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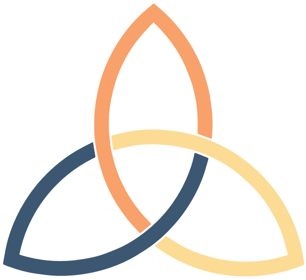

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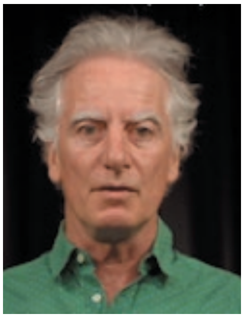

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Our Short Talks

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We recently organized the first edition of *Substantia Short Talks* to discuss some hot topics within the community of our journal. It was a recorded online event, that took place online on July 1, 2021, at 4 pm CEST.

In 2020, during the Covid-19 pandemic that forced us to restrain or limit our social and cultural activities, we thought to offer a lively cultural happening to strengthen our interactions and to ponder on some remarkable issues that affect our lives as scientists and citizens in a globalized world.

Examples that came up to our minds were quite some. Just to mention a few: the protection of intellectual property and the worldwide distribution of life-saving drugs (e.g. the anti-Covid vaccines) at very low costs; the relationship between science and politics, i.e. Black Lives Matter and the harsh debate between some international scientific journals and publishers; or the denial of freedom and democracy and even the lack of scientific dissemination in some countries, and so forth.

Not to speak about the side effects of the frenzied race to publish and the slavery to bibliometric indicators. What are the most important forces that drive research and dissemination in science today?

And what can we do to improve the state of the communication between the society and scientists? What does the pandemic have to say in this respect?

These are only a few among the several questions that spring from our minds.

And their echo often reverberate in *Substantia* as key points of some articles.

These are the reasons why we decided to organize these "short talks" as a parallel contribution to our efforts to make science more transparent.

This time our event features three contributions on peer review, big science and on the most advanced outcomes of current studies carried out by a young researcher in a specific field of Chemistry.

Each contribution lasted 20 minutes, leaving room for questions and answers.

We began with Seth Rasmussen from North Dakota State University in Fargo, who spoke about "The good and the bad of peer review".

Peer review started in 1831 in the UK with Willian Whewell who proposed to receive the comments of two fellows of the Royal Society on submissions to the *Philosophical Transactions*.

Peer review truly is the central core of scientific publishing. It is necessary to guarantee the reliability of a paper, in the scientific community but also before the society.

This process is the real core for the publication, of a reliable, solid and trustable article.

Interestingly, not so many people know that there are different kinds of peer review: single blind, double blind, post-publication, open, transparent, and collaborative peer review.[1]

Sometimes the process is rough, for different reasons, and the editorial staff has to handle this crucial and delicate step very carefully. In any case this is by far the most important stage in the publication process.

Then it was the turn of Helge Kragh, from the Niels Bohr Institutet in Copenhagen. He gave an historical overview on "Big Science: Opportunities and Challenges". This is a key issue with strong political ramifications. In fact big projects are so expensive that only governmental agencies can provide the necessary financial sources. They may also include other non scientific roles, such as managers, technicians, officers, secretaries, public accountants, and so forth. The work is usually carried out in a centralized system of large scale facilities

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where big and sophisticated, very expensive machines are employed, for example particle accelerators (CERN in Europe) or neutron sources (ORNL in the US).

The term "big science" was introduced by Derek J. De Solla Price, in a 1963 book that presented an overview of the 1962 Brookhaven National Laboratory Pegram Lectures.[2]

Certainly the topics and questions addressed in big projects are of paramount importance for science and for the society, however some significant drawbacks exist. For example the incredibly huge number of co-authors,[3,4] sometimes larger than 5,000! This fact has important negative consequences, for example the impossibility to establish each author's credits (who did what), practical problems (e.g. answering the reviewers), and ethical issues. Of course when such a gigantic amount of money is invested, labs and instruments must work full time, with the consequence that methodologies and techniques may take the advantage over topics and science.

The third contribution was from Andreas Lesch, a young electrochemist working at the University of Bologna. His presentation "Electrochemical detection of viable bacteria and biofilms" addressed some hot topics, particularly in view of the next pandemic that some expect will be due to antibiotics resistance in pathogens,[5] and of controlling the growth of biofilms on all kinds of surfaces.

Electrochemistry concepts and techniques can be very useful in the detection of viable bacteria, particularly when time is a key issue for establishing the correct therapy. The main conclusions of the presentation were the production of flexible and reproducible electrodes through inkjet printing,[6] their application to detect viable bacteria,[7] and the opportunities given by scanning electrochemical microscopies for investigating biofilms.[8]

In line with *Substantia*'s vision and scopes this talk on the most recent advances in research in this particular field, was combined with the two previous contributions that do deal with current science activities but in another way.

This attitude of the journal springs from our inter- and multidisciplinary interests.

Today science is deeply divided, there are only few chances to exchange high level information between scientists working in different fields. In other words, the unification of knowledge is a fantasy, due to the over-specialization and to the reluctance to make contents and concepts easily available to other scientists. It is not a question of science popularization, it is a question of sharing. And of promoting truly interdisciplinary studies.

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Feature Articles

Dante Alighieri Science Communicator

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Abstract. This paper deals with the issue of communication and dissemination of scientific knowledge outside the circle of specialists. In particular, in the occasion of the 700th anniversary of the death of Dante Alighieri, we will focus on the program for the popularization of knowledge outlined by Dante in the *Convivio* and *De Vulgari Eloquentia*, as well as several examples taken from his *Divine Comedy* concerning mathematical and natural sciences. Some solutions for communicating science proposed by Dante, such as the explanations of principles and scientific methods within a narrative framework (now often called the storytelling method), in addition to dialogues between characters, anticipate methods for science communication used by several authors after him. Examples are provided to show the depth of Dante's knowledge concerning the basic concepts and methods of mathematics, physics and natural sciences (such as chemistry, meteorology, astronomy etc.). In addition, the examples demonstrate how effectively Dante used analogies and metaphors taken from sciences within his poetry.

Keywords: Science popularization, Dante Alighieri, Divine Comedy, Medieval philosophy

1. INTRODUCTION

In Europe, during the 12th Century, there was a considerable spread of knowledge due to translations of texts from Greek and Arabic into Latin, especially in Toledo (south of Spain) and Palermo (at the court of Frederick II of Sicily), two cities where a mixture of Arabian, Greek and Latin cultures thrived side by side for many years, as well as in several other places. Authors whose works were translated into Latin included Aristotle, Ptolemy, Euclid, Archimedes, Alhazen, and Al-Khwarizmi, together with Chinese and Indian texts imported in Europe through Arabic versions. Such an abundance of Latin texts triggered the creation of a network of universities that used Latin as a *lingua franca* and favored an intensive exchange of international scholars and texts. The universities of Oxford, Coimbra, Paris, Montpellier, Bologna, and Salerno were founded in the 12th century, and those of Cambridge, Salamanca, Toulouse, Orleans, Naples and Padua in the 13th century (see e.g. Greco, 2014). In these universities the arts of the *Trivium* (grammar, rhetoric, dialectic) and those of *Quadrivium* (arithmetic, geometry, music, astronomy) became common subjects for all students.

At the same time, most particularly in the 13th century, *Abacus schools*, used by the emerging classes of merchants, craftsmen, artists, bankers and their sons, were created in many Italian cities. In these schools, popular (vulgar) Italian language and writing, as well as basic mathematics, accounting, mechanics and other subjects, were taught mainly through examples for practical purposes. Dante probably attended this kind of school when he was a child, as he was the son of a merchant, and as an adult he probably attended some lessons at universities as well, in Bologna and Padua, perhaps even in Paris. Therefore, he was probably familiar with both kinds of knowledge – the more theoretical kind taught in Latin at universities and the more practical one taught in the vulgar language at Abacus schools.

Moreover, Dante became used to Italian vulgar poetry, which originated at the court of Frederick II in Sicily and was adopted by many poets and scholars who shared this passion with Dante.

In the 13th century new knowledge and new texts (written in Latin) became more generally widespread in Europe, from the *Liber Abaci* by Leonardo Pisano (Fibonacci) to *Optics and Mathematics* by Robert Grosseteste, *Treatise on Astronomy and Astrology by* John Sacrobosco and *Summulae Logicales* by Pedro Hispano, just to quote a few. All these texts were addressed to an intellectual élite. Indeed, many scholars held an elitist idea of knowledge, especially regarding philosophy and science (often known as natural philosophy). This was, for example, the opinion of Islamic scholar Averroes (Cordova 1126 - Marrakech 1198), a famous philosopher, doctor, judge, and author of commentaries on Aristotle, who stated that teaching humble people was a wasted effort, and even dangerous because it could lead to misunderstandings, and could be a source of discouragement and humiliation for those who did not have the tools to understand. By contrast, Dante Alighieri (Firenze 1265 - Ravenna 1321) held a very different opinion. He firmly expressed a democratic idea of knowledge which should be provided to everybody, although at different levels and through different tools. He discussed these ideas in two unfinished books: *Convivio* (written in the vernacular) and *De Vulgari Eloquentia* (in Latin). In these two treatises Dante outlined a detailed program for the dissemination of knowledge. Indeed, *convivio* means banquet, a table that offers the participants the difficult "food" of knowledge, accompanied by the bread that will facilitate its assimilation. In fact, this work is a kind of encyclopedia in which Dante explains the great philosophical themes of his time in a language which is comprehensible even to non-specialists, themes ranging from linguistics to science, cosmology and politics. In the preface Dante explains why a book like *Convivio* is needed and why it is written in the vernacular instead of Latin. Moreover, he clearly states that "all men naturally desire to know" and "science is the ultimate perfection of our soul".

In *De Vulgari Eloquentia* (On Vulgar Eloquence), written slightly earlier, Dante examines the problem of the most suitable language to spread knowledge in a universal, clear and effective way. After a comparison between Latin and the vernacular, Dante considers the "excellent vernacular speech, common to all Italians, which can be learned without other rules by imitating the nurse"; in other words, the native language. It was written in Latin as it was addressed primarily to the scholars of the time, in order to show them the beauty and usefulness of Italian popular language. Its objective was the search for a natural language that could be understood by all Italians, obtained through a comparative study of different regional dialects and of the way these evolved, in order to find the words and expressions that could be appreciated by people of any Italian region. Finally, in this book Dante analyzes the more suitable metric structures for the poetic form of *canto* (or song), which is a literary genre developed in the Sicilian School of poetry. This poetic form, thanks to its metre and use of rhyme, allowed Dante to produce a poem which was suitable for being read out loud and easily memorized so that it could be learned and repeated even by illiterate people. That is exactly what Dante will do in the *Commedia*, called *Divina* by Giovanni Boccaccio.

It is worth noting that Dante also identifies another difficulty that was emerging in the 13th century. This concerned the specialization of languages within the various professions – thus anticipating a problem that would become a major obstacle to the spread of knowledge today, as maintained by C.P. Snow in his famous essay "The Two Cultures" of 1959. In order to describe this problem, in *De Vulgari Eloquentia* Dante proposes his own personal reworking of the well-known biblical legend of the Tower of Babel, where the external influence of God who confuses languages, is replaced by an endogenous, or evolutionary, explanation of the differentiation of languages. After reporting the classical version:

> Almost the whole of the human race had collaborated in this work of evil. Some gave orders, some drew up designs; some built walls, some measured them with plumb-lines, some smeared mortar on them with trowels; some were intent on breaking stones, some on carrying them by sea, some by land; and other groups still were engaged in other activities - until they were all struck by a great blow from heaven. Previously all of them had spoken one and the same language while carrying out their

> tasks; but now they were forced to leave off their labours, never to return to the same occupation, because they had been split up into groups speaking different languages.

Dante provides his own explanation:

> Only among those who were engaged in a particular activity did their language remain unchanged; so, for instance, there was one for all the architects, one for all the carriers of stones, one for all the stone-breakers, and so on for all the different operations. As many as were the types of work involved in the enterprise, so many were the languages by which the human race was fragmented; and the more skill required for the type of work, the more rudimentary and barbaric the language they now spoke.

Today we would say that doctors speak using their own specific language as do physicists, mathematicians, chemists, philosophers, etc., and as a result they no longer understand each other. Hence, someone is needed (the scientific journalist, the populizer, etc.) who is responsible for finding a way to communicate knowledge to everyone by using a common suitable language

In the *Divina Commedia,* many passages can be noticed in which the author shows that he is perfectly at ease not only with astronomy (which is obvious given the structure of the entire work) but also with arithmetic, geometry, logic, physics, and natural sciences in general, to the extent that he uses the stories and the dialogues included in the *Comedy* to communicate scientific concepts and theories, sometimes even at a rather sophisticated level for his times. In the following we shall examine and comment on some of these passages.

2. PHYSICS AND MATHEMATICS IN PARADISE

Let us start from *Paradiso*, Canto 2 (94-106), where Dante clearly illustrates the method of experimental science three hundred years before Galileo. He uses the words of Beatrice, his beloved guide throughout the trip in Paradise, to state how strong his faith in laboratory experiments is. Dante and Beatrice are ascending towards the first heaven of the Moon and the poet asks her what is the origin of the moon spots. Beatrice invites him to express his opinion and Dante attributes the phenomenon to the greater or lesser density of the celestial body (see e.g. Greco, 2009). Beatrice then announces an explanation that, based on an experiment, will refute Dante's theory:

Da questa instanza può deliberarti 94
esperienza, se già mai la provi,
ch'esser suol fonte ai rivi di vostr'arti.

[From this objection an experiment
can free you, if you ever try it,
for from experience derives the source of all your arts.]

That is to say: an experiment can reveal the fallacy of your explanation, as experiments are the starting points of all your knowledge. The statement is peremptory: all your knowledge (down on Earth) comes from experiments. Note that in this case experience is used to disprove definitively, and not to prove something – a form of what six centuries later Karl Popper will propose as the "Falsification Principle", a way of defining science from non-science, which is at the basis of the scientific method. However, Beatrice does not limit herself to such a statement, as she immediately moves on to the description of a real laboratory experiment:

Tre specchi prenderai; e i due rimovi 97
da te d'un modo, e l'altro, più rimosso,
tr'ambo li primi li occhi tuoi ritrovi

Rivolto ad essi, fa che dopo il dosso 100
ti stea un lume che i tre specchi accenda
e torni a te da tutti ripercosso.

Ben che nel quanto tanto non si stenda 103
la vista più lontana, lì vedrai
come convien ch'igualmente risplenda

[Take three mirrors, and place two of them at
the same distance from you, and let your eyes find
the third more distant and between the first two.

Facing toward them, have a light from behind
you shine on the three mirrors
and return to you reflected from all three.

Even though the more distant image
is not as extended in size, you will see
that it is equally bright there]

We will not dwell on the details of the experiment but rather highlight the point that Dante, through the words of Beatrice, is suggesting that an experiment be carried out on Earth in order to understand an astronomical phenomenon, thus affirming that the laws of terrestrial physics coincide with those of celestial physics. Galileo will have to work hard on such an argument in order to convince Aristotelians in the 17th century. And even the statement about experience as the main source of knowledge sounds quite advanced for his time, as it anticipates what will become commonly accepted only after the scientific revolution of the 17th century.

In this regard, it is also important to mention Dante's opinion about alchemists, as he imagines them to be expelled without any appeal, in the Tenth Bolgia of Hell, where they join the company of falsifiers and swindlers. In fact, in Canto 29 of *Inferno*, Dante meets some alchemists who are tormented as they are not able to see anything on account of the darkness. Two of them, Grifolino of Arezzo and Capocchio of Siena, present themselves to Dante.

«Io fui d'Arezzo, e Alberto da Siena», 109
rispuose l'un, «mi fé mettere al foco;
ma quel per ch'io morì qui non mi mena.

Vero è ch'i' dissi lui, parlando a gioco: 112
"I' mi saprei levar per l'aere a volo";
e quei, ch'avea vaghezza e senno poco,

volle ch'i' li mostrassi l'arte; e solo 115
perch'io nol feci Dedalo, mi fece
ardere a tal che l'avea per figliuolo.

Ma nell 'ultima bolgia de le diece 118
me per l'alchìmia che nel mondo usai
dannò Minòs, a cui fallar non lece».

[«I'm from Arezzo, and Albert of Siena»
one of them replied, «had me burned,
but I'm not here for what I died for there.

It's true I told him, jokingly, of course:
"I know the trick of flying through the air", '
and he, eager to learn and not too bright,

asked me to demonstrate my art; and only
just because I didn't make him Daedalus, he had me burned by one whose child he was.

But here, to the last bolgia of the ten,
for the alchemy I practiced in the world
I was condemned by Minos, who cannot err».]

In other words, even if Grifolino died because Alberto of Siena ordered to burn him as a consequence of his false claim about his ability to fly, after his death Minos, the judge and guardian of Hell, condemned him to the Tenth Bolgia just because he was an alchemist. It is important to point out that in the time of Dante alchemy was considered a method to investigate and imitate Nature, as stated by the other alchemist speaking to Dante:

sì vedrai ch'io son l'ombra di Capocchio, 136
che falsai li metalli con l'alchìmia;
e te dee ricordar, se ben t'adocchio,

com'io fui di natura buona scimia». 139

[then you will see that 1 am the shade of Capocchio, who falsified metals with alchemy;
and you must remember, if I eye you well,

how good an ape I was of nature."]

In other words, Capocchio believes that Dante should remember him as a good imitator of nature. Despite this, the poet places him in Hell, among those who took advantage of their knowledge to get rich by deceiving others.

Now we go back to Paradise, but we move onto mathematics, as there are really many references to this discipline in the Comedy (for a more complete treatment of this topic, see e.g. D'Amore, 2001, or Bischi, 2015). We start from *Paradiso*, Canto 33, where the Poet wonders about the difficulty to understand the mystery of the Incarnation, that is, the concept of how Christ can be both human and divine at the same time. This is not impossible for God, but difficult to demonstrate by a limited human mind. How could Dante find an example to explain such difficulty? He refers to the famous (unsolved) problem of Greek geometry known as the problem of squaring the circle, i.e. finding the sides of a rectangle whose area is equal to that of a circle of a given radius:

Qual è 'l geomètra che tutto s'affige 133
per misurar lo cerchio, e non ritrova,
pensando, quel principio ond' elli indige:

tal era io a quella vista nova; 136
veder voleva come si convenne
l'imago al cerchio e come vi s'indova.

[Like the geometer who is all intent
to square the circle and cannot find,
for all his thought, the principle he needs:

such was I at that miraculous sight;
I wished to see, as was fitting
the image to the circle, and how it enters therein]

This mathematical problem reminds Dante of the mystery of the Incarnation, that is, two things of a different nature, one penetrated by the other. This problem was impossible to be solved in Euclid's geometry because, in ancient Greece, geometry problems had to be solved by geometric constructions involving only the use of an ungraduated ruler and a compass. Such an approach constitutes a form of mental gymnastics, or a test of skills. Indeed, Dante knew very well how to calculate the area of a circle, and in fact he uses the approximation 22/7 = 3.1428... (often used instead of π

= 3.1415... in the Abacus books of the Middle Ages) to measure a circular bolgia. Thus, the poet's suggestion is really remarkable: the squaring of the circle (as well as the Incarnation of God) is not impossible to achieve in principle, but it becomes impossible to understand it if resorts only to the use of limited tools, such as a ruler and compass in geometry or the human mind in theology. Of course, this example is not easily understood by any reader of the Comedy, as it requires a deep knowledge of Greek geometry.

Similar arguments apply to the following passage, taken from *Paradiso,* Canto 28, where a reader is assumed to know the legend behind the invention of the game of chess often reported in Abacus books as an example of the exponential growth of compound interests. In this passage Dante uses the metaphor of sparks issuing from a fire to describe the number of angels revolving around God. But how many are them? The poet could write "so many as the stars in the sky", or "so many as the grains of sand in the sea". By contrast, Dante prefers to use an arithmetic argument:

> L'incendio suo seguiva ogni scintilla; 91
> ed eran tante, che 'l numero loro
> più che 'l doppiar delli scacchi s'inmilla
>
> [Each spark followed its fire,
> and they were so many that their number enthousands
> itself beyond the doubling of the chessboard.]

Dante refers to the famous legend of Sissa Nassir, a court magician, and inventor of the game of chess, to whom the Persian king promised the reward he desired for his invention. The witty inventor then made an apparently modest request: taking the chessboard, the usual square formed by 8 by 8 squares, he asked for a grain of wheat on the first square; twice as much, that is 2 grains, on the second, twice as much again, that is 4, on the third; and then 8, 16, 32 … up to the last 64th square, where 2^{63} grains are required. But as soon as the king realized that the total quantity of grain required to meet the demand was so huge, being of the order of ten billion of billion of grains, instead of rewarding Sissa Nassir he had him killed. This legend was reported as an example in many abacus books, as this "game of doubling" (or exponential increase) was used as a template for calculating compound interest, and used by banks in Dante's time, when commerce and entrepreneurial activities started to ask for loans, often at rates that today would undoubtedly be defined as usury.

With these two examples, we have seen how Dante was familiar with both learned mathematics (such as Euclid's *Elements*) taught in Latin at universities, and practical mathematics, the kind taught in the vernacular in Abacus schools.

Keeping to the subject of mathematics (and of kings), let us turn to the story of Solomon reported in *Paradiso*, Canto 13 (88-103). Solomon was king of Israel from 970 to 931 BC, and he was famous for his wisdom and knowledge. He became king at a very young age, and the Bible says that the Lord appeared to him in a dream and told him: "Ask me what I must grant you" and Solomon replied: "Lord my God, you made your servant reign in place of David my father. But I am a boy; I do not know how to rule. Give your servant a mild heart, that he may know how to do justice to people, and how to distinguish right from wrong". It pleased the Lord that Solomon had asked for wisdom in ruling, and he said to him: "Why did you ask for this thing, and did not ask for yourself a long life, nor riches, nor the death of your enemies? Behold, I grant you a wise and intelligent heart, but I also grant you what you have not asked for, that is, riches and glory such as no king ever had".

Dante reports the essence of this legend, but in doing so he replaces the requests Solomon did not make with his own wishes:

> Non ho parlato sì che tu non posse 94
> ben veder ch' el fu re che chiese senno
> acciò che re sufficiente fosse,
>
> non per sapere il numero in che enno 97
> li motor di qua sù, o se necesse
> con contingente mai necesse fenno,
>
> non si est dare primum motum esse, 100
> o se del mezzo cerchio far si puote
> trïangol sì ch'un retto non avesse.
>
> [I have not spoken in such a way that you cannot
> see clearly that he was a king asking for the wisdom
> to be a worthy king,
>
> not in order to know the number of the
> Movers up here, or if necesse
> with contingent ever made necesse ,
>
> not si est dare primum motum esse,
> or whether in a semicircle one can make
> a triangle that lacks a right angle.]

In other words, Dante would have asked God information about the number of angels (appointed to move planets and stars), or whether in a logical proposition a necessary premise combined with a contingent one will give a necessary consequence (a problem which is not trivial, and had already been tackled and negatively resolved by Aristotle), or whether there can be a first motion, i.e. which is not derived from another motion, or, finally, if a triangle that does not have a right angle can be inscribed in a semicircle.

Dante proposes these questions as examples of something false, because they contradict modes of logical necessity. If there is a motion, then necessarily there is a cause, i.e. another motion that generated it (inertia principle will be proved later, by Galileo). If a triangle is inscribed in a semicircle, then necessarily that triangle is rectangular, a direct consequence that the sum of all three angles is equivalent to a flat angle, which follows from the axiom of parallels (the so called 5th postulate of Euclid geometry). Now, while the statement of physical nature is linked to the question of the existence of God, who was able to create everything from nothing, therefore also to originate movements from nothing, the last statement concerns a rather unexpected example from geometry. Moreover, it expresses a doubt about the validity of a basic axiom of Euclidean geometry, in particular the fifth postulate. This may raise the question as to whether alternative geometries can exist, namely the non-Euclidean geometries that will be introduced in the 19th century. Probably we are going too far with our imaginations and we are also pushing Dante's imagination too far.

A similar argument applies to the following passage, found in *Paradiso*, Canto 15 (55-57) where Dante has just met his ancestor Cacciaguida and wants to tell him that he is so wise and forward-thinking that he seems to understand his words before he speaks, as if Cacciaguida were able to read his thoughts. The description of this situation, expressed by Cacciaguida's words while talking to Dante, may suggest to a modern mathematical reader a method for the construction of the whole set of natural numbers based on the principle of induction:

Tu credi che a me tuo pensier mei 55
da quel ch' è primo così come raia
da l' un , se si conosce, il cinque e 'l sei ,

[You believe that your thought flows to me
From him who is First, just as from one, if known, ray forth both five and six,]

This is a very famous phrase that Cacciaguida addresses to Dante: you believe that all your thoughts come to me from God (from him who is first) just as all numbers can be derived from number one (for example six comes from five by adding one). In modern notations we would say "given number 1, then from n we get $n+1$ by induction. However, this general notation that uses variables instead of numbers, was not yet used in Dante's time. For this we have to wait for François Viète in the 16th century. Dante just takes two consecutive numbers at random, such as 5 and 6, to say that this rule applies to all numbers. This mathematical metaphor used by Dante is really remarkable as it can be seen as a metaphor of Creation as well, because one can generate an infinite number of objects by just starting from unity.

3. METEOROLOGY, PROBABILITY AND CHEMISTRY IN PURGATORY

Let us descend now into Purgatory, where Dante meets Bonconte da Montefeltro in Canto 5 (88-129). Bonconte was the military leader of the Ghibellines of Arezzo against the Florentine Guelphs in the battle of Campaldino in 1289. Bonconte suffered defeat, he died during the battle and his body was never found. The whole story is interesting, showing a struggle between the powers of good and evil for his soul, and since he had uttered the name of Mary with his dying breath and shed a tiny tear, the heavenly faction prevailed and brought his soul into Purgatory. However, a demon took possession of his body and dispersed it into a river flood after a big storm. The description that Bonconte gives to Dante about the weather situation leading up to the storm is a page of intensive scientific revelation.

What is remarkable is the way Bonconte introduces himself (*Purgatorio* Canto 5, 88) «Io fui di Montefeltro, io son Bonconte» («I was from Montefeltro, I am Bonconte») – where the usage of both past and present tense means that when alive on Earth, he belonged to the noble family of Montefeltro whereas now in the life beyond, he is just himself. This shows the way in which Dante choses any detail with a precise meaning.

Let us now turn to Bonconte's description of the separation of his soul from his dead body and of the storm that caused the loss of his body in the river.

Io dirò vero, e tu 'l ridì tra ' vivi: 103
l'angel di Dio mi prese, e quel d'inferno
gridava: "O tu del ciel, perché mi privi?

Tu te ne porti di costui l'etterno 106
per una lagrimetta che 'l mi toglie;
ma io farò de l'altro altro governo!".

Ben sai come ne l'aere si raccoglie 109
quell' umido vapor che in acqua riede,
tosto che sale dove 'l freddo il coglie.

Giunse quel mal voler che pur mal chiede 112
con lo 'ntelletto, e mosse il fummo e 'l vento
per la virtù che sua natura diede.

Indi la valle, come 'l dì fu spento, 115
da Pratomagno al gran giogo coperse
di nebbia; e 'l ciel di sopra fece intento,

sì che 'l pregno aere in acqua si converse; 118
la pioggia cadde, e a' fossati venne
di lei ciò che la terra non sofferse;

e come ai rivi grandi si convenne, 121
ver' lo fiume real tanto veloce
si ruinò, che nulla la ritenne.

Lo corpo mio gelato in su la foce 124
trovò l'Archian rubesto; e quel sospinse
ne l'Arno, e sciolse al mio petto la croce

[Now hear the truth. Tell it to living men:
God's angel took me up, and Hell's fiend cried:
"O you from Heaven, why steal what is mine?

You may be getting his immortal soul
won it for a measly tear, at that,
but for his body I have other plans! '

You know how vapor gathers in the air,
then turns to water when it has returned
to where the cold condenses it as rain.

To that ill will, intent on evilness,
he joined intelligence and, by that power
within his nature, stirred up mist and wind.

Then the valley, by the end of day,
from Pratomagno to the mountain chain,
was fogbound; and dense clouds charged the sky:

so that the saturated air turned into water;
rain poured down, and what the sodden ground
rejected filled and overflowed the deepest;

gullies, whose spilling waters came to join
and form great torrents rushing violently,
relentlessly, to reach the royal stream.

Close to its mouth the raging Archiano
discovered my cold body-sweeping it
into the Arno, loosening the cross]

Quite remarkable is the description (109-111) of the water cycle, due to water evaporation and then condensation into liquid water again when the steam, as it rises, encounters colder air layers. This provides a clear-cut explanation of a meteorological phenomenon that was not so clear to people living in the 13th century (see e.g. Cornish, 2004). Moreover, the description of the whole process of storm occurrence and water flow towards rivers is very rigorous and worthy of a scientific essay.

An often-quoted passage of Purgatory, dealing with mathematical ideas given by Dante in the *Comedy,* is the description of a game of dice in Canto 6 (1-3), where an anticipation of some flavor of the concept of probability can be noticed:

Quando si parte il gioco della zara, 1
colui che perde si riman dolente,
repetendo le volte, e tristo impara

[When the zara game starts,
the loser remains sorrowful,
repeating his throws, and sadly he learns]

In the *zara game* (Arabic word 'zahar' means 'dice'), which was very popular in Dante's time, each player bets a certain amount of money before three dice are thrown and each of the players, in the short time between throwing the dice and then stopping them, says a number – whoever guesses the result wins the prize. If no one guesses correctly, the amount of money to be won in subsequent games increases. Of course, probability theory has a role in the analysis of this game; however this theory did not exist at Dante's time, as we have to wait for Cardano (1501-1576), Galilei (1564-1642), Fermat (1601-1665) and Pascal (1623-1662) for these concepts to be introduced in mathematics. However, the combination of the two words "*repetendo …impara*" (*repeating … learns)* may reveal an intuitive, veiled awareness of the existence of probability laws. If a player learns, it means that there is something to be understood, hence Dante may be aware that not all outcomes are equally probable, in the sense that some outcomes are more frequent than others. Moreover, "*repetendo*" makes one think of a "frequentist" definition of probability, given by the number of occurrences of the event divided by the number of trials, as the number of trials tends to infinity. Naturally this is a rather modern interpretation that cannot be attributed to Dante. However, the sentence is surely intriguing, as it was in the question about triangles without right angles in a semicircle in the Solomon story.

Finally, in *Purgatorio*, Canto 7 (73-75) we can find evidence of Dante's knowledge of chemical elements. Indeed, after the enactment of the Orders of Justice in 1293, Dante joined the order of physicians and apothecaries (ancestors of our pharmacists) in order to participate in political life. In addition to medicines however, apothecaries also produced materials for painters, such as white lead, which is lead carbonate, and Dante in his *Vita Nova* tells of having painted. He painted on wood and therefore had to know the methods of preparation of the wooden boards before painting them. So, we may hypothesize that his joining the order of doctors and apothecaries was due to this practice, at least as a novice. A description of these materials is given in the following passage:

> Oro e argento fine, cocco e biacca, 73
> indaco, legno lucido e sereno,
> fresco smeraldo in l'ora che si fiacca,
>
> da l'erba e da li fior, dentr'a quel seno 76
> posti, ciascun saria di color vinto,
> come dal suo maggiore è vinto il meno.
>
> Non avea pur natura ivi dipinto, 79
> ma di soavità di mille odori
> vi facea uno incognito e indistinto.
>
> [Think of fine silver, gold, cochineal, white lead,
> Indian wood, glowing and deeply clear,
> fresh emerald the instant it is split,
>
> the brilliant colors of the grass and flowers
> within that dale would outshine all of these,
> as nature naturally surpasses art.
>
> But nature had not only painted there:
> the sweetness of a thousand odors fused
> in one unknown, unrecognizable.]

