zwingenberg. In 1678 he moved from Nieder-Beerbach to the nearby somewhat larger Nieder-Ramstadt as a

Figure 2. View of the ruins of Frankenstein Castle in 1818 by Johann Georg Primavesi (1774-1855). (source: Hessian State Archive Darmstadt, Signature R 4 No. 30788).

pastor. These three places, Zwingenberg, Nieder-Beerbach and Nieder-Ramstadt, were in the southern part of the Landgraviate of Hesse-Darmstadt, a protestant Lutheran state of the Holy Roman Empire (HRR), the German Empire of the time. Two different calendars were used in Germany between 1582 and 1700. Catholic states used the more modern Gregorian calendar, which is still in use today, while Protestant territories, whether Lutheran or Reformed, used the older and less accurate Julian calendar. At the time of Johann Conrad Dippel's birth the difference was 10 days. Therefore, according to the Gregorian calendar, he was born on August 20, 1673.

In his excellent study from 2001, Stephan Goldschmidt presented a detailed biography of Johann Conrad Dippel up to the year 1700. [8] Therefore, for the brief description of this period, we should follow his study, also because no new sources have been found for this period after Goldschmidt's study was published.

Goldschmidt assumed that Dippel attended the small Latin school in Nieder-Ramstadt between 1679 and 1685. The building of this school still exists today. It is shown in Figure 3. However, a modern commemorative plaque on the former school building indicates that it was a kind of elementary school for the town and the surrounding area, which cannot be described as a Latin school as in the Dippel literature. Dippel then went to the Paedagogium Darmstadium, a higher school in Darmstadt, the capital of the Landgraviate of Hesse-Darmstadt. Dippel completed his schooling there in 1691. On May 9, 1691, Dippel was enrolled in the register of the university in Giessen. His Latin language entry read: "*Joh. Con. Dippelius, Straetaemontano-Francostenensis*", that means "Johannes Conradus Dippelius from Frankenstein on the Bergstrasse". The Bergstrasse, literally Mountain Road, is an ancient travel route parallel to the Rhine, but situated higher on the edge of the Odenwald to avoid flooding in the Rhine valley. The University of Giessen was the only university of the Landgraviate of Hesse-Darmstadt located in the northern part of this state.

Figure 3. Old school house in Nieder-Ramstadt. (source: Photo by the author 2018).

Dippel finished the prescribed basic philosophical studies in Giessen in 1693 with obtaining the "*Magister*" degree. The thesis for his disputation was entitled "*De Nihilo*", i.e. "About Nothing". Dippel then started to study theology in Giessen until the middle or end of 1694. At that point, he had to interrupt his studies because of financial problems. For about one year, Dippel earned money as a private teacher for the children of a nobleman in the Odenwald forest. Then he decided to continue his studies in theology.

For this purpose he enrolled at the University of Strasbourg in Alsace. For centuries, Strasbourg had been a Free Imperial City of the German Empire. It was only annexed by France in 1681, 14 years before Dippel came to study here. Therefore, at that time, Strasbourg still had the character of a German Protestant city and not that of a French Catholic city. On August 2, 1695, Dippel was enrolled in the register of the University of Strasbourg as "*M. Johannes Conradus Dippelius, Darmstadio-Hassus*". So this time he stated that he came from Darmstadt in Hesse, perhaps because Frankenstein Castle on the Bergstrasse was not well known in Alsace. In addition to studying theology, Dippel began to give first public sermons in Strasbourg. Besides that, he dealt with chiromancy and began first medical studies. A tutor position provided him with additional financial means. But Dippel was also active in student associations, there were brawls and trouble with the city authorities, so that in August 1696 he fled head over heels from Strasbourg to his Hessian homeland.

Dippel continued his study of theology in Giessen from spring 1697. At the same time he worked for one year as a prince's tutor for one of the sons of the Landgrave of Hesse-Darmstadt, which brought in a good income. If he wanted to give lectures at the university himself as a private lecturer, he still had to take an exam. After some quarrels with his professors, Dippel held his habilitation disputation on July 8, 1697. He was now allowed to lecture in the field of theology at the university and his aim was either to become a pastor like his father and others of his ancestors or to get a permanent position at the university. But he, still a *magister* not a *doctor*, was not to achieve either goal.

In order to explain this, it is important to know that Dippel had switched from strictly orthodox Lutheranism to Pietism during his time as an aspiring theologian in Strasbourg. He quickly made a name for himself as a radical Pietist, mainly through two printed pamphlets in 1697 and 1698. In these two books and later in almost all other publications, he used the author's pseudonym *Christianus Democritus*. The first book was entitled *Orcodoxia Orthodoxorum* (= *The hellish doctrine of orthodoxy*), the second one *Papismus Protestantium Vapulans* (= *The beaten papacy of the Protestants*). Despite the Latin titles, these were German-language treatises. With these two writings, which harshly opposed the orthodox Lutheran variant of Protestant Christianity, Dippel ended his prospects of a career in the Protestant church for good. The government of Hesse-Darmstadt began an investigation against him and his time at Giessen University was over. In the next few years until 1704, Dippel lived again with his parents in Nieder-Ramstadt, but he also traveled a lot in the Hessian area and began to work together with various church dissenters such as Johann Henrich Reitz (1665-1720).

DIPPEL'S BOOK *WEG-WEISER ZUM LICHT UND RECHT (= GUIDE TO LIGHT AND JUSTICE)*

In 1704 Dippel published the first edition of the two volumes of his book *Weg-Weiser zum Licht und Recht* (= *Guide to light and justice*). [9] A third volume was announced, but never appeared in print. In an *addendum* at the end of the second volume it is stated that this *addendum* was written on March 23, 1704. So we can assume that Dippel completed this work in the first half of 1704, the time when he was still living in his native Hesse. Dippel moved to Berlin in late autumn of that year. The second edition of these two volumes was published in 1705. At that time, Dippel had already established himself in Berlin.

The second volume of this work with the title *Weg-Weiser zum Licht und Recht in der äußern Natur* (= *Guide to light and justice in outer nature*) contains two sections which are of special interest if we study Dippel's activities as a chymist.

The first section is *Fata Chymica*, the preface of the second volume of the *Guide to light and justice*. In this text, Dippel told the story of how he became a chymist. The second section of interest is chapter 7 of the second volume entitled *Kurtze Anatomie derer in so weit unspecificirten Cörpern der eusseren Natur als des Feuers, des Wassers, der Erden, und der Lufft. Und was endlich unter dem Namen, Licht und Recht, in der Natur zu verstehen sey* (= *Brief anatomy of the unspecified bodies of external nature, i.e. fire, water, earth and air. And finally what is to be understood under the name of light and justice in nature*). Close reading shows that in this text and at a few places in the other chapters of this volume Dippel's chymical theory from that time is explained in great detail.

DIPPEL'S BEGINNING AS A CHYMIST ACCORDING TO HIS *FATA CHYMICA*

In most of his writings, Dippel did not refer to himself as an "Alchemist", but as a "Chymist" and he usually called the corresponding natural science "Chymie" not "Alchemie". So he was, in his German mother tongue, already in line with the modern so-called "New Historiography of Alchemy". [10] According to his *Fata Chymica*, he had a lot of time after he had published his highly controversial theological book *Papismus Protestantium Vapulans*. This book appeared in print in mid-1698, perhaps in June. In the following time, in the second half of 1698, he received an alchemical book from a pastor who was a friend of his, in which the *Experimenta* of Raymundus Lullus, the *Twelve Keys* of Basilius Valentinus and other classics of alchemy were printed. Dippel mainly studied *Lullii*'s *Experimenta* and decided to try his hand at alchemy at the next opportunity.

He reported about what happened some time later:

> In secret, I came across a chymical manuscript, which opened the way to a tincture in a very laborious way; which I resolved to follow at the earliest opportunity because both the method and the first matter were somewhat simpler than what I had found in *Lullio*. [11]

It was a text written by "a certain *Medicus* from Montpellier" called "Faber", i.e. Pierre-Jean Fabre (1588–1658). That was the process that he then successfully reworked, during which time he had to change his place of residence several times:

> To put it briefly, among all this incommodity I prepared within 8 months a tincture which, as soon as it was received, transmuted 50 parts of ☽ or ☿ into gold; which made me not a little happy and amazed. [12]

So Dippel informed us here that he had produced the tincture, i.e. the philosophers' stone, within 8 months and that he was able to convert 50 times the amount of silver or mercury into gold. Can we believe him? Certainly not.

However, Dippel then went on to report that he was from now on very liberal with his money. He bought an estate for 50,000 fl. from a “certain baron” at a place where there was a glassworks and other necessary “*Requisitis*”. There he wanted, together some friends, further investigate chymistry. At first, Dippel was only able to make a small down payment for the estate.

> To pay off this sum all the more conveniently, I wanted to increase and enhance the remaining quantum of my prepared tincture by multiplication. But unfavorable fate and an oversight in the preservation of fire shattered my glass in the process of this work, and what had taken so long to prepare perished in a moment. Especially since a strange and unfavorable salt from the ashes in which the glass had stood had completely altered and separated the tincture, parts of which I could otherwise have salvaged. [13]

By multiplication, so the alchemists believed, the potency of the tincture could be increased. So obviously Dippel worked on such a process when he lost the tincture altogether. Dippel now had to put off the baron to a new payment date. Dippel then attempted to make the tincture again. However, he wanted to achieve this in a faster way in just two instead of eight months.

In order to make some money during this time, Dippel sold various chymical particular recipes and thus made some money, 4,500 guilders. Of this he paid the baron a sum of 1,500 fl., the rest melted between his fingers. But crucially, he failed to reproduce the tincture again. Dippel reported:

> In my precipitated work I gradually learned that in chymistry all haste and shortening of time is an infallible *dispendium* and the shortest way from one error to another. I wanted to force nature and burned my fingers in all the work I did. [14]

With this unsuccessful work three years passed. Dippel got more and more problems with his creditors and became the ridicule of his neighbors and his relatives. For example, they called him a great fool or archdeceiver. Dippel continued:

> But some felt sorry for me, and could scarcely believe how it could have been possible that so clever a mind could have been so presumptuously implicated in the follies and messes of the wretched laboratory workers. Others thought it a strange judgment upon me, for speaking blasphemous words against the holy places, and confusing the world with my theological writings. Others even believed that I was playing an adventurous comedy with diligence, in order to draw people’s minds into the light the better, and to hide my things, which were already quite obvious, with such chimeras. [15]

According to Dippel, he had now in fact learned that in addition to knowledge and diligent work in such matters, a higher hand was at the helm, without whose direction the desired end could never be found. He could now easily see the reason why so many lovers of gold lose all their goods over the *lapide*; since even he, as an “*Adeptus*”, had roamed about for so long in vain.

So this is what Dippel himself told about his beginnings in chymistry. It is interesting that Dippel referred to himself as an *Adeptus*, meaning someone who knows how to make and use the *Lapis Philosophorum*. Therefore, this foreword from 1704 could also be seen as a kind of advertisement for the gold maker Dippel. Perhaps it helped him to be summoned to Berlin towards the end of 1704 as a promising alchemist?

DIPPEL’S CHYMICAL THEORY ACCORDING TO HIS *GUIDE TO LIGHT AND JUSTICE IN OUTER NATURE*

If studied by a chemist-historian, Dippel’s book *Guide to Light and Justice in outer nature* and especially it’s 7th chapter gives us new insight into his chymical theory. But what is interesting for us begins with a statement in the first chapter in which we can read:

> So let us confidently say that all currently existing hypotheses, of the old and new natural researchers, such as *Epicuri* and *Cartesii Atomi*, of *Aristotelis* and his successors 4 elements; of the Paracelsists, and of the Chymists in general three *Principia Sal*, *Sulphur*, and *Mercurius*, the more recent *Alcali* and *Acidum*, … are proving as much as nothing. [16]

So Dippel rejected the established teachings, particularly those of the four Aristotelian elements (fire △, water ▽, earth 🜃, air 🜁) and the three Paracelsian principles (sulphur 🜍, mercury ☿, salt ⊖). Regarding the latter, he also remarked in chapter 7: the illusion “of three visible *principiis*”, namely “*Sale*, *Sulphure*, and *Mercurio*” only arose in the “philosophers and chymists” “due to a lack of more thorough knowledge.” [17]

But what does he want to put in their place? This is explained in various places in the second part of the *Guide to Light and Justice*, for example in one place Dippel wrote that the whole

> basis of true chymistry, which noble and correct art is concerned solely with drawing out the pure form of fire and light and elevating it to permanence in fire. … so chymistry is generally content with this purpose, when it

> can, through a thorough separation, separate out the pure form of light and fire … and make it permanent in the fire through purer added *matrices*; [18]

Elsewhere he stated:

> For it is, according to my experience, all about separating the light and fire form, and nothing else, from the natural bodies. Plants and animals easily give off such *principia*, solely through the *motum* of the kitchen fire, but metals and other earthly, firmly closed bodies require a wet fire and appropriate solvents, through which the light form is freed of the bands of the dark *Matricis*. [19]

Dippel developed the idea of a "light and fire *principium*" from the Aristotelian element fire. [20] Basically, as early as 1704 he tried to replace the three established alchemical principles with the new "light and fire principle". Superficially, this points somewhat in the direction of Georg Ernst Stahl's (1659-1734) emerging *phlogiston* theory, but also to Wilhelm Homberg's (1652–1715) *matière de la lumière* [21] and, as we will see later, to Dippel's preference for phosphorus as the starting point for the production of the philosophers' stone. However, the difference between Stahl's *phlogiston* principle and Dippel's "light and fire principle" is enormous. While Stahl postulated an immutable principle which would be exchanged between the reactants in chemical reactions, Dippel's principle was to be released from substances by separation, but then "raised to perfect permanence in fire". Then it is the philosophers' stone, the "*lapis philosophorum*". With this "tincture" it is then possible "to make gold and silver out of base metals". This "*lapidis*" would also be suitable for "medicine, in the human body" because it has "along with the highest subtlety also the highest fixity". So this was nothing more than another theory of the philosophers' stone, the *lapis philosophorum*.

DIPPEL'S CHYMICAL THEORY FURTHER EXPLAINED IN A LETTER EXTRACT IN THE *MELLON COLLECTION OF ALCHEMY AND THE OCCULT*

In the *Mellon Collection of Alchemy and the Occult* we can read an extract from a German language letter written by Dippel and dated March 1716. [22] It is interesting for the present study that this letter also contains fragments of Dippel's chymical theory. So he wrote that for the tincture "the substance of the △ itself, which must really grasp itself as the *principium Agens* in a matter" would be necessary. So there is Dippel's fire and light principle again. Furthermore, Dippel explained in the text that the "substance from the △" would pass through the walls of the vessels standing in the fire, also through glass walls, and then "unite" with the contents of the vessels "*intimo* with it". According to Dippel, it is a saline substance from the fire that would permeate the walls of the vessel. Mercury would be used in the process only to facilitate the "ingress" of the substance of fire. These are again interesting insights into Dippel's chymical world of thought.

It has to be added, that an English translation of this letter extract can be found in the *Manly Palmer Hall collection of alchemical manuscripts*. [23] However, this is not a literal translation, but rather a free one, which does not always correctly capture the meaning of the original German text.

DIPPELIANA IN THE ARCHIVAL COLLECTION OF COUNT AUGUST ZU WITTGENSTEIN IN BAD LAASPHE

Today's Bad Laasphe was only Laasphe in Dippel's time, the small capital of one of the two small counties of Wittgenstein. In the private Princely Archive of Sayn-Wittgenstein-Hohenstein in the Rentkammer Wittgenstein near castle Wittgenstein in Bad Laasphe two folders are kept which deal with Johann Conrad Dippel's connection to Count August David zu Sayn-Wittgenstein-Hohenstein (short: Count August zu Wittgenstein) roughly for the time of Dippel's stay in Berlin since 1704 until his death 1734 and a few years later surrounding questions of Dippel's heritage. [24] The majority of the material is however from the time in which Dippel lived in the Wittgenstein counties (1729 to 1734). This Dippeliana collection also contains 10 letters written by Dippel himself between 1727 and 1734. We will come back to this collection in due time.

The area of the former county of Wittgenstein is now part of the German federal state of North Rhine-Westphalia, but is located directly on the border to the federal state of Hesse. In the Early Modern period, the county of Wittgenstein was under dominating Hessian influence. Since 1357 the county of Wittgenstein was ruled by the counts of Sayn, therefore the name Sayn-Wittgenstein for the ruling family. In 1603, the county of Wittgenstein was divided into the northern Berleburg and the southern Wittgenstein halves. These two counties, Sayn-Wittgenstein-Berleburg and Sayn-Wittgenstein-Hohenstein existed until the French period in Germany in the beginning of the 19th century.

Count August David zu Sayn-Wittgenstein-Hohenstein (1663-1735) was an almost life-long friend of Dippel from 1701 to his death. He came from the line of the Counts zu Sayn-Wittgenstein-Hohenstein residing in Laasphe. From 1698 his older brother Henrich Albrecht zu Sayn-Wittgenstein-Hohenstein (1658-1723) ruled the small county, while Count August zu Wittgenstein sought foreign services. We find him in January 1701 as a privy councilor and *envoyé extraordinaire* of the Electoral Palatinate at the coronation of Friedrich I as the first King in Prussia in Königsberg (today Kaliningrad, Russia). From December 1701 he was Oberhofmarschall at the Prussian royal court in Berlin, a very influential and well-paid position. In December 1710, however, he was relieved of his offices as part of the disempowerment of Count Johann Kasimir Kolbe von Wartenberg (1643–1712), who had been in charge of government affairs up to that point. Wittgenstein was temporarily imprisoned in the Spandau citadel and then expelled from the country after paying a large sum. This meant severe humiliation for an imperial count. After that he was again in the service of the Electorate of the Palatinate until in 1719 he was placed alongside his brother as co-regent and finally, after his brother's death in 1723, became the sole regent of the small county of Sayn-Wittgenstein-Hohenstein. While his brother was strongly influenced by Pietism and opened the county to and sponsored all possible and impossible radical pietists, separatists, mystics, inspired and other sectarians, Count August zu Wittgenstein was a staunch opponent of such ecclesiastical dissenters. Assuming the regency of the county, he ruled with an iron fist, driving out the separatists and being merciless to the old-established population as well. This led to countless lawsuits that were conducted by him or against him.

But Count August zu Wittgenstein, who by his own admission had known Dippel since 1701, was also a passionate alchemist. He was not alone in this at the Berlin court. On the contrary, in the first decade of the 18th century, numerous more or less well-known alchemists were drawn to the royal Prussian residence city on the Spree to try their luck there. And the leading figures of the Berlin court, the king himself, Counts Wartenberg, Wittgenstein and Wartensleben and many others were very much interested in the alchemical production of gold.