In the second Terrace of the Ante-Purgatory, the poet Sordello shows Dante and Virgilio the flowery valley where the negligent princes are located: in their lives they were guilty of neglecting their spiritual and earthly duties. Dante sees that nature here is luxuriant and beautiful as the grass and flowers have such vivid colors as to surely win the most precious and refined hues used by painters, such as gold, silver, emerald. And the spectacle is not only visual, as the flowers give off a scent that mixes a thousand sweet smells. This can be seen as proof of Dante's knowledge about chemicals (which give rise to colors and smells). In other words, we believe that Dante's involvement in the world of the apothecaries, where chemistry took its first steps, gave him more knowledge and understanding than the pseudoscientific alchemy practitioners, as mentioned in Section 2.

4. LOGIC AND GRAVITATION IN HELL

Let us now turn to *Inferno*, Canto 27 (112-123), where among the fraudulent advisers we find Guido da Montefeltro, father of Bonconte, duke of Urbino from 1293. He was also a Ghibelline military leader, and won many important battles often against the Papal army. Then he became a friar and entered the Franciscan monastic order in Assisi in 1296, where he died in 1298.

While he was in the monastery, Pope Boniface VIII asked him for advice in order to win a difficult battle. Guido argued that he could give him a suggestion but it would involve a lie, and Guido knew that as a friar he could not commit such a sin. But Boniface told him, "don't worry, I can absolve you before you commit it". Hence, the Pope absolved him in advance and Guido was allowed to give his fraudulent advice. When Guido died, Francis of Assisi personally picked him up to take him directly to Heaven (this was a privilege of the Franciscan friars). However, something unexpected happened due to a logical reasoning, a typical argument of formal logic which nowadays can be expressed by the symbolism of logical operators or set theory. Here is the beginning of the story:

> Francesco venne poi, com'io fu' morto, 112
> per me; ma un d' i neri cherubini
> li disse: "Non portar: non mi far torto.
>
> [Francis came later, when I had died,
> for me; but one of the black cherubins
> told him: 'Do not take him, do not wrong me.]

Here Guido is telling his story, starting from St. Francis who went purposely to take him ("for me"), but a black cherub, that is, an angel of Hell, ordered St Francis not to take him. It may seem really implausible that an anonymous black cherub gives orders to St. Francis, but as Dante will reveal to us, he is not just any cherub, because he is a logician as well. Notice that here we have a struggle between the powers of good and evil similar to the struggle we have seen for the soul of Bonconte da Montefeltro, the son of Guido. However, here the outcome will be different:

> Venir se de dee giù tra 'miei meschini 115
> perché diede 'l consiglio frodolente
> dal quale in qua stato li son a' crini;
>
> ch' assolver non si può chi non si pente, 118
> né pentere e volere insieme puossi
> per la contraddizion che nol consente".
>
> Oh me dolente! come mi riscossi 121
> quando mi prese dicendomi: "Forse
> tu non pensavi ch' io loico fossi"!
>
> [He must come down among my slaves,
> Because he gave the fraudulent counsel,
> since when, until now, I have been at his heels;
>
> for he cannot be absolved who does not repent,

nor can one repent and will together,
because of the contradiction, which does not permit it.'

Oh wretched me! how I trembled
when he seized me, telling me: "Perhaps
you did not think I was a logician!"]

The black cherub asserts that Guido must instead go down with him to Hell because he gave fraudulent advice, after which the cherub was always at his heels – a powerful image implying that the devil follows the sinner from the moment a sinful action is committed until he manages to take him to Hell. But Dante's masterpiece comes with logical proof to demonstrate that putting Guido in Paradise is a contradiction with respect to the laws (i.e. the axioms) of the Church. In fact, one cannot absolve someone who does not repent, nor is it possible to repent of sin and at the same time want to commit it, because this would lead to a contradiction. In short, faced with the evidence of a logical demonstration there is no getting round it. Not even St Francis, founder of the order, can counteract.

A question naturally raises concerning the level of Dante's knowledge about logics. A possible answer comes from the following statement in *Paradiso*, Canto 12 (134-135):

… e Pietro Ispano, 134
lo qual giù luce in dodici libelli

[… and Peter of Spain,
who shines down there in twelve volumes]

where Dante says that Peter of Spain (or Petrus Hispanus) was famous on Earth ("shines down there") being the author of the twelve chapters that make up the *Summule logicales*, a compendium of formal logic that was the reference manual on Aristotelian logic in use in European universities for more than 300 years. Dante does not mention the fact that Petrus was also a Pope under the name of John XXI. In short, according to Dante, Peter of Spain was famous for writing texts on logic, not for being a Pope. Therefore, we can deduce that Dante, having read and appreciated such a text, was able to understand and handle subtle questions of logic such as the one raised by the black cherub. And, of course, he used the *Commedia* to communicate such knowledge to people who did not have access to universities.

As a final example (among many others) of science vulgarization through the pages of the *Divina Commedia* we propose a passage from the last Canto of *Inferno*, Canto 34 (100-111), where Dante uses a remarkable narrative trick to describe the force of gravity as a centripetal force field directed towards the center of the Earth. In order to explain this, Dante tries to describe what should happen while passing through the center of the Earth, where in the *Commedia* Lucifer is located (see Figure 1, where the spatial structure of the Dante's universe is illustrated).

The last portion of Hell, before it is closed by the horrible hairy body of Lucifer located at the center of the Earth, is formed by the last area of Cocito, the Giudecca, where the traitors of the benefactors are severely punished by being imprisoned in ice. Dante and Virgilio move towards Lucifer and the Latin poet invites the disciple to embrace him around his neck while looking for the right moment to step over the Lucifer's body in order to continue the trip beyond the center of the Earth to the other hemisphere. When the monster's wings are open enough, Virgil clings to Lucifer's hairy ribs and descends along the demon's flanks, then, out of breath, he turns and clings to the hairy legs, beginning to climb upwards. Dante, attached to his neck, does not realize what really happened, and he wrongly believes that they are returning back to the Giudecca. In fact, before twisting around Lucifer, he feels the force of gravity pushing him, while now he feels it opposing his direction of motion. Because of this he thought he had inverted the direction of his movements, like when you go downhill and then you retrace your steps when going uphill. This is the reason for the following questions, which reveal how Dante remains confused due to the centripetal direction of gravity force:

«Prima ch'io de l'abisso mi divella, 100
maestro mio», diss'io quando fui dritto,
«a trarmi d'erro un poco mi favella:

ov'è la ghiaccia? e questi com'è fitto 103
sì sottosopra? e come, in sì poc'ora,
da sera a mane ha fatto il sol tragitto?».

Ed elli a me: «Tu imagini ancora 106
d'esser di là dal centro, ov' io mi presi
al pel del vermo reo che 'l mondo fóra.

Di là fosti cotanto quant' io scesi; 109
quand' io mi volsi, tu passasti ′l punto
al qual si traggon d'ogne parte i pesi.

[«Before I am uprooted from the abyss,
my master», said I, when I was erect,
«speak to me a little to help me out of error:

Where is the ice? and he, how is he fixed
so upside down? and how, in so little time
has the sun made the passage from evening to morning?"

And he to me: «You imagine that you are still

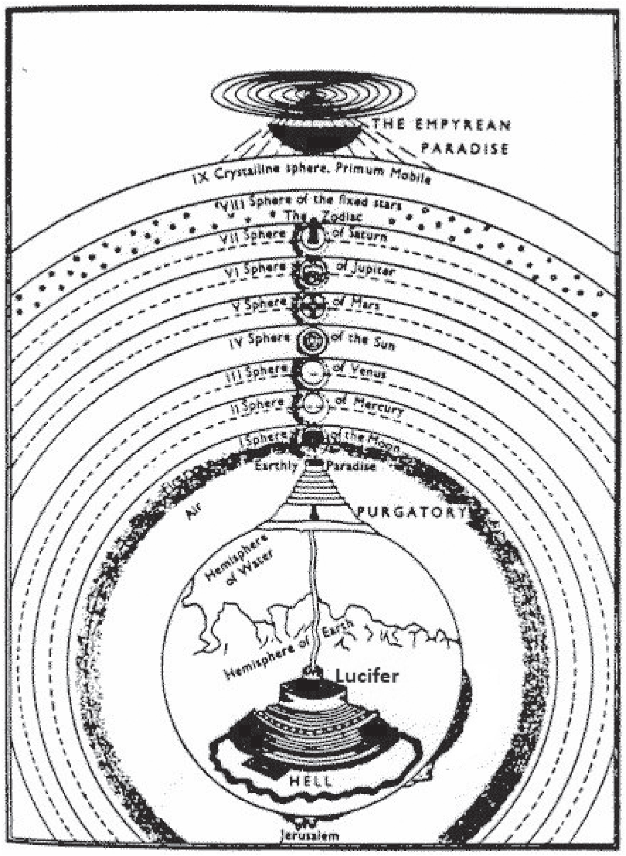

Figure 1. Schematic picture of Dante's travel described in the *Divine Comedy.*

> on the other side of the center, where I laid hold
> on the fur of this evil worm that gnaws the world.
>
> You were on that side while I descended;
> when I turned, you passed the point
> toward which the weights all move from every direction.]

The narrative trick of the illusion of moving back instead of passing through the center (so that Dante cannot realize why he sees Lucifero reversed, why he cannot see the ice of the Giudecca again, and why he suddenly sees the light instead of darkness) is really a clever way of explaining centripetal gravity force. It is not easy to understand the first time by a lay reader, but is undoubtedly effective in order to stimulate the imagination. Dante also explains quite clearly what happens when moving from the northern to the southern hemispheres with regards to daylight and darkness. In short, Dante once again shows an effective use of storytelling in order to make important scientific knowledge popular, while at the same time respecting the metrics and the use of rhyme.

CONCLUSIONS

In this article we described and commented on several passages taken from the *Divina Commedia* by Dante Alighieri which deal with Medieval science. We started from experimental physics (an experiment of optics) and ended with theoretical physics (description of gravitation), running the gamut of alchemy, geometry, arithmetic, logic, meteorology, chemistry. Such concepts and methods are described by Dante through a narrative device, or storytelling, as well as dialogs between Dante and his tour guides (whether Virgilio or Beatrice) or the souls he encounters during his imaginary journey to the afterlife. Hence, we believe that Dante can be seen as one of the first, and most important, science communicators, or, in current language, a *testimonial* or an *influencer*, communicating the importance of scientific knowledge (see also Gilson, 1999, 2001).

Science communication has a rich history related to long traditions and cultural factors, which are now embedded into more extreme forms like *science outreach* and *public engagement*, that is, the set of activities and events designed for the dissemination of research results and scientific knowledge in general among people. Osborne and Monk (2000) provide an overview of key motivations for science communication. First, there is the utilitarian argument, which states that people involved will gain technical skills and knowledge that will be useful to them. Secondly, the economic argument posits that advanced societies require a technologically skilled workforce and, at the same time, the results of research funded by Goverment or other institutions must be explained to financers. Thirdly, the cultural argument claims that science represents a "shared heritage" and it should be recognized as a wide part of our culture. Finally, the democratic argument asserts that science affects most major decisions in society, therefore it is important that both politicians, managers and citizens are able to interpret basic scientific information. Dante was mainly motivated by the democratic argument, however even the economic argument can be considered relevant to his time as the emerging classes involved in economic activities needed to increase their knowledge.

Of course, even nowadays not only scientists, but also scientific journalists, writers and intellectuals in a broader sense contribute to reaching such goals (see e.g. Capozucca, 2017).

Dante Alighieri was very active as a science communicator, as he clearly outlined in the *Convivio* and *De Vulgari Eloquentia*. The pioneering methods he used to diffuse knowledge among people were not only aimed at involving non-academics, such as the emerging classes of merchants, traders, artisans and bankers, but they also included illiterate people.

In order to appreciate the extent to which the methods for science communication used by Dante in the *Divina Commedia* are modern and forward-looking, we propose two short passages from two contemporary well-known Italian writers. The first one was written by Umberto Eco in the weekly Italian magazine "L'Espresso" (April 28, 2005):

> A seasoned belief wants things to be known through their definition [...]. I am among those who believe that even scientific knowledge must take the form of stories. [...] our knowledge (even the scientific one, and not only the mythical one) is woven of stories.

The second one is taken from a letter written by the Italian writer Dino Buzzati, addressed to the intellectual, poet and engineer Leonardo Sinisgalli, founder and director of the magazine *Civiltà delle macchine* (house organ of Finmeccanica, the main Italian group of firms dealing with advanced mechanics, robotics etc.) where the letter was published in the January issue of 1956, p. 78:

> In *Civiltà delle macchine* the scientists and technicians speak as technicians and scientists as if they were addressing people of the same level, they don't smirk, they don't soften their voices, they never have the air of saying, "Things are much more difficult and complex, but for you, stupid and ignorant people ...". The normal rule of science popularization is that scientists stoop to readers'. Here it is the reader who rises.

As argued several times in this article, both these modern points of view can be found in Dante's pioneering dissemination work, thus confirming his role as modern science communicator and his enduring legacy 700 years after his death.

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Feature Articles

Spin Temperature and Dynamic Nuclear Polarization. From the History of Researches (1949–1983)

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Abstract. An attempt is undertaken to acquaint the reader with a history of research and applications of dynamic nuclear polarization (DNP) in the most concise form the main focus on the first three decades of DNP research, and the history of the discovery and development of multiparticle DNP and its relationship with the spin temperature approximation are outlined in some detail. The article emphasizes the role of such researchers as Anatol Abraham, Maurice Goldman, Michel Borghini, Thomas Wenckebach, Vadim Atsarkin, Boris Provotorov, Maya Rodak, Mortko Kozhushner, Levan Buishvili, Givi Khutsishvili. As far as possible, the contributions of many other scientists are considered. The establishment of a uniform temperature for nuclear spins due to the effect of spin diffusion was first proposed by Nicholas Blombergen in 1949. The content of the article is based on the bibliography available in the public domains, in particular on the memoirs of the research participants, and first of all on the materials of Atsarkin's 1978 review in Sov. Phys. Uspekhi and on the oral history of the development of the multiparticle concept of DNP effects, collected from the speeches of the participants of the Moscow seminar "Problems of Magnetic Resonance" in 2001. A simplified description of the effects of DNP and a summary of the history of their discovery is given in section "Introduction". The brief biographical data and portraits of participants in the DNP study are given in Appendix 1, and a selected bibliography on the problems of DNP and spin temperatures is given in Appendix 2. The bibliography divided into four sections according to the time and type of publication (I - historical research, memoirs; II – monographs, reviews; III - original publications 1953 - 1983; IV – some original publications of a later time, mainly during the transformation of DNP into an method for the implementation of nuclear magnetic spectroscopy and tomography in the interests of chemistry, biochemistry and medicine). The widespread use of DNP methods is evidenced, for example, by the fact, that by now company Bruker BioSpin has installed about 50 gyrotron based spectrometers for DNP operating up to 593 GHz worldwide to date.

Keywords: Magnetic Resonance, Dynamic Nuclear Polarization, Nuclear Spin.

1. INTRODUCTION

1.1. General remarks

The degree of polarization is determined by the relative excess among the spins of some type such a one with a lower energy of interaction with the magnetic field. Therefore, this configuration is stable. The lower a lattice temperature T_L is, the greater an excess of spins at the lowest quantum levels. The higher the induction of the magnetic field in which the sample is located, the higher the degree of polarization. The increasing of magnetic field's induction B_0 causes enhancement of polarization. This method of increasing polarization was once called the "brute force method". The increase in polarization with decreasing lattice temperature is also natural. That is why experiments with polarized nuclei at low absolute temperatures $T_L \leq 4.2$ K are so widespread. The thermal polarization P_{S0} regardless of T_L, for example, for spins $S = ½$ is equal to:

$$P_{S0} = \tanh\left(\frac{\gamma_S \hbar B_0}{2kT_L}\right) \tag{1}$$

Hereafter γ_S is the gyromagnetic ratio for electron spins, γ_I is the gyromagnetic ratio for nuclear spins, $\hbar = h / 2\pi$ is the Planck constant, k is the Boltzmann constant. The total paramagnetic moment of each type of spins $I=½$ with a total number N and gyromagnetic ratio γ_I and magnetic moment μ_I under conditions of interaction with lattice located at the absolute temperature T_L is equal (for $\mu_I B_0 << kT_L$) to:

$$M_0 = \frac{(\gamma_I^2 \hbar^2 N B_0)}{2kT_L} = \mu_I . P_I \tag{2}$$

However, it turns out to be possible, using magnetic resonance and other "pumping" methods, to create quasi-equilibrium configurations with anomalous depletion of the lower levels or even with an excess of spins at higher energy levels. It is dynamic nuclear polarization (DNP). Under conditions of continuous action of an alternating electromagnetic field with a frequency close to the ESR resonance of paramagnetic centers (PC), the Zeeman system of nuclear spins takes on a temperature T_I that differs from the lattice temperature, and therefore:

$$|M^*| = \eta M_0 = \frac{(\gamma_I^2 \hbar^2 N B_0)}{2kT_I} \tag{3}$$

where $\eta \leq \frac{\gamma_S}{\gamma_I}$ is "the enhancement coefficient" or enhancement of nuclear polarization. The dynamic nuclear polarization for nuclei with γ_I may be of the order of thermal electron polarization for PC with γ_S.

For an arbitrary spin number I, the corresponding values of the total magnetic moment and, therefore, the integrated intensity of the NMR signal are [Abragam. II.1961. Chapter VIII]:

$$M_0 = \frac{\left(\gamma_I^2 \hbar^2 N B_0 I(I+1)\right)}{3kT_L} \tag{2a}$$

$$|M^*| = \frac{\left(\gamma_I^2 \hbar^2 N B_0 I(I+1)\right)}{3kT_I} \tag{3a}$$

Anomalous polarization is characterized in conditions DNP (in the simplest case relatively high temperatures) by formula (3a), similar to (2a), but with the positive or negative *inverse temperature* of the nuclear Zeeman system possibly much more in absolute value than the inverse lattice temperature) $|T_I|^{-1} >> (T_L)^{-1}$.

Methods of dynamic polarization of nuclei employing ESR saturation began to develop in 1953. The mechanism of DNP was discovered and elementary magnetic resonance acts of one kind of electron spins S directly interacting with nuclear spins I was studied (*Overhauser effect (OE)* [Overhauser. III. 1953A;1953B; Carver and Slichter. III.1953]). The processes were discovered soon [Abraham M., Kedzie, Jeffries III.1957] with a saturation of the combined resonance $A_{(\pm)(\mp)}S_\mp I_\pm$ of the spins of two particles (an electron and one of the nuclei). In *the so called solid effect (SE)*, the result is achieved due to the microwave-induced forbidden electron-nuclear transitions $A_{(z)(\pm)}S_z I_\pm$, when each of the transitions *two spins*: S and I. The latter DNP mechanism is effective for solid dielectrics with a high density of polarized nuclei I (see below about nuclear spin diffusion) and was discovered by Abragam [Abragam, Proctor. III. 1958]. In previous formulas $A_{(i)(k)}$ are the components of hyperfine interaction tensor.

Later (1963-1967), the mechanisms were observed evidently with excitation of processes involving three spins (two electron and one nucleus, so called "electron-nuclear cross-relaxation" (ENCR) or cross-effect (CE)) through saturation on the wings of the ESR lines [Kessenikh et al. III.1963; Hwang and Hill. III.1966A; 1966B].

The DNP mechanisms involving many electron spins were discovered almost simultaneously (1962 - 1968). In such mechanisms of nuclear polarization, the so-called *thermal mixing (TM) and dynamic cooling (DC)* DNP occurs due to the transfer of *collective energy of electron spin-spin interactions, i.e., we are faced with an essentially multiparticle effects* [Abragam, Borghini. III.1962; Provotorov, Kozhushner. III. 1967]. This was immediately confirmed in the important experiments performed by Atsarkin, Mefed, Rodak [Atsarkin et al. III.1967], by Dutch physicists [Wenckebach et al. III.1968; 1970], and by French physicists. The detailed analysis of the relationship between TM and CE is given by Wenckebach (see [Wenckebach II.2016; IV.2017; IV. 2019A;2019B]. The first steps of discovery and mastering of these two late DNP mechanisms were considered in the article [Atsarkin, Kessenikh. I.2012]. If we talk about dynamic polarization through the excitation of transitions between mixed electron-nuclear states, then this effect is provided usually by *the nuclear spin diffusion* inside the array of matrix nuclei (see for example [Khutsishvili.III. 1954; Khutsishvili.II.1968]), although it also manifests itself on the nuclei of the substance dissolved in the matrix. It should be noted that the diffusion mechanism of nuclear spins in a solid-state matrix was first suggested by N. Blombergen before the discovery of DNP processes [Blombergen. III.1949].

When the dipole-dipole and exchange interactions in the system of electron spins of the paramagnetic centers (PC) are sufficiently large and their energy is at least comparable to the energy of effects leading to inhomogeneous ESR broadening, the effects of dynamic cooling (thermal mixing) with a multiparticle transfer of polarization from the electron spin-spin reservoir to the nuclear Zeeman system come to the fore in the DNP mechanisms.

2.THE THERMAL MIXING OR DYNAMIC COOLING. UNDER THE SIGN OF PROVOTOROV'S THEORY

The mechanisms of DNP and related phenomena discovered or predicted earlier remained in the repertoire of researchers and were successfully developed further. The Overhauser effect in nuclear spin systems with different resonant frequencies has become an almost routine method in nuclear magnetic resonance [Noggle., Schirmer. II.1971.]. Numerous studies in weak magnetic fields (up to the induction of Earth's magnetic field) have also been partially based on the Overhauser effect. The "solid effect" discovered by A. Abragam was successfully used for proton polarized targets. Separate studies of the three-spin ENCR (CE) mechanism have also been performed. However, the main direction of research on DNP and related phenomena in the 1960s-1970s was the study of the effects of thermal mixing of the nuclear Zeeman system with the subsystem of dipole-dipole interactions of electron spins discovered by Boris Provotorov.

Anyone who dealt with the problems of magnetic resonance in the 60s-70s will immediately remember what works [Provotorov. III.1961; Provotorov. III.1962] mean and what role they played in the development of this field of science.

The essence of Provotorov's theory is that there exist an inverse temperature and one more inverse temperature, which are the inverse temperatures of the Zeeman interaction and the dipole-dipole interaction. The concept of two temperatures is applicable both in a coordinate system rotating with the frequency of a radio-frequency field and in a laboratory coordinate system, and the schools of A. Abragam - M. Goldman and A. Redfield (see classical monographs [Goldman.II.1970; Abragam and Goldman.II.1982]) predominantly use a rotating system coordinates. The relationship between the inverse temperatures of the two reservoirs is determined by *Provotorov's equations*. Here is the record of Provotorov's equations in the classic monograph by M. Goldman in the laboratory system:

$$\frac{d\alpha'}{dt} = -W\left\{\alpha' - \frac{\Delta}{\omega_0}\beta\right\};\ \frac{d\beta}{dt} = W\frac{\Delta}{D^2}(\omega_0\alpha' - \Delta\beta) \qquad (4)$$

where $\Delta = \omega_0 - \omega$ (detuning the microwave frequency ω from resonance); $D = \gamma H_L$, – the average shift of the resonance frequency of each of the dipoles in the local field H_l (that is, in the field caused by neighboring dipoles); Factor proportional to the square of the amplitude of the resonant magnetic field $W = \pi\omega_1^2 g(\Delta)$ – the probability of transition between spin magnetic sublevels under the influence of a rotating magnetic field with amplitude [redacted], where $g(\Delta)$ – line shape function. The prime at a'= [redacted] in Goldman text corresponds to the Zeeman temperature in the laboratory system, while the author of [Goldman. II.1970] and his immediate colleagues consider most of the problems in a rotating coordinate system. The value $\beta =$ [redacted] is a inverse temperature of spin-spin reservoir introduced in Provotorov's works.

It should be stressed for formal thermodynamics that the revolutionary idea of Provotorov was to assign two temperatures to a single system of spins. This was theoretically a controversial innovation, especially because – except in the high temperature approximation—these two temperatures cannot be assigned to two separate energy reservoirs. J.Philippot – [Philippot. III.1964], considered the inverse Zeeman temperature as a chemical potential and the inverse dipolar interaction temperature as the real inverse temperature.

The method of two reservoirs proposed by Provotorov for a system consisting of one kind of spins turned out to be extremely fruitful. This method is suitable both for systems with several resonance lines, and for spin systems with spins of different types, with sharply differing values of gyromagnetic ratios. The case when the resonance frequency of spins with a low γ_I value is close to the width of the resonance line of spins with high γ_S is especially interesting.

Wenckebach in his article [Wenckebach. IV.2019B] points out the approximation of the fluctuating field introduced by Buishvili [Buishvili. III.1965 – 1966], Provotorov and Kozhushner [Provotorov and Kozhushner. III.1967; Kozhushner. III.1969] and subsequently further developed by Goldman [Goldman et al. IV.1974] — the case of generalized approach taking into account the interaction of nuclear spins with the whole dipole reservoir of electron spins. The version of the multiparticle DNP mechanism was the most popular in 1960s years. Note that Soviet researchers in the 60s and partly 70s accounted for at least 20% of that invisible college that dealt with the problems of spin temperatures and spin polarizations. Of those who were directly involved in the development and experimental verification of Provotorov's theory, mention should be made primarily of Mortko Kozhushner, Oleg Olkhov from the Institute of Chemical Physics, Maya Isaakovna Rodak, Vadim Atsarkin, Anatoly Yegorovich Mefeod, Sergey Morshnev et al from the Institute of Radio Electronics of the USSR Academy of Sciences (USSR AS), as well as Georgian physicists Givi Khutsishvili, Levan Buishvili, Mikhail Zviadadze et al.

The influence of both the above-cited and subsequent articles of Boris Provotorov on the development of theoretical and experimental work in the field of magnetic resonance in the 1960s and 1970s was very important and their significance has survived to this day. In 2001, the All-Moscow Seminar "Problems of Magnetic Resonance" under the direction of V.A. Atsarkin devoted his 158th meeting to the fortieth anniversary of Provotorov's first works (see the publication of the abridged transcript of the seminar [NMR, EPR and theory of condensed systems of magnetic dipoles. I. 2004]). Boris during the execution of his pioneer works was a young employee of the theoretical group headed by A.S. Kompaneets at the Institute of Chemical Physics of the USSR AS. Boris did not hide the fact that he was significantly influenced by the work of Alfred Redfield (USA) devoted to the saturation of magnetic resonance [Redfield. III.1955].

In continuation and development of the successes of French physicists, Provotorov's ideas were picked up and developed by Maurice Goldman and Anatole Abragham with Michel Borghini. Already before 1964, Abragam and Borghini published the results of the implementation of the Provotorov's idea on existence of the electron spin-spin (SS) reservoirs and the implementation of a new DNP mechanism. In Atsarkin's article [Atsarkin. 1978] the results of the application of Provotorov's theory included in the actually review work of Abragam and Borghini [Abragam and Borghini. II.1964] are formulated as one of the options for thermal mixing (compare the Fig.1): Under conditions of microwave pumping at frequency $\Omega = \omega_S + \Delta_p$ which saturates the ESR line with a small offset Δ_p from the resonance, the values of β_{SZ} and β_{SS} become quite different. Whereas the Zeeman subsystem is heated (β_{SZ} decreases but remains positive), the inverse temperature $|\beta_{SS}|$ value increases dramatically, reflecting strong change in the mean energy of the secular dipole–dipole interactions. The strong cooling of the SS reservoir is represented in Fig. 1 by a steep Boltzmann distribution of populations inside the SS band.

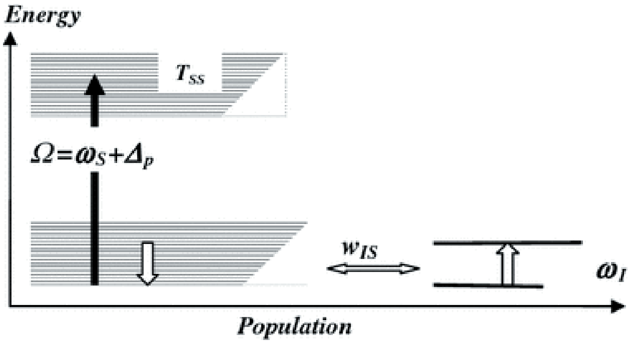

Figure 1. Diagram of the mechanism of induced thermal mixing according to Abragam – Borghini [([Atsarkin. II.1978]). See text for explanation.

In the frames of the quasi-equilibrium model, this phenomenon is explained by the transfer of the energy $|\hbar\Delta p|\bullet\hbar\Delta p$ to (at $\Delta_p > 0$) or from (at $\Delta_p < 0$) the SS reservoir at every act of quantum absorption. In the former case, particularly, the upper levels of the SS band are overpopulated and β_{SS} is negative, see Fig. 1. Here is a diagram of the induced thermal mixing mechanism. *Horizontal bars* reflect populations of corresponding energy levels in the electronic (*left*) and nuclear (*right*) systems. The *arrows* show transitions induced by the microwave pumping (*black*) and electron–nuclear dipolar interactions (*light*) .

We add, using the valuable remark of the head of the 2001 seminar V.A. Atsarkin (see [NMR, EPR and theory of condensed systems of magnetic dipoles. 2004]), that the French physicists a year before the appearance of the work [Provotorov. III.1961] seemed to have anticipated Provotorov's ideas about two energy reservoirs in the spin system. Atsarkin said: "Their experiment [Goldman and Landesman. III.1961] was carried out in such a way that in a weak field saturates the quadrupole resonance of chlorine isotopes (in paradichlorobenzene), thereby shifting the dipole temperature in the common dipole reservoir of chlorine and protons. Then the field was introduced adiabatically, and a signal of protons was enhanced (a kind of DNP). Goldman writes [Goldman.I.1996] – he carried out the experiment

– writes that when they got this result, they still doubted how all this could be explained, but there was L. Solomon, who explained this phenomenon to them in the mentioned way. I would not want a dispute about priorities to arise here, because in fact, I must honestly admit that Abragam dealt with spin temperature much earlier than all of us put together. And, of course, people absent here at the seminar, French physicist, they have the same memories. Therefore, when discussing priorities, one must understand all this. Of course, Abragam's laboratory at Saclay was the research engine of the spin temperature, and they thought a lot on this issue there".

French physicists evidently again proved to be at the forefront in mastering new approaches to the theory and method of DNP. But their Soviet colleagues in this time did not fall behind them significantly. The idea of Kozhushner and Provotorov about the direct contact of an SS reservoir with a nuclear Zeeman (IZ) reservoir was formulated in 1964 at a conference on magnetic resonance in a solid, held in Krasnoyarsk. The publication [Kozhushner and Provotorov.III.1967] was, however, delayed due to purely technical reasons, but its result was already known and even actually experimentally confirmed in the works of Rodak, Atsarkin, Mefe~~o~~d, Morshnev, Ryabushkin (see also [Kozhushner. III.1969]). Intensive research towards the approval of the two-reservoir theory of spin temperatures including the study of systems with number of lines in ESR spectrum [Atsarkin et al. III.1967] was initiated by Maya Rodak at the Institute of Radio Electronics of the USSR Academy of Sciences (USSR AS).

Let us to say a few words about the exceptional role of Maya Rodak in the development of Provotorov's theory. Magnetic resonance data make it possible to measure not only the Zeeman temperature, but also the spin-spin temperature, as was shown in the series of Provotorov's works. The integral intensity of the spectral line of magnetic resonance absorption serves as a measure of the Zeeman spin temperature (this is well known), and the shape of the contour of the magnetic resonance absorption line makes it possible to establish the spin-spin temperature (this fact in itself and the algorithm for such determination were the subject of works by Provotorov and his followers). But Rodak first developed a detailed theory of the experimentally observable and well-expressed effect (induced radiation in a part of ESR line) under saturation conditions in 1964 [Rodak. III.1964]. At the same year Provotorov and his disciple Mortko Kozhushner put forward the idea of thermal mixing of electron spin-spin and nuclear Zeeman systems. Due to this mixing, the inverse temperature of the nuclear Zeeman reservoir will tend to the inverse temperature of the electron dipole-dipole reservoir (dynamic cooling). Maya Isaakovna recalled in 2001 at the seminar "Problems of magnetic resonance" two conferences Colloque AMPERE in Ljubljana – 1966 and Colloque AMPERE in Grenoble – 1968, where she was a "scientific tourist":

"I brought to Ljubljana a small calculation from a series of physical consequences of Provotorov's theory. Here I should note that when Boris Nikitovich and I met at the beginning of 1963, I brought him a calculation just for cross-relaxation. It was simply striking that cross-relaxation draws energy from the dipole-dipole spin-spin reservoir. And in parallel with this, at saturation on the wing of the line, the same spin-spin reservoir is also touched, its temperature changes. These two processes can be somehow related and by changing the detuning and saturation on the wing, you can probably influence cross-relaxation. I was very happy when he accepted my calculation well. And then he immediately recommended my work at Soviet JETP, and we established good relations. But by 1966, even in the fall of 1966, when the Colloque AMPERE was in Ljubljana, we did not have an experiment. And all these four years, quite a lot of effects were predicted, which, from the point of view of the experiment, seemed not at all easy. Like Provotorov, I was confronted with mistrust all the time … For this reason, this trip to Ljubljana was very important for me, because I saw a completely different attitude of our foreign colleagues there. So, even on the eve of the congress, in the evening at such a cocktail party, where all the participants got to know each other, J. Jeener came up to me. He was a professor at the University of Brussels, a serious theorist of the Prigozhin school and at the same time a skillful experimenter … So he came up, said that he was interested in Provotorov's theory, read my articles, requested me to send them. It was Jeener who responded to Provotorov's very first publications with a large article entitled "Thermodynamics of spin systems in solids", which appeared in Phys. Rev. in 1964 [Jeener et al. III. 1964.], and he sent it to Provotorov as a preprint back in 1963, this proves his benevolence. In this article, he not only brilliantly outlined the physical foundations of Provotorov's theory from a general standpoint, but also presented the data of his experiments. These experiments were on harmonic cross-relaxation of nuclear spins in lithium fluorine (lithium fluoride) and it turned out, contrary to old ideas, that the tendency of cross-relaxation is by no means the establishment of a single temperature. The temperatures turned out to be different, and the more volatile spin-spin temperature changed most sharply.

After my report on the "Theory of Magnetic Resonance" section [Rodak. III.1967], Redfield approached me. I was told that his classic work 1955 was his graduate thesis. And by the time of our meeting he was already an internationally recognized scientist. As you know, in this classic work of his, he described magnetic resonance in a solid at strong saturation. Provotorov does not require saturation at all; he has a different criterion: the smallness of the alternating field in comparison with the local one. And Redfield, therefore, rightly, back in 1963, noted that Provotorov - these are literally his (Redfield's) words – "…filled the gap that existed in the theory of magnetic resonance in solids – threw a bridge across the gap." As far as I remember, in his famous book Abragam even writes directly that for H_1, for a variable field much smaller than the local one H_{loc}, the question remains, so the theory is by no means complete.

Abragam actually opened the congress. He made the first plenary lecture on the dynamic polarization of nuclei [Abragam. III. 1967], by the way, he did it in French, apparently in opposition to the Americans. Half of the audience did not understand him. Our entire delegation got to know him while walking around Ljubljana, it was facilitated by the fact that he knows Russian perfectly. Afterwards, we talked more than once, and at the end I dared to complete the task that Boris Nikitovich gave me, he was very angry with Abragam, and I decided to reconcile them. And so I just asked him why he had not responded in any way to the first work that Boris had given him in the fall of 1961 in the form of typescript. Abragam, as was typical for him, said that he did not understand anything. And then he noticed that he also did not understand and appreciate the classic work of Redfield at first. I would also like to remind you that there were several physicists who by this time, although they were not represented at AMPERE, worked in the same direction as Provotorov. They did conduct experiments, among them Goldburg, work in 1962 [Goldburg. III.1962]. All of them referred to Provotorov … Franz and Slichter - later works of 1966 [Franz and Slichter. III. 1966] and, of course, Goldman, who in 1964 in the French Journal de physique [Goldman. III.1964] introduced the term "Provotorov theory", and later used it many times.

So, by 1966, our foreign colleagues recognized Provotorov's theory and were very interested in it, at a time when, as we know, and as it was said at our seminar, many of our Russian colleagues had a lot of objections against Provotorov's theory, up to 1966».

In 1968 Maya Isaakovna had already brought to the AMPERE meeting the results of the experimental work she initiated. Rodak herself and their co-authors and colleague confirmed the effects expected from the results of Provotorov. Among the results reported in Grenoble were data on an explicit connection between electronic cross-relaxation (and hence the temperature of the spin-spin reservoir) and the dependence of the nuclear polarization enhancement on the frequency of microwave irradiation of a ruby sample, which has two well-resolved lines in the EPR spectrum at frequencies close to 10 GHz. For these data see works [Atsarkin et al. III.1967; Atsarkin et al. III.1968] (see Fig. 2)

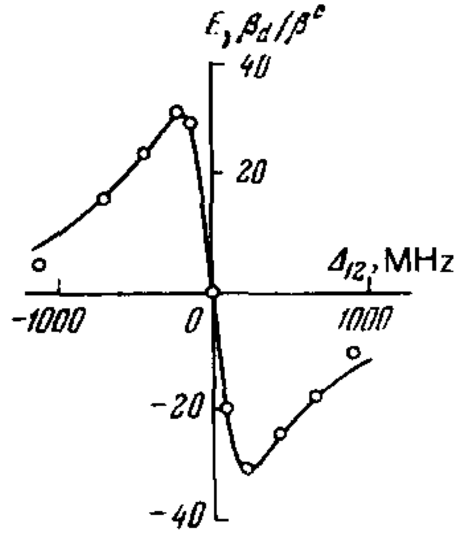

Fig. 2. Enhancement of polarization of ^{27}Al (η, here E_J,open circles) and degree of DDR cooling β_{SS}/β_L(here $\beta_d/\beta_{0,}$ solid curve) as a function of the detuning Δ_{12} between the two ESR lines involved in the cross-relaxation (one of them is saturated by the high-frequency field) [Atsarkin et al; III 1969].]. $A1_2O_3$ crystal with 0.03% of Cr^{3+}, T^o=1.9 °K, B_0=0.33 Tl.

A group of Dutch physicists began the DNP research [Swanenburg et al.1967]. Similar and very interesting results on induced thermal mixing of nuclear Zeeman reservoir with dipole electron-electron reservoir in DNP were obtained at 1968 and later. The future classic of DNP W.T. Wenckebach joined to this group and took part in verification of direct DC mechanism [Wenckebach et al.III.1968, Wenckebach et al.III.1969] too. They studied the so-called Tutton salts $ZnK_2(SO_4)_2$. $6H_2O$ with an admixture of paramagnetic copper-II ions, where the ESR spectra have a hyperfine structure due to the scalar interaction of electron spins with nuclei of isotopes $^{63.65}$Cu. These studies were continued successfully ([Hoogstraate et al. III.1973; Wenckebach et al. III. 1974] etc). An interesting result was obtained by comparing the DNP pattern in such samples at 14 K and 1.5 K. This experiment was also described in the review [Atsarkin. II.1978] (see Fig.3 from review). To some extent, the

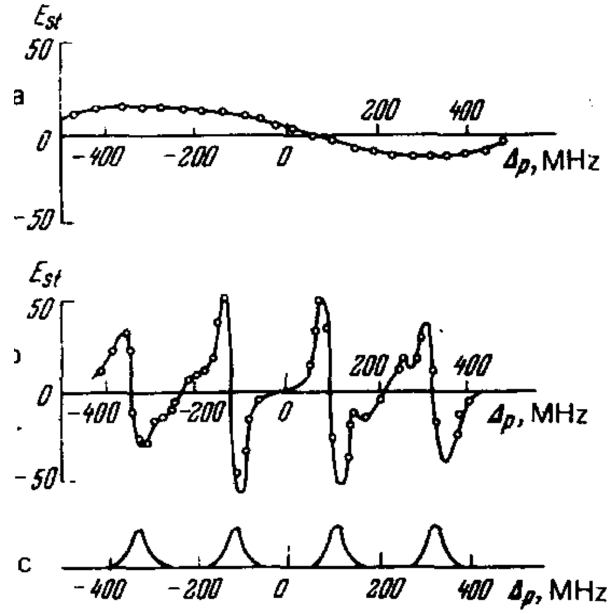

Fig. 3. Enhancement of polarization of protons η (here *Est)* in a crystal of $ZnCs_2(SO_4)_2 \cdot 6H_2O$ with 0.5% of Cu^{2+} as a function of the detuning Δ_p of the high-frequency field relative to the center of gravity of the ESR spectrum ($B_0 \approx 0.3$ Tl) [Wenckebach et al. 1974]: (a) T^o= 1.5 °K, (b) =14 °K, (c) ESR spectrum of the Cu^{2+}ion.

averaging of the obtained polarization over all possible dipole cross-relaxation effects as the electron spin-lattice relaxation time increases with decreasing absolute temperature, which is obvious from the figure, reminds of a similar effect in irradiated polyethylenes. Such an averaging (and there merge of maxima) leads to an effect that we call "spreading of the DNP maxima" [Kessenikh. et al. III.1964] and, of course, to a sharp decrease in the polarization enhancement.

3. SOME RESULTS OF EARLIER PERIOD AND FURTHER DEVELOPMENT OF DNP RESEARCH

3.1. Results of the first three decades of research on the effects of DNP. Leadership of French physicists and contribution of Soviet researchers

The first period of DNP research, in our opinion, ends by the early 1980s, but it makes no sense to indicate a more precise date than, say, the date of publication of a fundamental review [Atsarkin. II. 1978], and then a monograph [Atsarkin. II.1980], that, unfortunately was not translated into English. The 1970s, and early 1980s were also marked in the history of the DNP by the editions of more famous monographs [Goldman. II.1970] and [Abragam & Goldman. II.1982]. In the Soviet Union, by the 1960s and early 1970s, there was a fairly significant cohort of researchers of DNP and other phenomena studied in the spin temperature approximation. The works of the scientific schools in field of magnetic resonance in the Institute of Radio Engineering and Electronics, the Institute of Chemical Physics and the Institute of Physics of the Georgian Academy of Sciences made a significant contribution to the development of ideas about DNP and are wide known. The important results of applications of the DNP method to the study of nuclear reactions were obtained at the Joint Institute for Nuclear Research in Dubna. Research on DNP in the late 1960s-1970s and up to the mid-1980s continued to be most successful in France. The Saklay Nuclear Research Center has become a real Mecca for DNP specialists. As a remarkable example of the unification of scientific forces from different European countries under the auspices of the Saclay Center, we cite a link to the work of the ever-memorable for Czechoslovakia 1968 with the co-authorship of the Soviet specialist V.I. Lushchikov and Czech Odehnal on the DNP of protons in lanthanum-magnesium nitrate with a paramagnetic impurity of dysprosium ions [Odehnal, Loutchikov and Ezratty. III.1968]. In the late 1960s and early 1970s, unique research led by Abragam and Goldman (partially with the participation of the Dutch physicist Wenckebach). These researches led to the achievement of almost 100% polarization of fluorine nuclei in a single crystal of lithium fluoride, which made it possible to observe phase transitions of the spin system of nuclei into magnetically ordered states - nuclear ferromagnetism and nuclear antiferromagnetism [Chapellier. Goldman. Chau. Abragam. III. 1969; Jacquinot, Wenckebach, Chapellier, Goldman, Abragam. III. 1974] etc.

Japanese an American physicist Akira Masaike recalls at 2014 the role of Abragam's disciple Michel Borghini in the development of DNP methods for high energy physics [Masaike. I.2016]: «High energy spin physics began in early 1960s. It was pointed out that studying the spin dependent forces is one of the most important issues for particle physics. Therefore, it became an urgent need to measure the spin parameters of particle reactions. In order to realize such an experiment, it was indispensable to polarize the target protons…

The success of the dynamic polarization was amazing-event for high energy physicists, since it promised a new field of particle physics. At the International Conference on Polarized Targets held at Saclay in 1966, the known Australian physicist R. H. Dalitz pointed out that the polarized target may lead to especially illuminating information on three major areas in particle physics:

(i) High energy scattering where Regge-pole exchange is dominant.
(ii) Tests of time-reversal invariance for electromagnetic processes.
(iii) Hadron spectroscopy. Many resonant states had been observed for mesonic and baryonic states. In the attempt to classify and understand these hadronic states, the first need is for the determination of the spin and the parity for each state.

The *first experiment with the polarized target* was performed to measure the correlation parameter C_{nn} for p-p scattering at 20MeV by Abragam, Borghini, Catillon P., Coustham J., Roubeau P. and Thirion J. at Saclay in 1962 [A. Abragam et al. III. 1962]. The experiment was done with a polarized beam on polarized protons in LMN. The *first pion-proton scattering experiment* was performed at Berkeley (Bevatron) by Chamberlain, Jeffries, Schutz, Shapiro, and van Rossum in 1963 [Chamberlain O. et al. III. 1963.] In this experiment it was necessary to measure both angles of pion and proton in order to check the coplanarity, since the background from complex nuclei were enormous. Neutron transmitted through polarized protons are polarized, since neutrons with spin anti-parallel to the proton spin are scattered away. L. Shapiro at Dubna proposed to make a polarized slow neutron beam using an LMN filter in 1966.‡ Ishimoto et al. made a polarized neutron beam using an ethylene glycol filter at KEK in 1976 [Deregel et al. IV.1980.]. The method was used for parity violation experiments with polarized neutrons of 0.02 1 eV at Dubna [Dragichesku et al. III.1964], KEK and Los Alamos in 1980s».

3.2. Renaissance of methods of dynamic polarization at the turn of the millennium

Research on dynamic polarization continued throughout the 1980s and 1990s in the UK, USA, Switzerland, Japan, and elsewhere. However, in the USSR in the mid-1980s, these studies receded into the background, at the Lebedev Institute and in one of its heirs, the Institute of General Physics of the USSR AS, such studies were no longer resumed, at the Joint Institute for Nuclear Research they dropped to a minimum, at other Institutes they were occasional character. Due to the difficulties in the development of instrumental methods and the limited possibilities for the further growth of human and financial resources for fundamental research, these works began to gradually curtail.

Meanwhile, in the West, another revolution in experimental technology was taking place. Although gyrotron generators of millimeter and submillimeter electromagnetic waves appeared in the USSR, they were widely developed and applied only in Western Europe and in the USA. At the same time, a tendency arose to apply jointly the methods of DNP and sample rotation at a magic angle (MAS) to study a solid. The capability of getting higher induction of magnetic fields continued to grow steadily thanks to the application of superconducting solenoids available for the experiment (see the first DNP research with use of girotron microwave generator of terahertz frequencies in laboratory of Robert Griffin [Becerra et al. IV. 1993]), and the search for new solutions in preparing a sample with a paramagnetic impurity and in setting up the experiment did not stop. Methods for obtaining ultra-low temperatures (for example, using a solution of helium-3 in helium-4) were also improved. The last possibilities were also available in the USSR (in Dubna and Kazan, for example), but the fact is that in Europe and the USA all the numerous new achievements of experimental technology could be used jointly, while in Soviet laboratories they remained available separately. Therefore, at the next stage, scientists from Russia and Georgia could no longer be at the forefront of DNP, and they could only recall their past achievements in studying the problems of spin temperatures and DNP [NMR, EPR and theory of condensed systems of magnetic dipoles. I. 2004]. Along with the growth of experimental possibilities, the DNP method has a powerful and solvent consumer - high-resolution NMR of rare isotopes of organogenic elements carbon and nitrogen, in the first place, as well as of course NMR of protons and phosphorus-31 nuclei in biochemically important substations. Specialists in NMR of complex organic compounds were already backed by their customers – chemical enterprises, pharmaceutical companies and medical institutions.

In particular, the idea arose to use the instantaneous melting of a sample with enhanced in 10^4 and more times polarization nuclei using a laser and transfer the sample to a high-resolution NMR spectrometer (“dissolution DNP” [Ardenkjaer-Larsen et al. IV.2003]), Then, after the operations of multidimensional NMR spectra recording, which were usual by the 2000s, it was necessary to return the sample to the installation to obtain DNP and repeat this field cycling or “shuttle” procedure a sufficient number of times to accumulate signals with a good signal-to-noise ratio.

Finally, at the beginning of the new century, the research team of the Francis Bitter Magnetic Laboratory (FBML) at the Massachusetts Institute of Technology (USA) grew stronger. Since 1992 Robert Griffin has been the head of this laboratory. In 2004, an article [Hu, Griffin et al. IV. 2004] appeared in which the problem of the influence on the DNP mechanisms of the inhomogeneity of the distribution of paramagnetic centers was solved in the simplest and demonstrable way. The authors were the first to use TEMPO-type biradicals as a paramagnetic impurity to excite DNP. Since then, the arsenal of DNP mechanisms has firmly included the pairwise paramagnetic impurities – biradicals and, accordingly, the mechanism of electron-nuclear cross-relaxation (ENCR), briefly called the cross-effect (CE).

4.CONCLUSION

In conclusion, let us recall the main findings from Atsarkin's fundamental review concerning the general state of DNP research in the late 1970s and early 1980s (see also monograph [Atsarkin. II.1980] and, of course, the well-known monograph [Abragam and Goldman. II. 1982]).

1) The spin-spin reservoir model (Provotorov's two-reservoir model) was confirmed. Experiments on dynamic nuclear polarization played an important role in this.

2) A high and in some experiments almost one hundred percent nuclear polarization was obtained, which made it possible to study the dependence on the spins of particles of scattering by protons and deuterons of polarized beams of protons, neutrons and hadrons.

3) Extremely high nuclear polarization made it possible to observe magnetically ordered states of nuclear spins (nuclear ferromagnetism and antiferromagnetism).

We also point out that in early years only in the review and monograph by Atsarkin a special type of DNP mechanism - electron-nuclear cross-relaxation (ENCR) cross-effect (CE) - was discussed. Studies of this mechanism were not completed by that time. In the works of that time, the effects of the spatial inhomogenity of the distribution of paramagnetic centers in the specimen were neglected. Hence, it was unclear what the possible reason for the predominance of this mechanism ~~was~~. Also, in those years, and perhaps even later, the effect of a bottleneck in DNP, caused by long spin-lattice ESR relaxation times at low temperatures, was not studied in detail.

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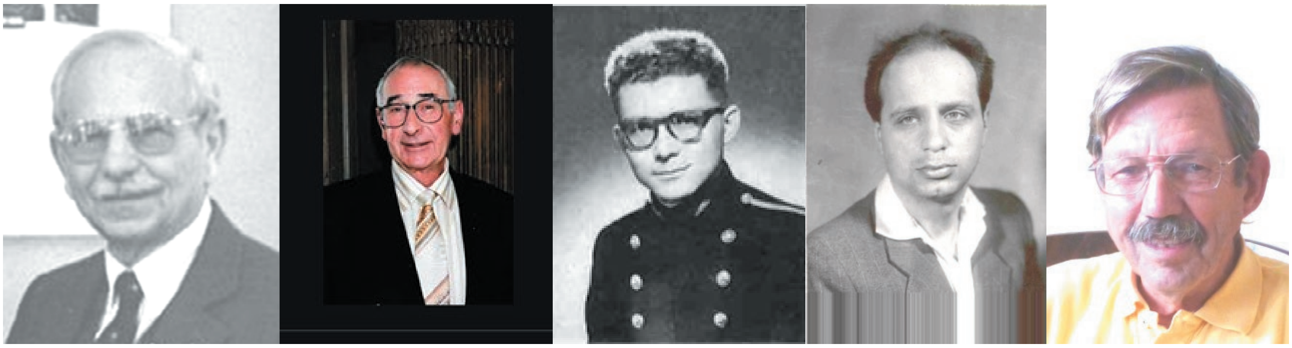
NOTES

1. Some authors believe that in this case there is no actual thermal mixing. However, we will adhere to the concept of V. Atsarkin set out in the text, according to which this is a variant of *induced* thermal mixing.
2. The transcription of the Russian surname "Lushchikov" ("Loutchikov") causes difficulties (see link below).
3. Japan: KEK-Ko: enerugi: kasokuki kenkyu.kiko: "High Energy Accelerator Research Organization". KEK exists from 1950.

APPENDIX I GALLERY OF PORTRAITS.
SOME LEADING RESEARCHES WHICH STUDIED THE PHENOMENA CONNECTED WITH SPIN TEMPERATURE AND DYNAMIC NUCLEAR POLARIZATION

From left to right: Alfred Overhauser (USA, 1925-2011); Charles Slichter (USA, 1929-2019); Carson Jeffries (USA, 1922-1995); Jean Jeener (Belgium, 1933-2016).



From left to right: Anatole Abragam (France, 1914-2011); Maurice Goldman (France, 1933); Michel Borghini (France, 1934-2012); Vadim Atsarkin (USSR (Russia). 1936); W.T. Wenckebach (Netherland, USA, 1943)

From left to right: Boris Provotorov (USSR (Russia). 1931-2001); Maya Rodak (USSR (Russia.). 1923-2015); Mortko Kozhushner (USSR (Russia). 1937-2020); Givi Khutsishvili (USSR (Georgia). 1921-1969); Levan Buishvili (USSR (Georgia). 1933-1996).

APPENDIX II.
SELECTED BIBLIOGRAPHY CONSIDERED WORKS DEVOTED INVESTIGATIONS AND APPLICATIONS OF DNP AND SPIN TEMPERATURE MODEL

References (Structured by topics and time)

i. Some abbreviations:

Journal of Experimental and Theoretical Physics: ZhETF – *Zhurnal eksperimentalnoy i teoreticheskoy fiziki [Soviet Journal of Theoretic and Experimental Physics – Soviet JETP]*

Advances in physical sciences: UFN – *Uspekhi fizicheskikh nauk [Soviet Physics Uspekhi ; later Physics Uspekhi]*

Journal "Solid state physics": FTT - *Fizika tverdogo tela [Sov.Phys. Solid State]*

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Feature Articles

Can Non-Recyclable Plastic Waste Be Made Environmentally Sustainable?

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Abstract. After death the fraction of living matter which is not biodegraded (shells, bones, corals, carbonaceous deposits) becomes environmentally sustainable. This is not the case for plastics so that these wastes should be either recycled or made environmentally inert and stored in secure repositories as a resource for future generations. Chemistry has offered different solutions to this problem, and each brings about advantages and disadvantages when compared to other options. One further possible route could consist in the enrichment of the plastics waste in carbon content ("carbonization"), in analogy with the production of charcoal from wood, but we hope to stimulate a debate about all the other possible routes among scientists and engineers in the involved fields.

Keywords: plastics waste accumulation and dispersion, circular economy, carbonization of plastics waste.

1. INTRODUCTION

There is a growing concern about the accumulation and dispersion of plastics waste.[1-4] Plastics have become indispensable for human life and for industry, but their high chemical stability makes most of them not completely degradable when dispersed in soil, fresh and sea water, and in air, unless it was properly designed to be biodegradable. Most plastics are obtained from fossil oil,up to about 10-12 % of the global production, according to an IEA report published in 2018.[3] Even using the best plastic waste management practices,[5-9] models predict that an important fraction of plastics waste (more than 22% in 2050) will accumulate,[10] especially in surface water and oceans, reaching a mass of 500±100 Mt in 2050.[3]

In oceans these wastes are able to create true plastic islands, that reached in 2018 an overall surface of $1.6{\cdot}10^6$ km^2, corresponding to about 6 times the surface of France, in the Pacific Ocean only.[3] Plastics waste degradation is accelerated by irradiation from the UV component of sunlight and by some mechanical wearing, with the continuous production of smaller and smaller debris, maintaining a substantial chemical integrity.[11-17] Energy recovery as heat, steam, or electricity by burning plastics wastes, that in 2016 represented the fate of as much as 40% of plastics waste,[3] is strongly discouraged because of the production of greenhouse gases and pollutants.[1-3,13] As it will be better detailed below, different strategies have been proposed for reusing and recycling plastics waste,[18] but its large fraction that accumulates in landfills and, what is much more dismaying, in surface waters and oceans, is generally not adequately considered. Although we are not pure specialists in the field, general common sense considerations led us to give our little contribution to drive the attention of the scientific community of chemists to this important problem in order to be allowed to say "I do my part of the job"

2. CIRCULAR ECONOMY AND PLASTICS WASTE

There are several different ways to define circular economy. According to the European Commission's Implementation of the Circular Economy Action Plan, approved in 2019, Circular Economy is:

> A system aimed at eliminating waste, circulating and recycling products, and saving resources and the environment.[19]

In a recent review focused on the plastics waste, it is stated that:[9]

> [the] concept of "circular economy" (CE) commonly refers to the "take-make-use-break-make" concept, where the main goal is to create economic impetus from the waste. It also enables the close-looping of product – waste – building block cycle.

However, as remarked for instance by Kümmerer *et al.*,[5] a complete recycling of plastics waste is practically impossible, unless plastics materials are purposely designed, and in fact a huge amount of wasted plastic residues is actually dispersed in the environment.

A closer look at natural living systems action to maintain environmental sustainable cycles can give some further insight in extending the concept of circular economy. Indeed, after completing their vital cycle, the fate of living matter "waste", besides a small quantity of volatile compounds, which are dispersed in the atmosphere, water or in soil, is mostly bio-recycled. Only a negligible fraction of it is burned as a consequence of natural events, such as fires caused by lightning, or by volcanic eruptions. However, a more or less important fraction of living matter waste is made of mineralized remnants. For instance, bones buried in soil last nearly unchanged for centuries, shells of aquatic animals are accumulated in lakes, seas, oceans floors and eventually become rocks, and coral colonies are able to build up entire islands. Finally, fossil carbonaceous deposits (coal, oil and natural gas) were originated by large amounts of living matter deeply sunk in soil. All these long-lasting living matter wastes share the important property to be environmentally sustainable, or inert. In conclusion, the natural ecology *is not strictly circular*, but the produced "waste", which is not recyclable is *environmentally sustainable*. Therefore, it is reasonable to ask ourselves why we cannot follow a similar route for the management of plastics waste, by proposing that all what cannot be biodegraded or used as feedstock for recycling[18] shall be treated to become environmentally inert and stocked in secure repositories, for future use as matter and energy resource.

3. OVERALL MANAGEMENT OF THE PLASTICS WASTE

Plastics often consist in one or more co-polymers along with several additives such as plasticizers, flame retardants, coloured agents, ultraviolet-light stabilizers, antioxidants that are difficult to separate during the recycle process leading to waste of time, money and material. The bottleneck of recycling is the preliminary separation and fractionation of the present compounds. Therefore recycling is often considered only at the atomic or molecular level with possible loss of the intrinsic properties of the products compared to those of the same products in the original waste. In January 2018 the European Commission announced a vision for Europe's new plastics economy substantially based on a new model of economy: from linear to circular economy. So the following commitments are considered to be implemented:

- all plastic packaging used in Europe must be reused or recycled by 2030;
- more than half of the plastic wastes must be recycled;
- plastic sorting and recycling capacity must be extended fourfold by 2030:
- some 10 million tons of recycled plastics are to be used for new products by 2025.

Mechanical recycling consists in transforming the plastic waste in raw material without any substantially modification of its chemical structure. It is the largely most adopted method in Europe but due to the presence of additives the process cannot recover more than 60-70% of the original wastes. The recycled materials find the same application as the original plastic wastes, in any sector of our today common life.

If separation and filtration of additives is omitted to save time and money, the obtained products are mainly used in mixed formulations applied to building works such as streets, bridges and other infrastructures. An alternative way is based on a selective dissolution of the plastic waste followed by filtration and evaporation of the solvent, but the real innovative process of recycle is based on chemical and biotechnological processes especially applied in the case of wastes of polyethylene terephthalate (PET), nylon and polyurethane. Among the chemical processes, pyrolysis consists in heating under vacuum which will result in a final product that contains a mixture of liquid and gaseous hydrocarbons.[4,20-23] De-polymerization can be obtained, at least for PET by means of microwave radiation.[24] Hydrogenation is a degradation that involves a treatment with hydrogen followed by heating, and in this case the products are olefinic hydrocarbons (ethylene, propylene, butadiene). Gasification is obtained by heating at high temperature (800-1600 °C) in the absence of air that results in a mixture of hydrogen and carbon monoxide. Chemolysis, glycolysis, methanolysis, amminolysis are all de-polymerisation processes that produce low molecular weight products, which can be used as reagents of multiple synthetic reactions and represent *an alternative route*, that results in the formation of chars (solid carbonaceous materials) and gaseous hydrocarbons. However, these solutions do not contribute to the "decarbonisation" of our society: the products are intended to be used as fossil fuels so contributing to further increase the anthropogenic greenhouse effect.

An innovative way of recycling is the enrichment of plastics wastes in C content. This process leads also to the recover of hydrogen and other heteroelements. The final products can be stored in the same sites where the raw material was extracted, such as exhausted carbon mines and fuel deposits, reproducing a stock of inert raw material to be used in the future.[25]

The main problem of this option is to have the proper catalyst able for the extraction of hydrogen and other elements similarly to what was obtained with the charcoal from the thermal treatment of wood. As recently reported, a catalyst based on mixed iron and aluminum oxides acting under a microwave field of 1000 W seems to be able to extract hydrogen from plastics.

Also biotechnological methods were successfully applied to the recycling of plastics.[6] The discovery made by a group of researchers of Carbios and of the Toulouse Institute of Biotechnology[26] of an enzyme present in the leaves' compost has opened a new way to recycle PET with very promising results as the recycled material has the quite same properties of the original waste.

In the 25th August 2020 issue of the *Chemistry World* weekly Kyra Welter reports that an International Group of research was successful in obtaining a polymer able to be recycled in principle for an infinite number of times, during which it was depolymerized and the obtained monomer was re-polymerized and so on.[27,28] Contrary to mechanical recycling that changes the properties of the material after few cycles, monomerization can potentially bring to materials that can be recycled whenever needed without any limit and keeping the same properties of the raw starting material. The problem in this case is that monomerization, if not purposely designed for plastic materials is not an available chemical process.

The chemical modification of the existing hardly recyclable plastics can increase their lifetime and face three different problems: first, in general polymers easily decomposed do not present good properties; second, the obtained products behave better in many common applications; and, third, if one wants to have good mechanical properties for the new product it is necessary to control the stereochemistry of the polymerization. The integration of this option in the actual recycling systems could be difficult because of the multifarious variety of the plastic waste, increasing the number of the possible components. This point can only be solved by a very responsible behavior of citizens and of local Institutions.

In general, plastics waste treatment can entail a net cost, which is to be supported in view of the unbearable environmental damage of accumulation and dispersion of plastics waste.[4] In line with a recent proposal about carbon taxes, this cost should be recovered from special *ad hoc* taxes "*similar to a value added tax (VAT) [...] such that end users pay the full costs.*".[29] Indeed general taxation usually is not equally charged and distributed among taxpayers.[30] Note that actually many megatons per year of plastics waste are exported from Europe, Australia and North America to China and other countries,[3,4] entailing transport costs that could be avoided if sustainable domestic treatments are properly implemented.

4. DISCUSSION AND CONCLUSIONS

In this paper we shortly outlined some dismaying problems connected with the management of plastics wastes, and particularly, of the large fraction of this waste which is accumulated untreated in landfills as well as in surface and sea waters, even if an increasing commitment is advanced to reuse and recycle plastics waste by the various available procedures.[1] Any effort and strategy should be performed to avoid the dispersion of plastics waste in air, waters and soil, by securing and controlling any phase of deposit, and especially in the long-lasting landfills.