DIPPEL'S LETTERS TO BARON GEUDER GENANNT RABENSTEINER IN UTRECHT

In the State Archives of North Rhine-Westphalia, unit Westphalia in Münster a collection of 22 letters from Johann Conrad Dippel to his friend Baron von Geuder, genannt Rabensteiner[2] in Utrecht are preserved. [25] These letters were written in German or Latin between 1706 and 1715 and sent from Berlin, Amsterdam, Warmond or Hamburg to Utrecht. These letters are full of valuable information on Dippel's life at that time. But also new insights in his acitivities as a chymist and physician result from reading these letters.

Baron Friedrich Philipp von Geuder, genannt Rabensteiner (1659-1727), came from the aristocratic von Geuder family, which had lived in the German region of Franconia for centuries, especially in Nuremberg and Heroldsberg. He was a Pietist nobleman and secretly married to the widowed Duchess Ernestine Charlotte von Nassau-Siegen (1662-1732). The couple lived in Utrecht in the Netherlands and was part of an international Pietist network. Von Geuder and Dippel were close friends as can be seen from the letters Dippel wrote to von Geuder.

The first of these letters was sent by Dippel from Berlin to Utrecht in June 1706. This was apparently the letter accompanying a medicine that Dippel had sent at the request of the addressee. It is not clear what this medicine was, but the Baron could use it in "all current and future diseases", especially "in head diseases, and in women's diseases" as well. The dose was "from 60 to 80 drops in all [diseases] in distilled water." The second letter of July 27, 1706 contains two medical recipes, that of Dippel's wound balm including a description of a drastic animal experiment with a dog and a nail, and that of a "*Medicina ex Martialis*". The latter is perhaps the remedy that the first letter in this collection of letters was about.

DIPPEL'S WOUND BALM

Let's have a closer look at Dippel's wound balm, because although forgotten today it was thought to be an important remedy during his lifetime! Dippel told Baron von Geuder in the letter from July 1706:

> It is a wonder-worthy *spiritus* as shown by the test that I myself made on various animals at my lodge. And now I believe with certainty that no wound is fatal *per se*, even if it goes right through the heart, if only it were possible to leave the weapon in the wound for so long until someone would be present to apply this *spiritum* through a syringe, the blood would certainly be staunched and the wound would soon be consolidated.

He followed with a detailed description of one of his animal experiments:

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[2] Literally translated: Baron de Geuder named Rabensteiner

> We drove a nail through the head of a young dog, in the presence of a *Medici*, who, as a good *anatomicus*, had to show where the principal *ventricali* of the brain are located and the wound would be most fatal: The one who had driven the nail through and through, so that the dog was nailed properly, could not get the nail out again without using the greatest force and *desordre*, so that the dog's brains had not been stirred up in the head, but it was quite *ex animis*, nevertheless we appilorated several drops into the wound, and poured half a spoonful down his throat: The animal recovered *in momento*, the blood stopped, and before half an hour had passed, the dog barked at the chickens, that had endured the same fate, it also ate bread and whatever was served to it.

Dippel also stated in this letter that the recipe did not come from him at all, but from a French *medicus* who had immigrated to Berlin. Nevertheless, this medicine became known under Dippel's name.

The physician Johann Christian Kundmann (1684-1751) in Breslau (today Wroclaw, Poland), who received his doctorate from Stahl in Halle in 1708, reported in 1716 in his book *Kurtze Abhandlung vom Verstande des Menschen vor und nach dem Falle* about the "Dippelian wound balm". [26] He mentioned that Dippel had given a sample of it to the Licentiate Johann Samuel Carl (1677-1757) in Berlin. Carl would have traveled to Halle with it and the drastic animal experiment with a dog and a nail would have been successfully repeated by the Halle medical professor Friedrich Hoffmann (1660-1742). As a result, Hoffmann's colleague Stahl also carried out this experiment. [27]

The recipe for the wound balm, which was given by both, by Dippel in his letter to Baron Geuder and by Kundmann in his book, was quite simple: You had to prepare the squeezed-out juice of fresh herbs from 1) *Betonica* (betony): 1 pound, 2) *Cerefolio* (chervil): 1 pound and 3) *Sanicula* (wood sanicle): 1 pound. You had to mix these liquids and add 4 pounds of *Aceti vini destillati rectificati* (rectified wine vinegar, i.e. highly concentrated acetic acid) and further add 1 pound of rock salt (NaCl). This would be distilled together from a flask in a water bath and the wound balm is ready, more of a tincture from today's perspective. Dippel added: "You can add other *herbar vulnerarias* [wound herbs] if you like, but the basis are the first three."

Around 1730 in Berleburg, a list of Dippel's medicines was printed in two quite similar versions. [28] As number 5, this list also contained a *Tinctura Vulneraria*, i.e. Dippel's wound balm. It was remarked in this rare print:

> Otherwise it is known that all brain wounds in animals are cured by this tincture, and if you drive a nail through their head and just pour some of it into the wound and also half a spoonful down its throat, the animal will soon recover to be salvaged.

So roughly 25 years after the letter to Baron von Geuder, Dippel or one of his followers still told the same improbable, hardly to believe story. According to the print, the price of Dippel's *Tinctura Vulneraria* was 22 kreutzer per ounce (= 29.23 g).

JOHANN CONRAD DIPPEL IN THE DIARY OF SENCKENBERG

In the early 1730s, Johann Christian Senckenberg (1707-1772), later a physician in Frankfurt am Main who was more than 30 years younger than Dippel, was an admirer of the radical Pietist theologian, physician and chymist. In his later years, the wealthy Senckenberg whose children had all died before him was the founder of several charitable and scholarly foundations. He is famous for his extensive diaries. 53 volumes of diaries and 600 folders with further entries comprise approx. 40,000 pages. In the last decade the first volumes of his diaries have been transcribed by Vera Faßhauer [29] and Veronika Marschall. Through these efforts, much valuable information has become available to the research community.

In April and August 1732, Senckenberg visited Dippel two times in Berleburg, the last place of residence of the old Dippel. The long conversations that Senckenberg had with Dippel himself and with others about Dippel were recorded in his diary. They give us many previously unknown details of Dippel's life including his activities as a chymist. In addition to that, also in later diary entries after his return to Frankfurt, Dippel remained an important topic for Senckenberg.

This new or additional chymical information include a slightly different narrative of the discovery of the pigment Prussian blue in Berlin in 1706, Dippel's preference for phosphorus as the starting material for the philosophers' stone and last but not least Dippel's chymical activities during his time in Berleburg.

THE DISCOVERY OF PRUSSIAN BLUE ACCORDING TO SENCKENBERG'S NOTES OF DIPPEL'S OWN REPORT

On August 22, 1732 Dippel told Senckenberg the story of the discovery of Prussian blue in Berlin. [30] Dippel's story is slightly different from what Georg Ernst Stahl had reported in his 1731 book *Experimenta, Obser-*

vationes, Animadversiones, CCC Numero, Chymicae et Physicae. [31] For a long time Stahl's account was the basis for the written history of the discovery of Prussian blue. [32] But since Dippel was part of the discovery team, we can believe his story more than Stahl's who was not even living in Berlin at the time of the discovery of this blue pigment. [33]

Dippel wanted to prepare *sal volatile*, so his story begins. For this purpose, he calcined tartar, mixed the potash thus produced with dried ox blood and distilled *sal volatile* from this mixture and perhaps also his infamous animal oil. Potash is potassium carbonate K_2CO_3 and *sal volatile* is $(NH_4)_2CO_3$. *Sal volatile* was a chymical product of the time and was used as a smelling salt.

Dippel wanted to throw away the six pounds of residual "*sal*" or *caput mortuum* from this process. But his young laboratory assistant Rösser collected it, extracted the salt from the residue and, after drying, stored this salt in a sugar glass labeled as "*sal tartari*", i.e. potash. We call it "Rösser's potash", because this potash was contaminated. Today we know that it also contained cyanide CN^-, perhaps also some hexacyanoferrate(II) $[Fe(CN)_6]^{4-}$.

Some time later, after Rösser had meanwhile left the laboratory, the following happened: A certain "Lieutenant Diesbach" also worked in Dippel's laboratory. According to Dippel, Diesbach usually prepared Florentine lake and other colors. On that day, he wanted to produce Florentine lake again by using, among other chemicals, potash and alum.

Diesbach, whose full name was actually Johann Jacob von Diesbach (*ca.* 1670-1748) according to the Berlin church records, [34] produced the red Florentine lake from a carminic acid extract. For this purpose, dried and pulverized cochineal insects were extracted in a warm, slightly acidic aqueous alum solution. By adding the right amount of alkaline potash solution, aluminum hydroxide precipitates in the neutralized aqueous solution, on which the carminic acid molecules adsorb. After filtering off and drying, the red Florentine lacquer pigment is obtained. If the aqueous alum solution contains additional metal salts, a pigment with a different color is formed. The addition of ferrous ion, for example, shifts the color from red to violet. That is exactly what Diesbach had done that day. However, things turned out very differently than Diesbach had expected.

Senckenberg noted what happened according to Dippel:

> Diesbach picked up the glass which Rösser, who had already left Dippel, had only labelled as *sal tartari*. But he got *loco rubri coloris*, *caeruleum Berolinense*, made an agreement with the painters behind Dippel's back to deliver them so and so much, but got caught out because after the glass was empty there was no more paint that looked blue with the common *sal tartari*. He came to Dippel and reported it to him, who knew, told him to take *sal tartari* with *sanguine bovino* so he would get it, and it worked. [35]

Let us summarize: Dippel's *sal volatile* production led to the formation of cyanide which remained in the residue of the process. Because Dippel's assistant Rösser wrongly labeled it as potash only, Diesbach used it for his Florentine lake preparation. But the cyanide in the potash led, together with the iron Diesbach had added, to the formation of blue iron(III) hexacyanoferrate(II), i.e. Prussian blue, besides the Florentine lake. The reaction scheme of the first Prussian blue synthesis is shown in Figure 4.

Diesbach sold this blue pigment to painters, but could not reproduce the process, after the source of contaminated potash (Rösser's potash) was gone. He had to ask Dippel what was special with this potash and Dippel told him to calcine potash with dried ox blood and the preparation of Prussian blue could be reproduced. Therefore, we can consider both, Diesbach and Dippel, as the discoverers of Prussian blue.

This discovery happened in Berlin in the year 1706. We know this from an entry in a handwritten chronicle

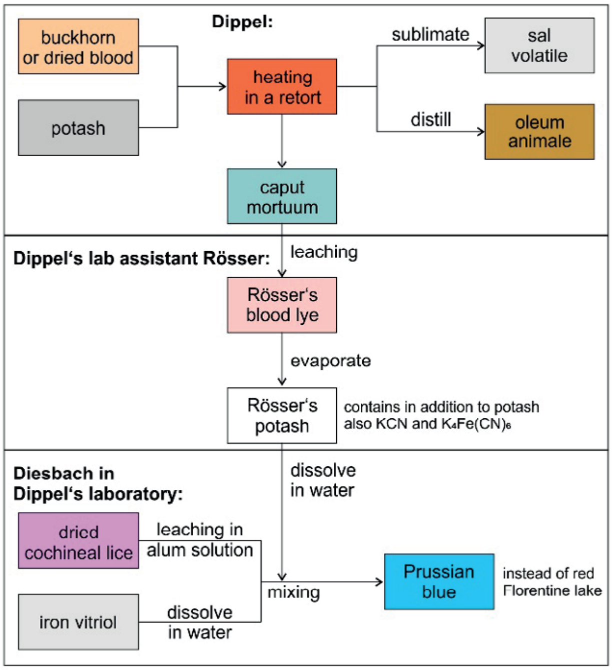

Figure 4. Reaction scheme of the first serendipituous preparation of Prussian blue by Diesbach using potash contaminated by Dippel and wrongly labeled by Rösser.

by Joachim Ernst Berger (1666-1734), Lutheran preacher in Berlin's Friedrichstadt district in which he recorded the first preparation of the "Prussian ultra-marine" by the "Swiss" Diesbach for this year. [36]

DIPPEL'S FLIGHT FROM BERLIN IN 1707 ACCORDING TO ARCHIVAL MATERIAL IN BERLIN

In the Secret State Archives of the Prussian Cultural Heritage Foundation in Berlin we can study a folder from which the events around Dippel's flight from Berlin in late February 1707 become clear. [37] Not much about chymistry can be found there, though. But let's tell the story:

The first thing we can learn from the material in this folder is that Dippel came to Berlin around early November 1704. In a letter he described that "I soon had to realize that because of alchemy, everyone was staring at me from all corners" and that "This pursuit meant that not only did I not do anything real in *Alchymices*, but I also resolved not to waste much time here." Roughly six months after Dippel came to Berlin he was so disappointed that he thought about leaving the city and try his luck elsewhere. Therefore he wrote a letter in Latin to the Swedish king Karl XII (1682-1718). Among other things, he wrote to the Swedish king that he wanted "to reveal his *arcanum* in alchemy to him as an inexhaustible source of wealth." [38] In addition, there was harsh criticism of the king and government of Prussia. So Dippel wrote:

> I see their monstrous crimes, in which court and government are completely immersed, as a divine sign, they impel me daily to promote my departure, and even if I alternately allied with one of the Firsts around the King, they would betray me for their meanness, I can predict that with certainty. [39]

and another example:

> Nor have I any confidence in the King's foul servants, who surround him on all sides, when he binds himself by solemn promises to any demands what they impede, known to the King or not, for I have already witnessed the *machinationes* of some of them.

Dippel did not send this letter directly to the Swedish king, but sent his servant to the Swedish "*envoyé*" in Berlin, Count Anders Lejonstedt (1649-1725), Swedish envoy in Berlin for the second time since 1703, "to be all the more certain about the address". Lejonstedt accepted the letter willingly and promised to forward it. However, when Dippel's servant approached him again after the agreed time:

> … so the count mentioned took a nasty turn on him, gave him the opened letter back, said he hadn't sent it away and didn't want to have anything to do with such things, yes, he even threw insults and threats around. [40]

One gets the impression that the Swedes had no interest in secretly poaching a chymist who was in the service of the Prussian royal court to Sweden. Against the background of the Great Northern War, in which Sweden was involved at the time, this is also understandable. The Kingdom of Prussia remained neutral in this conflict and Sweden certainly did not want to provoke Prussia into entering the war on the side of the enemy coalition. On the contrary, it was hoped that Prussia would take the Swedish side.

Roughly one and half year later, towards the end of 1706, a book was published by Johann Friedrich Mayer (1650-1712) a well-known orthodox Lutheran theologian. From 1701 he was general superintendent of Swedish Pomerania, professor of theology at the University of Greifswald and pastor of St. Nikolai in Greifswald. He was the most important Lutheran theologian in the German lands under Swedish rule. After the occupation of Saxony by Swedish troops in the ongoing war, Mayer had rushed to the Swedish camp at Altranstädt and conferred with King Karl XII about the increasing influence of the Pietists and what to do about it. In nearby Leipzig he then had his book "A Swedish theologian's short report about Pietists" printed without naming the author. [41] This book was a fierce but not clumsy attack on the Pietists. Mayer personally attacked various Pietists in this book, including the Pietists from Halle and also Dippel. Dippel reacted to this with his own polemic, which was called "Impartial Thoughts" for short. [42] At the instigation of the Swedish envoy, Dippel was arrested around February 7th because of his book, in particular because of the harsh criticism it contained of the Swedish king.

According to the royal order of February 12, the imprisoned Dippel was then to be released on bail of 2,000 thalers. On February 14, August Count zu Wittgenstein took over the bail "*sub hypotheca bonorum*", whereby Dippel was not allowed to travel from Berlin before the matter was resolved, had to be available to the commission and had to refrain from all writing on religious matters. [43] Dippel was released from prison the same day. Figure 5 displays the short letter Dippel wrote to Count August zu Wittgenstein asking him to take over the bail of 2,000 thalers.

A week after his release, on February 21, 1707, Dippel wrote a rather unwise letter to the Prussian General-Fiscal[3] Wilhelm Duhram (1658-1735). In this letter,

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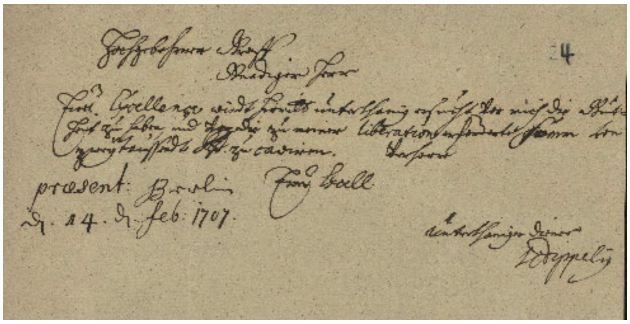
[3] General-Fiscal was a kind of attorney general.



Hochgebohrner Graff
Gnädiger Herr

present: Berlin
d. 14. d. feb: 1707

unterthäniger Diener
Dippelius

Figure 5. Letter from Johann Conrad Dippel to Count August zu Wittgenstein dated Berlin, February 14th, 1707 (source: GStA PK, I. HA Rep 9 Geheimer Rat Allgemeine Verwaltung D4c Fasc 24, f. 24).

Dippel wrote that among his still confiscated correspondence was a letter that he had written to the Swedish king in 1705. We have already discussed this letter. Dippel would fear that he would be questioned again about this letter and would like to avoid that by explaining it. He then went on to write that after his arrival in Berlin he had been put under great pressure because of his knowledge of alchemy and that he therefore wanted to leave Berlin again. That's why he wrote this letter to the Swedish king. Dippel then tried to explain further in his letter to Duhram why he had written so disparagingly about the Prussian court. However,

> there is nothing in it other than what is complained about at every table, at every assembly, and in every street by the subjects themselves. [44]

In any case, the letter to the Swedish king was dug out, and based on its contents, Dippel was to be arrested again. He found out about this in good time and fled from Berlin at the end of February 1707 via several intermediate stops to the Netherlands.

THE STORY OF PRUSSIAN BLUE CONTINUES

After Dippel left Berlin, Diesbach teamed up with the teacher and natural scientist Johann Leonhard Frisch (1666-1743). Together they produced and marketed Prussian blue over the next years and both earned a lot of money from it. This emerges from a collection of letters that Frisch sent from Berlin to Gottfried Wilhelm Leibniz (1646-1716) in Hannover between 1706 and 1716. [45]

Another letter preserved in the correspondence of Leibniz proves that Dippel also continued to produce Prussian blue during his time in the Netherlands. In this letter, written in French and dated August 17, 1714 from Paris to Leibniz in Hannover, Heinrich Hasperg, church councilor and secretary to Duke Anton Ulrich von Braunschweig-Wolfenbüttel (1633-1714), reported on "the blue color for the miniature … that is made in Berlin":

> A German in Holland called Herr Dipelius also makes it and I brought a sample here [to Paris], but it's not as nice as the color made in Berlin. [46]

Until the end of the 1710s, the discoverers of Prussian blue had a kind of manufacturing monopoly, but then the first recipes began to appear underground, both incorrect and correct ones. But still only a few knew how to make Prussian blue. That was over, however, with a publication in the renowned *Philosophical Transactions of the Royal Society* in 1724. [47] Now anyone who could master the necessary chymical manipulations could make Prussian blue himself. The price then collapsed rapidly.