As remarked, in view of the global warming problems, it should also avoided and restricted any treatment of plastics waste releasing CO_2 and other greenhouse gases into the atmosphere. In addition, the products of plastics waste recycling suitable as fuels should be preferably if not mandatorily used as feedstock for the chemical industry, so sparing mineral oil resources, or stored in secure repository.

A general strategy for the plastics waste management was proposed in the conclusions of a recent review about microplastics (tiny specks of plastics of micrometer size) by Hale *et al.*:[13]

> Most plastics are inexpensive to manufacture. Hence, there is little financial incentive to reuse them. To support a circular lifecycle, the upfront price of plastics must incorporate end of life costs. Currently, low volume plastic users and associated ecosystems bear a disproportionate burden (e.g., remote islands are now being littered with plastic debris). This environmental injustice echoes that of climate change and sea level rise. Landfills may be mined by future generations as resources become scarce and technologies improve. Optimization of such "dumps" into "repositories" is worthy of consideration. Political initiatives across borders should seek to accomplish these goals.

However, by considering the amounts and the rate of accumulation in landfills, in our opinion it is urgent to find also sustainable technical routes to transform the untreated or not recyclable plastics waste into "inert" matter which should be stored in secure repositories, such as exhausted mines of coal and other minerals, or impermeable quarries, as a resource for future generations. It could be objected that a large fraction of plastic waste is already environmentally "inert", as it lasts almost unchanged for hundreds or even thousands of years,[14] if properly saved. There are at least two reasons to propose a further treatment of plastic waste. First, the chemical nature of plastic materials makes their use as a feedstock in the future rather difficult and expensive, so that saving more homogenous materials would be preferable. The second reason is that the recovery of hydrogen, fluorine and other elements could help in reducing or even offset the cost of the treatment. In addition, the danger of a dispersion of degraded plastics in air and waters (especially as microplastics) would be contrasted, and the amount of the final waste could be reduced. All this can be obtained by the enrichment of the plastics waste in C content ("carbonization"). Examples of chemical processes that can achieve this result are discussed by Chen *et al.*[25]

If this proposal is considered unpractical or too expensive, we wonder whether there are there other ways to obtain environmentally sustainable materials from plastics waste.

In conclusion, on one hand, we urge scientists and engineers working in the field of plastics materials to think and propose practical solutions to this problem, and on the other hand we hope that a fruitful discussion about the ways to avoid accumulation and dispersion of plastics wastes will involve a larger scientific, technological, political and especially social public.

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Research Articles

Translations of Roscoe's Chemistry Books into Japanese and Hebrew - Historical, Cultural and Linguistic Aspects

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Abstract. This research studies two translations of Henry Enfield Roscoe's chemistry book of 1872 into Japanese (1873) and Hebrew (1929). Roscoe's original chapter on candle burning is presented, in which he manifested his attitude to chemical experiments. The Japanese and Hebrew historical backgrounds of the translations, as well as their cultural and linguistic aspects are discussed. Roscoe's relations with Japanese scholars are presented. The study moves between events in three countries, England, Japan and Israel. The importance and complexity of translation of science and its later results are discussed.

Keywords: translation of chemistry, Henry E. Roscoe, Japanese language, Hebrew language, candle burning.

TRANSLATION OF SCIENCE

Transferring knowledge from one culture and language into another target language that does not yet have a suitable vocabulary for the subject studied is an intensive human endeavor; creating new, appropriate vocabulary in order to look at the behavior of nature is the topic of this research. Inventing language in a new scientific discipline depends on contemporary knowledge in that field. Within the process of translation, the subject matter changes some of its features to suit the culture, the beliefs and understanding of the target people and their language. As Bensaude-Vincent stated in her article "The Language of Chemistry": *Language plays a key role in shaping the identity of a scientific discipline* (Bensaude-Vincent 2003).[1] The new thought and new terminology serve to augment the discussion and practices of the scholars and people using the target language. Later, the new terms go on to infiltrate and fertilize the daily language of the people. According to Montgomery,

> In rendering technical knowledge mobile between peoples and through the centuries, translation has been a crucial force behind both the creation and the continual refertilization of science (Montgomery 2000).[2]

Following are translations into Japanese and Hebrew of Roscoe's *Science Primers Chemistry* for school. Roscoe's explanation about the candle burning experiment highlights the historical and cultural background of the translations, the chemical terminology of the languages and what translation of science may lead to.

ROSCOE'S LIFE AND HIS EARLY CHEMISTRY BOOKS

Henry Enfield Roscoe (1833-1915) was an English chemist who spent a few years in the laboratory of Robert Bunsen in Heidelberg before returning to England in 1857. The same year he moved to Manchester, organized and revived the chemistry department of Owens College, which was incorporated into Victoria University in 1880. His main fields of research were Vanadium and photochemistry. After retirement from Victoria University in 1887 he moved to London and became a Member of Parliament, devoting time to several scientific committees. He was elected president of the Chemical Society in 1881 and was a founder-member and first president of the Society of Chemical Industry in 1881 (Roscoe 1906).

The early chemistry books by Roscoe were *Lessons in Elementary Chemistry* (Roscoe 1866) and *Lessons in Elementary Chemistry: Inorganic and organic* (Roscoe 1868). Roscoe's book *Chemistry* in the *Science Primers Series* was published in London by MacMillan addresses the following topics: Fire; Air; Water; Earth; Non-Metallic Elements; Metals; Results (Roscoe 1872). *Science Primers Chemistry* (1872) was a part of a series that included physics, geology, logic, botany etc.[3] It was also published in the United States of America by D. Appleton and Company, New York 1872. Editions of the book are still being republished. Those books have been translated into more than nine languages. The book *Lessons in Elementary Chemistry* was translated into Russian, Italian, Hungarian, Polish, Swedish, Modern Greek, Japanese and Urdu.[4] Translations of *Science Primers Chemistry* appeared in German, Icelandic,[5] Polish, Italian, Japanese, Bengali, Turkish, Malayan, Tamil[3] and Chinese.[6] As Osawa stated, *it is a proof to the excellence of the small book* (Osawa 1978).[7]

A short, original English text of Roscoe (Roscoe 1872) and its Japanese (*kogaku* 1873) and Hebrew (Oirbach 1929) translations are presented and studied in the following chapters. A copy of Roscoe's book in Japanese was given to the current author by Kida Akiyoshi in Kyoto in 2014; this led to the following research.

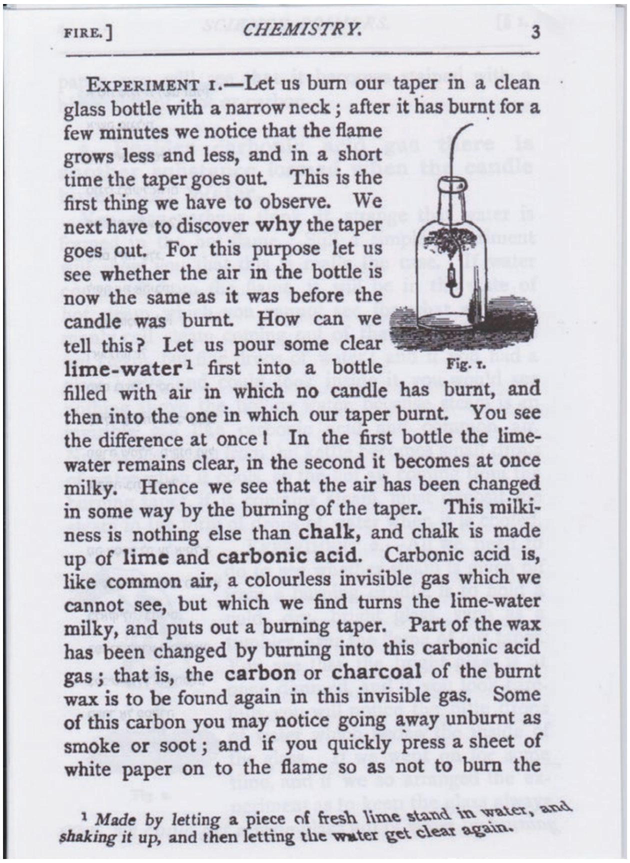
The experiment of the burning candle is the first experiment presented and explained by Roscoe and his translators. In addition to the observation of the chemical phenomena, Roscoe explained what a chemical experiment is and its importance.

ROSCOE: SCIENCE PRIMERS CHEMISTRY

The first chapter discusses the chemistry of air, water, earth and starts with fire.

Original texts from Roscoe's book:

> 2. What happens when a candle or a taper burns?
> The wax as well as the wick of the taper gradually disappears as the taper burns, and at last all is gone – wick, wax, and all. What has become of the wax? It has disappeared. Is it lost? So far as our eyes are concerned certainly it is lost, but so is the ship which sails away on the sea, and yet we know that the ship still exists though we do not see it; and so the lump of sugar appears to be lost when we put it into a cup of hot tea, and yet we know that the sugar is not really lost, because the tea is made sweet. Now we must look for the wax of our taper in another way; we must put a question to Nature for her to answer, and we shall always find that our question, if properly asked, is always clearly and certainly answered. We must



FIRE.] *CHEMISTRY.* 3

EXPERIMENT I.—Let us burn our taper in a clean glass bottle with a narrow neck; after it has burnt for a few minutes we notice that the flame grows less and less, and in a short time the taper goes out. This is the first thing we have to observe. We next have to discover **why** the taper goes out. For this purpose let us see whether the air in the bottle is now the same as it was before the candle was burnt. How can we tell this? Let us pour some clear **lime-water**[1] first into a bottle filled with air in which no candle has burnt, and then into the one in which our taper burnt. You see the difference at once! In the first bottle the lime-water remains clear, in the second it becomes at once milky. Hence we see that the air has been changed in some way by the burning of the taper. This milkiness is nothing else than **chalk**, and chalk is made up of **lime** and **carbonic acid**. Carbonic acid is, like common air, a colourless invisible gas which we cannot see, but which we find turns the lime-water milky, and puts out a burning taper. Part of the wax has been changed by burning into this carbonic acid gas; that is, the **carbon** or **charcoal** of the burnt wax is to be found again in this invisible gas. Some of this carbon you may notice going away unburnt as smoke or soot; and if you quickly press a sheet of white paper on to the flame so as not to burn the

Fig. 1.

[1] *Made by letting* a piece of fresh lime stand in water, and *shaking* it up, and then letting the water get clear again.

Figure 1. Candle burning experiment.[9]

> make an Experiment, and if this is properly made we shall never fail in the end to get the information we want.[8]
> […] and if you quickly press a sheet of white paper on to the flame so as not to burn the paper, you will see that it becomes stained with a black ring of soot or carbon.
>
> 3. Besides carbonic acid gas there is another substance formed when the candle burns, viz. Water.[10]

In the experiment described above the taper in the bottle was burnt, the fire was stopped, and (some of) the material disappeared from sight. The question Roscoe asked is what happened to the material of the candle, did it disappear completely? He addressed the question to Nature and the answer he gave after performing more experiments is that the carbon of the wax was turned into colorless carbonic acid and water. In a further experiment adding lime to the bottle in which the candle burnt it changed color to turbid white by forming calcium carbonate. The calcium of the lime (calcium hydroxide) reacted with the carbonic acid gas to produce calcium carbonate.

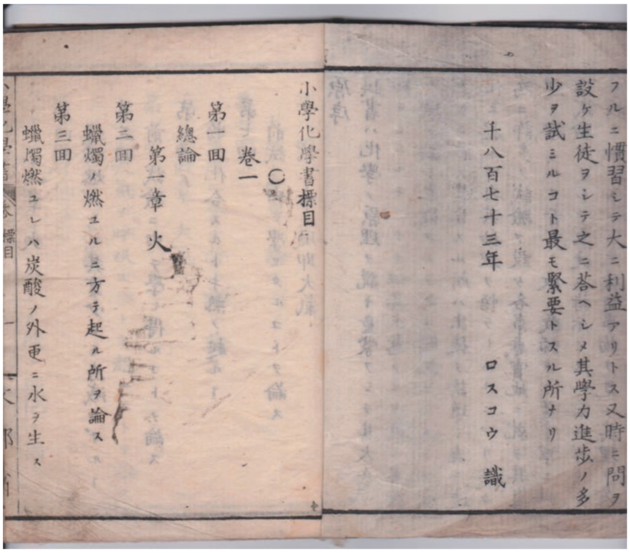
Roscoe didactically stresses the aim of the experiment and its result:

> We want to know what happens when a candle burns. We have learnt –
> 1. That a candle soon goes out if it be burnt in a bottle of air.
> 2. That a colorless invisible gas called **carbonic acid** is formed in the bottle after the candle has burnt.
> 3. That the carbonic acid gas comes from the carbon or soot contained in the wax.
> 4. That the **water** is also formed when the candle burns.[11]

The experiment gave answers to the question, thus Roscoe emphasized that chemistry is an **Experimental Science** [bold letters are in the original book]. However, Roscoe's statement that we shall always get the right answer if we ask the proper question is open to debate. The English text can be seen on-line in the Web.[12]

THE JAPANESE TRANSLATION OF ROSCOE'S TEXT

The Japanese translation of Roscoe's *Chemistry* book was published by the Ministry of Education 文部省 *mombusho* in 1873, translated by Ichikawa Seizaburou 市川盛三郎, titled *kogaku kagakusho hyoumoku* 小學化學書標目 *Chemistry Book for Elementary School*. The author of this article possesses a hand bound volume 1 of 1873. Its title page is presented in Fig. 2. There are many holes made by worms during one hundred and forty eight years since it was wood block printed, but still, in spite of the holes and the brownish background of the pages, it is clearly readable. The full translation was published in 1874 (Osawa 1978, Yamaguchi 2017). Japanese book can be seen on-line in the Web.[13]



フルニ慣習シテ大ニ利益アリトス又時ニ問ヲ
設ケ生徒ヲシテ之ニ荅ヘシメ其學力進歩ノ多
少ヲ試ミルコト最モ緊要トスル所ナリ
千八百七十三年　ロスコウ　識

小學化學書標目
○
巻一
第一回
總論
第一章ニ火
第二回
蠟燭ノ燃ユルニ方テ起ル所ヲ論ス
第三回
蠟燭燃ユレハ炭酸ノ外更ニ水ヲ生ス

Figure 2. Front page of Roscoe's book 十八百七十三年 ロスコウ 小學化學書標目 1873 Roscoe kogaku kagakusho hyoumoku *Chemistry Book for Elementary School.*

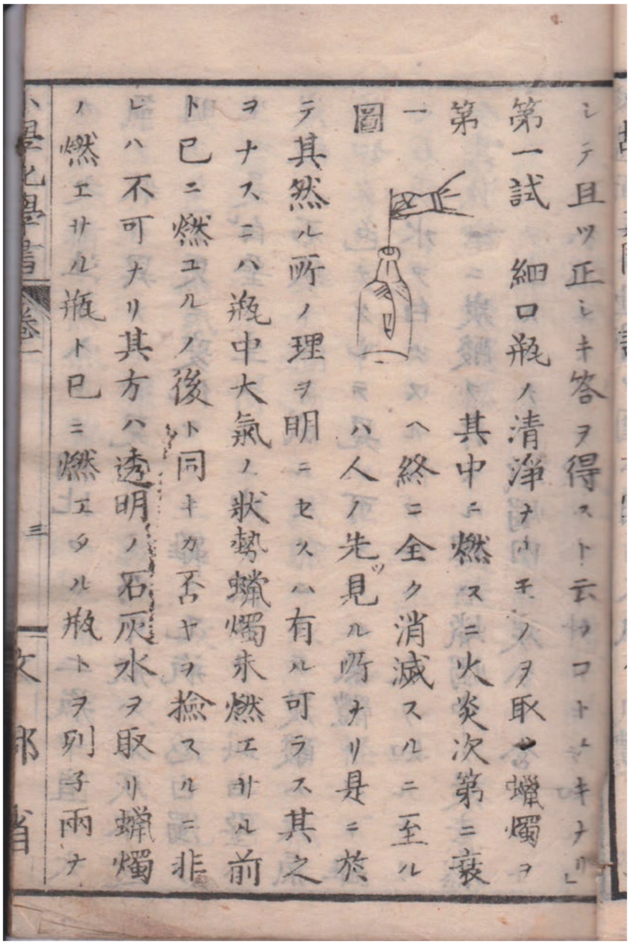
The experiment of candle burning in its Japanese translation is presented in Fig. 3. The figure of candle burning is the first of 36 figures, shown and discussed by Roscoe in his book. The Japanese translation of the English text is written in kanji, Chinese characters that convey meaning, and also in katakana, the phonetic square Japanese script.

This style is different from current use of kanji and hiragana, the phonetic cursive syllabaries. (B. Frellesvig).[14] The old writing style and some old characters will be discussed below. The pronunciation of the text in Romaji, adapted to today's writing and reading is presented in note.[15]

The Japanese text follows the English description in the paragraph on candle burning and running an experiment. According to Sato Shin it cannot be considered a good text by today's standards.[16] This is understood as we know that understanding chemistry and the language of chemistry have developed since 1873, examples follow.

THE HEBREW TRANSLATION BY PESACH OIRBACH, *HIMIA*, CHEMISTRY

Figure 4 presents Oirbach's Hebrew translation of Roscoe's arguments on the disappearance of things and



小學化學書　巻一　三　文部省

シテ且ツ正シキ答ヲ得スト云フコトナキナリ
第一試　細口瓶ノ清淨ナルモノヲ取リ蠟燭ヲ
第一圖
其中ニ燃スニ火炎次第ニ衰
ヘ終ニ全ク消滅スルニ至ル
ハ人ノ先ツ見ル所ナリ是ニ於
テ其然ル所ノ理ヲ明ニセスハ有ル可ラス其之
ヲナスニハ瓶中大氣ノ狀勢蠟燭永燃エサル前
ト已ニ燃ユルノ後ト同キカ否ヤヲ檢スルニ非
レハ不可ナリ其方ハ透明ノ石灰水ヲ取リ蠟燭
ノ燃エサル瓶ト已ニ燃エタル瓶トヲ列子兩ナ

Figure 3. Candle burning experiment in Japanese, 1873.

חימיה 6

חדשות בדבר טבעם ומהותם של הגופים הללו. אלא טרם נכָּנס
לתוך תורת החימיה של האויר, המים והאדמה, נחקור לדעת
את האש, מפני שהיא ידועה לנו פחות מהם.

I הָאֵשׁ

ב. מַה מִתְהַוֶּה כְּשֶׁדּוֹלֵק נֵר שֶׁל חֵלֶב?

החלב וכן גם פתילת הנר פוחתים והולכים בשעת
בעירתם עד תומם. מה נעשה בהם? נעלמו מן העין. האבדו
ואינם עוד? ודאי שאבדו מעינינו, כי הלא אין אנו רואים עוד
אותם. אך הן גם הספינה המפליגה בים נעלמת מעינינו מאחורי
האופק, על תרנה ועל מפרשיה, ואף־על־פי־כן אין אנו מפקפקים
במציאותה ובקיומה. גם גזר הסוכר שאנו נותנים בקָפֶה החם נעלם
מן העין, ואף־על־פי כן ברור לנו שלא הלך לאבוד ולא בטל
קיומו, כי הלא הוא שהמתיק את הקָפֶה. אל נא נשפוט
אפוא למראה עינינו לבד ונבקש את ישותו של הנר שנשרף
בדרך אחרת. הבה נציע שאלתנו לפני הטבע. והיה אם אך
שאול תשָׁאל כהלכה מצוא נמצא תשובה
ברורה ונכונה עליה. לתכלית זו נעשה
נסיון, וכשיהא זה עשוי בדיוק נמרץ תמָּצא
לנו תמיד התשובה הנכונה שאנו מבקשים.

נסיון א׳ — נכנים נר דולק בבקבוק
נקי של זכוכית בעל צואר צר. כעבור
שעה קלה נראה את השלהבת פוחתת
והולכת עד שתדעך ותכבה. דבר זה מיד
יעורר בנו את החפץ לדעת מדוע כבה
הנר. לתכלית זו נבדוק את האויר הנמצא

ציור א׳

Figure 4. Candle burning experiment in Hebrew, 1929.

the explanation about setting an experiment. The full Hebrew text of Experiment 1 on candle burning is presented in note 17.[17]

The Hebrew content follows faithfully the English original. It is written with somewhat elevated language, adding explanatory details that are discussed below.

In the following section, history, culture and linguistic aspects of the texts and the significance of its translations are presented and discussed.

HISTORICAL, CULTURAL, AND LINGUISTIC ASPECTS OF THE TRANSLATIONS

Historical background

In 1873 Japan and in 1929 Palestine-Israel, processes of the nation's revival evolved. The Japanese people shortly after Meiji Restoration of 1868, which moved the Tokugawa feudal rule and put the Emperor back to its seat, strived to reform and to unite the country. The Jews since late nineteenth century, started returning and renewing life in their ancient, Biblical motherland. These processes of nation building formed the need for updated scientific knowledge including chemistry. Hence, the motives to translate Roscoe's chemistry teaching book in both countries.

The Japanese translation of Roscoe's book

By 1873 the Ministry of Education of the new regime in Japan published the Japanese translation of Roscoe's *Science Primers Chemistry* book under the title *Chemistry Book for Elementary School*. How come the Ministry of Education decided to translate Roscoe's book, rather than a book by any other author? Three potential reasons are presented in notes.[18, 19, 20] However the Iwakura Mission is the only one of those three that might have had Roscoe's *Science Primers Chemistry* book.

Thus, Griffis holding Roscoe's book Elements in Chemistry, Inorganic and Organic, Kume Kunitake Diary emphasis on chemistry education during the travel of the Iwakura Mission, specifically during the visit in Manchester, at Roscoe's laboratory in Owens College, and Ichikawa's-Ritter's copy, might have influenced the Ministry of Education to order the translation of Roscoe's latest book.

Cultural aspects of the translations

Looking at the differences between the original English text and its Japanese and Hebrew translations, how faithful are they to the original text, are there any changes and what might be the reasons for these changes?

In order to explain the disappearance of the candle wax during burning, Roscoe presented two cases for the disappearance of items out of our sight and yet we are aware of their existence. Those cases serve to emphasize the fact that although the burning candle in the bottle has disappeared, its material is present in other forms. In the first case, a ship is going away and we do not see her any longer; nevertheless, we are sure of its existence. The Japanese translation tells about a ship, *fune*, 舟, that cannot be seen, without any additional information. The Hebrew translation broadens the description, telling about a ship with masts and sails, sailing beyond the horizon. This description is more figurative, adding more features to the original text.

The second case tells about material that disappears and actually changes its state. Roscoe told of a lump of sugar that enters into a cup of hot tea. The sugar disappeared, yet we are aware of its effect since the hot tea became sweet. This example tells about an English custom in which a lump of sugar is introduced into the tea. The Japanese translation of hot tea changed it into water, *mizu*, 水, not even hot water that has a different character *yu* 湯. The water becomes sweet therefore we are aware of the sugar dissolving effect. Since the Japanese do not sweeten their tea, in order to make the description closer to the Japanese experience, the English tea description is replaced by water. The Hebrew translator went even further: instead of hot tea the description is of a piece of sugar put into coffee. The reason for this change is not clear. Was coffee more popular than tea in Israel in 1929? There is no evidence for that. It can be said in general that the Hebrew translation uses a more elevated linguistic style than the English does, New Hebrew terms are used, and in an elaborate style. Oirbach wrote improved examples and a somewhat more detailed story. The vocabulary is widened, the style is new and the existing culture affects the terminology chosen for the translation.

There is a large time gap between the Japanese translation of 1873 and the Hebrew translation of 1929: understanding chemistry had progressed in the world between those almost sixty years. Moreover, the main difference is related to the translators. The Japanese translator had very little to rely on. Earlier chemistry translation in Japan were the seven volumes of *Seimi Kaiso*, Introduction to Chemistry, by Udagawa Youan published during 1836-1847 (Udagawa 1836-1847, Tanaka 1975, Siderer 2017). Udagawa Youan studied more than twenty books in Dutch on chemistry before he composed *Seimi Kaiso* (Dōke 1973, Azuma 2015, Siderer 2021). Perhaps Udagawa Youan's *Seimi Kaisou* books on chemistry might have been good sources for chemistry vocabulary if the translator Ichikawa Seizaburou had access to them. In distinction, the Hebrew translator Pesach Oirbach was born in Kishinev, Moldova, in 1877 and died in Tel-Aviv, 1945. He was a teacher, school principle, an author, researcher of nature and wrote books for teaching natural sciences. He immigrated to Palestine-Israel in 1908 (Wikipedia, 21.4.2021 Oirbach's biograph).[21]

Oirbach had the advice from Engineer M. Vinik (1886-1966) and other experts on the officially chosen and invented terms by a large group of scholars. Moreover, members of the Hebrew Language Committee in Mandatory Palestine-Israel had earlier studied chemistry in the countries they immigrated from, and they had already learnt chemistry in Russia and Germany (Simchoni 1949, Leibovitch 1951, Shapiro 1959). So when they came to coin Hebrew chemistry terms their scientific basis was much better than that of the Japanese translator Ichikawa. It enabled the Hebrew translator Oirbach to choose terms and to present a more elaborate translation. Nevertheless, we see in the next section that not all the terms Oirbach used has survived, and they were replaced by other, more appropriate terms. An example can be seen in Yizhak Klugai, a professor of the Technion, Israel Institute of Technology, who translated *General Chemistry* by Linus Pauling in 1965.

JAPANESE CHEMISTRY LANGUAGE AND TERMINOLOGY

The first English-Japanese chemistry dictionary was published in 1891 by Tokyo Chemical Society that later became the Chemical Society of Japan. It has English alphabetic order of the terms and the Japanese term opposite it. Some of the terms in the text above were modified during several changes of rules for writing kanji. During the years there were several committees that considered, omitted, added and modified kanji writings and kanji usage (Gottlieb 1995). The text under study itself has very few periods to mark the end of a sentence. Also, several of the syllables in the text like *ha, sa, su, ki, ku* are nowadays pronounced *ba, za, zu, gi, gu* respectively and are written with inverted commas (") at the right top of the character, not present in the old text, (e.g. は>ば、き>ぎ、く>ぐ) . Following are examples of few of the words written in kanji in the text and their modernized character (Denshi Jisho, 2017):

- 燈 (*tou*), lamp, an old kanji is replaced today by 灯 (*tou*) meaning lamp, and also in a combination: instead of 燈心 (*toushin*) it is now written 灯心 (*toushin*), meaning (lamp)/wick.
- 蠟燭 (*rousoku)* in the text, now an obsolete term, was changed into its variant 蝋燭 (*rousoku),* meaning wax, candle. The old term 蠟 (*rou*) having 25 brush strokes was modified to 蝋 (*rou*), having 14 strokes only.
- 氣體 (*kitai)* meaning vapor, gas, nature, atmosphere, was modified to 気体 (*kitai).* 気 (*ki*) stands for spirit, mind, air, atmosphere, mood. 体 (*tai*) means body, substance, object, reality. In this case both characters were modified: 氣 > 気, 體 > 体.
- 大氣 (*taiki*); 大 (*tai*) large, simplified letter 気 (*ki*) air, atmosphere. 大気 (*taiki*) atmosphere. In the text, talking about the atmosphere in the bottle.
- 石灰水 (*sekkaisui*), limewater, the term is formed by combination of three characters: 石 (*seki*) stone, 灰 (*hai*) ashes, 水 (*sui*, *mizu*) water.
- 造化 (*zouka*) creation/nature/the universe. 造 (*zou*) create, 化 (*ka*) change, take the form of, -ization. It is a word that is used in Shinto faith: 造化 の三神.[9]

Other chemistry related terms:[22]

- 燭 *(akari*) light, candlepower. Also written 灯 (*hi*)
- 炎上 (*enjou*) blazing/destruction
- 壓 (*ats*u) pressure. Its variant 圧 has 5 strokes instead of 17 in the old term.
- 環 *(wa, kan)* ring/circle
- 玻璃 (*hari*) glass / quartz (Buddhist term)
- 盃 (*sakazuki*) glass, cup
- 実地試験 (*jichchi shiken*) practical experiment, 実地 (*jichchi*) practice.

The language of chemistry is a specific topic in language planning. Chemistry and other sciences as well have to adapt to international rules for naming. The Japanese text of the chemistry book of the nineteenth century is written in a combination of kanji characters and katakana phonetic syllabaries. Current chemistry is written using Kanji, hiragana replace katakana; katakana is used for foreign names. The chemical elements and compounds have their Japanese names but chemical formulas and equations are written according the Western conventions. The Japanese names of the elements have either a Japanese word, e.g. iron, 鉄 (*tetsu*), or are written by katakana following foreign words, e.g. manganese, マンガン *mangan*, or use a combination of kanji character and katakana, e.g. iodine, ヨウ素 (*youso).*

HISTORY OF WRITING CHEMISTRY BOOK IN HEBREW

After the Hebrew people were exiled from their biblical Land of Israel the Hebrew language was not a daily spoken language. However, for many hundreds of years it was kept for reading the Bible, in prayers, and in writing and reciting religious services. Since the eighteenth century, when Jewish people started returning to and living in the Land of Israel then under Ottoman (Turkish) rule, that was followed by the League of Nations British Mandate for Palestine (1920-1947), there arose a gradual need to define, revive, restore and renew the spoken and written Hebrew language. In 1890 the *Committee of the Language* was established in order to plan the language. In 1953, after the 1948 Independence of the State of Israel, the *Committee* became the Academy for the Hebrew Language (Iair G. Or 2016).

The editorial preface by the publisher of the Hebrew translation of Roscoe's book presented his motivation in the beginning of the book:

> Textbooks for the studying youngsters and for everyone who seeks knowledge, this is a need that is felt every day in the life of the Hebrew school in the Land of Israel and outside of it....Chemistry book is the first in this series of books.…"*Daat*" [knowledge] books are meant not only for the younger ones needs, but also for the people, mainly those young ones who devote their days to labor and the evenings for studying (Torah). (Oirbach 1929, pp. 3-4).[23]

A study by Noach Shapiro (1900-1964) surveyed the historical development of the Hebrew terminology for chemistry. It shows the long various periods in which scholars of the Hebrew language paid attention to Nature and gave names to physical materials. Shapiro pointed at biblical names of six metals that remained unchanged in modern time, those are gold, silver, copper, iron, tin and lead; he added names of different forms of gold and silver. Shapiro emphasized that chemistry teachers among

Jewish immigrants to the Land of Israel in the 1920s felt the absence and need for Hebrew vocabulary and teaching books (Shapiro 1959, Shapiro1 1964). Leibovitch explained the discussion, dispute and agreement between the members of *Vaad HaLashon* committee and the committee for chemistry terms of the chemistry teachers organization concerning the construction of the names of chemical compounds (Leibowitch Y. 1951).[24] Interestingly, those metals of the ancient world have their names in Chines-Japanese kanji, since they were also known in ancient Asia. Those are: gold 金, silver 銀, copper 銅, iron 鉄, tin すず (金属 metal, old time's name) and lead 鉛 Sugahara 1990). Hebrew terms were also changed, as is shown in Table 1. Names of the elements in Hebrew carry biblical names in Hebrew, e.g. iron, ברזל *barzel*, or foreign name in Hebrew, like neon, ניאוןneon, or modified foreign names to adapt to the Hebrew sound, e.g., manganese, מנגן *mangan*.

THE STYLE OF THE LANGUAGE OF OIRBACH'S *HIMIA*

Looking at titles of the scanned page on Fig. 4: title 1. **הָאֵשׁ** The fire (*HaEsh*) and the following subtitle ב. מַה מִתְחַזֶּה כְּשֶׁדּוֹלֵק נֵר שֶׁל חֵלֶב? What is presented when a candle of tallow is burning? (*Ma mitchaze keshedolek ner shel chelev?*) Those two lines and the last sentence in that paragraph are written with what is called *nikud*, punctuation, small marks that serve as vowels to facilitate and clarify the reading. Most of the rest of the text is written without those. Currently the *nikud* is used mainly for writing children books, poetry, and to help reading words that might have more than one meaning when it is differently pronounced and punctuated. In the text, the words **בַּקָּפֶה** in the coffee (*bakafe*) and **הַקָּפֶה** the coffee (*hakafe*) are also punctuated, to make their reading clear.[25] (Incidentally, an interesting panel discussion for the Japanese term for "coffee" is described in: Okayama Dutch Learning Group, 2016).[26]

Hebrew terms in Oirbach's translation were those accepted by the committee for chemistry terms near *Vaad HaLashon*, Language Committee. The list has some eighty one terms. Fifty two of the terms are in use today, by chemists and by the general public. Twenty nine terms are not in use today, replaced by other words. A few examples of terms not in use today and their recent alternatives are listed in Table 1 and discussed below.

This author does not remember using the word retort or *abik* while working in the chemical laboratory, even though one finds them in the Hebrew dictionary, meaning a tool for distillation; the foreign name *kolba* was used. The Concise Hebrew Dictionary by A. Ben Shoshan *HaMilon Ha'ivri HaMerukaz*, (HaMilon Ha'ivri HaMerukaz, 1972) divides the literary sources of the vocabulary presented into five categories: the Bible, Talmud and ancient scrolls from Judea Desert, medi-

Table 1. Oirbach's *Himia* terms translated from English and German[27] and recent Hebrew terms.

English	German	Hebrew term in *Himia*	Hebrew reading	Hebrew term today	Hebrew reading
Retort	*Retorte*	אביק	*abik*	אביק	
Lunar Caustic	*Höllenstein*	אבן-התופת	*Even-HaTofet*	כסף חנקתי	Kesef chankati $AgNO_3$
Alkali	*Lauge*	בורית	*Borit*	1.אלקלי 2. בסיס	1. alkali 2. basis
Galena(Lead Sulphide)	*Bleiglanz*	ברק עופרת	*Brak Oferet*	עופרת גופריתית	Oferet gofritit PbS
Marsh-gas	*Sumpfgas*	גז ביצה	*Gaz bitza*	מתאן	Methan CH_4
Fire damp	*Grubengas*	גז מחפורת	*Gaz machporet*	גז מיכרות: מתאן, פחמן דן-חמצני, פחמן חמצני, חמצן, חנקן	Gaz michrot: Mines gas: CH_4, CO_2, CO, O_2, N_2
Prussian Blue	*Berlinerblau*	כהל ברליני	*kohel Berlini*	כחול פרוסי	Kachol prussi $Fe^{III}_4[Fe^{II}(CN)_6]_3$.
Magnesium	*Magnesium*	מגנון	*Magnon*	מגנזיום	Magnezium
Ferrycyanide	*gellbes Blutaugensalz*	מלחת	*Malachat*	פריציאניד	Ferricianid
Gold leaf	*Blattgold*	רדי זהב[01], עלי זהב	*Radey zahav*, *Aley zahav*	עלה זהב	Aley zahav

eval literature, new literature since the Haskalah (Age of Enlightenment) including press and spoken language and terms from foreign languages.[28] The word "Borit" comes from the Talmudic literature, a name of a wild plant that contains Saponin, which dissolves in water to produce emulsion with oil, like soap. Borit is also a synonym for soap, *sabon*. Hebrew uses the foreign word gas, pronouncing "gaz", but gives the chemical names of methane and other gases for "Gaz Bitza" and "Gaz machporet". Prussian blue is translated today to "Kachol prussi", meaning Prussian blue. Magnesium and Ferrycyanide are pronounced similar to their foreign names, not using Oirbach's term. "Aleh Zahav" meaning golden leave remained in use today.

ROSCOE'S INFLUENCE ON CHEMISTRY STUDIES IN JAPAN

How much was Roscoe involved in the education of Japanese chemists? After Meiji Restoration, 1868, the Japanese authorities invited foreign teachers to teach chemistry. The ministers felt the need to start modern technology and modern industry for the benefit of the people and the country's prosperity. Moreover, they sent students to study abroad, supported by the Ministry of Education. A few students were sent to Owens College, Manchester. Other students were sent to University College, London.

The connection of Japanese scholars with Roscoe did not end with the 1873-1874 translation of *Science Primers Chemistry*. In his autobiography Roscoe mentioned his Japanese chemistry student Sugiura Shigetake 1877-1879, and Y. Kiraga 1878-1879 and wrote with appreciation his recollections of his Japanese students.[29]

The Japanese who studied abroad were influenced by what they saw, by the cultures they were exposed to and what they learned in foreign countries. After their return to Japan some of them were appointed as school teachers, others had government and prefectural administration positions and a few others became professors in the new universities. They introduced what they have absorbed into the scientific thought, teaching and administration of their own country.

Roscoe had an influence on Japanese researchers and chemistry education since 1872 and later. The translated chemistry books were edited and republished in later editions. Osawa lists eleven books related to Roscoe between the years 1874-1889. There were several translators and reviewers, and different books titles. Kaji mentioned Ira Ramsen's popular book *The Elements of Chemistry: A Textbook for Beginners*. Originally published in 1887, it included a classification of elements based on valency but made no mention of the periodic law. Kaji listed its Japanese translations.[30, 31, 32]

FURTHER PROMOTION FROM THE WEST TO JAPANESE CHEMICAL EDUCATION

Western chemistry education in Japan was achieved from two directions. The Japanese students who studied abroad and returned to Japan after spending some months or years in European countries or in America. After returning to Japan they could get positions in industry, in governmental and prefectural administration, or as teachers in schools and in the developing universities. Gradually they developed the Japanese chemical and technological terminology. There is a list of more than one hundred and fifty Japanese who studied chemistry abroad during Meiji era 幕末明治海外渡航者総覧 *Bakumatsu Meiji kaigai tokō-sha sōran* (published 1992). The list includes their birth year, the countries they went to, the year(s) of their return to Japan, the positons they held after returning.[33]

Another source of studying chemistry came from the foreign chemistry teachers in Japan and the translation of their courses by their Japanese students. Discussed above are Griffis and Gratama. Other teachers like William Robert Atkinson, a British chemist who taught at *Tokyo Kaisei School* during the Meiji Period,[34] and the American teacher D. Penhallow teaching in Hokkaido, included in their curriculum to their Japanese students local Japanese materials and what is available in the Japanese environment for teaching natural sciences, including chemistry and botany. Penhallow later wrote about his experience in Japan.[35]

David Wright in his thorough study on *Translating Science, the Transmission of Western Science into Late Imperial China 1840-1900*, looks at various aspects of translation (Wright 2020). Wright explains the subtitle Transmission. His study concentrates on China, but the more general view he developed can apply to Japan, even though the methods and approach for translation science were different between China and Japan. In China, in the official translation offices, the translation was carried out by collaboration between Chinese translators and a Western scholar, whereas the Japanese translated mainly by themselves. Wright looks at translation model of transmission that "includes the political, social, economic and historical matrices within which the translation is conducted, affecting not only the nature of the process but also its velocity and acceleration."[36] We have looked in this study into aspects of culture, linguistic, history and politics. After Meiji Restoration, there was a change from the reluctance of the Edo era feudal rule to the spread of Western knowledge among the common people, and there evolved the recognition of the new regime in the need for modern knowledge in order to modernize Japan. That recognition caused the support for translation and publishing a basic chemistry teaching book by the Ministry of Education in 1873, as a part of the general new rules for basic education.

HIGHLIGHTS OF WORLD RECOGNITION IN CHEMISTRY IN JAPAN AND ISRAEL

For early twentieth century international collaboration on nomenclature see *Japan's Engagement with International Chemistry (1900-1930)* (Kikuchi 2017). A Japanese-English Chemistry Dictionary presents the current rules for Japanese chemistry nomenclature (Gewehr 2007). The Japanese Society for the History of Chemistry (*Kagakushi Gakkai*) published a comprehensive Encyclopedic Dictionary on the History of Chemistry that is now available to the Japanese readers (Encyclopedic Dictionary 2017).

Both Japan and Israel developed prosperous chemical industries. There have been Nobel Laureates from both countries in recent years, their history deserves another study.

In 2016, the superheavy synthetic element 113, discovered by Kyushu University professor Kosuke Morita, head of a team of scientists, was officially given the name nihonium, after the Japanese name of their country Nihon or Nippon. Nihonium is the first element to be discovered in an Asian country. It might be said that the translation of chemistry from the West into Japanese in the nineteenth century, and all the educational, theoretical, experimental, technological and industrial chemistry that followed, culminated into these Japanese achievements.

SUMMING UP

The practice of chemistry and chemistry teaching were involved in carrying knowledge across continents from the eighteenth to the twentieth century. The chapters above presented the transformation of the original English book in chemistry (1872) from England to America, then to Asia in 1873, to Finland in Northern Europe, and to the Middle East in 1929. Within the translations new terminology for the specific discipline chemistry was required and invented. Later authors of chemistry texts used the old terms, changed them, or rejected and replaced them with more appropriate terms. Those translations were the building blocks for increasing the number of people that have access to chemistry and its theory, to deepen modern knowledge in the respective countries, supporting modern approach to chemical manufacturing industry.

What conclusions the reader can draw from this comparison as a whole? This comparison reflects the dynamics of language movement between people and thru time. This is true for languages in general, and in this study for the case of the science of chemistry in Japan and Israel.

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NOTES

1. Bensaude-Vincent **2003**, 174.
2. Montgomery **2000**, 270.
3. Roscoe's Autobiography **1906**, 151.
4. Roscoe Autobiography **1906**, 150.
5. Icelandic Efnafrædi **1879**, cited by Morris **2015**, 174.
6. Chinese translation of Roscoe's *Science Primers Chemistry* **1886**. Received with thanks from Chang H. 2017.
7. Osawa **1978**. The book size is 18x12 cm, including 16 drawings of experiments in 35 folded pages. *Mr. Roscoe's Chemistry* 羅斯珂氏化学 was co-translated by Sugiura Shigetake 杉浦重剛 and Miyazaki Michimasa 宮崎道正, one of the first three graduates of Tokyo University Department of Chemistry (Kikuchi, correspondence of 23 April 2017). This is probably a translation of Roscoe's 1866 book *Elements of Chemistry* (Osawa **1978**).
8. Roscoe **1872**, 2.
9. Roscoe **1872**, 3.
10. Roscoe **1872**, 4.
11. Roscoe **1872**, 5.
12. Roscoe's *Science Primers Chemistry* book is available on line at: https://archive.org/details/bub_gb_8RsNAAAAYAAJ/page/n3/mode/2up

13. The chemistry book in Japanese is available on line at: https://archive.wul.waseda.ac.jp/kosho/ni04/ni04_03127/ni04_03127_0001/ni04_03127_0001.html
14. Frellesvig **2011**, 14 sec.1.1.2.5 *manyōgana;* pp. 158-162 sec. 6.1.2, Kana (hiragana, katakana, hentaigana). The hiragana and katakana developed as reduced shapes of *man'yōgana*. Kanji letters as they are read phonetically, not logographically. There are two sets of fifty kana letters: hiragana stands for the cursive set, katakana are the square shaped letters set. Mixed writing of kanji and kana started in the middle of Heian period (794-1185).
15. Professor Shin Sato is acknowledged for providing the following Romaji transcription for reading the text of the candle burning experiment in Fig. 3.
    小学化学書巻一 *shougaku* (orally: sho-gaku) *kagakusho kan ichi*
    p.1
    Roscoe shi sen
    Ichikawa Morisaburo yaku
    [Skipped]
    The Japanese description of the candle burning, Experiment 1:
    Dai ichi shi hosokuchibin no seijou naru mono wo tori, rousoku
    sono naka ni moyasu ni (sono naka de moyasu to) kaen shidai ni otoro e
    shimai ni mattaku shoumetsu suru ni itaru wa hito no mazu miru tokoro nari.
    Kore ni oite sono shikaru tokoro no ri wo akiraka ni sezuba aru bekarazu.
    Sore wo nasu ni wa binchuu taiki no jousei, rousoku imada moezaru mae
    to sude ni moyuru no nochi to onaji ki ka inakaya wo kensuru ni arazareba fuka nari. Sonohou wa toumei no sekkaisui wo tori, rousoku no moezaru bin to sude ni moetaru bin to wo narabete hakari na
    p.4
    Gara kore wo sosogi irete ai kurabureba ni binchuu tadachi ni taiki
    no jou no koto naru wo miru beshi. sunawachi koubin wa sekkaisui
    toumei ni shite sara ni henka sezu to iedomo otsubin wa tachimachi
    hakudaku wo shouzu. kore hakua wo shouzuru ni yorite shikaru nari.
    kono hakua wa tansan to sekkai to yori naru mono ni shite, tansan wa
    taiki no gotoku iro wa naku shite miru bekarazaru kitai nari to iedomo
    sekkaisui wo shiroku suru sei aru nite kore wo shiru nari.
    ima, sono binchuu ni tansan no son suru ri wa rousoku chuu no tanso mo
    ete kore wo shozuru nari. rousoku nai ni tanbun wo fukumu koto
    wa sono ichibu moezu shite kemuri to nari masaru nite shiru beku, mata
    sumiyaka ni hakushi wo motte honoo ue yori ooi asseba
    sono tanso kuroki wa to narite tsuku wo miru nari.
    dai san kai
    rousoku moyuru wa tansan no hoka sara ni mizu wo shouzuru koto.
16. Sato S. comments in correspondence of 1 April 2017.
17. The full text of Experiment 1 on candle burning is presented in Hebrew:
    נסיון א' – נכניס נר דולק בבקבוק נקי של זכוכית בעל צוואר צר. כעבור שעה קלה נראה את השלהבת פוחתת והולכת עד שתדעך ותכבה. דבר זה מיד יעורר בנו את החפץ לדעת **מדוע** כבה הנר. לתכלית זו נבדוק את האוויר הנמצא עתה בתוך הבקבוק, למע[ן] דעת אם עודנו כזה שהיה מתחלה, טרם דלק הנר בבקבוק. וכיצד נבדוק? – ניצוק מעט מי סיד צלולים* בשני בקבוקים, שאחד מהם יהיה מלא אויר אשר נר לא דלק בו, והשני יהא זה שהנר דלק בו וכבה. מיד נכיר את ההבדל: בבקבוק הראשון יהי המים **צלולים** ובשני – **עכורים**. מכאן ראיה, כי ע"י בעירת הנר חל שינוי באויר. מהו שנוי זה – תסביר לנו עכירות המים (מי הסיד). המים לא נעכרו אלא על ידי קירטון, וזה עשוי **מסיד חי ומחומצה-פחמנית**. החומצה הפחמנית היא גז חסר צבע, זך ושקוף וסמוי מן העין, ממש כאויר, אלא שהוא עוכר מי סיד צלולים ומכבה נר דולק. נמצא שחלק מן החלב נהפך והיה לחומצה-פחמנית, כלומר, הפַּחְמָן או הפחם הכבוש בחלב שנשרף נתגלגל בגז סמוי מן העין. חלק מפחם זה נראה לנו בדמות עשן או פיח: אם שקע לרגע פסת ניר לבן בשלהבת הנר נראה, כי הניר לא יאוכל באש אלא כעין כתם שחור ועגול של פיח יוטל בו. ופיח זה אינו אלא פחם שלא הספיק להשרף.
    ג. מִלְּבַד חֻמְצָה-פַּחְמָנִית מוֹלִידָה הַבְּעִירָה עוֹד חוֹמֶר אַחֵר מָיִם.
18. Potential source for the awareness of the Japanese Ministry of Education was the copy of the book ordered to Japan by William Elliot Griffis (1843-1928), an American graduate (1869) of Rutgers University at New Brunswick, who was invited to teach chemistry to youngsters in remote Fukui in Japan and started teaching there in May 1871. In a letter of 15th July 1871 to his sister Margaret in Philadelphia he wrote: "… Send one copy of Roscoe's Chemistry, latest American edition, by mail, it costs $1.50…" (Yamashita 1965). Uchida mentioned Griffis reading to his students in Fukui from a copy that used to belong to Kusakabe Taro, who studied in Rutgers and died there. When Griffis came to Japan shortly thereafter, he brought with him Kusakabe's personal effect. It is possible that after reading to his students in Fukui from Kusakabe copy on 12th July, Griffis

wrote the request cited above. After moving to Tokyo in January 1872 Griffis was involved in preparation of curriculum for a new university and in 1872-74, he taught chemistry and physics at *Kaisei Gakkō* (the forerunner of Tokyo Imperial University).

The three chemistry books that are noted by Griffis in the Library of Fukui are:

1. H.L. Roscoe, Lessons in Elements of Chemistry: Inorganic and Organic (New York, 1868).
2. W.A. Miller, Elements of Chemistry: Theoretical and Practical, 4th edition (London, 1867).
3. J.E. Bowman, An Introduction in Practical Chemistry, Including Analysis, 5th edition (London, 1866) (cited by Uchida p. 247, and by Edward R. Beauchamp p. 33, both in Edward R. Beauchamp and Akira Iriye Eds. in *Foreign Employees in Nineteen Century Japan*, 1st edition **1990**.

After returning to America Griffis published and lectured about Japan. His book *The Mikado's Empire*, 1895 edition, had a new edition in 2007 and printed on-line in 2015.

19. The Iwakura Mission Diary, the Mission's accumulated oral and written information. The statesman Iwakura Tomomi (1825–1883) headed the Iwakura Mission (December 1871-1873) that was sent to America and Europe in order to introduce the new Japanese regime; to renegotiate the commerce treaties of 1859; and to observe and study Western systems of law, commerce, transportation, education and others ways of life in the countries they visited. In his Diary (*Nikki*) of the Iwakura Mission its historian Kume Kunitake observed chemistry studies and industry in several places. He wrote and emphasized the need of the Japanese to learn the fundamentals of chemistry (In Liverpool, Kume True Account 2002, vol. II p. 143). While in Manchester during 4th-9th October 1872 the Iwakura Mission visited the chemistry laboratory in Owens College (Kume True Account 2002 vol. II chapter 29 pp. 190-191, Japanese pocket edition 2009 p. 182). It is possible that the Mission's visitors have collected Roscoe's *Science Primers Chemistry* book during the visit and sent it to Japan. The book first edition was already mentioned in a letter by Huxley dated 11th April 1872 (Roscoe 1906, p. 148).
20. Ichikawa Seizaburou assistance to Hermann Ritter.

    The translator Ichikawa Seizaburou (alas Morisaburou), later changed his name to Hiraoka Morisaburou (1852-1882), studied at University College London between 1866 - June 1868 when he had to return to Japan due to the fall of the Bakufu regime. He became a teacher of higher education for the Ministry of Education and an assistant of the German chemist Hermann Ritter (1827~1874). Ritter taught chemistry and physics in Osaka and Tokyo in English, and succeeded the Dutch chemist Koenraad Wolter Gratama (1831-1888). Gratama stayed in Japan for five years from 1866 to 1871 and taught chemistry in Osaka chemistry school, *seimikyoku*, which was built in 1869. Osaka chemistry school was closed in Meiji 3, 1871 and moved to Kyoto. Ichikawa saw Roscoe's earlier chemistry book that was used by Ritter. Ichikawa moved to Tokyo on May 1873 and about that time he made the translation that was published in 1873 and 1874 (Osawa 1978). Ichikawa went again to England and was in Manchester Owens College studying physics during 1877-8 and 1878-9 and published physics book under the name Hiraoka Morisaburou.
21. Oirbach assisted the renowned poet, translator and editor Chaim Nachman Bialik (1873-1934) when he came to Kishinev to write a report, and later famous poems, about the Kishinev Pogrom that took place there in 1903. Thanks to Dr. Ruhama Albag and Agnon House for the information concerning the acquaintance between Oirbach and Bialik.
22. 金箔 *kinpaku* Golden leaf. In Kanazawa city– *kinpaku* production survives to-date.
23. Oirbach, **1929**, pp. 3-4.
24. Leibowitz **1951** Vol. 18 (ח”י) p. 104-105.
25. Adding punctuation in order to distinguish between הקָפֶה *hakafe* meaning 'the coffee' and הַקָפָה *hakafa* meaning 'surrounding'.
26. The suitable characters for the word "coffee" were searched by the scholar Udagawa Youan (1798-1846), when he introduced the word コーヒー ko-hi- and 咖啡 written by *ateji*, phonetic pronunciation of the kanji, not its meaning. He wrote 27 kanji combinations and 6 katakana combinations before he chose the combination that satisfied him:

    コーヒーの当て字
    各比伊, 歌兮, 迦兮, 可喜, 哥非乙, 哥兮, 骨喜, 架非, 咖啡, 黒炒豆,
    可非, 膏喜, 茶豆湯, 架菲, 豆の湯, 和蘭豆, 加非, 雁喰豆, 過
    稀, 可否, 香湯, 滑否, 滑韭, 骨非, 茶豆, 架啡, 煎豆湯
    コオヒー□ コーシー□ コーヒィ□ カウヒイ□ コヲヒ豆□ コツヒイ
27. Oirbach English and German in Word List. The Hebrew terms in this list were mostly accepted by *Vaad HaLashon* based on the suggestion of M. Vinik (1886-1966). pp. 111-114.

28. המילון העברי המרוכז *HaMilon Ha'ivri HaMerukaz*. Page facing inside front cover 1972.
29. Roscoe, 1906, pp. 113-115. Sugiura Shigetake 杉浦 重剛 (1855-1924), In Britain (1877-1879), and Y. Kiraga (1878-1879.) Roscoe wrote: "…Since that time I have had several letters from my Japanese friends and pupils, some of which are interesting:" A letter from Y. Kiraga 1878-1879, at the Technical Institute, Asakusa, Tokio, Japan, October 1st 1886. Kiraga (formerly known as Sadam Takamatsu) apologized for not writing since he returned to Japan and happily announced his appointment as a chair of Technical Chemistry in the established Technical Institute by the Ministry of Public Instruction, devoting himself to the chemistry of dyeing. Kiraga sent to Roscoe a copy of his "maiden work" on guidance of dyeing for the dyers.
30. Osawa, Table 2, pp. 857 (75), **1978**.
31. Osawa, vol. 29, No. 10, p. 72-79, (854-861), **1978**
32. Kaji **2015**, p. 287; notes p. 300 no. 13, lists several translations of Roscoe and Ira Remsen's books. p. 301 no. 15. Ira Remsen, *The Elements of Chemistry: A Textbook for Beginners*, London: Macmillan, **1887**.
33. After returning from studies abroad, Japanese chemists various field of research include: academic research on fertilizer, agricultural chemistry, applied chemistry, beer brewing, biochemistry, cement making, chemical education, chemistry of sake brewing, common salt production, components of oriental drugs, copper engraving- lithograph, dyeing, electrochemistry, gunpowder production, industrial gas, industrial pharmaceutical production, inorganic chemistry, internal medicine, isolation of glutamate – *ajinomoto* (the element of taste), manufacturing of window glass, meat-making, metallurgy, minting, paint manufacturing, paper making engineering, physical chemistry, plant physiology, oil and sugar manufacturing, organic chemistry, wine brewing, and more**.**
34. William Robert Atkinson, a British chemist. Atkinson stayed in Japan during September 9, 1874 - September 8, 1878 and February 3, 1879 - July 4, 1881. He taught agricultural studies at *Tokyo Kaisei School* and Faculty of Science, University of Tokyo. He concentrated on Natural produce of Japan, e.g. studying the brewing method of sake (Japanese liquor) and the dye that is used for dyeing cloths, indigo blue dye, that he called "Japan blue".
35. David P. Penhallow *Japan*, McGill University Magazine 3 (April **1904**), pp. 88-103.
36. Wright, **2000,** Chapter 12. The Translation of Western Science. P. 403.
37. Kikuchi **2017** p.17.

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Research Articles

First Steps: Synthetic Ammonia in the United States

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Abstract. The synthetic ammonia industry, originally based on Fritz Haber's 1909 invention of a catalytic high-pressure method as scaled up by Carl Bosch at BASF, grew globally in the years following World War I, based on the processes of Brunner, Mond & Co. (Britain), Luigi Casale (Italy), Georges Claude (France), and Giacomo Fauser (Italy). The ammonia was mainly converted into ammonium sulphate fertilizer. There was less impetus in the United States for taking up these developments, because America relied on ammonia from its by-product coking ovens and coal gas works, sodium nitrate (Chilean nitrate) from South America, and calcium cyanamide as manufactured by the American Cyanamid Company. Even when a synthetic ammonia industry started up in the United States, it was on a smaller scale than in Europe. However there emerged just before the Wall Street Crash two major producers of synthetic ammonia, Allied Chemical and Du Pont. This article presents a historical reconstruction of the early synthetic ammonia industry in the United States focusing on the 1920s, paying particular attention to Du Pont's success, which relied on the ammonia process of Casale. Standard accounts suggest that Du Pont acquired Casale technology as the result of a straightforward business acquisition. However, the situation, as shown here, was far more complex. Du Pont had to engage in aggressive litigation in order to acquire rights to the Casale process in 1927.

Keywords: synthetic ammonia, Casale process, Niagara Ammonia Company, Allied Chemical, Du Pont.

INTRODUCTION

The 1920s were the take off years for science-based chemical industry in the United States. This is nowhere better illustrated than in the realm of coal-based synthetic organic chemistry, in which American firms drew on German technology to master and even excel in the production of colorants and, later, novel products, such as pharmaceuticals, derived from the dye intermediates.[1] The need to catch up with Germany, and to invent new products for new needs, such as the automobile industry, stimulated unprecedented research and development. The growth and diversification of the US chemical industry was tremendous, and included development of novel polymers, and expansion at firms engaged in electrochemical technologies. Some of the most significant developments drew on catalyzed, high-pressure industrial chemistry, following introduction of the Haber-Bosch synthetic ammonia process by BASF in 1913.[2] In this area of chemical technology, however, the United States was a late starter. Relative to the synthetic dye industry, the parallels, particularly with imitation of German dye technology, are more difficult to discern. This article will explore the several reasons, as well as the early development of the US synthetic ammonia industry.

The extraordinary success of the Haber-Bosch synthetic ammonia process in contributing to Germany's industrial effort in the production of munitions during World War I was widely acknowledged.[3] After the cessation of hostilities, BASF was not prepared to license the process, preferring instead to use it as a bargaining tool in attempts to gain access to various international tie-ups and also to control the global market in nitrogen fertilizer. This pretention to world leadership, however, spawned imitators, and rivalry.

Here we recount two related but distinct stories—insofar as they concern similar technologies and their transfers across the Atlantic from Europe—in the development of the large-scale American synthetic ammonia industry. One concerns the Allied Chemical & Dye Corporation, whose process originated with one of its predecessor firms, and was similar in operating conditions to the Haber-Bosch process. The other describes the Du Pont corporation's entry into synthetic ammonia, based on the acquisition of the processes of Georges Claude (France) and Luigi Casale (Italy) that were worked at around four times the pressure of the Haber-Bosch process. It was the Casale process that enabled Du Pont to become an American technology and market leader in high-pressure chemistry. For this reason I focus mainly on Du Pont's entry into what was also a completely new venture, based on a novel technology that relied on sophisticated engineering expertise, and that was decidedly removed from synthetic dyes. The background involves the transfer in 1927 of Casale technology from an ambitious but struggling start-up to Du Pont, which planned a major scale up of ammonia manufacture, mainly for the fertilizer market, particularly of ammonium sulphate.

At the outset, it should be pointed out that massive transatlantic technology transfer from Europe, whether of dyes or of high-pressure chemistry, by whatever means, was part of a pattern that impacted on the entire American chemical industry during the 1920s. Much of this encounter has been well analysed, including the mergers and acquisitions, and the partnerships with Europan firms, that led to the rapid growth of major corporations. Shortages of vital chemicals as a result of the cutting off of imports from Germany during World War I provided the impetus for diversification, and for the foundation of start-ups that mastered many features of synthetic organic chemistry, often using information gleaned from sequestered German patents. In some cases, the war enabled the survival and expansion of struggling firms. In others, firms denied access to intermediates made in Europe drew on processes that under peacetime conditions were not economically viable. What is absent in many cases from the historical record are accounts of the complexities of how this industrial transformation was achieved at a more detailed level. This account is an attempt to compensate for the lacunae in one specific sector, though it serves as an outstanding indicator of what was achieved overall by 1930. Its contemporary relevance to the historian resides in the oft neglected focus on the technologies involved; they are often overlooked in accounts that are more focused on business history.

As is frequently the case in the pursuit of industrial history, archival sources are limited, often long ago lost in fires and explosions or discarded following mergers and acquisitions. Fortunately there is adequate material to guide us at the Hagley Museum and Library, in Wilmington, Delaware, in examining an important part of the early history of synthetic ammonia in America. We are aided by the few articles on developments in the United States published between 1930 and the early 1950s, particularly since records of technical progress at Du Pont are mainly absent.[4] While the fragments of history may not make a whole, they can certainly aid our understanding of how the synthetic ammonia industry evolved in America.

Among the handful of novel, successful ammonia processes developed in Europe around 1920, the most widely adopted, and successful, was that of the Italian chemist and entrepreneur Luigi Casale, who requires a brief introduction.

LUIGI CASALE

Luigi Casale (1882-1927) studied chemistry at the Royal Polytechnic of Turin (Reale Politecnico di Torino), where he graduated in 1908. His teacher was Arturo Miolati (1869-1956). During 1909-1912, Casale worked under Michel Fileti at the Turin Institute of Chemistry, where he received his postgraduate degree in 1910.[5] Publicity surrounding the successful outcome of Fritz Haber's work at Karlsruhe on a high-pressure synthetic ammonia method no doubt stimulated Casale's interest in physical chemistry and gas reactions at high pressures. During 1912-1913, Casale undertook research in physical chemistry under Walther Nernst, in Berlin, and kept in touch with the latest developments in the thermodynamics of gas reactions, as well as their commercial utility. After returning to Italy, Casale undertook research in organic chemistry, as assistant of Miolati, during 1913-1915, while retaining an interest in synthetic ammonia.

During World War I, after studies on war gases, Casale worked at industrial concerns, including the electrochemical firm IDROS (Società IDROS; it derived its name from idrogeno and ossigeno), founded on 19 February 1916, to supply hydrogen to the Italian navy for dirigible and other aerial balloons, and oxygen for oxyacetylene welding. IDROS was located in Terni, Umbria, close to Italy's main steelworks company. Hydroelectricity provided an inexpensive source of power for IDROS. Around 1917, while at IDROS, Casale began to study the synthesis of ammonia from its elements. By 1920, assisted by the American physicist and inventor René Lepreste (1876-1941), Casale had invented a high-pressure ammonia process. The main inventive concepts included application of far higher pressures (at up to 850 atmospheres) than used in the Haber-Bosch process (around 200 atmospheres) and a converter made of ordinary steel that survived the huge stresses. As with the Haber-Bosch process, unreacted gases were recirculated to the converter through a closed loop. The yield of ammonia was around fifteen to eighteen per cent, compared with five to eight per cent for the Haber-Bosch process. The use of ordinary steel in Casale's converter was made possible by the forced cooling action on the inner casing of the converter shell of the mixed reactant gases, hydrogen and nitrogen, that were introduced under pressure (Figure 1). As a result of the very high pressure, the converter required a less active iron catalyst than needed for the German process. Surrounding the inner catalyst chamber was a concentric heat exchanger, providing heat for the incoming gases. Overheating in the region of the catalyst was prevented by allowing some ammonia to remain in the recirculated gases, thereby slowing the reaction down.