Today almost 300 years have passed since the manufacturing instructions for Prussian blue were published and this compound is still used as a pigment. In the meantime, however, it has also found other areas of application. It serves as an antidote for poisoning with thallium or radioactive caesium and as a sensor material for determining the concentration of certain substances, such as hydrogen peroxide. Many other applications are still being tested or are being examined on a laboratory scale, such as the use of Prussian blue as an active substance in batteries and electrochromic windows or its use in modern imaging processes in medical technology or even to combat tumors. [48] Surprisingly, several details in the composition, structure and chemical reactions of Prussian blue are still open more than 300 years after the discovery of this amazing compound. [49,50]

DIPPEL'S STAY IN THE NETHERLANDS 1707-1714

We had already heard that Dippel left Berlin for the Netherlands in 1707. Most of the newly discovered information about Dippel's time in the Netherlands we owe to the Rabensteiner letters, which we have already mentioned above. After arriving in the Netherlands, Dippel first lived in Amsterdam. This was reported by Kundmann who visited Dippel in early 1708 in Amsterdam. We can see this also from nine letters in the Rabensteiner collection which were dated Amsterdam between 1709 and 1711 and from the copy of another letter to a certain Herr Bergmann in Darmstadt dated Amsterdam, August 3, 1709. [51]

But, it is interesting to note that Dippel's letters to Baron Geuder were sent from Warmond between October 1710 and early June 1711. Warmond is a small village just north of the university town of Leiden. From a brief remark by Dippel, which Senckenberg recorded in his diary, one can conclude that Dippel had bought an estate there, near Leiden. [53] What brought Dippel to this place? He, who, as far as is known, had never studied medicine, wanted to do a doctorate in medicine. However, it was not until April 1, 1711 that he enrolled as magister "*Johannes Conradus Dippelius Hassus*" in the register of the University of Leiden. And already on April 17th he defended his theses and received his doctorate in medicine. It can therefore be assumed that he has already been working on his planned doctorate before he enrolled and perhaps wrote his soon to become famous doctoral thesis entitled "*Vitæ Animalis Morbus et Medicina*" in Warmond.

In older biographies of Dippel it is usually mentioned that he lived in the Netherlands in Maarssen near Utrecht. But no letter from Maarssen is among Dippel's 22 letters to Baron Geuder, only the last Dutch letter, written during his urgent departure on September 19, 1714, contained a crossed-out "Maarssen" as a sending location. But this maybe explained by the fact that it is not a long way from Maarssen to Utrecht, only a few kilometers, so that information could be exchanged personally between the two friends. But from the content of several letters [54] and from some notarial agreements [55,56] it becomes indeed clear that Dippel lived in Maarssen in his later years in the Netherlands. Here he owned an estate called Vredenhoef. This "buitenplaats" can easily be identified and it exists still today, however, the appearance of the house has probably changed a lot. It is located on the Straatweg, the old street between Utrecht and Amsterdam. In front of the house flows the Vecht, a small river that flows from Utrecht to the Gooimeer, a lake on the edge of the IJsselmeer. Figure 6 shows the Vredenhoef as it looked in 1836. It was built in the mid-17th century in the Dutch Classicist style; construction was probably started in 1666. It is not known who built the house. In Dippel's time, the house had a stable, a garden, plus an orchard and a vegetable garden. The tea house on the river was built later. From the above mentioned letters we can also conclude; that Dippel had still to pay the purchase price for the estate which also included a "*laboratorio*".

Figure 6. Buitenplaats Vredenhoef in Maarssen in 1836 (source: lithographic print by P.J. Lutgers / Desguerrois & Co, Amsterdam in the collection of the author).

DIPPEL'S ANIMAL OIL BECOMES FAMOUS

After Dippel had received his doctorate in April 1711, he now, as a M.D., printed his theses again and his *Vitæ Animalis Morbus et Medicina* became a well-selling book. [57] Therefore, it was reprinted several times and also translated into German as "*Die Kranckheit und Arzney des thierisch-sinnlichen Lebens*" (=*Maladies and Remedies of the Life of the Flesh*). Of particular interest is a German-language critically annotated and appendix edition from 1736. [58] The editor and commentator, who knew Dippel well and was a well-versed physician and chymist, remained anonymous, but perhaps it was Johann Samuel Carl.

Through *Vitæ Animalis Morbus et Medicina*, Dippel's animal oil became widely known, although he dedicated only a very small part of this book to it. He wrote:

> I cannot avoid, for the benefit of the neighbor, to share a remedy which, as I have experienced myself very often, drives away all abating fevers, even if you have taken it only once, and with a quite wonderful effect, for the sick were overtaken by a pleasant sleep; and if at times they had passed about fifteen hours in sweet repose, with the face blooming and vivid in color, they arose fresh and healthy after they had slept through the attack of fever. [59]

The remedy would not bring sleep in healthy people, but even 30 hours of sleep in epileptics, after which they would also be cured. "*Medici*", who had seen this,

> almost no longer doubted the truth of the philosophical stone and the universal remedy, although it was nothing more than a very small remedy despised by the apothecaries, but which had been worked out with great patience.

That all sounds very unbelievable: someone with fever sleeps 15 hours, an epileptic 30 hours at a time after taking the remedy and then they are immediately completely healed, while a healthy person does not fall asleep at all!

However, according to Dippel, this remedy has "a very penetrating and rather unpleasant smell" but

> a pleasant and savory taste … It is namely a distilled oil from all parts of the animals, separated from its salt, which has been rectified and purified through the retort without any addition of anything else until it no longer leaves any black, burnt deposits, which is only attained after the 15th repetition.

The dose was said to be 30 to 40 drops. – This rather short section of his dissertation established the fame of Dippel's animal oil.

In the critically annotated edition of 1736, the commentator on Dippel's animal oil warned that

> not a single example has been seen that it presented anything worth mentioning, let alone wonderous.

It was much more frequently "shown that it was downright harmful". This "miracle oil so splendidly highlighted" is "not worth a damn" [60] and: "Those who love their lives should leave the stuff out and get rid of it." [61] Before that he had briefly remarked that "it is very often distilled from ox meat or ox blood". In order to keep it colorless, it has to be distilled several times from potash (K_2CO_3), possibly also from burnt lime (CaO). The work was "mad and tedious". So the commentator, who knew Dippel and his animal oil well, hardly had a good word to say about this mixture of substances.

The commentator also knew Dippel's "so highly and much praised light and fire *principium*". However according to him, Dippel "basically" did not "know and understood" this principle by himself, for otherwise

> he would never have done such chymeric things, and would have presented something far more real and useful to the world. [62]

DIPPEL'S FLIGHT FROM THE NETHERLANDS TO HAMBURG AND ALTONA AND HIS TIME THERE (1714-1719)

In September 1714, Dippel fled head over heels by ship from the Netherlands to Altona, which at the time was part of the Danish dominions in northern Germany. [63] He stayed there and in the much larger neighboring Free Imperial City of Hamburg until 1719. It is not yet known why he left the Netherlands. But there were rumors in Germany that

> he had to flee Holland not only because of a few very unfortunate cures, but also because through many expensive alchemical operations which ended in vain he had accumulated great debts to a certain great lady. [64]

In Altona, Dippel was a protégé of the Danish governor Christian Detlev Graf von Reventlow (1671-1738). Not much is known about Dippel's chymical activities at that time, but it is clear that he was also working in the laboratory. Christoph Heinrich Dornemann (1682–1753) from Hamburg, for example, mentioned in a letter from May 1715 to the Pietist professor Johann Heinrich May (1688–1732) in Giessen that Dippel was very

> busy with laboratory work. … I suspect that he is searching for gold, although he found a medicine lately, and our gentlemen pastors are also looking for the same with him … . [65]

These were, in particular, Messrs. Heinson, i.e. Johann Theodor Heinson (1663-1726), senior pastor of St. Peter's Church and Winckler, i.e. Johann Friedrich Winckler (1679-1738), senior pastor of St. Nikolai Church, who "did their utmost to find the *lapidem*". If that were to be true, these people interested in alchemy would have been the two most important Lutheran-Orthodox preachers in the Free Imperial City of Hamburg.

Heavy disputes between Dippel and the various local authorities in Altona and the surrounding Danish controlled region (e.g. Glückstadt, Pinneberg) began in 1717. In early 1719 Dippel fell also out with his protector Reventlow and in the course of the affair he was imprisoned in May 1719 and eventually sentenced to life imprisonment in September of the same year. [66] He had to serve this on the Danish island of Bornholm.

DIPPEL IMPRISONED ON THE DANISH ISLAND OF BORNHOLM 1719-1726

On the island of Bornholm, Dippel was imprisoned in the mighty fortress of Hammershus on the Northwestern corner of the island. Today a picturesque ruin, it was still an impressive and functional fortification in Dippel's time. But Dippel was the last prisoner who was incarcerated in Hammershus. After his release the decay of the building began.

Not much is known about Dippel's nearly seven years in Hammershus, but close reading of the preface of one of his books, [67] the study of some letter's in the Dippel-letter collection of Count August zu Wittgenstein and of some entries in Senckenberg's diary give us at least an impression of his chymical activities there. So in

1732, Dippel reported to his visitor Senckenberg in Berleburg that in Hammershus he

> was only able to do little or next to nothing in *chymicis* in his prison, and only built a furnace for simple *extraction*. [68]

In mid-1725, the last year of his imprisonment had begun, Dippel was visited by Christian Pagencopen from Hamburg, an emissary of Count August zu Wittgenstein. For Dippel's book *Eröffnete Muhtmassungen und Merckwürdige Gedancken* (= *Opened Conjectures and Remarkable Thoughts*) Pagencopen wrote the preface signed with his initials C.P. only, but since Pagencopen also wrote several preserved letters on the same subject to Count August, we know that it was him who wrote the preface. In a letter dated Hamburg, September 5, 1725 [69] Pagencopen reported Count zu Wittgenstein about his visit of Dippel in his arrest on Bornholm. From the preface of the book and from this letter we learn that Dippel lived in a small detention room on the fifth floor of the central mantle tower of the fortress. However, he was allowed to prepare his own meals in the hall in front of his cell and also to produce medicines there himself, which he would distribute to patients who came to him frequently. Dippel's visitors were always accompanied by a senior officer and a noncommissioned officer, with the latter remaining in the hall while the other went into the small detention room together with the visitor. Figure 7 shows the ruin of the mantle tower as it appears today.

Figure 7. Ruin of the mantle tower of Hammershus on the Danish island of Bornholm. Dippel was imprisoned here on the top floor for about seven years. (source: Photo by the author 2019).

Although Dippel the chymist could obviously only produce some medicine during his time on Bornholm the Danish royal court was also interested to receive more information about Dippel's gold making attempts. This can be shown by a letter from Dippel from February 1724, in which he answered questions from the governor of Bornholm Niels Madsen West (1666-1752) about his gold making. Dippel wrote:

> Meanwhile, I can say so much *in general* that the *productum* will far exceed the cost, but whether it will turn out 10,000, 100,000, or 1,000,000 remains to be seen.

Regarding the cost of carrying out the experiments, Dippel replied: "600 *Reichsthaler*" and the duration: "one and a half years". Whether the gold produced is good ducat gold?: "The gold must not only be ducat gold, but far better…". [70] So in this case, too, we see Dippel's typical exaggerations when he wrote about his chymical knowledge. And there is no evidence that royally sponsored gold-making experiments with Dippel's recipes actually took place in Denmark.

In June 1726, Dippel, sentenced to life imprisonment, was released from prison on condition that he had to leave Denmark immediately and never to set foot in Danish lands again. He had been in the Hammershus prison for six years and ten months.

DIPPEL'S SWEDISH PERIOD 1726-1728

Dippel next went from Bornholm to Sweden and stayed in that country for almost two years until March 1728. Ironically, after his release from prison, Dippel actually wanted to return from Bornholm to his native Germany. But since the shipping connections via southern Sweden (Skåne) were better, he first traveled to Ystad in Sweden in order to get to Germany from there. But then he followed the invitation of a Swedish Pietist merchant Johan Hoffmeister (1699–1744) from Kristianstad and accompanied him to that place, where he lived for the next few months. Here Dippel became a center of the Swedish Pietist movement.

It is interesting to note that the Swedish king at that time was a compatriot of Dippel from Hesse, Fredrik I (1676-1751, king of Sweden from 1620), the son of the landgrave of Hesse-Kassel. This Swedish king invited the physician Dippel, meanwhile an international celebrity, to come to Stockholm. After some hesitation Dippel finally moved to the Swedish capital and arrived there in mid-January 1727.

Not much is known about the chymical work done by Dippel in Sweden. About one episode he informed Senckenberg. According to him, he had

> given Count Frölich in Sweden an opportunity to work on the phosphorus, and he completely distilled ☉ mixed with it into a ☿ium, which the *comes* held very highly … . [71]

This Count Frölich is probably one of the descendants of Carl Gustav Frölich (1637–1714), a general in the Swedish infantry, perhaps Count Bengt Frölich (1684–1744), a Swedish follower of Dippel.

Elsewhere it was reported that

> various bigwigs in Sweden held Dippel for a great gold maker and tried to learn this art from him; but finally found themselves deceived in their opinion. [72]

This may have happened in Stockholm, where Dippel lived in the house of the wealthy Elias von Walcker (1660-1733). Dippel must have impressed Emanuel Swedenborg (1688-1772) as well. Swedenborg, an inventor and scientist, later also a mystic theologian, was perhaps among the guests of Dippel in von Walcker's house. Alfred Acton (1867-1956) wrote

> Swedenborg's intercourse with Dippel was probably and perhaps exclusively on the scientific or rather the chemical side of his learning, and among other things, on his claim to make gold – not exactly, as it would seem, a claim totally to transmute metals, but to draw gold from them. [73]

Swedenborg's words concerning the "Dippelian Experiment" according to Acton were:

> When Dippel was staying in Sweden, he preached his process as a sure argument for the transmutation or augmentation of gold from metals; for he promised by this art and process to extract more gold from copper than can be done by any common way. [74]

Swedenborg also recorded this in one of his books as an "*experimentum quoddam Dippelianum*": According to this, one part of copper is mixed with 2 parts of saltpetre, placed in a crucible, which is closed and heated in the reverberatory fire. After cooling, the obtained mass is pulverized in a mortar and placed in a flask together with *spiritus vini rectificatus*. This flask is then kept in mild heat for a day, during which time the *spiritus vini* turns red. Put this red *spiritus vini* in another flask. The leaching of the red color from the mass is repeated. The red spirits are combined and distilled into a recipient. A *materia rubra* or *sal rubrum* remains behind in the flask. This *sal rubrum* is mixed with half the amount of silver lime and placed in a crucible. After melting and cooling, you get a *regulus*, which after separation with aquafort gives quite a lot of gold lime. [75]

This recipe reminds on Dorothea Juliana Wallich's (1657-1725) theory of extracting the colouring soul (*anima tingens*) or tinging sulphur out of several materials, among them copper, and introduce this soul into silver to produce gold. She had published this in her book *The Mineral Gluten* in 1705. [76] This was a so-called particular recipe, not a process description for the philosophers' stone. So, Dippel used essentially the same procedure as Wallich, although details of the process may be different. Interestingly, in Sweden, a country with huge copper mining industry, Dippel tried to impress people with a chymical recipe for extracting *anima tingens* from copper to transmute some silver into gold.

But if we look at this recipe with the eyes of an chemist, it seems to be very dubious. If you add copper metal to a saltpetre (potassium nitrate KNO_3) melt, blue-green copper nitrate will be produced, accompanied by red fumes of nitrogen dioxide. Copper nitrate can be dissolved in ethanol, but this is also a blue-green solution not a red one. And if we distill off the ethanol from this solution, a blue-green solid will be found, not a red salt. A red copper compound would be copper(I) oxide Cu_2O, but this should not be produced by the process described by Dippel. Maybe this is the reason why the Swedish bigwigs felt themselves deceived by the chymist Dippel.

But much more important for Dippel's fate in Sweden were the quarrels around his theological writings. Their content and the fact that he found a substantial number of followers in Sweden led the Swedish clergy to work on his extradiction from this country. Finally, Dippel was forced to go. He left Stockholm in early December 1727, and Sweden in March 1728.

DIPPEL AND THE TINCTURE MADE FROM PHOSPHORUS

So what about the phosphorus that Dippel introduced to Graf Frölich in Sweden? From some entries in the Senckenberg diary, from several other documents in the Senckenberg collection and from a recipe which was found in the manuscript collection of the State and University Library in Hamburg it is now established knowledge that Dippel wanted to produce the philosophers' stone from phosphorus. He pursued this idea for more than three decades, from at least 1701 until his death in 1734.

Dippel's first acquaintance with phosphorus as a raw material for the production of the philosophers' stone seems to have been an alleged transmutation in 1701 in Frankfurt am Main. Dippel must have been very impressed. He reported about this to his visitor Senckenberg in Berleburg in 1732:

> Back then, the projection happened at Saltzwedel's, and he had the laboratory work done at his place … in *phosphoro*, … and that's what it was supposed to be, … at that time you could almost smell the *operationis ex stercore et urina* [operations from feces and urine] in Ff. [Frankfurt am Main] on every street, … he always had the laboratory workers collect the human feces in baskets. [77]

According to Johann Conrad Creiling's (1673-1752) collection of transmutation stories, this transmutation was carried out by a journeyman apothecary named Godwin Hermann Braun from Osnabrück in the Apothecary shop At the Swan in Frankfurt in the presence of the owner Nikolaus Saltzwedel (1651-1726) and other distinguished persons, and "a lead ball weighing 2 lots and otherwise also lead and ☿*um* turned into good gold with his tincture". A "principal piece of the tincture" was "*Phosphorum … ex regno animali …*". [78] So the tincture for the Frankfurt transmutation was made from phosphorus, which in turn was derived from human urine and feces.

In the archived collection of Senckenberg's writings and correspondence there is also a "*copia* of Mr. Saltzwedel's process which tinges ♄ in ☉": [79]

> *Recipe*, 14 bowls of human excrement without urine, put them in the sun so that they get a thick black crust on top, take this off and put it in a flask … whereupon is a blind helmet, put it in the sun again until you get the *Spiritum phosphori* made from this (which will be so strong that one can light powders with it), with this *spiritu* extract the *TR* [tincture] from the crusts, when all is out put the *TR* in a circulating glass, and leave it well circulating in the ☉ [sun], but then pass it over *per alembico*, the *TR* left in *fundo* tinges ♄ in ☉, but there must be a large phosphorus addition and it must be dissolved in the *TR*, so that it is in digestion for 4 days, if it is not tinging yet, some *phosphoro* is to be added until 4 drops transform 1 quint ♄ into good ☉. *NB.* in May, June, and July the matter must be collected.