The process, for a given output, used smaller equipment than employed in the Haber-Bosch process. This also applied to the French process of Georges Claude, of Air Liquide, which was worked at 1,000 atmospheres. Moreover the energy requirements in the Casale and Claude processes were not much greater than required in units that were operated at considerably lower pressures. A major difference with Claude's high-pressure process was that the latter, as a result of its design, which involved passage of reactant gases through a series of converters (without recirculation), required special steels in order to withstand the severe operating conditions. One important advantage of the two eponymous very high-pressure processes of Casale and Claude was that they gave directly anhydrous ammonia, in contrast

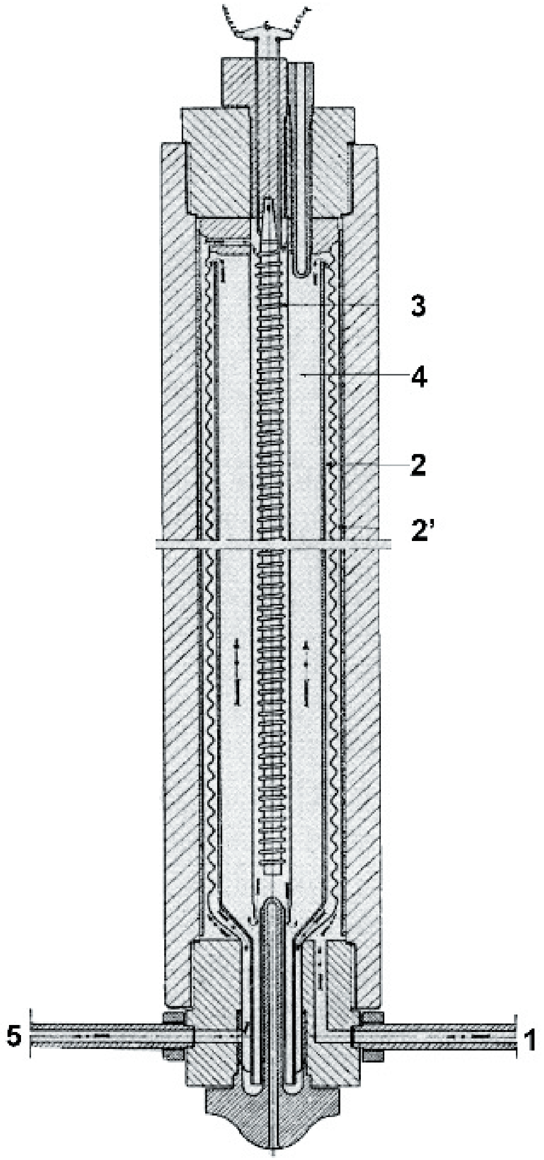


Figure 1. Casale ammonia converter (reactor), 1920s. Key: 1, gas (nitrogen-hydrogen) inlet; 2, 2', concentric annular spaces, divided by corrugated partition; 3, electrical heater; 4, catalyst space; 5, ammonia and unreacted nitrogen-hydrogen outlet. Redrawn from A. Miolati, *Synthetic Ammonia and the Casale Process. Amplified edition of a lecture delivered the 27th February 1927 at the Institute of Chemistry of the Polytechnic School of Prague* (transl. G. Impallomeni, 2009). "L'Universale" Tipografia Poliglotta/Ammonia Casale SA, Rome, 1927, p. 24.

to processes carried out under Haber-Bosch conditions which required expensive refrigeration equipment to achieve an anhydrous product.

Casale erected a pilot plant in an old iron works belonging to the Terni steelworks company (from 1922 Società per l'Industria e l'Elettricià Terni). In April 1921, he founded Ammonia Casale SA, in Lugano, Switzerland, which soon licensed the technology to entrepreneurs, companies, and state organisations in Japan and Europe. Though patents were filed in the United States, there was little interest in Casale's and other synthetic ammonia processes. America was well supplied with nitrogen products, through entrenched businesses and processes. Here we need to understand the background to the nitrogen fertilizer market in the United States.

NITROGEN PRODUCTS IN THE UNITED STATES

Three products enabled self-sufficiency in nitrogen compounds for use as fertilizers, and contributed to a healthy export trade in ammonium sulphate. The sulphate was the main nitrogen fertilizer, produced from the ammonia from by-product coking ovens that were rapidly replacing the beehive ovens from which valuable products were lost. In 1925, the United States ammonium sulphate capacity from many of the 10,000 by-product coking ovens was "well over 600,000 tons."[6] Imported Chilean nitrate was widely used as fertilizer, notably in citrus growing regions. The third important source of fertilizer nitrogen was calcium cyanamide, as manufactured by the American Cyanamid Company on the Canadian side of the Niagara Falls from 1910.

During 1924-1925 the import of Chilean nitrate into the United States grew considerably, including through the involvement of the increasingly diversified Du Pont company. From the nitrate, Du Pont manufactured nitric acid, which was essential in production of explosives, dyes, and other products.

There was a new route to nitric acid, much used in Europe: catalytic oxidation of ammonia (the Ostwald process). Conversion of ammonia derived from cyanamide and from coking ovens into nitric acid using this process had been achieved just prior to World War I by, respectively, American Cyanamid, at Warners, New Jersey, and the Solvay Process Company, at Syracuse, New York. However the earlier method of making the acid starting with Chilean nitrate was generally favoured for both economic and technical reasons until the late 1920s. This is one reason why Du Pont had a not inconsiderable interest in the Chilean nitrate industry.

Ammonia for Refrigeration

In contrast to the situation in postwar Europe and Japan—where the synthetic ammonia industry was often backed by government self-sufficiency programmes related to both fertilizers and explosives—the early interest in synthetic ammonia in the United States was in supplying the more restricted refrigeration market. Ammonia was used as an industrial refrigerant well before World War I, notably by Armour & Company of Chicago that was involved in meat packing and storage. The coal gas manufacturers were sources of aqua ammonia (ammonia water) used to produce the anhydrous ammonia for industrial refrigeration. Anhydrous ammonia was shipped in cylinders. From around 1890, the Harrisburg Pipe & Pipe Bending Company manufactured the cylinders from hand-welded steel pipes. After 1910, following the lowering of an import tariff, seemless high-pressure gas cylinders made by Mannesmann in Germany were imported into the United States. Harrisburg responded by producing a quenched and drawn heat cylinder of lighter weight, which could be handled by one man, instead of two as previously. In 1923, the production of anhydrous ammonia used in industrial refrigeration came to 23,966,000 pounds, valued at $6,415,000.[7] Domestic refrigerators that relied mainly on sulphur dioxide for cooling were introduced later in the 1920s.[8]

Armour had pioneered large scale long-distance transportation of otherwise perishable foodstuffs in refrigerated railroad cars. This was far more important than in Europe, where transportation involved much shorter distances, and in generally cooler climates. Brewers were among the other important consumers of ammonia for refrigeration.

The leading distributor in the east was the National Ammonia Company, of St Louis, formed in 1889 at the initiative of Edward Mallinckrodt, of the Mallinckrodt Chemical Works, by merger of five large producers of ammonia (subsequently other companies in the ammonia business were acquired). By the early 1900s there were factories in both St Louis and Philadelphia, and branches in Canada and Australia, offering both anhydrous and aqua ammonia. On the west coast, the Pacific Ammonia & Chemical Company, managed by Robert P. Greer, monopolised the market in anhydrous and aqua ammonia. Pacific Ammonia, founded in San Francisco in the 1890s, moved its manufacturing base to Seattle in 1908-1909. By 1920, it was represented by agencies in Japan, China, the Philippines, the Hawaiian Islands, and British Columbia. In 1922, Pacific Ammonia became associated with National Ammonia; the two stockholders in Pacific Ammonia, with almost equal holdings, were

National Ammonia and Robert Greer. National Ammonia retained its strong interest in distributing ammonia to the refrigeration market, but did not compete with producers and distributors of nitrogen fertilizers.

The FNRL and Its 3-Ton Per Day Ammonia Unit

Despite the range of commercial nitrogen products available in the United States, interest in high-pressure ammonia processes and general nitrogen fixation was certainly not lacking. From March 1919, the role of synthetic nitrogen compounds as fertilizers and in production of nitro compounds for munitions were investigated at the state sponsored Fixed Nitrogen Research Laboratory (FNRL) in Washington DC, under the aegis of the U.S. Army's Nitrate Division. During 1919, American military officers visited the BASF ammonia facility at Oppau, in the French zone of occupation. Though they were not always welcome, they made useful observations, and, probably surreptitiously, procured samples of catalysts, that ended up on the test benches of the FNRL.[9] In just over half a decade, its staff resolved most of the chemical and technical problems related to the ammonia synthesis. Thus, Alfred T. Larson developed a catalyst similar to that used in the Haber-Bosch process, no doubt based on analysis of samples obtained from Oppau, and patents for German recipes. This contributed to the success of the FNRL in producing synthetic ammonia, at around 200 atmospheres pressure, drawing on pure hydrogen obtained by electrolysis of water in cells provided by the Electrolabs Company of Pittsburgh.[10]

From 1924, the results of the FNRL were made freely available to chemical firms and entrepreneurs; many of its chemists subsequently contributed to the US synthetic nitrogen industry.[11] Larson, for example, joined Du Pont. The FNRL's 3-ton per day (tpd) synthetic ammonia unit became a model for a handful of American firms, all working on a small scale. The most expensive input was hydrogen, for which operators of the FNRL process relied mainly on by-product hydrogen from electrochemical processes in locations where abundant hydroelectric power was available. First to adopt the FNRL process, in 1924, was the Pacific Nitrogen Corporation, at the Seattle works of Pacific Ammonia (then associated with National Ammonia). The entire installation was erected under the supervision of FNRL staff. In this case, dedicated cells produced the hydrogen, which was far more costly than by-product hydrogen. Next, during 1924-1925, was the Mathieson Alkali Works, at Niagara Falls, followed in 1926 by the Roessler & Hasslacher Chemical Company, also at Niagara Falls (Table 1).[12] These firms manufactured ammonia for the refrigeration market or for use in production of other chemicals. Thus, Roessler & Hasslacher relied on in-house by-product hydrogen from electrolytic production of sodium, and used the ammonia to manufacture sodamide (sodium amide), for its sodium cyanide process. The small scale of working with FNRL type units, as compared with manufacture in Europe and Japan, did not permit economic production of nitrogen fertilizers.

At best, the FNRL had aided in the creation of a minor branch of chemical industry. However, nitrogen fertilizers based on synthetic ammonia required large-scale operations and economies of scale. This was achieved in Europe by merging the two cultures of engineering and chemistry. Ammonia Casale SA was a front runner in this endeavour.

CASALE IN AMERICA

Here we turn to the story of the introduction into the United States of the Casale ammonia process. Luigi Casale not only promoted and, unlike BASF, licensed his process but also served as a contractor, supplying Italian made converters, compressors, and associated equipment to clients. At first there were no rivals: Claude's process faced difficulties with converters; and the Italian process of Giacomo Fauser, under Montecatini, was confined to Italy. The first licensee of Ammonia Casale SA was Noguchi Shitagau (founder of the Nitchitsu corporation) in Japan, who met with great success and within a short time was ordering additional converters. Casale converters were put to work in Belgium, France, Switzerland, Spain, and elsewhere.[13] Figures of nitrogen consumption in the United States clearly suggested to Luigi Casale that here was an untapped and potentially vast market for synthetic ammonia, including for use in refrigeration. In 1923, following the filing of certain key patents on his inventions, Casale set about the creation of a new enterprise, Niagara Ammonia Company, Inc., established in New York City. This American branch of Ammonia Casale SA would not only engage in licensing arrangements and the supply of equipment, but would also undertake manufacture on American soil, using converters and compressors imported from Italy. Casale's Niagara Ammonia would not only be a showpiece for Americans to admire, but its product, usefully, would not be subject to import tariffs on ammonia.

Ammonia Casale SA also established in New York The Ammonia Corporation (Figure 2). It retained ownership of the Casale patents in the United States.[14] Also involved, as an assignee jointly with Luigi Casale of cer-

Table 1. Synthetic ammonia facilities, United States, 1927.

Name	Location and process	Rated daily capacity, tons of ammonia	Daily operating rate, tons of ammonia	Yearly nitrogen equivalent in tons (based on 350-day operation)
Atmospheric Nitrogen Corp.	Syracuse, NY (Solvay/Allied), *General Chemical*	30	30	7,750
Lazote, Inc. (Du Pont)	Charleston W. Va. (Belle), *Claude*	25	15	4,350
Mathieson Alkali Works	Niagara Falls, NY. 3 tpd in 1925, *American*	10	10	2,900
Niagara Ammonia Company (to Du Pont, 1927; ceased operating July 1927)	Niagara Falls, NY, *Casale*	13 (17)	8	1,250 (approximately six months)
Roessler & Hasslacher Chemical Co. (to Du Pont 1930)	Niagara Falls, NY, *American*	3 (increased to 9 tons, 1928)	3	865
Pacific Nitrogen Corp. (to Du Pont 1927)	Seattle, Washington, *American*	3	3	865
Great Western Electrochemical Co.	Pittsburg, California, *American*	1	1	290
Commercial Solvents Corp.	Peoria, Ill. Southwest of Chicago, *American*	15	0	Converted to methanol, shortly after inauguration in 1927.

Sources: F. A. Ernst, *Fixation of Atmospheric Nitrogen*, Chapman & Hall, Ltd., London, 1928, p. 121. F. A. Ernst, F. C. Reed, W. L. Edwards, "A Direct Synthetic Ammonia Plant," *Industrial and Engineering Chemistry*, August 1925, *17*(8), 775-788. Editorial, *Industrial and Engineering Chemistry*, August 1925, *17*(8), 772. F. A. Ernst, M. S. Sherman, "The World's Inorganic Nitrogen Industry," *Industrial and Engineering Chemistry*, February 1927, *19*(2), 196-204, on 199. Notes: *American* = based on the Fixed Nitrogen Research Laboratory (FNRL) method. The original source of hydrogen at Syracuse was water gas, until May 1927, when in house by-product hydrogen became available. Niagara Ammonia Company used its electrolytic cells for generating hydrogen, as well as purchasing by-product hydrogen from the adjacent Hooker Electrochemical plant. Pacific Nitrogen used electrolytic hydrogen from its dedicated cells; Mathieson and Great Western used by-product electrolytic hydrogen. Commercial Solvents used by-product hydrogen from fermentation.

tain of Casale's patents, was René Leprestre, who was based, in part at least, in New York. The Ammonia Corporation assigned patent rights and provided funding to Niagara Ammonia; they were to share any licensing compensation.

Reports of successful operation of the Casale process must have gone a long way towards convincing American investors, especially those with interests in electrical power, to back Casale. As a result, the principal external backer was the Electric Bond & Share Company, a major utilities trust originally founded by General Electric in 1905.[15]

Around four-fifths of both preferred and common stock in Niagara Ammonia were held by The Ammonia Corporation, while around one-fifth of the stock was held by Electric Bond & Share, represented by the banker and entrepreneur Henry J. Pierce (1859-1947).[16] The Electric Bond stock was held in the name of nominee Frank L. Smiley (1871-1948) a dealer in utilities stocks. Ammonia was in some ways an unusual investment for Electric Bond & Share, which was mainly involved in power stations and electrical infrastructure, including interurban and street railways. However, the chemical industry was a major, and rapidly growing, consumer of electricity, and synthetic ammonia, which relied on electrically powered machinery, no doubt offered a novel area for diversification. (The interest in synthetic ammonia at Electric Bond & Share, later EBASCO, continued until well after World War II.)

Other investors included the New York stockbroking houses A. Iselin & Company, which had close connections with Europe, and H. T. Carey & Company. There was also David Barker Rushmore, an engineer formerly at General Electric, and an enthusiast for hydroelectric power generation. In 1923, Rushmore published the second edition of a book, co-authored with Eric A. Lof, on power stations.[17] In the same year, Lof drew up a report on atmospheric nitrogen fixation. The Iselin firm held the stock certificates of Ammonia Casale SA investments in the United States.

To all intents and purposes, the aspirations of The Ammonia Corporation were based on a business plan

INCORPORATED UNDER THE LAWS OF THE STATE OF NEW YORK

AP2

100

Full Paid and Non-Assessable

The Ammonia Corporation

The Corporation is Authorized to Issue [illegible] Shares of A Preferred Stock and [illegible] Shares of B Preferred Stock, each having a Par Value of $100 Per Share, and 10,000 Shares of Stock without Nominal or Par Value

THIS IS TO CERTIFY that A. Iselin & Co is the owner of One hundred Shares of the A PREFERRED Capital Stock of THE AMMONIA CORPORATION transferable [illegible] the holder hereof in person or by duly authorized Attorney upon surrender of this Certificate properly endorsed.

The Preferred Stock of the Company [illegible] over the Common Stock in the manner set forth on the reverse side of this Certificate.

A PREFERRED

WITNESS the seal of the Company and the signatures of its duly authorized officers affixed this 30th day of July, 1923.

Treasurer

Frederick Pope

President

Figure 2. Stock certificate, The Ammonia Corporation, preferred stock, assigned to A. Iselin & Co., 30 July 1923. Iselin held the stock certificates of Ammonia Casale SA holdings in The Ammonia Corporation and the Hydro-Electric Chemical Company. From: The Ammonia Corporation, A Preferred Stock. Records of E.I. Du Pont de Nemours & Co. Absorbed companies. Manuscripts and Archives Department, Hagley Museum and Library, Wilmington, Delaware, Accession 500, series II, part 1, box 67. Author's photograph. Reproduced with permission.

aimed at marketing the Ammonia Casale brand in North America, underpinned by proven success, and patent protection. In terms of rated converter capacity, of around 7-8 tpd, the Casale process certainly offered far more than the processes based on the Fixed Nitrogen Research Laboratory's 3-tpd unit, which in 1923 had not yet been introduced on an industrial scale, and the then problematic Claude process. The only viable rival was the General Chemical Process, of Allied Chemical, which was confined to Solvay operations at Syracuse (See next section). The Ammonia Corporation, it must have seemed, stood to benefit from growth in demand for nitrogen products, including, the founders probably anticipated, the fertilizer market, that would bring in substantial royalties following the signing of licensing agreements. This differed from arrangements elsewhere, in which sole licenses for given countries or geographical regions were sold to chemical manufacturers, without, it appears, direct investment from Ammonia Casale.

THE GENERAL CHEMICAL PROCESS

The first attempt to introduce a catalytic high-pressure synthetic ammonia process in the United States was made by the General Chemical Company (a consolidation of twelve companies established in 1899), just prior to the outbreak of war in Europe. Much interest had been generated after the demonstration by BASF of Haber's method at the Eighth International Congress of Applied Chemistry, held in New York in 1912. This was followed by careful scouring of the available literature and patent applications concerning the process. At General Chemical, Frederick W. de Jahn and colleagues developed a process similar to that of BASF, and discovered an iron catalyst incorporating sodamide. The company put together a small pilot plant during 1915-1916. Subsequent government supported wartime experimental work based on the process was not successful. However, by 1919 these studies enabled General Chemical chemists to overcome several technical problems, including a suitable steel for the converter shell, and devise an improved catalyst.[18]

In late 1919, General Chemical and the Solvay Process Company brought together their interests in synthetic ammonia through the Atmospheric Nitrogen Company, in order to set up an ammonia unit at Solvay's Syracuse works.

The development of the General Chemical process benefitted greatly from the free exchange of technical information between Solvay Process and the British firm Brunner, Mond & Company, in accord with arrangements dictated by the Belgian licensor of the Solvay ammonia-soda process, Solvay et Cie. This included details of the catalyst used in the Haber-Bosch process, samples of which were taken by Brunner, Mond investigators during their visits to Oppau in 1919.[19]

In 1920, General Chemical, Solvay Process, and five other firms, including National Aniline & Chemical (a merger of four firms dating from 1917), were absorbed into a new behemoth, Allied Chemical & Dye Corporation. This was one of the first major interwar mergers in the chemical industry, preceding those that led to I.G. Farben (1925), and Britain's ICI (1926). It was in many ways a response to concerns arising from the fact that Du Pont and BASF had begun discussions on the opening of a Haber-Bosch facility in the United States, much to the chagrin of General Chemical and Solvay Process, who were anticipating collaboration with BASF in a similar venture. In the end, Du Pont failed in its dealings with BASF, and for a while lost interest in synthetic ammonia.[20]

On 8 August 1921, Atmospheric Nitrogen started up what became known as the General Chemical synthetic ammonia process at Syracuse. The initial rated output was 9-tpd. The source of hydrogen was water gas, obtained by the reaction between steam and red hot coke, the latter available from Semet-Solvay coking ovens. This followed the success of BASF and Brunner, Mond with water gas processes.

Nitrogen was initially obtained by air liquefaction. In September 1921, William Henry Nichols, chairman of Allied Chemical, "caused a deal of surprise" when he announced this considerable achievement at a luncheon during the American Chemical Society's 62nd meeting, held at Columbia University.[21] In 1922, however, the German observer Bruno Waeser suggested that the process was facing technical difficulties.[22] Moreover, the Syracuse anhydrous ammonia was not at first well suited to refrigeration due to the presence of impurities, as a result of which distillation equipment had to be introduced. Some ammonia was probably used to produce sodamide for the Allied Chemical synthetic indigo process, and for manufacture of sodium cyanide. Its potential for use in the Solvay ammonia-soda process was also significant.

Published figures of the rated annual output of Syracuse ammonia indicate growth from 3,000 tons in 1921 to 7,750 tons in the mid-1920s.[23] This increase took place following the decision of the head of Allied Chemical, Orlando Weber, to invest heavily in synthetic ammonia and inorganic products at the expense of dyes and other organic chemicals.[24] Allied Chemical's ammonia process was not made available for licensing. By 1925, Allied Chemical had embarked on construction of a large synthetic ammonia facility, using the modified General Chemical process, at the new Hopewell, Virginia, factory of Solvay Process. It opened in late 1928, and relied for hydrogen on water gas made from coke brought in from Allied's remote coking ovens. The first product made at Hopewell was anhydrous ammonia, soon followed by the fertilizers ammonium sulphate and sodium nitrate. For the first time in the United States, economies of scale enabled synthetic ammonia to compete in the agricultural fertilizer market with Chilean nitrate, coking oven and gas works by-products, and calcium cyanamide.

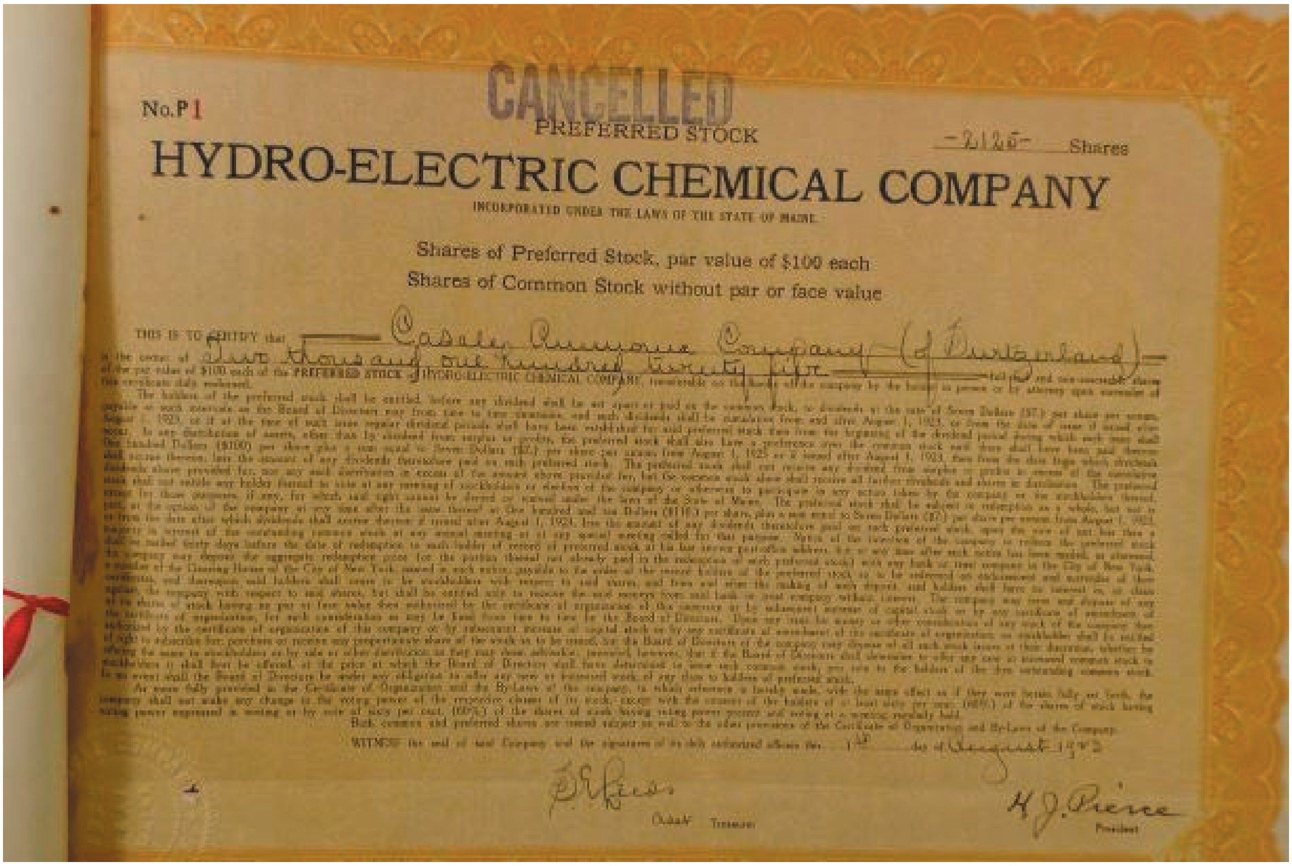
According to historian of the US chemical industry Williams Haynes the Syracuse ammonia unit continued in service, as had been the case earlier, as a pilot facility for process development, while markets for synthetic ammonia were being investigated.[25] However, with downsizing, following construction at Hopewell, there was an alternative source of hydrogen at Syracuse. From May 1927, the new Solvay electrolytic plant there supplied by-product hydrogen for the synthetic ammonia unit, in addition to chlorine for dye manufacture at the nearby factory of National Aniline (part of Allied Chemical), and caustic soda for local manufacturers of artificial silk (viscose). For development purposes, there were advantages in employing electrolytic hydrogen. It was pure, unlike that from the water gas process (which required extensive purification to prevent poisoning of catalyst). Also, reliance on electrolytic hydrogen permitted intermittent, small-scale, operation, unlike the coke-based processes. These factors were also important in deciding the source of hydrogen at the FNRL, and also at Casale's American factory. The Syracuse experimental unit continued to operate until well into the 1930s.[26]

AMMONIA CASALE SA IN AMERICA

The function of the Niagara Ammonia Company, as its name might suggest, was to operate the Casale process at Niagara Falls, the hub of the US electrochemicals industry. In this connection there was also an associated Casale enterprise, again with the close involvement of Electric Bond & Share, the Hydro-Electric Chemical Company, founded in Maine in July 1923 (Figure 3). Hydro-Electric's holding company was the Chemical Investment Corporation, also established in 1923 (Table 2).[27] The president of Hydro-Electric Chemical was Henry J. Pierce, again representing Electric Bond & Share. Among the investors (and later a director) was the New York lawyer Josiah Turner Newcomb, the special council for Electric Bond & Share. A director, and holder of a single share, was René Leprestre. The interests of Electric Bond & Share and Ammonia Casale in America were now closely intertwined. Together they embarked on an ambitious venture aimed at dominating certain novel and emerging sectors of the US chemical industry, based on electrochemicals and high-pressure technology.

Colonel Frederick Pope

The president of both The Ammonia Corporation and Niagara Ammonia was the Harvard educated chemical engineering consultant and entrepreneur Colonel Frederick Pope (1877-1961), a resident of New York.[28] Before 1914, following stints in mining operations, including in South Africa, Pope had studied aromatic nitro compounds, those used to make modern explosives and synthetic dyes. During World War I, it was later claimed, he opened the first new American synthetic dye



No. P1

CANCELLED

PREFERRED STOCK

-2125- Shares

HYDRO-ELECTRIC CHEMICAL COMPANY

INCORPORATED UNDER THE LAWS OF THE STATE OF MAINE

Shares of Preferred Stock, par value of $100 each
Shares of Common Stock without par or face value

THIS IS TO CERTIFY that Casale Ammonia Company (of Switzerland)

is the owner of Two thousand one hundred twenty five

H. J. Pierce
President

Figure 3. Stock certificate, Hydro-Electric Chemical Company, preferred stock, in the name of the Casale Ammonia Company (often used in English language documents for Ammonia Casale SA), 1 August 1923. From: Hydro-Electric Chemical Company, Stock Certificate book, 1923-28. Records of E.I. Du Pont de Nemours & Co. Absorbed companies. Hagley Museum and Library, Wilmington, Delaware, Accession 500, series II, part 1, box 848. Author's photograph. Reproduced with permission.

Table 2. Ammonia Casale SA investments in the United States, 1923-1927.

Holding corporation	Affiliate	Place and year of foundation	Date of transfer of stock to Du Pont	Fate
The Ammonia Corporation		New York, 1923	May-June 1927	Bankrupt, February 1928
	Niagara Ammonia Co., Inc.	New York, 1923	May-June 1927	Bankrupt, February 1928
Chemical Investment Corporation		1923	1927	
	Hydro-Electric Chemical Company	Maine, 1923	October 1927 (to Lazote December 1927)	

Notes:

The Ammonia Corporation: In 1923, Ammonia Casale SA held 2,000 shares of preferred stock, and 3,050 shares of common stock, in The Ammonia Corporation.

Niagara Ammonia Co., Inc.: The second largest stockholder was Frank L. Smiley, nominee for Electric Bond & Share Company, whose holdings were transferred to Du Pont in May 1927.

Hydro-Electric Chemical Company: The authorised capital was $750,000, with 20,000 shares non par. Ammonia Casale SA held 2,125 of preferred stock, and 7,840 of common stock. The Chemical Investment Corporation, the holding company for Hydro-Electric Chemical, held 5,000 preferred stock, out of a total of 7,500 (later increased to 9,000), and 10,191 common stock. A major stockholder in the Hydro-Electric Chemical Company was Bonn & Co., whose holdings were transferred to Lazote in 1929.

factory, prior to specialising in gas warfare in the United States and France. In 1918, before the cessation of hostilities, he took from England to the United States details of the technology for producing mustard gas by the Levinstein process, which was taken up at Edgewood Arsenal. In 1919, he was among the technical experts who visited German chemical factories, in his case twice, to follow up developments in organic chemical and dye manufacture and the production of toxic chemicals. Pope's brief published account does not indicate the sites that he visited, though they probably included the synthetic ammonia facility of BASF at Oppau.[29] His Chemical Warfare Service colleague Theodore Sill visited Oppau, which he described as a wonder of modern technology. What Pope saw or heard about Oppau must have aroused in him an interest in the potential for high-pressure industrial chemistry.[30] Above all, it was Colonel Pope's status as an experienced entrepreneur, with an extensive network of contacts, that recommended him to the American Casale enterprise.

HYDROGEN FOR NIAGARA AMMONIA

As with all synthetic ammonia processes, the main operational cost was associated with production of hydrogen, at first obtained by electrolysis in locations where abundant hydroelectric power was available. On the United States side of the Niagara Falls firms such as Hooker Electrochemicals manufactured chlorine, alkali and chlorinated organic compounds, as well as making available by-product hydrogen, from its electrolysis process. In 1918, Hooker first supplied hydrogen to a joint enterprise, Hydrofats., Inc., for hardening vegetable oils.[31] Hydrofats, located on Hooker's land next to the latter's Niagara Falls factory, ceased operating in 1922. In the following year, the former Hydrofats site was leased by Hooker to Niagara Ammonia, whose directors included Willard E. Hooker, youngest son of the founder of Hooker (Elon Huntington Hooker, 1905).

In November 1923, a contract with Electrolabs for purchase of a hundred and sixteen of its 5,000 amp cells, including their installation, at a cost of $40,356, was approved, as was a contract with the General Electric Company for "motor generators, exciters, switchboards, etc., being the complete apparatus to furnish direct current at the proper voltage to the cells, for the sum of $45,308:00." Niagara Ammonia director A. E. Bonn, previously at American Cyanamid, reported that the Electrolabs cells at the FNRL "had been entirely satisfactory." (Bonn, through Bonn & Company, was an investor in the American Casale enterprises.) Also, it was reported that the two-month old Casale ammonia plant in Japan was so successful that an order had been placed for two additional converters, each with a rated daily capacity of 7 ½ tons of ammonia. Hydroelectricity from the Niagara Lockport & Ontario Power Co. (which was independent of Electric Bond & Share) drove all machinery at Niagara Ammonia, including compressors and circulation pumps, and provided power for the electrolysers. Niagara Lockport also supplied electricity to the Syracuse factory of Solvay Process.

The source of nitrogen for the ammonia process was based on another of Luigi Casale's inventions, the removal of atmospheric oxygen from air by its reaction with hydrogen, the so-called burning of air.[32]

To protect the considerable investment in high-pressure chemistry, that would soon reach well over half a million dollars, the board of Niagara Ammonia discussed acquisition of a license for a German synthetic ammonia process from the Chemical Foundation, Inc., which held sequestered German patents on a number of nitrogen processes as well as on synthetic organic chemicals.[33] This would be of value to Niagara Ammonia should the Casale patents in the United States come under threat through litigation arising from patent disputes. The precaution was justified. This was still the start-up period, based on a relatively new industrial technology, with unknown risks, at least in the United States: "It was the consensus of opinion that approval to the taking out of that license [from the Chemical Foundation] should be be given only as a measure of defense, since the Casale patents under which this Company would operate, have not as yet been the subject of judicial determination and there are certain claims which might give rise to litigation and the consequent expense and loss... approval was deemed wise as a matter of business precaution." The drawing up of a contract with the Chemical Foundation was "unanimously approved."[34]

In December 1923, Frederick Pope, in his role as president of Niagara Ammonia, reported that progress in construction work at the Niagara Falls site was satisfactory. The first consignment of machinery had arrived from Italy. Bonn advised that there might be some delay in receiving a second seaborne shipment of machinery from Italy, and that there "is a substantial amount of machinery on the third boat."[35] The machinery included Casale converters, probably manufactured at the Terni steelworks. An alternative source was the Italian works of Armstrong SA, a subsidiary of the British engineering firm Armstrong Whitworth, at Pozzuoli, in southern Italy, that manufactured Casale converters for installation at the Nera Montoro synthetic ammonia factory, located near Terni.[36] Also from Italy were the special high-pressure compressors, manufactured by the firm of Pignone, of Florence, and circulation pumps. In 1922, Pignone introduced the first commercial multistage compressor suited to the synthesis of ammonia under Casale's operating conditions.

During May 1924, Niagara Ammonia first received by-product hydrogen from Hooker.[37] Though Niagara Ammonia intended to generate its own supply of hydrogen from the in-house electrolysers, the availability of hydrogen from Hooker was a useful reserve supply.

On July 30, Pope reported that this was the first occasion when he could report actual production, "the plant having operated off and on during the month of July, making about 72,000 pounds of ammonia, which at 15¢ a pound, amounts to $10,800." The monthly bill for hydrogen was approximately $5,000. The payroll was about $4,000, and cost of supplies $600. Pope believed that "the plant profit, excluding overhead and sales expenses, could be about $1,000."[38]

However, Niagara Ammonia was forced to delay sale of its anhydrous ammonia until quality issues had been dealt with. Pope drew attention to the fact that for use as refrigerant the anhydrous ammonia was unacceptable to an important potential customer, and distributor, Armour & Company, "as it contained more than the allowable percentage of water and foreign gases." This difficulty could be overcome by the installation of a distilling apparatus, costing between ten and fifteen thousand dollars. The decision to install suitable distillation equipment was based on a report from D. T. Kiley of Armour & Company, whose chief chemist, J. R. Powell, visited the Niagara Ammonia factory. Kiley's report revealed the difficulties involved in producing ammonia for the refrigeration market, and not just at Niagara Ammonia.

> Our chief chemist, Mr Powell, has returned from Niagara Falls and I am enclosing to you a copy of his report. You will see that it is going to be necessary for you to put in another still. The Syracuse people [Allied Chemical/Solvay Process] had the same trouble and their ammonia was condemned by the trade until after they had installed an extra still to put out an anhydrous ammonia that was equal to that made by other manufacturers.
>
> I know that you will go into this at once, as you personally know that should we send out any ammonia that was not fully equal to that made at Syracuse, the Niagara ammonia would get a 'black eye' that would take a long while to get over and our competitors would take advantage of it. You may rest assured that the first ammonia we put out will be watched closely and they will all be buying cylinders and testing the ammonia and if it isn't 'up to snuff', you can bet the consumers are going to know about it through them.

Powell found contamination of the anhydrous product with moisture and foreign gas that was three or four times greater than required of an ammonia suited to the exacting requirements of the refrigeration market. An Italian representative of Ammonia Casale had been on hand during Powell's visit and "seemed thoroughly convinced that the source of the water was the accidental introduction of small amounts of oxygen with the gases before they entered the system."[39]

Colonel Pope observed that Henry Pierce, as a member of the Niagara Ammonia board, "has been of great service to the company while abroad, in urging Dr. Casale to come to the United States the middle of August, and in following the delivery of the Italian machinery for the third unit of our plant." If the three units were identical, this indicates, on the basis of published reports of rated capacities, that each one was of around 7-tpd capacity. On the same occasion, funds were approved for completion and "tuning up" of the first unit.[40]

Not long after, Luigi Casale visited the United States to deal with his business interests there. According to Casale's professor, Arturo Miolati, Casale attended an event with Fritz Haber in New York, which must have been around the time of the Benjamin Franklin centenary celebrations, held in Philadelphia during September 17-19, where Haber was a speaker.[41]

CHANGES AND CHALLENGES AT NIAGARA AMMONIA

The Departure of Fredrick Pope

On 14 November 1924, Colonel Frederick Pope tendered his resignation, as president, of Niagara Ammonia, and apparently of other Casale interests, and was replaced by Henry Pierce. On the same occasion, anticipating substantial investment in scaling up, or at least in making improvements, it was resolved that the "president be authorized to borrow from The Ammonia Corporation the sum of $150,000, in such amounts as might be required, upon this company's notes, at the rate of 6% per annum."[42] By early 1925, Willard Hooker had been appointed a vice president of Niagara Ammonia.[43]

Pope perhaps foresaw difficulties, including the great expense of generating hydrogen from electrolysers at the Niagara Falls operation.[44] That may have suited Europe and Japan, where strong political and strategic commitments and local and state support were significant factors in the adoption of hydroelectric power. In the United States, electricity, though widely available, was expensive. Very few additional electrolysers were installed at Niagara Ammonia. The actual output of synthetic ammonia never exceeded 8-tpd, which was considerably less than the combined rated capacities of the converters.

Lured away by new challenges, Pope's experience at Niagara Falls, and of the new synthetic ammonia technology of Luigi Casale, was timely and put to good use. Pope became involved in the Nitrogen Engineering Corporation (NEC), founded in 1926, which offered an ammonia converter based on a process that was far better adapted to large scale production than the so-called "American" process of the FNRL. The co-inventors of the NEC process, Louis C. Jones and Major Charles O. Brown, had previously been employed by Allied Chemical. Pope also became associated with the Chemical Construction Company (Chemico), an engineering firm based in Charlotte, North Carolina, that in 1929 acquired NEC, and held patents on novel catalytic processes, including the Selden vanadium catalyst for sulphuric acid, and that had developed a process for oxidation of ammonia to give nitric acid. In 1930, Chemico was acquired by the American Cyanamid Company. Cyanamid's Chemical Construction Corporation (still referred to as Chemico), offered design and construction services for high-pressure plant, and other equipment. Around 1930, Pope was involved in introduction of the NEC process in the Soviet Union, perhaps after convincing the Russians that it was better suited to their conditions than the Casale process (which was introduced at one site in Russia in 1928). In June 1932, at a time when the Soviet Union was anxious to gain diplomatic recognition from the United States, the Russians managed to gain his assistance.[45] However, Pope's relationship with the Russians was not smooth. He ceased dealing with them in 1934.[46] Later, he was closely associated with attempts to introduce American Cyanamid's (Chemico) chemical technologies in China, Mexico, Egypt, and elsewhere.

The Hydro-Electric Chemical Company and the Liljenroth Process, and Royalties on Ammonia

In 1924, an interest in production of mixed nitrogen-phosphorus fertilizers, and at the same time a new source of hydrogen, led Hydro-Electric to back the electrothermal phosphoric acid-hydrogen method of Frans Georg Liljenroth, of Stockholm, Sweden. Phosphorus, produced by reduction of phosphate rock in an electrically heated furnace, was reacted with steam to afford phosphoric acid and hydrogen. The Phosphorus-Hydrogen Company had been established in New York to promote the process in the United States, and during 1925 began experimental work at the Niagara Ammonia factory. Chemist Thomas Edward Warren, who worked at Niagara Falls on the Swedish process in 1925, recalled that the intention was to move away from ammonia for use in refrigeration towards synthetic fertilizers, in particular ammonium phosphate, and phosphoric acid, as well as generating hydrogen from the Liljenroth process for use in the ammonia process.[47] However, the Liljenroth process was not taken up in practice.

Hydro-Electric, like Niagara Ammonia, also promoted the Casale process. One item in its correspondence file is of interest for revealing the royalty rates, and also the difficulty in finding licensees. During 1925, the royalty on the Casale process was fixed at 5 dollars per ton. On 9 December 1925, the board of Hydro-Electric discussed a reduced royalty, to be "granted by this Company at any time within two years from and after the date of this meeting, the royalty rate to be fixed ... at not less than 0.4¢ per pound of NH_3." Board member Charles Hardy voted against this proposal because he considered that it was not good for business to reduce the royalty rate from 5 dollars per ton until the latter "had been refused by some of the prospective licensees" (of which there were few, if any).[48]

The discussion on royalty rates had been stimulated by the abrupt 50 per cent fall in the price of anhydrous ammonia late in 1925. The price of aqua ammonia also fell, though less sharply. This encouraged widespread oxidation of ammonia into nitric acid, and the use of the acid in manufacture of sulphuric acid, in particular using processes developed by Du Pont and Chemico.[49] However, this hardly helped Niagara Ammonia and other companies that relied on sales of synthetic ammonia for the industrial refrigeration market. They had a hard time matching the price of ammonia from the other sources.[50] By 1926, the ammonia suppply industry in general was suffering from severe competition and a glut. The Niagara Ammonia Company, operating at less than half capacity, faced an uncertain future, and not just as a result of an increasingly difficult trading environment.

In March 1926, at a meeting of the directors of Niagara Ammonia, it was revealed that the company was in debt to the tune of $600,000, for one loan, and $25,000, for a second loan, to The Ammonia Corporation. The repayment dates for both loans were extended from April 1st to May 20th.[51] On May 17th, the redemption date was extended until July 20th.[52] These and other heavy debts owed to The Ammonia Corporation would remain on the books. This state of affairs arose from the precariousness of Niagara Ammonia's situation in 1926. It was facing heavy losses, apart from those arising out of substantial cuts in the price of anhydrous ammonia. For various reasons, the daily output target could not be met. Though there were plans to enter into the nitrogen fertilizer business at Niagara Ammonia, the facility was too small to compete with the major producers of nitrogen products for agriculture. As with the operators of FNRL units, the scale of working with electrolytic hydrogen was both limiting and expensive. By 1926, the main investors had sunk well over half a million dollars into the venture and had seen no return. Debts were mounting up, and, with the reduced price of ammonia, a turn to profitability did not seem likely. Investors must have been wary of injecting additional funds into an enterprise that was confronting several challenges, including from a new, and powerful, player in the industry.

DU PONT AMMONIA

Du Pont's interest in synthetic ammonia was revived early in 1923, following somewhat exaggerated claims concerning the Claude process made by a representative of Air Liquide to Du Pont's Norwegian born and German trained Fin Sparre, director of the Development Department, and head of much of the corporation's diversification programme. Sparre had previously been against embarking on manufacture of synthetic ammonia, though he expressed a strong interest in oxidation of ammonia to nitric acid. What impressed him now was the high yield achieved at pressures far greater than used in the process of Allied Chemical, possibly sufficient to make the latter obsolete, and the potential of catalyzed high-pressure technology.[53] Samuel K. Varnes of Du Pont, writing in 1947, observed that when in October 1923 a Du Pont commission travelled to Monterau, France, to investigate Claude's pilot plant they were somewhat disappointed.[54] Claude advised Du Pont that his process was not yet fully developed. The first steel converters were incapable of withstanding the severe operating conditions. By 1924, major improvements had been made, with the introduction of special alloys for the converters. As a result, in the summer of 1924, Du Pont acquired exclusive US rights to the Claude process from Air Liquide.[55] To formulate a nationwide marketing programme, Du Pont also acquired National Ammonia, the major US distributor of ammonia for refrigeration purposes. Du Pont now prepared to repeat its success with organic chemicals in the area of nitrogen products.

Du Pont's stated original intention was to enter the market for ammonia as refrigerant, distributed through National Ammonia, and later move into oxidation of ammonia, to nitric acid, and production of nitrogen fertilizers. National Ammonia would thereby begin to play a new role in the nitrogen distribution business. On 21 May 1925, jointly with Air Liquide, Du Pont incorporated in West Virginia the firm Lazote, Inc. Air Liquide provided 25 per cent of the capital in this partnership. Fin Sparre was appointed president of Lazote. Construction work began on an ammonia factory at Belle, East Kanawha County. Soon after, Du Pont announced that Georges Claude had on 30 June 1925 received letters patent 1544373, assigned to Lazote, "covering broadly a method of conducting the synthetic operation wherein the pressure-sustaining wall is cooled by the incoming gases which are preheated by heat exchange with outgoing gases from the zone of reaction." Tellingly, "Lazote, Inc., is prepared to enforce its rights under this patent and prevent infringement thereof."[56]

A catalyst testing laboratory, under the supervision of chemical director Roger Williams, and modelled after that of the FNRL, was installed at Du Pont's Wilmington Experimental Station. Alfred Larson, as noted previously at the FNRL, conducted further investigations at Wilmington. The Belle facility, where hydrogen was produced from water gas, and nitrogen from producer gas (blow-run gas, or blow gas), both made from coke, opened on 1 April 1926. Du Pont announced that it was represented by its distributor, the National Ammonia Company.[57]

The Claude process did not come up to expectations.[58] There were problems with the high-pressure, or hyper-, compressors ("hypers"), water gas and gas purification equipment, liquefaction plant, and converters.[59] The rated capacity, of 20-tpd, was difficult to achieve. Aware of the difficulties, and dangers, including explosions and casualties, Du Pont began to take an interest in the Casale process, no doubt in part because, having invested in hypercompressors, it wished to continue working with pressures way beyond those used in other synthetic ammonia processes (all of which Du Pont intended to outperform). Apart from these considerations, Casale's process was still the only independent, well-tried process suited to large scale production available for licensing in the United States in 1926 (the German Mont Cenis and the Nitrogen Engineering Corporation processes were new, and the Italian Fauser process was in the hands of Montecatini, which had only just started to consider licensing arrangements). While access to Casale's process could have been obtained through a licensing agreement with The Ammonia Corporation, Du Pont chose another way, acquisition of the Casale ammonia patents in the United States.

CHALLENGING THE CASALE PATENTS

The way to capture the superior Casale technology was to engage in litigation based on a patent suit, in which it would be argued that the Casale patents infringed certain of Claude ammonia patents. This would bring about the downfall of existing interests in the Casale process in the United States and open the way for Du Pont's acquisition of Casale technology. In 1926, Lazote commenced proceedings against The Ammonia Corporation and Niagara Ammonia, in Buffalo, New York State, for patent infringement. Because the claims in the United States for both processes were construed as broad, the wording of certain of the Casale patents were open to attack. This mainly concerned the very high pressure, considerably greater than that of the Haber-Bosch process, which was a feature common to both the Casale and Claude processes. Du Pont, through Lazote, pushed for an injunction against Niagara Ammonia's operations, in addition to claiming damages.[60]

Niagara Ammonia, totally reliant on Casale technology, prepared to be tested in litigation. The company, facing difficulties, financial as well as operational, and unable to achieve its intended output of ammonia, was a weak contestant. Though no account of the proceedings appear to have survived, it is apparent that the indictment offensive engineered by Du Pont's high powered patent lawyers was sufficient to topple the defence. Matters were brought to a head during the last week of May 1927. The outcome was an out of court settlement, at a closed-door meeting, in the favour of Du Pont.[61] In view of the parlous state of affairs at Niagara Ammonia, what Du Pont offered may even have appealed to some of those associated with the Casale enterprises. The arrangement enabled Du Pont to aquire all rights to the Casale patents in the United States.

Du Pont, by injection of capital, also took over control of Niagara Ammonia, The Ammonia Corporation, and Electro-Chemical. A Du Pont press release from the Publicity Bureau revealed only the acquisition of patent rights from The Ammonia Corporation.[62] A boardroom reshuffle at Niagara Ammonia took place on 27 May 1927, at a meeting held in New York, followed on the same day by decisions on certain manufacturing operations at Niagara Falls. Pierce, the president, and the other Niagara Ammonia directors resigned. Du Pont senior people were installed in their places, with F. S. MacGregor as president, and W. S. Gregg as vice president.[63] As for The Ammonia Corporation, Pierce and his co-directors were summarily ousted, and replaced by Du Pont men, with MacGregor as president.[64] The changes were soon known in the trade. In May 1927, Herbert Humphrey of Britain's ICI ammonia facility at Billingham was on a fact finding mission in the United States, and was informed of the fate of Ammonia Casale interests.[65] By 6 June 1927, the day the transfer of patent rights was announced in the *Oil, Drug and Paint Reporter*, Du Pont was in possession of all stock in Niagara Ammonia.[66] This included Electric Bond & Share's former substantial interest, as held in the name of Frank Smiley. Arrangements began for the transfer of Ammonia Casale stock in Hydro-Electric to Du Pont.[67] MacGregor, Niagara Ammonia's new president, replaced Pierce as president of Hydro-Electric.

On the occasion of the May 27 shakeout, MacGregor recommended sale of the electrolytic plant, including the Electrolabs cells. Latterly (and perhaps for some time) the plant had relied on hydrogen purchased from Hooker.[68] (The Electrolabs cells remained in place, unused, until moved to Seattle in 1928; see later.) Undoubtedly, the high cost of hydrogen was a major contributor to the losses at Niagara Ammonia. The Niagara Ammonia factory ceased operating in July 1927.[69]

Du Pont made further share transfers and continued to reshuffle the boards. On 3 October 1927, Ammonia Casale's stock of 2,125 shares in Hydro-Electric were transferred to Du Pont, and, in turn, on 22 December 1927 they were transferred from Du Pont to Lazote (Table 3). Du Pont people elected to the board of Hydro-Electric were Jasper E. Crane (member of the executive committee responsible for international affairs, and vice president of Du Pont from 1929), and engineer Frederick A. Wardenburg.[70] On 30 December 1927, Du Pont transferred its stockholdings in the Hydro-Electric Chemical Company, the Phosphorus-Hydrogen Company, and the Chemical Investment Corporation, to Lazote. Crane was appointed chairman of the board of directors of Lazote Inc., and Wardenburg, until then vice president, was appointed president, replacing Fin Sparre.

On 26 January 1928, at a meeting held in the Du Pont Building, Wilmington, presided over by MacGregor, the voluntary petition in bankruptcy of the Niagara Ammonia Company was sanctioned.[71] On the same day, the directors of The Ammonia Corporation met at its offices in New York. Of the seven directors present, six agreed that because the corporation was unable to pay its debts (as a result of the failure of Niagara Ammonia) it was necessary to declare the corporation bankrupt.[72] MacGregor, as president of both Niagara Ammonia and The Ammonia Corporation, filed voluntary petitions in bankruptcy. The *New York Times* reported that the liabilities of Niagara Ammonia were $947,748, and assets $107,899. The principal creditor was The Ammonia Corporation, with liabilities of $839,249, and assets of $498,467. The corporation was indebted to Lazote for the sum of $821,714. The principal listed assets of the corporation were rights to "foreign" patents, namely those relating to the Casale synthetic ammonia process, valued at $350,000 (this sum probably included the Phosphorus-Hydrogen Company's patents). These valuable patents were now in the hands of Lazote. Plant, stock and fixtures of Niagara Ammonia were valued at $97,579, which in the newspaper report were assigned to The Ammonia Corporation, as creditor.[73] It had been an expensive business all round, but now, at least, Lazote was firmly in control of the Casale ammonia process, and the useful Italian-made high-pressure converters and equipment of Niagara Ammonia. The Ammonia Corporation and Niagara Ammonia, together Ammonia Casale's sole overseas venture, were laid to rest.

Du Pont immediately introduced the Casale ammonia process at the Belle Lazote facility. As a first step, the converters and machinery from the defunct Niagara Ammonia factory were shipped to Belle. Over the winter

Table 3. Holdings in common stock, Hydro-Electric Chemical Company, probably late 1927.

Bonn & Co., Inc. 980 (assigned 1923)
Jasper E. Crane 1
Luigi Casale 1 (deceased February 1927)
Chemical Investment Corporation, Wilmington, 10,191 (assigned 1923)
Lazote, Inc., 7,840 (originally assigned to Ammonia Casale, 1923)
Charles J. Hardy 490 (assigned 1923)
Ernest Iselin 1
G. A. Henrie 1
Josiah T. Newcomb 50 (assigned 1923)
Henry J. Pierce 200 + 200 (assigned 1923)
Walter U. Reisinger 1
Samuel K. Varnes 1
David Barker Rushmore 40 (assigned 1923)
Roger Williams 1
M. L. Farrell 1
F. A. Wardenburg 1
Total 20,000

Source: Undated typewritten list, "Stockholders – Hydro-Electric Chemical Company." Added, in hand, holders of preferred stock were listed as Bonn & Co. (250 shares), Lazote, Inc. (2,125 shares, from Ammonia Casale SA, also referred to as Casale Ammonia Co.), Chemical Investment Corporation (5,000), and Charles J. Hardy (120). Hydro-Electric Chemical Co., Stock certificate book, 1923-28. Records of E. I. Du Pont de Nemours & Co. Absorbed companies. Hagley Museum and Library, Wilmington, Delaware, Accession 500, box 848.

The authorised capital of Hydro-Electric was $750,000, with 20,000 shares non par. Casale Ammonia Co. (Ammonia Casale SA) in 1923 held 2,125 preferred, and 7,840 common stock in Hydro-Electric. The 2,125 preferred shares were transferred to Du Pont on 3 October 1927, and then to Lazote on 22 December 1927. The Chemical Investment Corporation, the holding company for Hydro-Electric, held 5,000 preferred stock, out of a total of 7,500 (later increased to 9,000), and 10,191 common stock. The Bonn & Co. holdings were transferred to Lazote on 28 February 1929. Apart from Ammonia Casale, Chemical Investment Corporation, and Bonn & Co., early investors were Charles J. Hardy, Henry J. Pierce, and David B. Rushmore.

Hydro-Electric directors in 1924: Henry J. Pierce (president), Clement R. Ford, A. E. Bonn, René Leprestre, Ernest Iselin, Charles J. Hardy, George S. Baker (resigned September 1925; M. L. Farrell became director in his place), George H. Howard, Frank McCommon. Hydro-Electric directors in May 1925: Henry J. Pierce (president), Clement R. Ford, R. L. Farrell, Ernest Iselin, J. W. Mooney, Luigi Casale, George H. Howard, Frank McCommon, Frank E. Southard. Southard, of Augusta, Maine, was a lawyer representing utility interests, probably including Electric Bond & Share. Hydro-Electric Chemical Co. Directors & Stockholders Minutes, 1924-26. Records of E. I. Du Pont de Nemours & Co. Absorbed companies. Hagley Museum and Library, Wilmington, Delaware, Accession 500, box 847.

of 1927-1928, Du Pont authorised three-fold expansion in output of synthetic ammonia, based on the introduction of the Casale process. New Casale-type converters were ordered for installation in a designated building.[74] By this time, Casale converters of 20-ton daily rated capacity were in general use.

Hydro-Electric was retained as a Du Pont subsidiary, probably in the hope that the phosphorus-hydrogen process, or other electrochemical processes might become viable. Lazote's arrangements with Casale interests presumably included access to a new feature, the ejector, a static piece of equipment which did away with the need for a gas circulation pump, as developed by Luigi Casale at Terni. This was an important consideration since reciprocating pumps and compressors working under the high pressure conditions required frequent attention, and there were always concerns over contamination of gas mixtures with lubricating oils.

DIVERSIFICATION AT BELLE

The success with ammonia encouraged Roger Williams to develop a high-pressure methanol process, using the same converters as employed in the ammonia synthesis. Methanol production was expanded greatly from around 1928. It was used in the production of formaldehyde (for Bakelite), antifreeze, and other large volume products. Significantly, by 1928 American inventors had developed four of the eight synthetic ammonia processes in use (General Chemical/Allied Chemical, Du Pont, FNRL, and NEC). However, it was Du Pont's entry into high-pressure chemistry that stimulated the development of more general high-pressure chemical production.

Technology transfer from Europe to Du Pont in the area of ammonia production included a contribution from Britain's ICI. At the end of the 1920s, ICI and Du Pont drew up an agreement for exchange of knowhow. ICI (into which Brunner, Mond had been merged in 1926) had an interest in Allied Chemical, through Solvay Process, and the agreement was strongly opposed by Orlando Weber. In November 1928, ICI severed its ties with Allied Chemical. Soon after, Du Pont representatives inspected the ICI Billingham ammonia factory. While much was learned, it was perhaps not readily applicable to the high-pressure processes at Belle. Probably of great interest were the water gas process for manufacture of hydrogen, which closely followed German technology, as copied from BASF, oxidation of ammonia to nitric acid, control instruments, and perhaps ICI's then early work on steam reforming of hydrocarbons for manufacture of hydrogen.

In 1929, following the increased reliance on Casale technology, Du Pont bought out Air Liquide's holdings in Lazote, a strategy that was adopted in other cases of joint ventures with European companies.[75] Du Pont's ammonia interests became the Du Pont Ammonia Corporation. By September 1929, expansion at Belle brought the rated daily capacity of ammonia to over 220 tons. In around 1930, the daily capacity at Belle was 100 tpd of ammonia by the Casale process, and 125-tpd by the Claude process.[76]

Reminiscences of managers and staff at Belle show that for a few years the Claude and Casale processes were confined to separate production areas; and the main early increase in production was due to the introduction of Casale technology.[77] The Du Pont synthetic ammonia process, through innovations adopted from the Casale process, had become the modified process of Du Pont.[78] Contemporary accounts, including by Du Pont personnel, speak of the excellence of Du Pont's ammonia process. The process, it was noted, "has decidedly new and advantageous features and represents a radical departure from the original Claude process."[79] Jasper Crane, writing in 1933, stated that the "best features" of the French and Italian processes "were adapted to … American conditions."[80] One author even referred to the "modified Casale process operated by Du Pont."[81]

In 1931, the assets of the Du Pont Ammonia Corporation were transferred to the new Ammonia Department, with Wardenburg as general manager. National Ammonia remained a separate Du Pont company, working closely with the Ammonia Department.[82] Further expansion at Belle during the early 1930s brought the annual rated capacity of synthetic ammonia to around 145,000 tons. Ammonia was converted into ammonium sulphate fertilizer, nitric acid, and other industrial products. A Sales Development Division investigated new uses for the ammonia. The location of the Belle facility, in the lower Kanawha Valley, well inland, and protected, was used to emphasise the strategic value of the site for purposes of producing nitrogen products important to the national defence.

Contrary to the early expectations at Du Pont, its very high-pressure process did not make the Allied Chemical (General Chemical) and similar processes carried out below 300 atmospheres obsolete. By the mid-1930s, Allied Chemical was responsible for 60%, and Du Pont for 40%, of synthetic ammonia produced in the United States. They collaborated in control of the fertilizer market, partly through Allied Chemical's Barrett Division, as distributor of ammonium sulphate. One important outcome of the availability of inexpensive synthetic ammonia was that during the 1930s it almost completely replaced Chilean nitrate as the source of the world supply of nitric acid. Anhydrous ammonia, from all sources, continued to be largely used as a refrigerant, though consumption relative to synthetic ammonia for fertilizer use was not great. National Ammonia remained Du Pont's distributor of anhydrous ammonia.

DU PONT INNOVATIONS

The Wilmington-based Du Pont was, for long periods of its history in the 20th century, the most innovative chemical company in North America. During and after World War I it became one of the leaders in aromatic organic chemistry, enabling massive expansion during the 1920s in the manufacture of synthetic dyestuffs and modern explosives. In dyes and other sectors Du Pont relied on its capabilities as a prolific dealmaker, particularly for access to new technologies. This is reflected in the long list of strategic acquisitions made by the corporation as held at the Hagley Museum and Library. How, and under what circumstances, those acquisitions were made, and for what reasons, varied according to the perceived needs of the corporation. In the case of ammonia, as this article has demonstrated, it was the failure of the expensive Claude technology, but the commitment to high-pressure chemistry, that was the stimulus for acquisition of the Casale technology that operated over a similar pressure range. Niagara Ammonia, The Ammonia Corporation, and the Hydro-Electric Chemical Company, are just three entries in the portfolio that direct historians to folders on absorbed companies. These Casale enterprises contributed to the great success with catalytic high-pressure chemistry achieved by 1930.

The lessons taken from this small but highly instructive episode relate to the balance of power between weak firms or start-ups with a useful technology and large corporations desperate to gain access to that technology. By delving deeply into the archival records, much about how and why has been revealed, directly and indirectly, concerning Du Pont's motives and actions for entering into a new area of the nitrogen industry. Above all, the fine detail of these acquisitions reveals far more than the overlapping stories of one struggling start-up and the initial failure of a major corporation when embarking on a completely new area of diversification. It concerns what was genuinely an important, and eventually highly successful, phase in Du Pont's interwar entry into a new sector of heavy chemical industry.

This provided a novel context for innovation, and, I argue, probably the key to one of the most profound transformations at Du Pont, ensuring that the corporation remained relevant in commercialization of new discoveries for decades to come. Though synthetic ammonia was certainly low in the list of Du Pont innovations, and at first hardly met the criteria for investment, it had a tremendous impact on the long term standing of a technology giant. Early on, research and development for new products based on high-pressure processes enabled Du Pont to alleviate the difficulties confronted by the loss-making Ammonia Department.[83] This helped to propel the corporation to first place as the leading innovative chemical firm in the United States, drawing on catalytic high-pressure technologies for industrial production of a proliferation of new of products, notably nylon, followed by other polymers, and later even broader diversification.[84] From 1930, there was also, from a different direction, the first chlorofluorocarbon (CFC) cooling refrigerant, Freon, commercialized by Du Pont, following research at General Electric. It was adopted for air conditioning, and later household refrigeration; in several uses it replaced sulphur dioxide and ammonia.[85]

Du Pont's expertise in ammonia technology, drawing on its acquisition of the Casale process, contributed to American preparedness for war after the government decided to construct ammonia factories for munitions production. Du Pont built the first government-owned contractor-operated facility, completed in 1941, at the Morgantown Ordnance Works, Monongalia County, West Virginia, with a capacity of 180,000 tons of nitrogen per year.

Du Pont, Pacific Nitrogen, and Roessler & Hasslacher Co.