Senckenberg's copy of a letter from Dippel to him takes the same line. Senckenberg had noted:

> Author J. C. Dippelio / You must know that I still have no other experience with the tincture than from *phosphoro* with which ☉ or ☽ is dissolved and also sublimated by appropriate manipulations, afterwards dissolved and abstracted in 🜈 *Rect.* and you have an *Elixir tingens* within a few weeks … [80]

So there it is, the tincture made from phosphorus! – Dippel then continued:

> Just because phosphorus requires a lot of effort and trouble and its handling is very dangerous for someone who has not learned the right laboratory techniques well and has not seen them with his own eyes, I have not yet been able to resolve to give part of it, but now I am well provided with it.

A corresponding recipe is the "*Dippelii Tinctura Universalis*" found in the manuscript collection from the Hamburg State and University Library. [81] Let's take a closer look at this process description now:

Dippel described that at first three preliminary works have to be carried out, namely:

i) to prepare *Vitriolus Martis* (iron vitriol = iron sulphate $FeSO_4$)
ii) to prepare *Spiritus Luminosus* and *Phosphorus* in stock, and
iii) to prepare a sublimated *Regulus Antimonis et Martis* resulting in *flores* that shine like diamonds.

The *Regulus Antimonis et Martis* should be an alloy of the metals antimony and iron, we also know about iron vitriol and phosphorus, but what is *Spiritus Luminosus*? A glowing or shining spirit? – If we use the analogy to the early modern terms: *Spiritus vini* = distilled wine = ethanol, *Spiritus salis* = distilled common salt NaCl = hydrochloric acid (HCl), *Spiritus vitrioli* = distilled vitriol salt, e.g. $FeSO_4$ = sulfuric acid (H_2SO_4), *Spiritus nitri* = distilled saltpetre (KNO_3) = nitric acid HNO_3, and continue with *Spiritus Luminosus* = distilled luminous matter, i.e. phosphorus = phosphoric acid (H_3PO_4)?

Back to the recipe of *Dippelii Tinctura Universalis*. Figure 8 displays the reaction scheme of this process description. According to this, A.) one part of the ominous *spiritus luminosus* is mixed with iron vitriol and sublimated to obtain a homogeneous sublimate, then B.) purified phosphorus is dissolved in the second part of the *spiritus luminosus* and purified by *cohobationes*, whereby one would obtain a *phosphorus liquidus*.

What could Dippel mean by *phosphorus liquidus*, a liquid phosphorus? In his chemistry textbook *Einlei-*

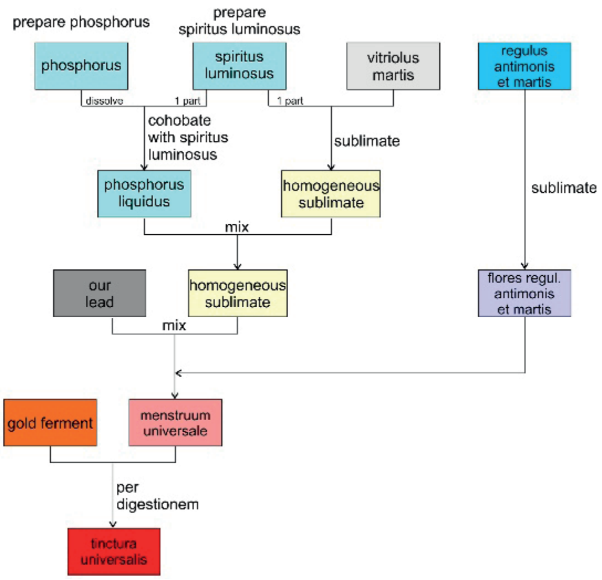


Figure 8. Reaction scheme of *Dippelii Tinctura Universalis* from the Hamburg State and University Library.

tung in die Chymie (= *Introduction into Chymistry*), [82] Hieronymus Ludolf (1708-1764) also described the production of "liquid phosphorus", which was said to be of great benefit. He further claimed: "This liquor shines brightly when you rub your hand with it and it doesn't do you any harm." Of course, this can by no means be real phosphorus, because it causes serious injuries when it comes into contact with the skin. Ludolf also remarked: "I haven't been able to do it yet because of its length, but I think it's practicable". At this point, Ludolf brought a recipe that he had not yet tried out himself. He had never seen *phosphorus liquidus* himself, and maybe Dippel hadn't either?

The melting point of pure white phosphorus is 44.2°C. If it is contaminated, it may melt at a slightly lower temperature, so that a chymist could easily obtain liquid phosphorus, but of course not with the properties described by Ludolf. Ultimately, what was meant by *phosphorus liquidus* at this point in the recipe must remain open.

In the next step C.) the *phosphorus liquidus* should be conjugated with the sublimate obtained under A.), which also results in another homogeneous sublimate. With this D.) "our lead" is dissolved. In addition, it should be noted that the adjective "our" before a substance in the alchemical arcane language of the time often meant that, as in this case, it was not lead, but something else that was then called "our lead" but its actual nature remained open. In step E.) you had to mix this mixture with the diamond flores. A steaming crystall, the *menstruum universale* would be created. This heated with gold ferment, results in the *tinctura universalis*. This recipe remains difficult to understand because some intermediate products cannot be identified. This includes the *spiritus luminosus* and *phosphorus liquidus*.

In the Senckenberg collection, too, there are several phosphorus recipes in connection with records of Dippel. The process description "*De Phosphoro*" is particularly interesting. This is much more detailed than what has just been discussed and the process is also very different. Figure 9 shows the corresponding reaction scheme.

According to this process, phosphorus is produced following the Kunckel method from putrefied urine with the addition of sand and purified by rectification (Figure

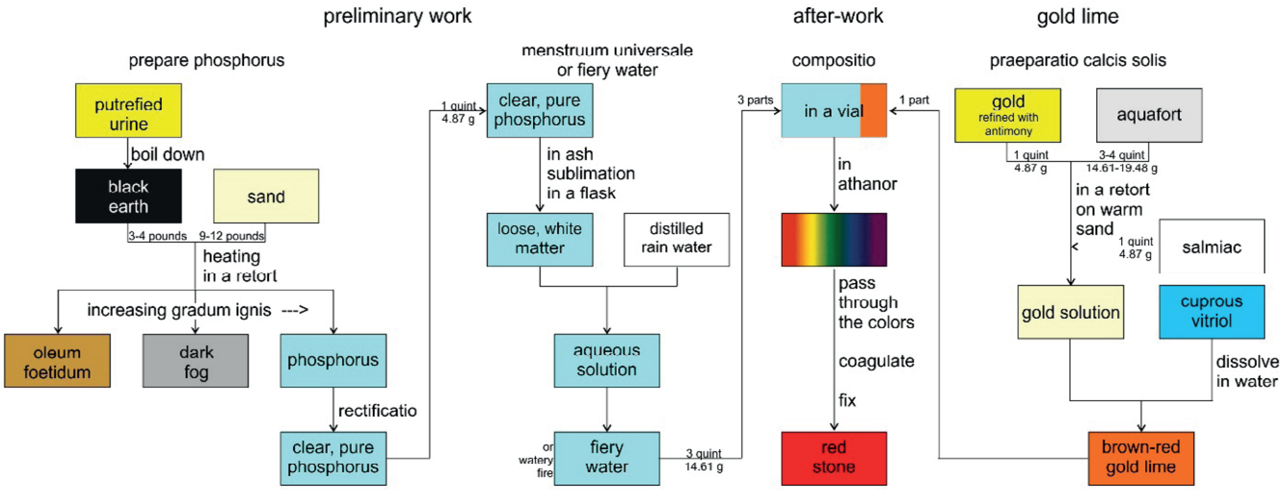


Figure 9. Reaction scheme of *De Phosphoro* from the Senckenberg collection.

9, left column). The "*menstruum universale* or the fiery water and watery fire of the philosophers" is then to be produced from this phosphorus (Figure 9, 2nd column from the left). For this purpose, "a quint of *phosphoro*" is gently heated in a glass flask with a helmet in an "ash oven" in such a way that the phosphorus does not over-distills and the vapors "always roll around in the flask". Over time, a "loose matter white as snowflakes" would build up on the bulb wall. This fluffy white matter can be interpreted as phosphorus pentoxide P_4O_{10}, which is formed as the phosphorus vapor circulates as a result of the reaction with the oxygen in air. The phosphorus pentoxide is then dissolved in distilled rainwater and some water is distilled from it. One then obtains the "fiery water and watery fire." That's the recipe. The "fiery water" can be interpreted as a more or less concentrated phosphoric acid solution H_3PO_4 in water.

A gold lime was then required, the production of which was described in the section "Praeparatio Calcis Solis" according to the right-hand column in Figure 9. In the alchemical literature, gold lime was usually understood to mean very finely distributed gold, not a gold compound, but still elemental, metallic gold. [83] To do this, purified gold ("poured through the antimonium") should be dissolved in aquafort (HNO_3) to which some salmiac NH_4Cl was added. Nitric acid containing chloride dissolves gold. At a certain concentration ratio, this mixture is also called *aqua regia* because it dissolves the king of metals, gold. An aqueous solution of venereal vitriol, i.e. $CuSO_4$, should then be added to this gold solution, "this is how a beautiful brown-red and very subtle gold limestone precipitates". It would have to be tested experimentally whether gold is really precipitated. But gold can be precipitated very easily from an acidic solution of gold chloride if a suitable reducing agent is added.

In any case, with the "fiery water" and the gold lime, the starting materials for the next process step of the *compositio* were now available. To do this, one should put one part gold lime and three parts "of the *menstruo philosophico* or fiery water" in a vial, "melt the glass shut, set it in an *athanorum*, and let it … pass through the colors, coagulate and fix into a red stone." That is probably the philosophers' stone, the *Lapis Philosophorum*.

If you compare this entire reaction sequence with other alchemical process instructions for the production of the philosophers' stone, then the process from urine to the "fiery water" corresponds to the preliminary work for the production of the *menstruum universale* and the dissolution of the gold lime in the *menstruum universale* and the subsequent steps of going through the colors in the *athanor*, coagulating and fixing is the after-work.

The *multiplicatio* and the *fermentatio* are also briefly mentioned in the process description. The *multiplicatio* is again typically alchemical, you take the result of the preliminary work, the "fiery water", three parts and add one part of the result of the after-work, the red stone and let it go through the colors, coagulate and fix. The *fermentatio* refers to the *12th key of Basilius Valentinus*. In contrast to the Hamburg process description, this recipe from the Senckenberg collection can be followed and understood in every single step. The question would of course be at which point in the process description the actual chemical reaction is different from the one described. This should be the dissolution of the gold lime in the "fiery water", for gold does not dissolve in phosphoric acid.

There are several other process descriptions in the Senckenberg collection that use phosphorus as an important ingredient. However, we have discussed the most important of them. But there are of course other references in original sources that point to the importance of phosphorus for Dippel's chymical path to the philosophers' stone:

Among the Dippeliana in the archive in Bad Laasphe we also find a letter by Amsterdam apothecary Albertus Seba (1665-1736) to Count August zu Wittgenstein from January 1717. [84] From this letter we learn that "*Dippelius*" bought 20 ounces of "phosphorus" from Seba at a price of 22 guilders per ounce. This price would have been very cheap, wrote Seba, and he only sold it so cheaply for his "old friend". But even at that price, based on weight, phosphorus was more expensive than gold! It is somewhat surprising that Dippel as an experienced chymist would have preferred to buy the very expensive phosphorus rather than produce it by himself.

Dippel himself mentioned phosphorus already in his doctoral thesis *Vitæ Animalis Morbus et Medicina* from 1711:

> … the so strange fruit of the noble art of chymistry, namely the so-called phosphorus … which can be prepared from all liquid parts of the animals by the greatest power of fire, if they have been properly putrefied beforehand. … This phosphorus, no matter how well it is sealed in the jar and only aroused by the slightest heat, immediately bursts into flames; even if it is held under water, it still does not stop spewing flames and spreading them over the water… [85]

The latter is not true, because phosphorus burns in air but not under water and is therefore also stored under water.

DIPPEL'S CHYMICAL EXPERIMENTS IN LAASPHE AND BERLEBURG IN THE TWO COUNTIES OF WITTGENSTEIN

Eventually being expelled from Sweden, Dippel finally returned to Germany via Copenhagen in mid-1728. On the way, Dippel had repeatedly received letters from Count August zu Wittgenstein, who urged him to come to the county of Wittgenstein. Dippel then replied in a letter dated June 25, 1728 from Copenhagen to the count's representative Pagencopen and asked for "100 ducats to my travel". [86] The count would "find contentment for this and for everything else on my arrival" in Wittgenstein.

The first stop during Dippel's return to Germany was the Free Imperial City of Hamburg. In November 1728, Dippel wrote to Count August zu Wittgenstein again, thanking him for the 100 thalers he had sent. From Hamburg he went via Lauenburg, Lüneburg and Celle to Liebenburg near Goslar in the Prince-Bishopric of Hildesheim. A letter dated September 7, 1729 states that Dippel stayed there to "complete some chymical experiments on medicine and other curiosities in solitude". [87] When he was finally expelled from the Prince-Bishopric of Hildesheim, Dippel went to the counties of Wittgenstein, where he arrived in December 1729.

A few days after his arrival in Berleburg in the County of Sayn-Wittgenstein-Berleburg, a carriage brought Dippel from Berleburg to Laasphe in the County of Sayn-Wittgenstein-Hohenstein. For the first few months of 1730, Dippel was a guest of Count August zu Wittgenstein at the Wittgenstein castle near Laasphe. However, around mid-April 1730 he returned to Berleburg where he stayed the next four years.

What has happened, that Dippel left his old friend and supporter Count August zu Wittgenstein? We may find an answer to this in a letter that Dippel sent to Count August on December 24, 1731 from Berleburg:

> Hope with God that the annoyances and *criante* incidents between Your Excellence and your subjects were once resolved and brought to a good end, so I could, without hurting my conscience and without angering others, cultivate closer correspondence, and restore the old trust to Your Excellence. [88]

And on September 25, 1732 he wrote to Count August that he "finds the Wittgenstein Castle too restless and annoying to advance my affairs there". [89] Dippel also said to his young admirer Senckenberg:

> Count August in Wittgenstein, when he was still in Berlin, was much nicer than now, when he lives brutally with his children and harasses his subjects. [90]

To summarize, Dippel rejected the count's dealings with his subjects. During this time, the count tried to reduce the largely free peasants, who were only obliged to a little forced labor, to the status of serfdom. As a result, the count was widely hated. And that also affected the family, servants and friends of the count. Those who worked for him were despised by the population of the county.

In the four-year period that now followed, Dippel tried to create an opportunity to work out his chymical universal recipe in a suitable laboratory. With Count Casimir in Berleburg, where he now lived, he found no interest in it. He therefore remained in contact with Count August zu Wittgenstein and also resumed the old contact with his former sovereign, Ernst Ludwig von Hesse-Darmstadt (1667–1739), who was known for his passion for hunting and also as a keen alchemist.

First, Dippel tried to convince Count August to finance a laboratory in the small village of Schwarzenau, which belonged to the county of Sayn-Wittgenstein-Hohenstein but was closer to Berleburg than to Laasphe. The negotiations went through August Frensdorf (1693–1755), a councilor of the count. In the end, this failed because he asked the count for too much money and because he did not want to reveal too many details of his process to Count August.

Therefore, Dippel now turned to the Landgrave of Hesse-Darmstadt. In September 1732, they met in Breidenbach in Hesse-Darmstadt near the border with the counties of Wittgenstein. [91] The negotiations resulted in various draft treaties. First, Johann Conrad Dippel offered the landgrave his "*Arcanum chymicum*" for 100,000 thaler, to be paid from the income of the work with 5% interest. As the negotiations progressed, Dippel gave up the money and now wanted Frankenstein Castle, where he was born, as a fief for himself and the Dippel family. Namely "along with all dependencies, subjects and justices". Details about the *Arcanum* were not given in the documents, only that it

> should yield as much revenue … as the whole amount when the property should be sold according to the ordinary *taxa* and this with easy effort, without art and dangerous work, and with the help of only 3 to 4 people.

But the landgrave did not agree to this and the project was not carried out.

During Senckenberg's second visit to Dippel in Berleburg in 1732, Dippel also showed him "a ☽ regulus, which also contained some gold". [92] He "had dabbed the ☽ underneath with aquafort, there you could see the yellow ⊙." [93] Dippel also described the corresponding particular process to Senckenberg: According to this, 2 parts of mercury with one part of silver and a certain menstruum should be placed in a closed vessel in the fire. From letters [94] exchanged between Dippel and August zu Wittgenstein it becomes clear that this certain menstruum was "*olij vitrioli*" i.e. concentrated sulfuric acid H_2SO_4. This mixture of mercury, silver and sulfuric acid had to stand in the fire for 14 days. Thereafter, the vessel had to be opened and all liquid to be distilled away. Now fresh sulfuric acid had to be added to the remaining material and this had to be placed in a closed vessel in the fire again and so on. This process had to be repeated 10 to 12 times until everything would be fixed. Dippel thought that during these 140 to 168 days of heating the light and fire principle would move through the vessel walls into the reaction mixture. Mercury and *oleum vitrioli* would help this principle to enter the silver and transform some of the silver into gold. According to Dippel as noted by Senckenberg, this

> particular sample of ☽ and ⊙ is very lucrative, without much headache, to force ☿ into ⊙ and ☽, the yield is more than 200,000 thalers each year, but he doesn't know how to find a place to do it. [95]

So we have learned that besides his universal process based on phosphorus Dippel also worked in Berleburg on a particular process for the transmutation of parts of the silver used into gold. Senckenberg also noted about Dippel that

> he offered me that if he had a laboratory and I wanted to be with him for a while, I could do it … when he has set up the *Laboratorio*, I should come to him for a few weeks and leave happy. [96]

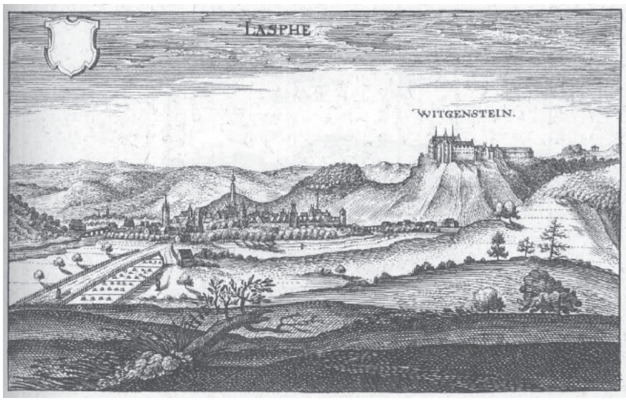


Figure 10. View on Laasphe and Wittgenstein Castle. Engraving by Matthäus Merian (1593-1650) published in *Topographia Hassiae*, Matthäus Merians Erben, Frankfurt am Main, **1655**. (source: Wikimedia Commons, https://commons.wikimedia.org/wiki/File:Laasphe_De_Merian_Hassiae_144.jpg , last access 10.4.2023).

DIPPEL'S DEATH

After hesitating for a few years, the 60-year-old Dippel finally went to Count August at Wittgenstein Castle in April 1734 to carry out chymical experiments together with the count. He arrived at the castle on April 12, but Count August had once again traveled to Wetzlar to the German Imperial Chamber Court. Dippel began to prepare the planned chymical experiments, but since "the most important *praeparata* … were locked away …" he could not continue the work. Was that the phosphorus he couldn't get hold of during the count's absence? In the last letter to Count August dated April 13, Dippel asked August zu Wittgenstein to give him or his son Count Friedrich permission to use these *praeparata*. [97] We do not know of a reply from the count to this letter. Twelve days later, early in the morning of April 25, 1734, Dippel was found dead in his bed in the living room provided for him. The count, who was still or again staying in Wetzlar, was immediately informed of Dippel's death. Dippel's belongings were sealed, his living room locked and a sentry posted in front of it.

Figure 10 shows Laasphe and Wittgenstein Castle high above the small town. Dippel died in the castle and was buried in the town church of Laasphe. A few days after Dippel's death, Count August zu Wittgenstein began to receive letters in which various people to whom Dippel owed money were trying to get their money back. These included Johannes Hummel (1700-1769) from Elberfeld and the "protection jew" Joseph Schmul from Marburg. Hummel had, as can be seen from the letters, also worked together chymically with Dippel. In addition, Johann Christoph Dippel from Grünberg, a son of Dippel's younger brother Johann Albert (1678–1717), reported to the count on behalf of Dippel's heirs. But since Dippel also owed the count a lot of money himself, none of the petitioners received anything.

On August 27, 1735, about 16 months after Dippel's death, Count August David zu Sayn-Wittgenstein-Hohenstein died at his castle above Laasphe at the age of 72. – An interesting note from October 1737 can also be found in Senckenberg collection. [98] It says about phosphorus: "But Count zu Wittgenstein has several pounds of the same and gives it cheaper" than the phosphorus from the "*Laboratorio*" of Godfrey in London, where it was sold at 50 shillings per ounce. Since Count August had already died in 1735, it must be his son and successor as regent, Count Friedrich zu Sayn-Wittgenstein-Hohenstein (1708-1756). Perhaps Count August had phosphorus produced or bought in larger quantities in order to obtain the philosophers' stone according to Dippel's instructions? And now that both Dippel and Count August had died, did Count Friedrich at least try to sell the phosphorus to make some money from it?

CONCLUSIONS

Many new archival sources connected with Johann Conrad Dippel have been found in the last 15 years. Combined with a close reading of some of Dippel's books they give a new account of Johann Conrad Dippel's life as a chymist. This closes a gap in the research of the biography of this important German theologian, physician and chymist from the turn of the 17th and 18th centuries. We learned that Dippel was a chymist with broad range of interests, spanning from recipes for medicines to transmutation processes by use of phosphorus. He also developed his own special chymical theory based on what he called the light and fire principle. This account shall serve as a starting point for the research community to explore the life of this popular figure more deeply to draw an accurate picture of this man and to refute the many wild speculations which are distributed on the internet.

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Historical Article

Martin Heinrich Klaproth (1743-1817), a Great, Somewhat Forgotten, Chemist

Juergen Heinrich Maar

Retired, Department of Chemistry, Federal University of Santa Catarina, Florianópolis, SC, Brazil
E-mail: juergen.maar@gmail.com

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Abstract. For various reasons, some of them linked to the evolution of the historiography of Chemistry, many recognized and important chemists in their time – and in ours, because of the legacy they left – are relegated to some degree of oblivion. One of these chemists, dead just over 200 years ago, is Martin Heinrich Klaproth (1743-1817), a key figure in the transition from phlogiston theory to Lavoisier's new chemistry and one of the creators of modern analytical chemistry, an empiricist who discovered many elements and polymorphism, author of remarkable chemical and mineralogical analyses and creator of archaeometry. This article presents the life, training and scientific production of a great, but less remembered, chemist, crossing the frontiers of Chemistry in many cases.

Keywords: history of chemistry, Martin Heinrich Klaproth, history of analytical chemistry, history of the discovery of the elements, mineral and mineral water analyses, archaeometry.

> As much as I worried about meeting the obligations that the chemist owes to Science, for whose progress he responds to, and the audience, to whom he reports the fruits of his labor; as much as I myself committed to imprinting on my analyses the greatest possible degree of accuracy and truth; many were the occasions when I realised how difficult this goal is.
> (Martin Heinrich Klaproth)

FORGETFULNESS

A little more than two hundred years ago, on January 1, 1817, died Martin Heinrich Klaproth, one of the most important, respected and productive chemists of his time. In the posthumous opinion of August Wilhelm von Hofmann (1818-1892), Klaproth was "for all times a model of the true scientist"[1], and yet today he is not remembered as deserved. Despite his great importance for the consolidation of Lavoisier's new chemistry, especially in the German-speaking academic world, even with the discovery or confirmation of new elements (uranium, zirconium, cerium, tellurium, titanium, strontium, chromium), with a systematic work in the fields of analytical chemistry (gravimetry, data processing) and of inorganic chemistry, with the creation of archaeometry (application of chemical procedures in archaeology), Klaproth's name is now not very common even among chemists. How is it possible that a researcher of enormous importance and influence in his own time is now somewhat forgotten? Forgetting would even be understandable if his proposals were currently not valid, or their empirical data wrong, but this is not the case.

Georg Edmund Dann (1898-1979), historian of pharmacy and professor of history of pharmacy at the University of Kiel, biographer of Klaproth, wrote about it in 1958:

> No chemical law, no theory, much less a hypothesis are associated with Klaproth's name. With his exact works of investigation he participated personally like few others in the establishment or confirmation of the bases of the new Chemistry. But from the results of his researches he did not develop any regularity or general law, he did not himself develop any theory from his data[2].

Brita Engel adds that Klaproth did not leave any longer text exposing in an integrated way his ideas and conceptions about the new antiphlogistic chemistry, to whose dissemination he contributed so much. He did not even write a textbook, which could offer an idea of his lectures, which can, however, be evaluated through an extensive manuscript of 588 pages, left by Arthur Schopenhauer (1788-1860), who studied at the University of Berlin in 1811/1812, not only with Fichte and Schleiermacher, but also with Klaproth. Another manuscript, by the physician Stephan Ferdinand Barez (1790-1858), complements Schopenhauer's. Both were transcribed and studied by B. Engel in 1987/1989[3].

A law. or theory, or reaction or reagent linked to the name of a chemist certainly perpetuates his memory along with the application that is made, to this day, of his law, theory, reaction, or reagent, even if the researcher who created them occupies a less prominent place in the general context of our science. Every chemist, and probably researchers from other areas, will know the names of Guldberg and Waage, Proust, Fehling or Mohr, but the aforementioned Klaproth, or Torbern Bergman, or Wollaston are less remembered. Although present in almost all histories of Chemistry, cited and quoted in papers, the real importance of his work should, in our opinion, be the subject of more detailed discussion.

Pharmacist, chemist and member of the Berlin Academy, Klaproth was self-taught. Has this fact contributed to some marginalization? This seems unlikely, considering Dalton, Davy and Faraday were self-taught, and obligatorily figure in all history of science texts, irrespective of ideologies. On the other hand, the academic community seems to value graduates from the academy itself: Mitscherlich, Klaproth's successor, coming from Göttingen and from Berzelius' laboratory, deserved a statue at the University of Berlin, but not Klaproth, whose contribution to Chemistry, however, far surpasses Mitscherlich's.

There may be extra scientific motivations minimizing Klaproth's contribution to the whole history of chemistry. Perhaps the most obvious case of forgetting and excluding scientists for unscientific reasons is the ostracism to which brilliant Austrian chemists were condemned after Austria's political and economic downturn in 1918: where do we still find figures such as Loschmidt, Rochleder, Lieben, Hlasivetz, Pfaundler, Redtenbach, authors of extensive empirical and theoretical work? The scientific isolation of Germany and Austria after the First World War (1914/1918) may have contributed to the ostracism or even oblivion of many scientists. Needless to say, opinions fluctuate with time and context, and sometimes the version is worth, not the objective fact.

There are reasons for some marginalization which are inherent to the scientific activity, and as such justifi-

Figure 1. Valentin Roses's pharmacy 'Zum weissen Schwan', in the Nikolaiviertel, in Berlin, lithograph, c. 1840, where Klaproth was assistant. (Edgar Fahs Smith Collection, University of Pennsylvania, Philadelphia).

able. But there are also reasons unrelated to science, arising from historical-political contexts, and thus not always justifiable. What matters is keeping, within the limits where this is possible, the historical records of a great man, and that is what we intend to do succinctly in this article. It does not intend, and should not be, a hagiography, but Klaproth's scientific activity and practice are such that few criticisms can be made. Of course there are controversies and questions of priorities, but these are normal in periods of great expansion of scientific knowledge. But there are other, much deeper – and more dangerous – motivations for the ostracism to which Klaproth and many other chemists were relegated, which we will present at the end of this essay; The importance of uranium, which Klaproth discovered in 1789, for nuclear energy, contributes to preserve his memory.

THE ORIGINS AND FORMATION OF KLAPROTH

Of humble origins, Martin Heinrich Klaproth was born on December 1, 1743 in the small town of Wernigerode, in the mountains of the Harz, the second son of the tailor Johann Julius Klaproth (? – 1767). The medieval town of Wernigerode was nominally part of the county of Stolberg-Wernigerode, but Count Christian Ernst of Stolberg-Wernigerode (1691-1771) ceded his lands in 1714 to the Kingdom of Prussia. The modest birthplace, narrow and 3 meters wide, was rebuilt after a great fire that devastated a large part of the town in 1751. With the destruction of his family's house, he moved to the home of relatives. His childhood was unhappy. Of his four brothers, one died young; Julius Christoph (1739-....) studied theology and was a Lutheran pastor and teacher, and Christian August (1757-1812) held a public office. From 1755 to 1758 Martin Heinrich Klaproth attended the *Gymnasium* (*Lateinschule*), but abandoned it before completing his studies, because of the rigor observed by some teachers. In Dann and Schwedt's current critique, instruction at the *Gymnasium* was comprehensive and modern, similar to Halle's famous *Franckesche Stiftung*. For C. Friedrich, the professor Johann Christian Meier (1732-1815), from the *Gymnasium*, aroused Klaproth's interest in Pharmacy. To ensure his livelihood, he participated in the church choir (*Chorus symphonicus*), giving rise to the deep religiosity that accompanied him throughout his life. Even with little education, from 1759 to 1766 he was apprenticed in Pharmacy at the *Adler und Ratsapotheke* (founded in 1575), with the pharmacist Friedrich Victor Bollmann (1712-1789), in the nearby city of Quedlinburg, becoming a pharmacist in 1766, at the age of 23. Between 1766 and 1771 he went to work as a pharmacy assistant at the *Hofapotheke* (Court Pharmacy) in Hannover, at Gabriel Heinrich Wendland's (1730-1796) pharmacy *Zum Engel* (located on *Mohrenstrasse* and now disappeared) in Berlin, and at the *Ratsapotheke* in Danzig (present-day Gdansk, Poland), then owned by the physician Johann Alexander Hevelke (1731-1806). He decided in 1771 to return to Berlin, to study with Johann Heinrich Pott (1792-1777) at the *Collegium Medico-Chirurgicum*, with Andreas Sigismund Marggraf (1709-1782) at the Academy of Sciences, and with the pharmacist Valentin Rose the Elder (1736-1771), with whom he learned not only chemistry, but also Latin and Greek.

The year 1771 marked Klaproth's professional life: he became Valentin Rose's assistant at his *Zum Weissen Schwan* (To the White Swan) pharmacy in Berlin, located on *Spandauerstrasse*, no longer in existence today. Rose, who had been a student of Marggraf and versed not only in pharmacy but also in chemistry (inventor of Rose's metal, a low melting point alloy) and in metallurgy, acquired the pharmacy in 1761. There worked and studied not only Klaproth, but also Sigismund Friedrich Hermbstaedt (1760-1833), who would take over the pharmacy in 1783, Conrad Heinrich Soltmann (1782-1859), Johann Daniel Riedel (1786-1843). Rose's pharmacy was a sought-after center of research and study. Still with Wilhelm Rose (1792-1876), grandson of Valentin the Elder, came to study pharmacy (1836/1840) the novelist Theodor Fontane (1819-1898), fellow countryman of Valentin Rose (in his novel "Effi Briest", from 1896, Fontane speaks of Carl Wilhelm Scheele and the discovery of oxygen, in the wake of manuscripts from Scheele's time then discovered by Adolf Erik Nordenskiöld). In his biographical writings "Von Zwanzig bis Dreissig" (1894), Fontane tells in a casual way his formation with Wilhelm Rose. The pharmacy, which in 1802 gained a new building designed by Karl Friedrich Schinkel (1781-1841), an exponent of classicist architecture that would characterize Berlin. The pharmacy was completely destroyed in 1945[4].

With the death of Valentin Rose the Elder in 1771, Klaproth took over the "White Swan" pharmacy, and the education of Valentin's four children, including Valentin Rose the Younger (1762-1807), later an important chemist and co-author with Klaproth of several articles. He also took care of the education of the children of Valentin the Younger, who died of cholera in 1807, Heinrich Rose (1796-1864) and Gustav Rose (1798-1873), later professors of chemistry and mineralogy, respectively, at the University of Berlin.

In 1780, Klaproth carried out the rigorous examinations required for the profession of pharmacist,

Figure 2. Martin Heinrich Klaproth (1743-1817). Engraving by Ambroise Tardieu (1788-1841), after a portrait by Eberhard Siegfried Henne. Public domain.

with a paper entitled "Treaty on Phosphorus, plus an annex on the preparation of the best distilled waters" (published in 1782). The year 1780 was another decisive year in Klaproth's career: in February he married Christine Sophie Lehmann (1748-1803), daughter of the famous mineralogist Johann Gottlob Lehmann (1719-1767), active in Saint Petersburg, and Marggraf's niece. Klaproth thus entered the Academy's innermost circle. In the same year, Klaproth bought the pharmacy *Zum Goldenen Bären* (To the Golden Bear) or simply *Bärenapotheke* (Bear's Pharmacy) pharmacy, located on the same street as the White Swan Pharmacy, right next to old *Nikolaikirche*. Klaproth renovated the pharmacy and installed a private laboratory there, in which he analysed dozens of minerals and discovered uranium. A plaque shows today the location where this discovery, so crucial in the future and for the future of Humanity, took place. Klaproth sold the pharmacy in 1800. The building was replaced in 1898 by a modern one, which in turn was destroyed in 1945. The complex of houses was restored to recall, although not reproduce, its original appearance in the popular *Nikolaiviertel*.[5]

In 1787 Klaproth was admitted to the Berlin Academy of Sciences, succeeding in 1802 Franz Carl Achard (1753-1821) as director of the laboratory. He began teaching at the *Collegium Medico-Chirurgicum* (1782), at the Mining School (1784), at the Military Academy (1787), and finally, in 1810, self-taught in chemistry and without a university degree, he was chosen to be the first professor of Chemistry at the new University of Berlin, on the recommendation of Wilhelm von Humboldt (1767-1835), the founder of the university. His colleagues were the physicists Paul Ermann (1764-1851) and Karl Tourte (1776-1847), the mathematician Johann Georg Tralles (1763-1822), the zoologist Martin Lichtenstein (1780-1857), the botanist Karl Willdenow (1765- 1812) and the mineralogist Christian S. Weiss (1780-1856)[6]. Klaproth's renown had crossed borders: he was a member of the Royal Society (1795), the Paris Academy (1804), the Stockholm Academy (1804), and the St. Petersburg Academy (1805). Fortnightly, he taught public Chemistry classes, in the spirit of the Enlightenment, approaching current topics, and spoke about chemical subjects at meetings and private events. After successive attacks of apoplexy (he had already suffered a heart attack in 1814) he died in the modest residence reserved for him at the Academy, on January 1, 1817, at the age of 74. He was buried in Dorotheenstadt cemetery, but his tomb, for which Schinkel had drawn a cross cast in iron, has not been preserved. In 1993, on the 150th anniversary of his birth, a plaque was placed in the cemetery. His successor at the university was Eilhard Mitscherlich (1794-1863), recommended by Berzelius (who had refused the post to which he himself had been invited). The university honors Mitscherlich with a bronze statue by Carl Ferdinand Hartzer in front of the side façade (1894), but does not honor Klaproth. Signs of an (almost) forgetting. Many of the places where Klaproth worked no longer exist – another factor that leads to oblivion – but other important places of interest for the scientist's life interested admirers can still be visited: the university, Wernigerode, Quedlinburg. The site of the old Academy building (on *Dorotheenstrasse)*, built in 1711 and destroyed in 1944, today is occupied by a parking building. In 1996, an iron monument by Ralf Sander (*1963) in homage to Klaproth, in the form of a stele, was installed next to the main building of the Technical University in Berlin. Johann Friedrich John (1782-1847) called *klaprothium* the element cadmium, discovered as an impurity of zinc (1817, Stromeyer; Klaproth had died shortly before). A crater on the moon was named Klaproth.

The infrequent citing of Klaproth is, perhaps, only paralleled by that of Marggraf – but in this case the sunset can be attributed to the fact that Marggraf was a phlogistonist, swept away (unfairly) by the 'house cleaning' proposed by some historians[7].

Martin and Christiane Klaproth had a son and four daughters, two died in early infancy. Klaproth's son Julius Klaproth (1783-1835) studied oriental languages against his father's wishes, travelled through Siberia and the Caucasus, was a member of the St. Petersburg Academy and settled finally in Paris. By the end of the 19th century his work was hopelessly outdated. Johanna Wilhelmine (*1787) married the *Bergrat* Heinrich Wilhelm Abich (1772-1844), and Charlotte Ernestine (1790-1868) married the Prussian General Moritz von Bardeleben (1777-1868).

THE WORK – THE THEORY

Considering the stage of development of Chemistry at his time, Klaproth's work is quite comprehensive and diverse. As we have seen, he left few general texts, but his view of Chemistry can be reconstructed from the notes of others (Barez, Schopenhauer), from his 218 articles, and his participation in several collective works, with other researchers, such as the five volumes from the "Chemisches Wörterbuch" ("Chemical Dictionary") written in partnership with Friedrich Benjamin Wolff (1765-1845). He left aside the French and Latin of the Academy's publications, writing exclusively in German.

Klaproth's theoretical contributions to Chemistry are two and they are interconnected: his general conceptions in the field of Chemistry and the necessary replacement of the phlogistonist theory by a more convincing antiphlogistonist theory, essentially that of Lavoisier. The clash provoked by the introduction of Lavoisier's antiphlogistonist theory in Germany is known[8], not a heated clash as is sometimes made to believe, but a clash anyway, using rational and scientific arguments, but also extra-scientific arguments of nationalist inspiration (after all, it was the period of the Napoleonic wars, the occupation of part of German territory by French troops and the dissolution of the Empire by Napoleon in 1806). The first defenders of the new antiphlogistonist theory in Germany were Johann Friedrich August Göttling (1755-1809), thanks to Goethe professor of Chemistry at the University of Jena, and Sigismund Friedrich Hermbstaedt (1760-1833), professor at the *Collegium Medico-Chirurgicum*. Göttling not only defended the new theory, but published a positive critique in 1794, "Contribution to the Corrections of Antiphlogistic Theory", while Hermbstaedt translated Lavoisier's "Traité" into German (1792). Klaproth read Hermbstaedt's manuscript, studied it, and repeated several of the experiments. Klaproth's position would be fundamental, since after becoming convinced of the validity and usefulness of Lavoisier's theory, he led the Berlin Academy in 1792 to officially adopt it. Klaproth was not content with theoretical considerations and the observations of others, but remade part of Lavoisier's experiments (despite the difficulty in acquiring the equipment), for example, the famous "pelican experiment", with which Lavoisier showed that there is no transformation of water into earth (the experiment seems anachronistic in the 18th century, but is linked to several natural observations, for example, rain and its effects on plant growth and nutrition). The experiment was remade, and Klaproth wrote: "*The formerly accepted belief in the conversion of water into earth is unfounded: analyzing the experiments which were intended to prove it, it was found that the supposed earth was glass, detached from the retort by the effect of friction and heat*"[9]. Converted, he wrote in 1792:

> The ease with which it was believed to be able to give from the phlogiston theory a satisfactory explanation for the most important chemical phenomena, led to forgetting that phlogiston is also a hypothetical entity, and that the system built on this theory would be solid and unshakable. With the almost daily increase in the sum of chemical knowledge, and especially in view of the discovery of gaseous species, there should finally be a review of this part of Chemistry. Among the researchers who are responsible for the greatest merits in this regard, Lavoisier is at the forefront, having convinced himself, after years of experience, of the insufficiency of Stahl's theory, overturning it entirely and introducing the current and new system, which it is also called antiphlogistic[10].

Accepting the new theory, the concept of element was also accepted, as proposed by Lavoisier, an element defined a *posteriori*, as the ultimate result of an analysis (Boyle's element was defined *a priori*). Klaproth mentions 51 *Elemente* or *unzerlegbare Stoffe* (= indecomposable substances), including among them light (*Lichtstoff*), heat (*Wärmestoff*) and 'electrical matter' (*Elektrische Materie*). There were 28 metals, 11 of which discovered while he himself was acting as a chemist (Lavoisier's table contained 33 elements, also including light and caloric)[11].

An original contribution by Klaproth to theoretical chemistry was the discovery in 1788 of polymorphism: the same compound can present itself in several different crystalline forms. Klaproth described two crystalline states for calcium carbonate ($CaCO_3$), calcite (trigonal, hardness 3, density 2.7) and aragonite (orthorhombic, hardness 3.5-4, density 2.95). (The hardness and density values are not from Klaproth's times; and the name "aragonite" was coined only in 1797 by Abraham Gottlob Werner [1749-1817] in Freiberg).

Given the above, the idea that Klaproth was averse to theoretical considerations cannot be maintained, and as a proof, B. Engel describes the theoretical conceptions of Klaproth's chemistry as follows[12]:

- he intends in his lectures to explain, clarify, fighting the view of chemistry as a "secret science";
- chemistry is not a rigid system, but an evolutionary path destined to approach the truth;
- the guideline of his work is clear objectivity, simplicity and accuracy – only experiments that can be repeated are of value as a proof;
- his own contributions are important to him as steps towards the apprehension of reality;
- his work is always descriptive, and whenever possible, quantitative.

Seen today, it is an almost positivist recipe, and certainly an empirical one, averse to unverifiable theorizations – it is in this sense that Klaproth is averse to theories. Consistent with its scientific beliefs, he abhors Alchemy, and unmasks many of the miraculous "elixirs" then in vogue. For example, he called into question the alleged alchemical transmutations in the famous case of Johann Semler (1725-1791), professor of theology at the University of Halle, who claimed to have been successful in obtaining gold: without knowing the "aid" of his servant, who had added traces of the precious metal to the jars. The mysterious "elixir" unmasked were the "Bestuscheff drops" (*Tincture Ferri Chlorati Aetherea*) for "evils of the nervous system", which were just a solution of $FeCl_3$ in ether dissolved in alcohol... the belief in miracle drugs is not of today.

Klaproth's theoretical stance can be understood from the way he converted from the phlogiston theory to the oxygen theory, but it can still be followed in all his "scientific genealogy", in which we can go back to the Paracelsian Daniel Sennert (1572-1637) , putting us in front of a current question: does the evolution and modification of chemical theory necessarily lead, in the creation of chemical knowledge, to ruptures (or new "paradigms", in the Kuhnian nomenclature)? Or, as we have said before, the development of new experimental techniques and methodologies (such as replacing the idea that chemical analysis is a 'comparison of samples' by 'searching for sample components') would not more likely lead to new 'paradigms'?

Sennert → Rolfinck → Wedel → Stahl →
Neumann → Marggraf → V. Rose → Klaproth
KLAPROTH'S SCIENTIFIC GENEALOGY

In Klaproth's case, the adoption of a new theoretical model did not change his laboratory procedures, but it did change the causality and interpretation of the empirical facts studied, excluding *a priori* experiments considered to be meaningless, and including others that his predecessors considered unnecessary. Klaproth became a phlogistonist not only with his teacher Valentin Rose the Elder, but with readings from his apprenticeship as a pharmacist, such as the texts of Johann Friedrich Cartheuser (1704-1777) and Jakob Reinhold Spielmann (1722-1783), and the option for the new theory did not change his practices: uranium and zirconium were discovered in the context of the phlogiston theory, cerium and tellurium already under Lavoisier's theory, without changing laboratory methods. At the time, there was a tendency to consider, alongside "theoretical chemistry" (the analyses referring to the 'system of chemistry'), also a "rational chemistry", which dealt with all aspects capable of 'converting chemistry into science'. The search for rational chemistry dates back to the times of Georg Ernst Stahl's theory of phlogiston (1660-1734) – the theory of phlogiston was a rational theory, albeit based on false premises – and Klaproth's and his contemporaries strong opposition to Alchemy is also owed to the phlogistonists.

Klaproth is directly associated with the discovery or confirmation of the discovery of seven elements. Uranium and zirconium are unanimously mentioned as discovered by Klaproth, in 1789. In the other cases – cerium (discovery simultaneously with Berzelius), titanium, tellurium, strontium, chromium – questions arise about priorities, but it is up to him to confirm the discovery and the characterization of the element. Klaproth's generosity made him give up many disputes, leaving to his colleagues the credit for the discovery. He had only had to confirm it, because, as James Marshall mentions, his articles were in any case appreciated, for the guarantee of a good analysis. Klaproth's righteous character did

Table 1. Elements discovered or confirmed by Klaproth.

Element	Discovery	Independent Discovery or confirmation
1782 Tellurium	Müller v. Reichenstein	Klaproth (1788), Kitaibel (1789)
1789 Uranium	Klaproth	
1789 Zirconia	Klaproth	
1790 Strontium	Crawford, Cruikshank	T.C. Hope, Klaproth
1791 Titanium	Gregor	Klaproth
1797 Chromium	Vauquelin	Klaproth
1803 Cerium	Klaproth	Berzelius

not want to anticipate Henry de Montherlant's (1895-1972) saying that the glory of the great corrodes and destroys that of the small. At a time of great expansion of chemical knowledge, the simultaneity of discoveries is inevitable, giving rise to the consequent disputes over priorities. Klaproth's work with the elements is closely related to the improvements he introduced in Analytical Chemistry, and by extension in chemical analysis.

THE WORK – THE ELEMENTS

Of all these discoveries, the one with the greatest repercussion – not only in the history of chemistry, but in the history of Humankind – was the discovery of uranium. The prehistory of uranium begins in the 16th century, when in the inhospitable and sparsely inhabited mountains and forests of the Metalliferous Mountains (*Erzgebirge*), on the border between Saxony (Germany) and Bohemia (Czech Republic) began an intense mining activity, of silver, tin and other metals, which quickly turned the region into Europe's largest mining center (Freiberg, Annaberg, Aue, Johanngeorgenstadt in Saxony, Joachimstal [Jachymov] in Bohemia). Despite depleted silver veins and competition from silver from the New World, the mines (then owned by the Austrian crown) continued to be explored in the 18th century, producing mainly cobalt and bismuth. There was in these mines a black mineral, which apparently had nothing to do with the silver ores, which the miners called *Pechblende* (from the German *Pech* = pitch, *Blende* = ore, literally 'pitch-colored ore'). The first to describe pitchblende was the naturalist Franz Ernst Brückmann (1697-1753) in 1727. Axel Frederick Cronstedt (1722-1765) considered it a silver mineral (1758), and Abraham Gottlieb Werner (1749-1817), a mineral associated with iron (*Eisenpecherz*). Klaproth, using new analytical procedures he had developed, analysed a Johanngeorgenstadt mineral in the laboratory of his "Bear Pharmacy" (July 1789), and found it to be a compound of a new element, which he called uranite, later uranium, in honor of the discovery of the planet Uranus, in 1781 by Sir William Herschel (1738-1822), his compatriot living in England since 1757. Altogether Klaproth analysed about 300 samples of minerals from Johanngeorgenstadt, today exhibited at the Museum of Natural History in Berlin, which also preserves the more than 4800 pieces from Klaproth's mineralogical collection.

Briefly, he dissolved pitchblende (some say it was a sample of torbernite, phosphate of uranyl and copper, $Cu(UO_2)_2(PO_4)_2$,) in nitric acid, and treated the solution thus obtained with potash (K_2CO_3), obtaining a "yellow precipitate", which redissolves with a new amount of potash. Heating the yellow precipitate with linseed oil gives rise to a black mass, which on further heating turns into a black powder; this, when heated in an oven with coal, leads to a brittle black powder, which Klaproth considered to be the new metal (uranium), but was actually its oxide UO_2. No other element known to Klaproth presented such properties, hence his conclusion that pitchblende contained a new element. The results of his experiments were reported by Klaproth to the Academy of Sciences at the session of September 24, 1789[13]. At a scientific meeting in a building that no longer existed, the Atomic Age was born, and as I have written elsewhere[14],

> in the year of the Fall of the Bastille, when Humanity began to glimpse the spirit of Freedom, Equality, Fraternity, the first seed of a spectrum that more than a century and a half later seriously threatened the future of Humanity was also (innocently) planted. And if, to our unhappiness, the dream of Freedom, Equality, Fraternity has not yet materialized, we are consoled by the fact that the specter is also dead or at least asleep.

Klaproth isolated the oxide from a new metal, and obtained several of its compounds, such as uranium acetate (1793). Metallic uranium was only isolated in 1841 by Eugène Melchior Peligot (1811-1890), reducing UCl_4 with potassium (UCl_4 was also synthesized by Peligot). It was necessary to await the discovery of a stronger reductant than those known at the time, like potassium (Davy, 1807), to reduce certain metal oxides to the corresponding metal (Berzelius developed a reduction procedure with potassium).

For most historians, two conditions are necessary to consider a "discovery" of a new compound: obtaining it in pure state, and its perfect characterization by analysis. I add a third observation: the existence of resources that allow obtaining chemically the element. In Klaproth's time there were no resources to chemically obtain metallic uranium, so Klaproth is its discoverer. (Lavoisier considered the "earths" as elementary – lime, magnesia, soda, potash, barite – as there were no resources to isolate the metal from them, but he suggested the possibility that in the future they would prove to be composed). There is a controversy between Klaproth and the Hungarian chemist Antal Ruprecht (1748-1814) about the conversion of oxides into metals, the "metallization" or thermal reduction of the "earths"[15]. Considering that the *calces* are metal oxides, and given the then-known possibility of obtaining the metals manganese (Gahn, 1774) and molybdenum (Hjelm, 1781) by reduction with coal, Ruprecht, a professor at the Schemnitz School of Mines, intended to be this reaction a general reaction of metal oxides. He built a furnace with which he obtained temperatures of 1600 °C, and claimed to have reduced barite, lime and magnesia to their respective metals (1790). Klaproth was unable to repeat Ruprecht's experiments, and the analysis showed that the supposed metals released in the three cases were impure iron fragments, probably released by the equipment. Klaproth considered the "metallization" as the "Schemnitz Illusion", *Schemnitzer Illusion*, and it would be "impossible in principle" to obtain the metals from these earths (1791). Szabadváry draws attention to the care that we must take in science with statements such as "impossible in principle", because by electrolysis Sir Humphry Davy (1778-1829) managed to obtain the metals from the aforementioned earths, a result that Klaproth, somewhat grudgingly, ended up accepting. The controversy is an example of a dispute in which both sides are right: Ruprecht was right because the "earth" actually contains a metal, Klaproth was right because it is really impossible to get the metal with chemical resources. At the time of the clash, Klaproth's empiricism had won.

Pitchblende is an emblematic mineral in the history of science. In the same pitchblende, now from Joachimstal (provided by the Vienna Academy, through its president Eduard Suess [1838-1914]), Pierre (1859-1906) and Marie Curie (1867-1934) isolated in 1898 polonium and radium.

Another element discovered by Klaproth in 1789, again as its oxide form and again in his pharmacy, was zirconium. After platinum, it was the first element to be isolated from a non-European mineral, zirconite (zirconium silicate, $ZrSiO_4$), a semi-precious stone from Ceylon (present-day Sri Lanka), already mentioned in the Bible. It was not the first time that an eminent chemist had studied zirconite: Torbern Bergman (1735-1784) isolated from it an "earth", which actually was a mixture of alumina, iron oxide and lime. Klaproth analysed the zirconite, noting that 70% of the mineral was constituted by a new "earth", the *Zirkonerde* or zirconia, ZrO_2. Isolation was quite difficult, especially separating the contaminating iron. Although Klaproth believed he had obtained an element, metallic zirconium was only obtained by Berzelius in 1824, by potassium reduction of $K_2[ZrF_6]$.

The discovery of cerium[16] (or *cererium*, as suggested by Klaproth) in 1803, simultaneously and independently by the teams of Klaproth and Jöns Jacob Berzelius (1779-1848), led to the single most serious controversy in Klaproth's career, leading to a harsh exchange of correspondence between the two, interrupted by Klaproth, as it was not leading to anything positive. The incident had a banal origin: when Berzelius and his collaborator Vilhelm Hisinger (1766-1852) sent the journal *Neues Allgemeines Journal für Chemie*, edited by Adolf Ferdinand Gehlen (1775-1815), their article communicating the discovery of the new element, the editor replied that he had already received an identical communication from Klaproth and Valentin Rose, and that, for reasons of chronology, he would first publish Klaproth's work in the current issue of the magazine, and Berzelius' in the next edition. Gehlen's correct decision (although he attributed the discovery of cerium to Berzelius) angered Berzelius' disciples active in Paris, who started a fierce controversy, finally appeased by Louis Nicolas Vauquelin (1763-1829): Klaproth, a man of righteous character and already an experienced and famous scientist, had no need to appropriate the discoveries of others, and from what he had been able to observe during the controversy, Berzelius and Klaproth independently discovered the new earth, practically at the same time. In his view the two researchers should to be considered the discoverers of the earth "ceria", an opinion today accepted by most historians of chemistry. Klaproth himself calmly accepted the priority given to the Swede. The element's name is an allusion to the asteroid Ceres, discovered in 1801 in Palermo by Giuseppe Piazzi (1746-1826).

Both Berzelius and Klaproth isolated the ceria earth from bastnaesite (name given by Berzelius, Klaproth called it ochroite), a mineral found by Frederick Cronstedt (1722-1765) in 1751 in the Bastnaes mines, which belonged to the Hisinger family. For the history of chemistry, more important than assigning the priority of the discovery to Klaproth or Berzelius, is the finding that both ceria and yttria, the latter discovered by Johan Gadolin (1760-1852) in 1794 (from a mineral found in the Ytterby feldspar mines, which Klaproth named in 1801 gadolinite) are sources for the future discovery of new elements – real elements, such as the rare earths, elements never confirmed, discovered twice or more, spurious or non-existent, but nevertheless extremely valuable empirical searches in the historical context of chemistry. For the methodology of scientific work, error or failure can be as illustrative as success.

Of the other elements mentioned, the most complex case is that of tellurium. In 1782, Austrian chemist Franz Joseph Müller von Reichenstein (1742-1824), mine inspector in Transylvania (then part of Hungary, now in Romenia), among deposits of gold discovered a mysterious mineral he called (1795) *aurum problematicum*, possibly an antimony mineral (it is now known to be $(Ag,Au)Te_2$, telluride of gold and silver, silvanite). Müller was averse to analyses, and the mineral was studied, among others, by Antal Ruprecht and Torbern Bergman, who also supported the thesis of an antimony mineral.

Finally Müller von Reichenstein sent samples of *aurum problematicum* to Klaproth. In general terms, Klaproth's analysis involves the dissolution of the mineral in nitric acid, the precipitation of gold and iron by adding potash, neutralization of the solution with hydrochloric acid: it precipitates the oxide of a new "semimetal", as yet unknown; we know today that it is tellurium oxide, TeO. In 1796 Klaproth visited Vienna, and there learned of the analyses of a mineral found by Paul Kitaibel (1757-1817) in 1789 in Hungary (manuscript, the article was never published). Klaproth, who was then busy with Müller's samples, confirmed them, but did not realize at first that they were the same oxide that existed in the *aurum problematicum* sample. Once confirmed the identity, Klaproth called the new element tellurium, in 1798 (from *Tellus* = the Earth, "our dear mother earth"), and was a kind of godfather to the tellurium.

The discoveries of the elements strontium (1790), titanium (1791) and chromium (1797) were confirmed by Klaproth. Klaproth was an independent discoverer of strontium in 1793, but he was not the first to obtain it (always in the oxide state, SrO, metallic strontium was only obtained by Davy in 1809, by electrolysis). Klaproth prepared, however, several strontium compounds (chloride, nitrate, acetate, tartrate) and definitively differentiated $BaCO_3$ from $SrCO_3$, and consequently BaO from SrO. Klaproth was studying at the same time the properties of $BaCO_3$ and $SrCO_3$. The name strontium is an allusion to the lead mines of Strontian, Scotland, where in 1787 William Cruikshank (c.1745-1810), a chemist from the Woolwich arsenal, found a new "earth", so he is known, next to Adair Crawford (1748-1795), also from Woolwich, as the discoverer of this element (1790). A more detailed study of the new species, even before Klaproth, is that of Thomas Charles Hope (1766-1844), professor at the University of Edinburgh (successor to Joseph Black). Hope obtained strontium oxide by heating the Strontian mineral, $SrCO_3$, which he named strontianite. Klaproth confirmed in 1793/1794 the discovery of titanium, isolating titanium oxide, TiO_2, from rutile or *schörl* (a kind of tourmaline). In other analyses, in 1797, Klaproth also isolated strontium from the mineral celestine, $SrSO_4$. The original discovery of titanium, in 1791, is due to William Gregor (1761-1817), in a Cornish mineral, menachite or ilmenite, from which he isolated a new "earth". The name "titanium" was given by Klaproth, a tribute to the Titans, children of Titania, the Earth goddess.

The history of chromium begins with the discovery in 1766 of the mineral crocoite (lead chromate) in the lead mines of Beresoff, near Yekaterinburg in Siberia, by Johann Gottlob Lehmann (1719-1767) (Klaproth's father-in-law). Louis Nicolas Vauquelin (1763-1829) analysed the mineral in 1789, but discovered nothing new. Only a further analysis by Vauquelin in 1797 led to a new metal, chromium (the name was suggested by Haüy and Fourcroy). In the same year, Klaproth isolated the same element from crocoite, but historiography generally attributes the discovery to Vauquelin, because of his previous experiments; others, like Gmelin and Kopp, consider it a simultaneous and independent discovery. For Dann, there is no reason to create a matter of priority Vauquelin – Klaproth about the discovery of chromium, as already in 1791 Johann Jakob Bindheim (1740-1825), then in Moscow, had analysed a Siberian mineral (crocoite), in which would exist a metal, maybe molybdenum; Vauquelin later identified the metal as chromium.

As for beryllium, even before knowing the element beryllium or glucinium, discovered by Vauquelin in 1802, Klaproth had analysed chrysoberyl[17], a mineral discovered in Brazil, first described by Christian August Hoffmann (1760-1814) and Dietrich Ludwig Karsten (1768-1810), both from Freiberg. Klaproth's (1795) analysis provided 71% alumina, 18% silica, 6% lime, 1.5% iron and 3% losses, total 99.95%. The current formula is $BeAl_2O_4$ (Seybert's analysis, 1824)[18].

Beryl, a silicate of aluminum and beryllium (emerald and aquamarine are variants containing metallic impurities) was analysed by Vauquelin, Klaproth and Bindheim.

THE WORK – ANALYTICAL CHEMISTRY

Anyone - like this author - who went through the banks and laboratories of Chemistry courses in the 1960s will recognize in Klaproth's discussion on Analytical Chemistry many of the operations he performed in practice, and much of the reasoning behind them. I think we are few survivors of an era of Analytical Chemistry in which exhausting manual labor performed the task of today's sophisticated instruments and techniques. I think – without nostalgia – that much of the magic of scientific practice has been lost...

Klaproth inherited an already reasonably well-structured Analytical Chemistry, fruit mainly of Torbern Bergman's (1735-1784) activity in this field. After Bergman, Klaproth joined Vauquelin as the greatest exponent of Analytical Chemistry of his time. According to Bergman, chemical analysis has as its purpose the search for the truth, and the analyses must be carried out with the greatest possible rigor. Analytical data already available should be reviewed with the utmost exemption. The analysis of the components of a compound should not be based on comparisons, but on independent identifications in each case. For that, the "wet route" methods are more indicated. Here are the general lines of Bergman's "philosophy of chemical analysis", for which he developed scripts and introduced new reagents. Bergman's conceptions in turn were influenced by earlier work by Marggraf, and many of his reagents already come from Boyle and Friedrich Hoffmann (1660-1742).

Following Bergman, Klaproth structured Analytical Chemistry on strong empirical bases, mainly gravimetry, which he structured as a scientific method of analysis. He emphasized some aspects he considered essential:

- to be subjected to analysis, chemical substances must be in the purest possible state;
- he emphasized the purity of reagents and developed procedures to purify them;
- the equipment must be chosen properly (he was perhaps the first to use agate and silica mortars).

In the particular case of gravimetric analysis, he introduced:

- heating the precipitates to constant weight;
- the precipitate of the reaction is not always the most suitable compound for weighing, and if ignition results in a more stable product, this should be used to determine the weight.

Regarding data processing, Klaproth was the first chemist to record exactly the data obtained, without the "corrections", which even chemists like Bergman and Lavoisier did when the sum of the data did not reach 100%. Precisely the reactions that do not reach 100% lead to the discovery or confirmation of new elements: the "correction" of the analytical data made the discovery of zirconium elude Bergman. In the aforementioned analysis of chrysoberyl, among the "losses" is the element beryllium, later isolated by Vauquelin (1802).

In the qualitative analysis, he made intensive use of hydrogen sulphide (H_2S) to obtain precipitates, a procedure later expanded by Heinrich Rose, and finally systematized by Remigius Fresenius (1818-1897).

In analytical practice he introduced potash fusion in a platinum crucible to convert minerals difficult to decompose into suitable analytes (1802).

THE WORK – CHEMICAL ANALYSIS – MINERALS

Having commented on Klaproth's contributions to Analytical Chemistry, and considering that Analytical Chemistry and chemical analysis are distinct concepts, some comments on the analyses carried out by Klaproth are also appropriate. According to Paschoal Ernesto Senise (1917-2010), Analytical Chemistry is a branch of chemical science and as such deserves a study with all the methodological rigor that characterizes a science; chemical analysis, on the other hand, is the simple routine, "*a set of methods and operations necessary to arrive at the determination of the composition of a compound*". Of course, chemical analysis does not dispense with rigor either, and Klaproth writes about it in the preface to the manual "Anweisung zur Chemischen Analyse" by the pharmacist Johann Friedrich John (1782-1847), professor at the University of Frankfurt/Oder until 1811 and later in Berlin:


Figure 3. Martin Heinrich Klaproth. Bust by Eduard August Lürssen (1840-1891), 1882. Courtesy Museum für Naturkunde, Berlin.

> […] it is not enough to follow in an analysis a theoretical procedure that gives a correct impression of the object [= analyte] to be worked on, but the experiments must be such that in repetition by several chemists, all working with the same accuracy, they always get the same result. The acumen of a chemist can easily be seen by reading his works, but we can only assess the accuracy with which he

> performs his experiments if we are present when he performs them, or if we repeat them. The two qualities are not always present at the same time. There is no lack of chemists who easily know how to solve the most complex problems, without apparently having to confirm a priori; but if we direct our attention to his skills as an experimenter, things soon take on a different image[19].

Here are the conditions that are still valid today for a correct chemical analysis, introduced as an obligatory systematic by Klaproth, and also allowing us to foresee the verification by other analysts defended by the empirical science of the nineteenth century. The difference, for the chemist, between accuracy and precision is also explicit**.**

Klaproth analysed a large number of minerals, among them, in addition to the aforementioned chrysoberyl (from Brazil), chrysolite[20] (brought from the Levante by his friend Hawkins), criolite (originating in Greenland, from where it came into the hands of Professor Peter Abildgaard [1740-1801]; Klaproth mentions the analyses of José Bonifácio de Andrada e Silva [1763-1838], who had received Abildgaard's samples) [21], olivine, alum, apatite, fluorite (previously studied by Scheele, Marggraf, Wenzel and Richter)[22], lepidolite, emerald (from Peru, a gift from Prince Dimitri Gallitzin [1723-1803])[23], topaz[24], opal[25], sapphire, garnet from Bohemia and the Orient[26], dolomite[27], lapis lazuli[28], borax or tincal[29], and mainly pitchblende. The samples were collected by Klaproth himself on excursions through the Dresden and Freiberg region, to Bohemia, to Pomerania; others were sent to him from around the world by friends, such as geologist John Hawkins (1761-1841), or researchers, like Alexander von Humboldt (1769-1859), and even by his son Julius Klaproth, who travelled the Caucasus and in Georgia.

Of Klaproth's mineral analyses, the most famous is certainly that of pitchblende, mentioned above, not only for the future consequences of the uranium discovery, but for the chemical aspects of this analysis, in addition to theoretical aspects, such as the "Schemnitz illusion". The qualitative detection of uranium, as practiced until the 20th century, was, in general, Klaproth's (little practiced in chemistry courses, not because of the risk, but because of the high cost of uranium). The various chemical treatments to which pitchblende was subjected resulted in a solution, identified in 1842 by Eugène Melchior Peligot (1811-1890) as uranyl nitrate, $UO_2(NO_3)_2$; the addition of NaOH leads to precipitation of sodium diuranate, $Na_2U_2O_7$, and H_2S precipitates uranyl sulfide, UO_2S. Briefly, Klaproth indicates in Table 2 the following composition of pitchblende, converted into percentage:

Table 2. Composition of pitchblende according to Klaproth.

Uranium Oxide	86,5%
Iron Oxide	2,5%
Galena (lead sulfide)	6%
Silica	5% (Total 100%)

All these mineral analyses are described in "Beiträge zur Chemischen Kenntnis der Mineralkörper" (1795/1815), with a great wealth of experimental details, the repetition of which would be idle here. A patient reading of all these analytical works, however, shows not only the rigor of Klaproth's work, but especially the ingenious use of the chemical and analytical resources then available.

Some of these mineral analyses are of special importance in the History of Chemistry, for example, that of leucite, a volcanic mineral from Italy, analysed in 1797. At the time, two "soft alkalis" were known, mineral mild alkali, or soda (Na_2CO_3), and vegetable mild alkali, potash (K_2CO_3), the latter obtained exclusively from vegetable ashes (from algae or marine plants). Although the elements sodium and potassium were only isolated in 1807 by electrolysis (Sir Humphry Davy), chemists were able to distinguish perfectly between soda and potash (1736, Duhamel de Monceau), as well as between sodium salts and potassium salts (Stahl). Klaproth discovered potash in leucite, and obtained for the first time in a mineral the "white plant alkali" (leucite is an aluminum and potassium silicate, according to Klaproth containing 53.750% silica, 24.625% alum and 21.350% of ' vegetable alkali')[30].

There is the curious case of siderite or hydrosiderite, a supposed element. In 1777/1778, Torbern Bergman in Uppsala and Johann Karl Friedrich Meyer (1733-1811) in Stettin were studying a curious variety of cast iron, which after being treated with sulfuric acid and further reduced, gave rise to a greyish-white powder, a possible element, siderite. The same variety of iron was also analysed by Klaproth, who found in 1783 that it was an alloy of iron and phosphorus (as phosphoric acid or phosphide)[31].

Another analysis of importance for the evolution of chemistry was that of guano, brought from South America by Alexander von Humboldt on his return to Europe in 1804. Humboldt entrusted samples for analysis to Fourcroy and Vauquelin in Paris, and to Klaproth. The French published their analysis in 1806, Klaproth in 1807[32]. Klaproth found in guano 16% of ammonium urate, 12,75 % of calcium oxalate and 10% of calcium phosphate. The results were similar, but far from those of a modern analysis (Klaproth found phosphates, oxalates, urea, ammonia). Guano has been known since the

16th century, but the first more detailed descriptions are by Amédée François Frézier (1682-1773), in his 1712/1714 travels, and by Antonio de Ulloa (1716-1795). In addition to Klaproth, Louis Nicolas Vauquelin (1723-1829) and Wilhelm August Lampadius (1772-1842) also chemically analysed guano. Other exotic materials brought by Humboldt were also subjected to analysis by Klaproth, such as the "pacos" from Peru (supposed silver mineral, actually 71% iron, 14% silver)[33] and the "mocha" from Quito, a volcanic material[34].

THE WORK – CHEMICAL ANALYSIS – MINERAL WATERS

The analysis of mineral waters, especially those that present a supposed or real curative aspect, attracted the attention of analysts and assayers since the Middle Ages, and with the improvement of analytical techniques these analyses multiplied from the beginning of the 18th century, involving many chemists, from Hoffmann and Bergmann to Berzelius, Liebig and Fresenius. Oskar Baudisch (1881-1950), an analytical chemist, dedicates an essay to the "magic and science of healing mineral waters". The "magical" aspect of the "cure" is, on the one hand, psychological, involving the entire atmosphere reigning in the mineral resorts, and on the other, even scientific, with the discovery in the waters of chemical principles that could account for certain medicinal effects (iodides, sodium sulfate, lithium salts) [35]. Klaproth also analysed mineral waters, two of which we will present here: the waters of Karlsbad, in Bohemia (today Karlovy Vary, in the Czech Republic), and the waters of the Dead Sea, the first due to the great importance of Karlsbad in the cultural context of the 18th and 19th centuries, attended by the European elite (Goethe, Beethoven, Berzelius, Chopin, Turgenev were regulars), and the second for the emblematic value for Christianity of the waters of the Jordan and the Dead Sea.

The first analysis of Karlsbad thermal waters is due to the spa's physician, David Becher (1725-1792), in 1770. Klaproth analysed them during his stay there in June 1789, in the company of his friend Count Carl Friedrich von Gessler (1752-1829). Klaproth determined the following components of Karlsbad water: 1000 parts by weight of water contains 5,478 parts of solids, distributed as per the table; the analysis generally confirms Becher's.

A new analysis was carried out in 1809 by the chemist Ferdinand Friedrich Reuss (1778-1852), professor at the University of Moscow. As early as 1802, Klaproth had published a recipe for making 'artificial Karlsbad water'. The production of artificial mineral waters was described in 1783 by Johann Carl Friedrich Meyer (1739-1811), a pharmacist in Stettin (now Szczecin, Poland), but even earlier Priestley and Bergman had already produced artificial waters. Berzelius published in 1823 a long article discussing the analysis of the waters of Karlsbad, in which he criticizes aspects of Klaproth's analysis, despite the usual rigorous procedure of the latter[37].

Table 3. Klaproth analysis of Karlsbad mineral waters[36].

Sodium sulfate (Glauber's salt)	2,431 parts
Sodium bicarbonate	1,345 parts
Sodium chloride	1,198 parts
Calcium bicarbonate	0,414 parts
Silica	0,086 parts
Iron oxide	0,004 parts

The Dead Sea is *par excellence* a sacred place for Judaism and Christianity, and its waters have a high symbolic value for Western Christian-Jewish civilization: their analyses combine the history of Humanity, the presence of mythical and transcendental values, the 'magic' side of science, and chemical analysis figures as a kind of 'centralizer' of the discussion. For centuries, pilgrims and explorers visiting the Holy Land brought back bottles with water from the Dead Sea and the Jordan River, and a first qualitative analysis of these waters was carried out by the English physician Charles Perry (1698-1780) in 1742. The first quantitative analysis was that of Pierre Macquer (1718-1784), in 1781 (it is the second quantitative analysis of natural waters, preceded only by seawater). After Macquer, many chemists occupied themselves with the emblematic water: Alexandre Marcet (1807 and 1813), Klaproth (1809, 1813), Gay-Lussac (1819), Hermbstädt (1822), Christian Gmelin (1827), Boussingault (1856)[38]. Table 4 shows Klaproth's data from 1813.

Klaproth's data broadly confirm Macquer's, but they were contested by Marcet.

In 1792/1793 Klaproth analysed the waters of Iceland's hot springs. John Thomas Stanley (1766-1850) had

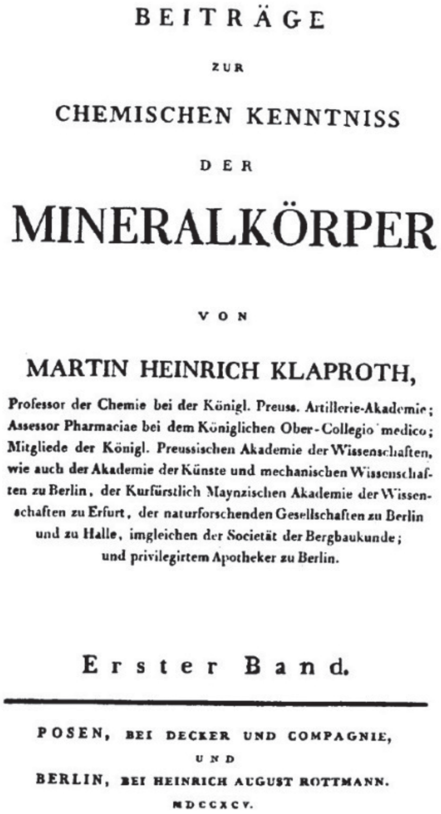
Table 4. Klaproth analysis of Dead Sea waters.

Chloride	206,5 g/liter
Sodium	38,2
Magnesium	35,9
Calcium	24,3
Potassium	traces

brought bottles of these waters from his expedition to the Faroe Islands and Iceland in 1789 and forwarded the samples for analysis to Klaproth and Joseph Black. The results of both are almost coincident (presence mainly of silica, sodium chloride, sodium sulphate)[39].

THE WORK – ARCHAEOMETRY[40]

Analyst that he was, it did not take long for Klaproth to apply chemical analysis to antiquities and archaeological objects: coins, metals, bronze and other metallic alloys, glass, ceramics, pigments, dyes, an applied branch of chemistry known today as Archaeometry. The term 'Archaeometry' is not Klaproth's, it was used for the first time in 1953, in a journal published by the Research Laboratory for Archaeology and the History of Art in Oxford. There are some analyses prior to Klaproth, e. g. the analysis of Chinese *paktong* by Gustav von Engeström (1738-1813) in 1776, and some 'archaeometallurgical' studies mentioned by T. Pownall in 1775[41]. Archaeometry is one of Klaproth's most interesting contributions, not only to Science, but to History itself[42]. Archaeology, erected in science essentially thanks to the efforts of Johann Joachim Winckelmann (1717-1768) in understanding Classical Antiquity, had an auxiliary arm in archaeometry, which allows not only to study the technological resources available to the ancients, but also to make inferences, such as determining trade routes, cultural influences, colonization start dates and others. Knowing the composition of ancient objects, it is also possible to restore works of art from the Antiquity. Klaproth had a special interest in history, and had a valuable collection of antiquities, thus being interested in the analysis mainly of metals (coins, weapons), but also of glass and medieval metallic objects. Klaproth began these analyses in 1785, and Earle Caley (1900-1984), a modern authority on the subject, considered them of great importance, as never before had anyone analysed such objects from a chemical, scientific point of view, nor was there a script until then, for the analysis, for example, of old coins[43]. It is no longer possible to confirm Klaproth's data, but modern analyses of coins from the same time and place confirms his results: for example, for a Roman coin from the times of Emperor Claudius, Klaproth found a composition of 77.9% of Cu and 21.1% Zn, and in 1869 the self-taught writer and chemist Ernst von Bibra (1806-1876), also interested in this subject, found for a coin of the same period the values 77,44% Cu and 21.50% Zn (the difference corresponds to traces of metals that escape the analytical procedures of Klaproth and Bibra)[44]. It is thus known, thanks to archaeometry, that the Roman coins of the 1st century were minted in brass and not in bronze. Josef Riederer (1939-2017), a chemist from the Berlin museums, repeated some analyses of Roman coins (1974), with results very similar to those of Klaproth. Table 5 shows some of the results.



BEITRÄGE
ZUR
CHEMISCHEN KENNTNISS
DER
MINERALKÖRPER
VON
MARTIN HEINRICH KLAPROTH,
Professor der Chemie bei der Königl. Preuss. Artillerie-Akademie;
Assessor Pharmaciae bei dem Königlichen Ober-Collegio medico;
Mitgliede der Königl. Preussischen Akademie der Wissenschaften,
wie auch der Akademie der Künste und mechanischen Wissenschaften
zu Berlin, der Kurfürstlich Maynzischen Akademie der Wissenschaften
zu Erfurt, der naturforschenden Gesellschaften zu Berlin
und zu Halle, imgleichen der Societät der Bergbaukunde;
und privilegirtem Apotheker zu Berlin.

Erster Band.

POSEN, BEI DECKER UND COMPAGNIE,
UND
BERLIN, BEI HEINRICH AUGUST ROTTMANN.
MDCCXCV.

Figure 4. Cover page of Klaproth's most important publication, 'Beiträge zur Chemischen Kenntnis der Mineralkörper'.

Table 6 compares the data of the analysis of an ancient mirror by Klaproth and Bibra.

In the case of studying old glasses, the weight of the sum of the weights of the components found does

Table 5. Analyses of Roman coins by Klaproth and Riederer[45]

Elements	Klaproth (1795)		Riederer (1974)	
	(sample 1)	(sample 2)	(sample 1)	(sample 2)
Copper	77,9	83,0	77,5	83,0
Tin	-	1,9	-	0,7
Lead	-	-	-	0,62
Zinc	15,5	15,15	22,1	14,45

Sample [1]: coins from the times of Claudius (41/54); sample [2]: coins from the times of Vespasian (98/117).

Table 6. Analyses of the metal of an ancient metal mirror, by Klaproth and Bibra[46].

Elements	Klaproth	Bibra
Copper	62	64,46
Tin	32	28,36
Lead	6	7,13
Iron	-	traces
Nickel	-	0,05

Table 7. Composition of old glass according to Klaproth.

Components (grains)	Red	Green	Blue
Silica	142	130	163
Lead oxide	28	15	-
Copper oxide	15	20	1
Iron oxide	2	7	19
Alumina	5	11	3
Limestone	3	13	0,5

not match the original weight of the sample, a fact that Klaproth does not explain, although he knew the fundamental aspects of glass technology since Antiquity. It is now known that the difference is due to the presence of sodium and potassium oxides, compounds not known in Klaproth's time. The importance of the knowledge of the basic theoretical aspects for correct chemical practice is evidenced in Klaproth's analysis of glass: for him copper was responsible for the color of red and green glasses, but different "forms" of copper. We would say today, different oxidation states of copper, Cu(+II) in red, Cu(+I) in green glass. Table 7 shows data from Klaproth's analyses[47].

In 1798 Klaproth published more detailed glass analyses, from glasses collected at the Villa of emperor Tiberius in Capri. Compounds in bold were in Klaproth's opinion responsible for the color of the glass. Klaproth found out that different 'kinds' of copper are responsible for both red and green color, a fact we explain today considering different oxidation states of copper.

It is worth mentioning the analysis of the ancients' electrum (in this case, a mineral sample from Siberia) [49], and, in the course of the analysis of many "earths", the analysis of the "earth of Lemnos" (*Lemnia Sphragis*), used by the ancient Greeks as antidote for poisons, and whose composition is, according to Klaproth: 66% silica, 14.5% alum, 6% iron oxide, 3.5% soda, 0.25% lime, 0.25% talc and 8% water[50].

Table 8. Analyses of Roman Glasses from Capri (Klaproth, 1798)[48].

Color	SiO_2	PbO	Cu_2O	CuO	Fe_2O_3	Al_2O_3	CaO
Red	72,8	14,4	**7,7**	-	1,0	2,6	1,5
Green	66,3	7,7	-	**10,2**	3,6	5,6	6,6
Blue	87,4	-	-	0,5	**10,2**	1,6	0,3

Other early 19th-century chemists were concerned with archaeometry: Jean Antoine Chaptal (1756-1832) analysed pigments found in Pompeii (1809), and Sir Humphry Davy (1778-1829) analysed the pigments used by the ancients in paintings[51].

And as we said, archaeometry ended up leading to the possibility of restoration and conservation of archeological objects and ancient works of art, today a routine in the laboratories of specialized museums. The first laboratory along these lines was that of Friedrich Rathgen (1862-1942), the "father of modern archaeological conservation", in the Berlin Museums (1888)[52].

THE WORK – ORGANIC CHEMISTRY.

Most of the history of Chemistry treatises consider Klaproth's contribution to Organic Chemistry to be minimal. They limit themselves to mentioning the discovery, in the mineral mellite (*Mellit, Honigstein*), of mellitic acid (*Honigsteinsäure*), $C_6(COOH)_6$, in 1799 (mellite is the aluminum salt of mellitic acid, $[Al(H_2O)_6]_2C_6(COOH)_6$, discovered in Artern, Germany, in 1789 by Dietrich Ludwig Gustav Karsten [1768-1810]) [53]. Mellytic acid is obtained by treating mellite with ammonium carbonate and precipitating alumina with ammonia. In 1776, Klaproth examined copal, a vegetable resin of various origins, used in the manufacture of varnishes. Copal was considered sometimes as a mineral, sometimes as a semi-fossilized resin (*succinum vegetabile indicum*) similar to amber[54].

In fact, Klaproth's interest was great not only in Organic Chemistry, but also in Physiological Chemistry, but as both were still taking their first steps, they hardly appear in his writings. However, they occupy an appreciable space in his lectures, as B. Engel discovered to her surprise when transcribing the aforementioned manuscripts by Barez and Schopenhauer. Surprising is the space given to the "components of organic bodies", almost 28% of the manuscript, almost the same extent as that devoted to minerals (30%), Klaproth's main field of research. "Organic bodies" include "flammable substances" and "substances from the animal kingdom". It is clear, according to Engel, that Klaproth not only taught his students Inorganic Chemistry, but also the knowledge taken as fundamental requirements for understanding Organic Chemistry and Physiological Chemistry that were beginning to develop, a particularly important aspect in courses that prepared physicians and pharmacists, still in the opinion of B. Engel[55].

THE WORK – PUBLICATIONS.

In addition to the routine publication of the results of his investigations – mainly chemical analyses – in various scientific journals, such as Crell's *Annalen der Chemie*, in Scherer's *Allgemeines Journal der Chemie* and in Rose's and Gehlen's *Neues Allgemeines Journal der Chemie*, there are also more comprehensive publications, some in partnership with other chemists. The most important of these works is undoubtedly "Beiträge zur Chemischen Kenntnis der Mineralkörper" (Contributions to the Chemical Knowledge of Minerals), in six volumes, published between 1795 and 1815 in Berlin, devoted the first five volumes successively to John Hawkins, Dietrich Ludwig G. Karsten, Vauquelin, Berthollet and A. von Humboldt. Also important is "Chemische Abhandlungen gemischten Inhalts"[56] (Chemical communications on various contents), Berlin 1815. In this book he describes, for example, the analyses of ancient coins[57] and glasses, Belustscheff's dye[58], analyses of minerals and products of plant origin, analysis of salt, ozokerite, meteorites[59], sugars and many other subjects. In 1797 the King of Prussia Frederick William III (1777-1840) commissioned a new pharmacopoeia, the *Pharmacopoeia Borussica*, which was developed by Klaproth, with the collaboration of Valentin Rose the Younger and Sigismund Friedrich Hermbstaedt (1760-1833). The *Pharmacopoeia* was developed according to the Lavoisierian theory, including nomenclature. Chr. Friedrich notes that the new pharmacopoeia already contains data on the chemical composition of the *simplices* as well as quality tests.

Klaproth wrote in partnership with Friedrich Benjamin Wolff (1765-1843) the "Chemisches Wörterbuch" (Dictionary of Chemistry), in five volumes (1807/1810), dedicated to Tsar Alexander I (1777-1825), translated in 1812 into French by Heinrich August Vogel (1778-1867), professor at the *Lycée Napoléon* in Paris; later four volumes of "Supplements" (1815/1819) were added. Wolff was Kant's student in Königsberg and for a long time taught Mathematics and Physics at the *Joachimstaler Gymnasium* in Berlin, and also wrote a didactic "Handbook of Chemistry". The "Systematisches Handbuch der Chemie" (Systematic Handbook of Chemistry) by Friedrich Albrecht Carl Gren (1760-1798), published in 1787/1794, merited a new revised edition by Klaproth in 1805 (Gren was an ardent advocate of phlogiston, but convinced of the assertion of Lavoisier's theories, sought to reconcile the two theories).

THE STUDENTS.

Raised to the university chair at the age of 67, Klaproth had there few students (we mentioned Arthur Schopenhauer before), but many studied with him at the *Collegium Medicum,* and in what Aaron Ihde considered the "best place to learn Chemistry" in the 18th century, the pharmacy[60]. Klaproth did not form a school, but his biographer Dann mentions 32 names he considers of some relevance who were his students, starting with Heinrich Rose and Gustav Rose, sons of Valentin Rose the Younger and later professors at the University of Berlin. Important was Adolf Ferdinand Gehlen (1775-1815), editor of several scientific periodicals and, since 1807, chemist at the Bavarian Academy of Sciences in Munich (where he died of intoxication while researching arsenic compounds). Johann Jakob Bindheim (1740-1825), about whom little is known, studied with Klaproth in the White Swan pharmacy, and later worked in Russia (1795/1804). Also should be mentioned Carl Willdenow (1765-1812), later professor of Botany at the University of Berlin, the pharmacists Johann Heinrich Julius Staberoh (1785-1858) and Johann Christian Schrader (1768-1826), active in the public health service in Berlin, and Jacques Peschier (1769-1832), the latter from Geneva[61].

A TENTATIVE EVALUATION

Looking at the life and work of the pharmacist and chemist Klaproth, it remains for us to assess the figure of the scientist at the time he was active. In Hufbauer's opinion, at the end of the 18th century the situation in German Chemistry was chaotic, and we can say that in the midst of this chaos, Klaproth's figure is a lone star[62]. In the 18th century there were outstanding and influential personalities in German Chemistry, coming essentially from Pharmacy and Medicine: the theorist Stahl, the empiricists Friedrich Hoffmann and Andreas Sigismund Marggraf, the technologist Johann Beckmann, but the situation deteriorated at the end of the century, not only because of the controversy between the "French chemistry" (read Lavoisier) and "German chemistry" (read Stahl's followers), a controversy fueled not only by scientific arguments, since it was predictable that the German chemists defended first the theory of their countryman Stahl. One cannot forget the influence of nationalist factors and especially the reflection of the decadence of academic chemistry, exhausted and without perspectives, revived in the end by the adhesion of Hermbstaedt and Klaproth to the new Lavoisierian theory, and, in Homburg's opinion, also by the radical reformulation of university laboratories. If at the end of the 18th century there were undoubtedly competent chemists such as Georg Ludwig Claudius Rousseau (1724-1794) or Heinrich August Vogel (1778-1867), there were also exotic characters such as Gottfried Christian Beireis (1730-1809) in Helmstedt, and Ferdinand Wurzer (1765-1844) in Bonn. Thanks to the rationality and empiricism that he imprinted on his scientific activities, Klaproth reversed the situation, just when the chemical community in Germany was beginning to organize itself, around 1790. After a youth of "suffering and hope", in his own words, the self-taught Klaproth raised all the steps of the Prussian medical bureaucracy and academic activity; as an internationally recognized scientist, he gave a new start to the chemical activity in Germany and influenced the pharmaceutical activity for 30 years. We conclude with the assessment that the chemist and historian of chemistry Thomas Thomson (1778-1842) made of his legacy[63]:

> Among the outstanding traits of his character is the incorruptible respect he had for all that was true, honorable and good; his pure love of science, without any reference to feelings of selfishness, ambition or avarice; his rare modesty, unaffected by the slightest boasting or arrogance. He was benevolent to all men, and he never uttered a word of spite or even offense directed at anyone around him. When forced to censure, he did so quickly and without bitterness, for his criticism was always directed at facts, never at people. His friendships were never the result of selfish calculation, but were based on his opinion of each individual's personal worth. […] To all this we can add a true religious feeling […] of the obligations of love and charity […] demonstrated, for example, in the commendable care he devoted to the education of Valentin Rose's children.

Here is the life, character, and work of our somewhat forgotten honoree.

EPILOGUE - A NECESSARY FINDING.

Why was Klaproth forgotten? The evils that affect historiography in general today also affect the historiography of Science: a refusal to accept causality, the gradual replacement of the Philosophy of Science by a Sociology of Science, the abandonment of a logically ordered method, the neglect of primary sources (which could lead to a historiography that is too "positivist", or even Rankean). In the case of the historiography of Science, there are also two dangerous trends: the mistaken belief that scientific creation is socially conditioned, and not by the logic underlying a method, and the appreciation of facts not for what they mean in terms of advances in scientific knowledge, but for the importance attributed to them in the social context. Many "theorists" of the History of Science, in their practice, no longer differentiate between objective science and subjective "doing science", are ignorant of the very notion of "science", and often forget that Chemistry is, after all, an experimental science. And many "theorists" of Science defend more and more the idea that knowledge is a "social construction" and not the consequence of the rigorous application of a pre-established scientific methodology that is periodically tested through the results obtained. Thus, they open the doors for the return of pseudo-sciences and for the emergence of themes that do not exist at all, such as a supposed "pre-Columbian science" (there were pre-Columbian techniques), or others that should already be buried, such as "Occult Chemistry".

The necessary integration of scientific culture to the Culture of Humanity as a whole is unfortunately done at the expense of scientific knowledge. Thus, names like Klaproth, like Bergman, Gadolin, Trommsdorff, Runge or Kolbe, all empiricists, left the scene. They are all deserving of a return. And in this regard "[*History] can help to better understand the scientific discovery itself, verifying the factors that acted in it, the figures that remained behind the scenes. Perhaps this way scientists and historians can rectify many glories and unearth many forgotten skeletons*"[64]. And the biographies serve as a backdrop against which all the events that led to a particular scientific discovery unfold, going beyond the limits of science itself. Biographies, far from hagiographies, make it possible to establish contacts between people – scientists and non-scientists – places and times, assess the spread of ideas and theories, in addition to allowing the identification of influences and scientific schools[65].

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Book Review

Review of *Research between Science, Society and Politics: The History and Scientific Development of Green Chemistry*. Johan Alfredo Linthorst, eds. Eburon Academic Publishers, Utrecht, The Netherlands, 2023

Andrea Goti

Department of Chemistry "Ugo Schiff ", University of Florence, 50019 Sesto Fiorentino (Firenze), Italy
E-mail: andrea.goti@unifi.it

This book is the publication of the Author's PhD thesis in History, discussed on February 2023 at the Faculty of Arts and Social Sciences of Maastricht University. Johan Alfredo Linthorst got a Master's degree in Chemistry at the University of Groningen in 2004 and a second Master's degree for teacher training in chemical education at Fontys University of Applied Sciences in 2005. He is involved in chemistry education at pre-university level since 2003. Parallel to his interest in teaching chemistry, including designing and publishing new experiments for students, he developed a personal interest in the history and philosophy of sciences and chemistry in particular. In this connection, in 2005 he started his research at Maastricht University as an external PhD candidate which culminated with his dissertation, which constitutes the present publication.

The subject of this book is well summarized by its sub-title: "The History and Scientific Development of Green Chemistry". Green Chemistry has been and continues to be a subject of intense debate among chemists themselves, starting from the term "green chemistry" itself, to continue with its scope, aims, significance, and character as a new discipline or not.

Green Chemistry, also referred to under many other designations, such as "safe chemistry", "benign by design chemistry", "sustainable chemistry" among the most frequent albeit not necessarily used with the same meaning, has emerged in the beginning of the 1990s as a new way of approaching a chemical synthesis considering all aspects under the point of view of safety and sustainability.

Chapter 1 of this text is devoted to the birth and emergence of Green Chemistry. Here, the reasons and the events that pushed to look at (synthetic) chemistry under a different and more environmentally oriented manner are summarized and analyzed. The emergence of this perception as a consequence of the negative image of chemistry raised by accidents in the chemical industries and by widespread pollution caused by production and use of chemicals are discussed. The key role played by environmental chemists, especially working at the Environmental Protection Agency (EPA) of the USA, in pursuing these ideas are introduced, as well as linkages among society, politics, and scientists. These connections, including the role of the respective chemical societies (ACS, American Chemical Society; RSC, Royal Society of Chemistry; KNCV, Royal Netherlands Chemical Society) in promoting this new way of thinking, are presented and discussed in great detail in the following three chapters, devoted to the rising and shaping of Green Chemistry in the USA (Chapter 2), UK (Chapter 3) and the Netherlands (Chapter 4). In Chapter 5, a picture of the subject under a more scientific point of view is given, again illustrating the development in chronological order. Thus, examples of reactions are reported which are evaluated about their greenness, also utilizing some of the proposed and mostly applied quantitative descriptors (eg, the atom economy percentage and the E-factor, among some tenths proposed up to date). The "Twelve Principles of Green Chemistry" listed by Anastas and Warner in 1998 in their booklet "Green Chemistry: Theory and Practice", which represent the first attempt to rationalize and define the concepts and scope of Green Chemistry seen as a new way of doing chemistry rather than a scientific discipline, are also showcased. Finally, Chapter 6 reports the Author's conclusions on the subject.

No doubts that the roots of Green Chemistry are to be searched in the USA, with the debate among scientists in the EPA following societal impulse and that USA politics (eg, with the Presidential Green Chemistry Challenge Awards program launched in 1995, inter alia) has largely contributed to its quick diffusion and acceptance among the general public. It is also true that UK and the Netherlands are among the nations that largely contributed to the diffusion of ideas of Green Chemistry in its infancy, albeit with notable differences that are exhaustively presented and discussed by the Author in Chapters 2 to 4. However, circumscribing the treatment to these three countries, although representative, is the major limit of this endeavour. Expanding the analysis at least to EU countries and EuChemS societies would have been appropriate. For example, in Italy the Green Chemistry issues have been recognized since the early 1990s already by the government, which approved the institution of the Interuniversity Consortium INCA-"La Chimica per l'Ambiente" ("Chemistry for the Environment") in 1993, which played a major role in the following years in promoting and diffusing the ideas and culture of a more environmentally friendly chemistry at national and international level. Nevertheless, this limit does not diminish the value of this work, which is the most comprehensive treatise on the history of Green Chemistry published up to date. Other studies on green chemistry and its emergence and history have appeared previously, which are recognized by Linthorst and summarized in Chapter 1, but are much more limited in scope and lack the wide breadth of intent and perspectives of this work. The Author made a huge effort, collecting an impressive amount of diverse bibliographic sources, in order to give solid foundation to his representation of the Green Chemistry movement and its connection with society, politics, funding agencies and scientific societies. This text is an invaluable source of information for both practitioners and novices and deserves to be read by all scientists interested to the subject.

From Introduction and Conclusions it appears that the phenomenon allows many interpretations concerning either the causes of its emergence and the motivations for its reception by the scientists. The different opinions opened a great debate, which still leaves open questions as apparent from the Conclusions. Despite its use as an umbrella term or for greenwashing operations, certainly abused, it is important as (synthetic) chemists to recognize that Green Chemistry has contributed substantially to multiply our efforts in pursuing procedures more respectable of the humanity well-being and of the environment. As a matter of fact, Green Chemistry guidelines have already pervaded our lives. As researchers, we are aware that the Green Chemistry principles are strictly connected to many of the 17 Sustainable Development Goals (SDGs) of the 2030 UNO Agenda for Sustainable Development. Moreover, every time we sign the DNSH (Do Not Significant Harm) declaration, eg, when applying for funding from the EU or National programs, we state to comply with those principles.

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Table of contents