For sake of completeness, it is worth including a brief account of Du Pont's two other acquisitions in early synthetic ammonia businesses, one on the west coast and the other on the east coast. The west coast venture, which we have already met, was the Pacific Nitrogen Corporation, of Pacific Ammonia, the affilitate of National Ammonia, in Seattle, Washington. Pacific Nitrogen, was incorporated in 1924. Its entire stock was acquired by Du Pont in 1927.

Pacific Nitrogen used the FNRL process to produce both anhydrous ammonia and ammonia liquor. In May and June 1928, the Seattle plant produced 2.98 tons of ammonia every 24-hour hours, in accord with the daily capacity of its single FNRL unit.[86] In April 1928, Pacific Nitrogen was authorised to receive the electrolytic cells of Niagara Ammonia: "App[ropriation]n $35,000.00 – Purchase and installation of 170 electrolytic cells owned by Lazote, Inc., and at present at the plant of the Niagara Ammonia Company, Niagara Falls, New York" (capitals in the original).[87] Their installation in Seattle was completed in July 1928. Caustic potash for charging the cells was due to arrive on July 22nd, "and it is anticipated that the cell installation will be ready for trial operation the latter part of August." On 31 December 1930, the Du Pont Ammonia Corporation, as owner of the stock of Pacific Nitrogen, arranged to take over its assets and property.[88] The Pacific Nitrogen factory, the last in the United States to use dedicated electrolysis cells for hydrogen in manufacture of ammonia, was closed down in the early 1930s.[89]

The east coast synthetic ammonia business was that of Roessler & Hasslacher Co., of Niagara Falls, where production based on a modified FNRL process, also at a rated capacity of 3-tpd, began in 1926. For synthetic ammonia, it relied on in-house by-product hydrogen from electrolytic manufacture of sodium, and, from 1928, by-product hydrogen piped to the factory from Hooker Electrochemical.[90] In 1928 the ammonia capacity of the facility was raised to nine tons daily. Uses included in the manufacture of sodium cyanide, as well as for general sale. In 1930, Du Pont acquired Roessler & Hasslacher Co.; in 1932 it became the R&H Division of Du Pont (and later the Electrochemicals Division).

CONCLUSION

Late in 1927, the leading American journal of industrial chemistry, *Industrial and Engineering Chemistry*, reported that "A belated start in the fixation of atmospheric nitrogen seems to have been overcome by the development of our own processes—so satisfactory as to more than hold their own in world competition."[91] The turning point in the establishment of a competitive American synthetic ammonia industry would be achieved from late 1928. Until then, production in the United States was on a small scale, and mainly for the refrigeration market. This, however, demanded purer ammonia than was at first available, as we have seen at Allied Chemical and Niagara Ammonia. Significantly, Allied Chemical's Syracuse facility, the first to operate with any degree of success, served mainly as an experimental facility. The same was true elsewhere, including at Du Pont, even if not intended. Du Pont, suffering from problems with the Claude process, had to look elsewhere. During 1926-1927, Du Pont resorted to patent litigation against a weaker rival, the group of financially troubled Casale-related firms, to gain access to the latter's process patents. Du Pont, after having acquired its intended trophy, as well as Casale equipment, quickly dismembered and bankrupted Niagara Ammonia and The Ammonia Corporation, and embarked on nitrogen fertilizer and nitric acid production, both starting with synthetic ammonia.

From late 1928, five years after success in Europe and Japan, and partly through changing economic conditions, the US synthetic ammonia industry began to stand its ground in production for the fertilizer market. Du Pont and Allied Chemical were the main producers; their competitive advantages arose from the large scales of production. However, not long before the Wall Street Crash the exuberance of the late 1920s was already being tested by the threat of global overproduction and overinvestment in nitrogen fertilizers. During 1929-1932, cutbacks were substantial. However, when recovery and renewed diversification began, there was an atmosphere of free and uninhibited innovation and extraordinary growth in the American chemical industry, especially at Du Pont. Synthetic nitrogen fertilizers and catalytic high-pressure processes, including for methanol, higher alcohols, and the spinoffs from research into synthetic gasoline, were at the forefront, stimulated by the examples of rivals in Europe. The new triumph of American high-pressure chemistry enabled innovations that became bargaining tools in dealing with foreign manufacturers. The export of Du Pont and NEC ammonia technologies and know how brought in considerable revenue. A decade on, in the mid-1940s, the US synthetic ammonia industry, following massive expansion for munitions purposes during World War II, had become a world leader, and was still growing.

Within the larger context of the growth and expansion of the American chemical industry, the ammonia sector represented one of the main areas in which diversification relied on the adoption of European technologies and acquisition of firms that offered novel product lines.[92] In this, Du Pont moved from the manufacture of dyes and intermediates, through inhouse research, and then into high pressures and synthetic nitrogen and related products. However, the delayed entry into the latter was in part due to the already high investment in imported nitrates that were necessary for production of nitric acid used in synthetic dye and explosives production. Once success had been achieved in synthetic ammonia at Du Pont, following acquisition of Niagara Ammonia, and the Casale patents, the conversion of ammonia by oxidation into nitric acid was a logical next step, as was invention of a synthetic methanol process, and conversion of ammonia into urea. This was the prelude to Du Pont's rise to first place among innovative American firms, particularly in the mid-1930s, with manufacture of nylon, which relied on synthetic ammonia. Allied Chemical may have been less innovative, but, significantly, sacrificed synthetic organic chemistry in order to enhance its role in ammonia production, with, from the late 1920s, an emphasis on nitrogen fertilizer production. In nitrogen products, there were strong parallels elsewhere, most particularly at the American Cyanamid Company which during World War I had converted its calcium cyanamide, based on a German process, and originally produced as a fertilizer, into ammonia for the manufacture of explosives, and of urea for Du Pont. The ammonia was oxidised in German-made plant, imported just before the war. American Cyanamid, however, moved into synthetic dyes later than Du Pont, with the acquisition in 1927 of the Calco Chemical Company, itself a merger of firms engaged in dyes and pigments.[93] In 1930, American Cyanamid entered into synthetic ammonia and methanol through acquisition of the Chemical Construction Company (Chemico) that had acquired the Nitrogen Engineering Corporation and its synthetic ammonia process. Chemico's synthetic ammonia process, like that of Du Pont, was soon after licensed to several European firms. From the 1930s, transatlantic technology transfer of high pressure and many other chemical processes, including for nitric acid, was just as likely to be from America to Europe (and elsewhere) as it was from Europe to America.

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55. Claude's first ammonia patent in the United States was no 1332460 of 2 March 1920. In 1921, he received a US patent for obtaining hydrogen from a gas mixture, and another for an apparatus suited to high pressure, high temperature exothermic reactions; in 1922, two patents for producing hydrogen and one for separating constituents in a gas mixture; in 1923, one patent for high pressure apparatus for production of ammonia, and one patent for a thermally insulated apparatus. Three of Claude's six US patents filed in 1924 covered the use of ammonia in production of ammonium chloride and sodium carbonate, which was relevant to the Solvay alkali process.
56. Claude Patent for a Method for Direct Synthesis of Ammonia, *Ind. Eng. Chem.*, **1925**, *17*(9), 985. Claude's US ammonia patents were assigned to Lazote.
57. Glancing Back Over 1926, *The Du Pont Magazine*, **1927**, *21*(3), 1.
58. Varnes, Pioneering in High Pressure, p. 14.
59. Hounshell and Smith, *Science and Corporate Strategy*, pp. 183-189.
60. W. Haynes, *American Chemical Industry: A History*, vol. IV. *The Merger Era*. D. Van Nostrand, New York, **1948**, p. 88. Meantime, National Ammonia Co. and Armour & Co. in 1926 had taken out licenses for ammonia processes from the Chemical Foundation.
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67. Hydro-Electric Chemical Co., stock certificates, transfer documents, 10 June 1927. Including affidavits of Guiseppe Albisetti, member of the council of administration, Ammonia Casale SA, and Luigi Calissano, manager of Ammonia Casale SA, before the consulate of the United States of America, Milan, Italy. Hydro-Electric stock.
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71. Du Pont, Wilmington, letters regarding meeting to be held on 26 January 1928 to consider voluntary petition in bankruptcy of Niagara Ammonia Company, Inc., 19 January 1928, Niagara Ammonia. Ammonia Corporation, Board of directors, meeting no. 41 (Special meeting), 26 January 1928; board of directors, meeting no. 42 (special meeting), 10 March 1928, Ammonia Corporation, box 66.
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Research Articles

The «D.I. Mendeleev's Periodic System of the Elements» Mural Near the Mendeleev Institute for Metrology in Saint Petersburg: How Metrologists Celebrated the 100th Anniversary of the Scientist

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Abstract. This article is timed to the celebration of the International Year of the Periodic Table of Chemical Elements, declared by the UN and UNESCO in connection with the 150th anniversary of the discovery by D. I. Mendeleev of the Periodic Law of Chemical Elements (1869). The article highlights the metrological activity of D. I. Mendeleev and tells about how in the scientific metrological center, he created the Main Chamber of Weights and Measures. Now the D.I. Mendeleyev Institute for Metrology (VNIIM*)* preserves the memory of the life and activities of the great Russian scientist and encyclopedist. Based on the research carried out in the archives of St. Petersburg and the funds of Metrological Museum, the article for the first time details the history of the formation of the Mendeleev memorial complex on the territory of VNIIM. The contribution of the institute metrologists to the creation of such famous sights of St. Petersburg as the monument to D. I. Mendeleev (sculptor I. Ya. Ginzburg, 1932) and the mural (mosaic) «D. I. Mendeleev Periodic system of elements» (1935) on the occasion of the 100th anniversary of the scientist is shown. All peripteries, related to the installation of the monument - table are described: a selection of options for the arrangement of elements, decoration, manufacturer and manufacturing techniques, coordination with various organizations, solving financing issues.

Keywords: D. I. Mendeleev, D.I. Mendeleyev Institute for Metrology (VNIIM), Metrological Museum, monument to D. I. Mendeleev, mural (mosaic) D. I. Mendeleev's periodic system of elements.

Figure 1. General view of the historic buildings of VNIIM, St. Petersburg, Russia, Moskovsky pr., 19. Photo from the collection of the Metrology Museum hosted by the D.I. Mendeleyev Institute for Metrology, November 2010.

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The year 2019 was notable for the two memorable dates associated with the name of D.I. Mendeleev, a great Russian scientist and encyclopedic mind of his time: February 8th marked by the 185th anniversary of the scientist's birth, and February 17th, the 150th anniversary of the Periodic Law that he discovered. To honor these anniversaries, the United Nations General Assembly, in liaison with UNESCO, proclaimed 2019 the International Year of the Periodic Table of Chemical Elements, and the global scientific community widely celebrated these events. The year started with the opening ceremony at the UNESCO quarters in Paris on January 29, 2019 and the closing ceremony took place on December 5, 2019, in Japan.

In Russia, most of the anniversary events were held in St. Petersburg, the city that played the most important role in the life and work of D.I. Mendeleev. It was in this city indeed that he studied at the Chief Pedagogical Institute (Главный Педагогический Институт) (1855), discovered the famous Periodic Law of Chemical Elements (1869), and gave lectures for 40 years in the city's largest higher educational establishments, such as Institute of Railway Engineers, Technological Institute, St. Petersburg University (1861–1890). Then he founded and headed the first scientific metrological establishment of the country – Main Chamber of Weights and Measures (1892–1907) – which is still functioning today under the name of *All-Russian Scientific Research Institute for Metrology* and is known to the world as the *D.I. Mendeleev Institute for Metrology (VNIIM)*. The scientist's name was appended to that of the Institute in 1945. The memory of the founder of scientific metrology has been held sacred at VNIIM for more than a century.[1]

The D.I. Mendeleev Institute for Metrology was instrumental in organizing and holding main Mendeleev-related events during the International Conference *Mendeleev-150* and *XXI Mendeleev Congress on General and Applied Chemistry*. During the visits to VNIIM, Russian and foreign guests got acquainted with the Institute's activities and with the unique heritage connected to Mendeleev. The historical site and architectural objects located on its premises feature the century-old buildings where D.I. Mendeleev lived and worked, the sculptural and painted portraits of the scientist, and the Metrology Museum. Of particular interest is the Mosaic Panel displaying Mendeleev's Periodic System, produced on the initiative of metrologists in 1935 to be appended on the wall of the building adjacent to VNIIM (at that time this building belonged to the Artillery School, now housing the Suvorov Military School). The story behind the panel and a number of other monuments to D.I. Mendeleev on the VNIIM's territory is associated with the 100th anniversary of the scientist's birth celebrated in 1934 and is the topic of the present contribution.

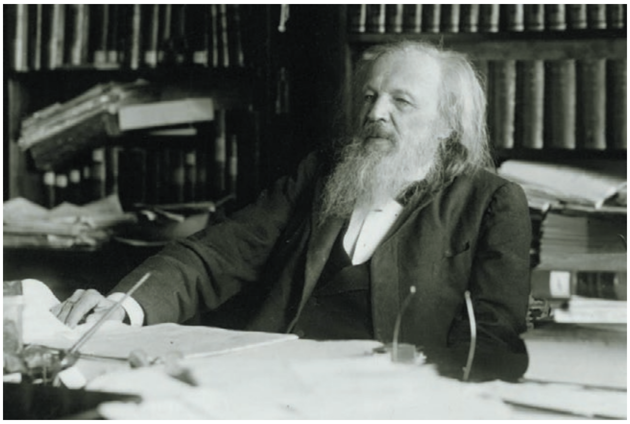


Figure 2. D. I. Mendeleev was the author and the main architect of the metrological reform in Russia (1892-1907). On his initiative, the Depot of Measures and Weights was transformed into a scientific metrological center – the Main Chamber of Measures and Weights (VNIIM since 1934). Photo from the collection of the Metrology Museum hosted by the D.I. Mendeleyev Institute for Metrology, 1904.

Figure 3. Employees of the Main Chamber of Measures and Weights, who worked with D. I. Mendeleev, posing in the first exhibit of the museum. Among them: Mikhail Mladentsev (former MCWM Scientific Secretary, sitting first from the left), Alexey Skvortsov (former personal secretary of D. I. Mendeleev, standing second from left), Alexander N. Dobrokhotov (standing third from left), Victor Mueller (standing fifth from left) and etc. Photo from the collection of the Metrology Museum hosted by the D.I. Mendeleyev Institute for Metrology, 1934.

HONORING THE MEMORY OF THE FOUNDER – CREATION OF THE MENDELEEV MUSEUM AND THE MONUMENT TO MENDELEEV IN THE MAIN CHAMBER OF WEIGHTS AND MEASURES

Back in 1925, in order to preserve the memory of D.I. Mendeleev and his work, his colleagues and students founded Mendeleev Group at the Main Chamber of Weights and Measures (MCWM). It consisted of the MCWM President Dmitry P. Konovalov (Chairman), Mikhail N. Mladentsev, Alexander N. Dobrokhotov, Victor A. Mueller, Alexey.V. Skvortsov, as well as the scientist's son, Ivan D. Mendeleev. They formed the Mendeleev Fund of the Main Chamber Museum, which was opened to visitors on December 16, 1928, on the day of the Annual Grand Meeting of VNIIM staff. The first exhibit, located in the scientist's office, showcased not only D.I. Mendeleev's contribution to the development of metrology science, but also the main stages of his life and work.[2]

In 1930, the MCWM began preparations for the celebration for the 100th anniversary of Mendeleev's birth. To organize the celebration an All-Union Commission was created. Among its members there were the Director of the All-Union Research Institute of Metrology and Standardization (VIMS; former MCWM, today the D.I. Mendeleev Institute for Metrology, VNIIM), the academician M.A. Shatelen, the Heads of Republican Chambers of Weights and Measures, as well as Mikhail N. Mladentsev, who headed the Mendeleev Museum at the Main Chamber of Weights and Measures - VNIIM from 1928 to 1941.

On May 6, 1930, the Commission heard the report of M.A. Shatelen on the main activities planned by metrologists to prepare the celebration.

The main proposal was to *"install a bronze monument* to *D.I.* Mendeleev *in the Main Chamber courtyard in front of the house where* scientist *lived"*. Previously, negotiations were held with the sculptor Ilya Ya. Gintzburg who *"agreed to donate his beautiful work – a statue of D.I. Mendeleev sitting in his chair"* and offered to cast and to install the monument, free of charge. According to D.I. Mendeleev's son and his widow, and to people who knew him well and worked closely with him, *"the statue bears a great resemblance to Mendeleev"*.

Ilya Ya. Gintzburg made a statuette depicting a scientist sitting in an armchair with a book in 1890, then D. Mendeleev posed for the sculpture for three months (from March to April). I. Gintzburg took this work as a basis when creating a bronze monument to Mendeleev in the *in the Main Chamber courtyard.* (The author's copy of this figurine, made by Ilya Gintzburg of plaster, is still kept in the collection of the Metrological Museum).

Other proposals included publication of his works, making a film and a book on D.I. Mendeleev's metrological activity, drawing (and printing) his portrait, etc.[3] The Commission decided to accept all those proposals submitted by M.A. Shatelen.[4] They were accepted by the decision of the 9th All-Union Conference of Verification Specialists and sent to the Chairman of the Council of Labor and Defense (STO) Standardization Committee on December 9, 1930. As a result, the Resolution of the STO All-Union Committee for Standardization Presidium dated December 20, 1930, decided to erect a monument dedicated to D.I. Mendeleev and to fund the corresponding work.[5]

Ilya Ya. Ginzburg redeemed his promises given to the Commission: he provided a model of the monument and supervised its casting and installation, all free of charge. The allocated funds were spent on materials – granite and bronze.

It can be seen that the D.I. Mendeleev monument was created within a relatively short period of time. Its inauguration coincided with the 25th anniversary of

Figure 4. Inauguration of the monument to D. I. Mendeleev in the square of the Main Chamber of Measures and Weights. Photo of February 2, 1932 Photo from the collection of the Metrology Museum hosted by the D.I. Mendeleyev Institute for Metrology. Note. The figure (bronze, granite) is 1.86 m, the pedestal of red unpolished granite is 1 m. The monument is under protection of the State and it was included in the List of Historical and Cultural Heritage Objects of Federal Importance by the Decree of the Government of the Russian Federation No. 527 dated July 10, 2001). The monument is also registered with the State Budgetary Institution of Culture "State City Museum of Sculpture" (since 1993) and included in the Museum Fund of the Russian Federation (Preservation Order dated September 18, 2019, Order of the State Inspectorate for the Preservation of Monuments No. 07-19-439/18). В 1934 г. All-Union Scientific Research Institute of Metrology and Standardization (VIMS) was renamed into the All-Union Scientific Research Institute of Metrology (VNIIM).

the scientist's death – February 2, 1932. The monument was placed in the MCWM courtyard on the very spot of the garden house favored by the scientist for taking a rest while living in the «Red House». D.I. Mendeleev is portrayed sitting on a chair with an open book in his hand surrounded by heavy volumes, manuscripts, and books, one bearing of them the inscription «Временник Главной палаты мер и весов» (Chronicles of the Main Chamber of Weights and Measures), which was the first metrological journal published in Russia on the initiative and under the leadership of D.I. Mendeleev. At the opening ceremony, academician M.A. Shatelen said: «*I hope, this monument is a precursor. Probably, our State will build a worthy monument to honor Mendeleev's 100$_{th}$ anniversary. But this small, one might say, homely monument, will be a place of pilgrimage for us, so to speak. Mendeleev is the founding father of our metrology. If we use extensive achievements of metrology, if we can legitimately consider our Institute, VIMS (All-Union Scientific Research Institute of Metrology and Standardization), to be one of the leading institutions of this kind on a global scale, we undoubtedly owe that to Dmitri Ivanovich*».[6]

CELEBRATING MENDELEEV THROUGH THE PERIODIC SYSTEM

On September 22, 1933, to prepare for the 100th anniversary of D.I. Mendeleev an Organizing Committee was created at VIMS for the "ceremonial honoring the memory of D.I. Mendeleev". It consisted of the Institute's staff: academician A.A. Baykov (Chairman), A.N. Dobrokhotov, S.Z. Snarsky (Director), profs. L.V. Zalutsky, M.F. Malikov, A.K. Kolosov, V.E. Murashkinsky, A.T. Gorbov, I.D. Mendeleev (son), and M.N. Mladentsev (Scientific Secretary).

The Committee was tasked with developing, approving, and supervising the list of events dedicated to the scientist's anniversary and the perpetuation of his memory, estimating the costs, liaising with other scientific institutions that wished to participate in the commemorative events.[7] Among the proposals received were among others: to rename the Mezshdunarodniy (International) Avenue into Mendeleev Avenue, to organize conferences, lecture courses, to republish D.I. Mendeleev works, to restore D.I. Mendeleev's estate in the village of Boblovo. The most interesting of the proposals received was to install a Mosaic Panel featuring Mendeleev's Periodic System of Elements on the wall of the Artillery School (today the Suvorov Military School) adjacent to VNIIM.

The making of the monument was discussed at the Organizing Committee meetings of 1933– 1934, including the issues related to expenses, contracting, styling and manufacturing, as well as obtaining the necessary permits.

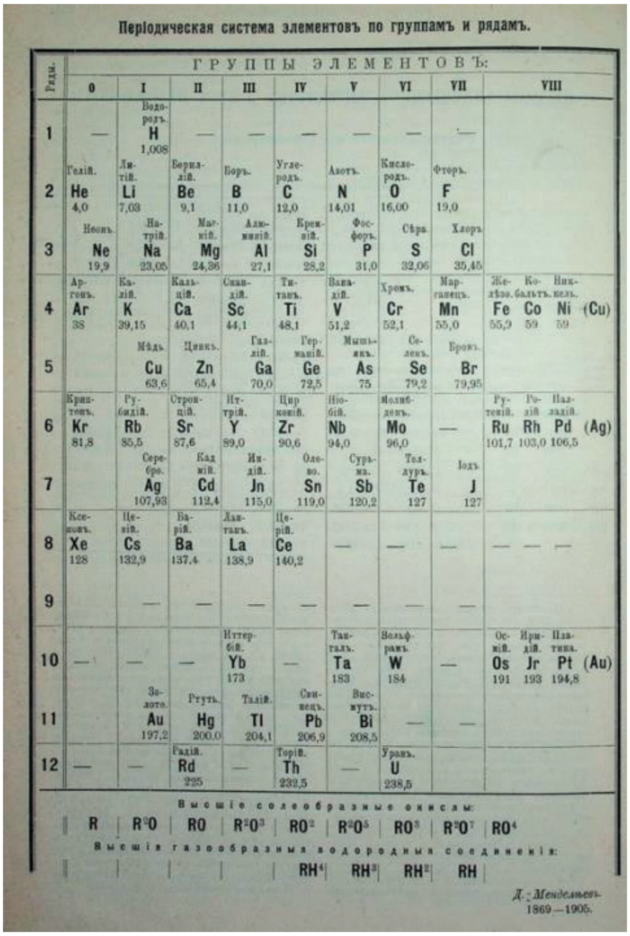
Negotiations were conducted with the Lomonosov Porcelain Factory, State Ceramic Research Institute and Russian Academy of Arts. Initially, it was planned to order the Table to be made of ceramic tiles at the Lomonosov Porcelain Factory art laboratory; however, during the negotiations held by Alexander K. Kolosov, it turned out that the monument would be ready only by the spring of 1934 (i.e. by the anniversary, but not by February 8). Yet still the most difficult was to decide which table should be used as a basis.

On December 27, 1933, the Organizing Committee discussed the proposal of A.I. Gorbov and M.N. Mladentsev, who were entrusted with drawing up a draft of the Table. They supported picturing the Table as it was printed in the 8th (1906) edition of D.I. Mendeleev's *Foundations of Chemistry*.[8] Some of the Committee members, including Ivan Dmitrievich Mendeleev, believed that "the Table would serve both as a monument, and a study guide, which would make it improper to depict the Table in 1934 as it was in 1906, because great changes have taken place since then".[9]

The discussion did not lead to a final decision, and VIMS Director S.Z. Snarskiy was charged with convening an ad-hoc meeting with academicians N.S. Kurnakov, A.B. Favorskiy, V.E. Tischenko, V.Ya. Kurbatov, S.P. Vukolov, I.Ya. Gintzburg, the representatives of the Lensovet Development Authority and VIMS public organizations to study drafts of the Table.[10] Thus, by January of 1934, two main issues - which of the proposed Tables should be chosen and who should be commissioned to manufacture it - remained unresolved.

On January 15, 1934, given the newly discovered disagreements, an extended Organizing Committee meeting was held to discuss the drafts of the Table. After an extensive debate, the Committee decided to opt for the Periodic Table proposed by Ivan Mendeleev. The Table published in the 8th edition of D.I. Mendeleev's *Foundations of Chemistry* was agreed upon as a basis, with addition of the elements discovered from 1906 to 1934. Protocol Resolution No. 11 states:

- to recognize, that all additions to the Table made after D.I. Mendeleev's death must be depicted in a different color,
- to recognize as desirable the addition of atomic weights to the Table, if no technical or esthetic considerations interfere with doing so,
- to ask the VIMS architect to prepare, according to instructions of A.K. Kolosov and I.D. Mendeleev, a draft of one or more symbols of the Table in full size



Періодическая система элементовъ по группамъ и рядамъ.

Ряды.	ГРУППЫ ЭЛЕМЕНТОВЪ:								
	0	I	II	III	IV	V	VI	VII	VIII
1	—	Водородъ. H 1,008	—	—	—	—	—	—	
2	Гелій. He 4,0	Литій. Li 7,03	Берилій. Be 9,1	Боръ. B 11,0	Углеродъ. C 12,0	Азотъ. N 14,01	Кислородъ. O 16,00	Фторъ. F 19,0	
3	Неонъ. Ne 19,9	Натрій. Na 23,05	Магній. Mg 24,36	Алюминій. Al 27,1	Кремній. Si 28,2	Фосфоръ. P 31,0	Сѣра. S 32,06	Хлоръ. Cl 35,45	
4	Аргонъ. Ar 38	Калій. K 39,15	Кальцій. Ca 40,1	Скандій. Sc 44,1	Титанъ. Ti 48,1	Ванадій. V 51,2	Хромъ. Cr 52,1	Марганецъ. Mn 55,0	Желѣзо. Кобальтъ. Никкель. Fe Co Ni (Cu) 55,9 59 59
5		Мѣдь. Cu 63,6	Цинкъ. Zn 65,4	Галлій. Ga 70,0	Германій. Ge 72,5	Мышьякъ. As 75	Селенъ. Se 79,2	Бромъ. Br 79,95	
6	Криптонъ. Kr 81,8	Рубидій. Rb 85,5	Стронцій. Sr 87,6	Иттрій. Y 89,0	Цирконій. Zr 90,6	Ніобій. Nb 94,0	Молибденъ. Mo 96,0	—	Рутеній. Родій. Палладій. Ru Rh Pd (Ag) 101,7 103,0 106,5
7		Серебро. Ag 107,93	Кадмій. Cd 112,4	Индій. Jn 115,0	Олово. Sn 119,0	Сурьма. Sb 120,2	Теллуръ. Te 127	Іодъ. J 127	
8	Ксенонъ. Xe 128	Цезій. Cs 132,9	Барій. Ba 137,4	Лантанъ. La 138,9	Церій. Ce 140,2	—	—	—	— — —
9		—	—	—	—	—	—	—	
10	—	—	—	Иттербій. Yb 173	—	Танталъ. Ta 183	Вольфрамъ. W 184	—	Осмій. Иридій. Платина. Os Jr Pt (Au) 191 193 194,8
11		Золото. Au 197,2	Ртуть. Hg 200,0	Таллій. Tl 204,1	Свинецъ. Pb 206,9	Висмутъ. Bi 208,5	—	—	
12	—	—	Радій. Rd 225	—	Торій. Th 232,5	—	Уранъ. U 238,5		
Высшіе солеобразные окислы:									
	R	R^2O	RO	R^2O^3	RO^2	R^2O^5	RO^3	R^2O^7	RO^4
Высшія газообразныя водородныя соединенія:									
					RH^4	RH^3	RH^2	RH	

Д. Менделѣевъ.
1869—1905.

Figure 5. "Periodic System of the Elements» published in the book by D.I. Mendeleev "Fundamentals of Chemistry". St. Petersburg. 1906.

Figure 6. Mosaic panel «D.I. Mendeleev's Periodic System of the Elements». Photo taken by E.Ginak, 2019.

in two versions: with the elements only and with both the elements and their atomic weights.[11]

In January 1934, on behalf of the VIMS Director S.Z. Snarskiy, letters requesting installation of the Table were sent to the Head of the Artillery School and the Lensovet Development Authority, and the corresponding permits were obtained.[12] However, the issue of contractor still had not been decided upon. Even the option of making a temporary table using oil paints was contemplated, but that was declined because of the unfavorable climate conditions in the city.

Only on June 5, 1934, an agreement was concluded between VIMS, represented by its Director, S.Z. Snarskiy, and the All-Russian Academy of Arts, represented by the Head of Mosaic Department, Vladimir A. Frolov, on manufacturing of the Table. The Agreement states, that "The Institute instructs, and the Academy takes on execution of the *memorial plate to Professor D.I. Mendeleev* with unpolished mosaics (letters and digits) on faux stone cement background with marble chips and with the same frame to place it on the side wall of the building adjacent to the Institute".[13] The memorial plate was manufactured by the Academy using its materials; 12 barrels of Portland cement required for the project were provided by the Institute; the work was delivered in form of separate completed square stones of reinforced concrete without notching in two stages; the delivery of the finished parts was carried out by the Academy at its own expense. All work on installation of the tablet was carried out by the Academy; the Institute constructed the necessary scaffolding and provided 2 workers and cement mortar to fix the square stones on the wall. The Institute would pay the Academy 21 000 rubles for the work. The deadline was October 15, 1934.[14] All parts of the "memorial plate", as it was initially called, were manufactured and delivered on October 16, 1934, according to the Acceptance Certificate.[15] Architectural design of the wall was developed by architect D.L. Krichevskiy. Inauguration of the Mosaic Panel with *Mendeleev's*

Periodic System of Elements took place on November 10, 1935. (The height of the monument is 9 m; the total area is 69 sq.m).

LIFE OF A MONUMENT «D.I. MENDELEEV'S PERIODIC SYSTEM OF THE ELEMENTS»

In 1983, during the preparation for the celebration of 150th anniversary of D.I. Mendeleev, VNIIM pointed out that the Periodic System Mural needed some repairs. There were proposals to amend the state of the Table and to add the elements discovered after 1934. To this end, VNIIM applied to the authoritative commission (it included well-known historians of chemistry: professors Alexander A. Makarenya and Igor S. Dmiriev) asking it to check the accuracy of the Table symbols and structure. Finally, it was decided to act according to Protocol No. 11 dated January 15, 1934 and restore the monument to its original state.

In 2013–2017, a comprehensive reconstruction and restoration of the military school buildings was conducted. VNIIM sent a request to the State Inspectorate for the Preservation of Monuments to provide for the preservation and restoration of the unique mosaic on the wall. The Metrological Museum provided to the restorers the necessary information from archives on the history of the Periodic System Mural and on its particular features. A number of obvious repairs were carried out: cleaning, washing, reinforcement, etc. There are no plans now to introduce any changes to the 1935 Panel. Order No. 556-r dated 15.12.2017 of the State Inspectorate for Preservation of Monuments lists the "barracks" building and the Table on its wall in the register of cultural heritage objects of regional importance "Complex of buildings of the Imperial Orphanage (Konstantinovsky Military School)".

Figure 6. Monument to D.I. Mendeleev and Mosaic mural « D. I. Mendeleev Periodic System of Elements», St Peterbsurg. Photo taken by E.Ginak, 2019.

CONCLUSION

Thus, thanks to the efforts of the staff of the Main Chamber of Weights and Measures (VNIIM), a unique memorial complex was created in 1932-1935 in the center of St. Petersburg, dedicated to Mendeleev and his famous discovery. It invariably attracts the attention of St. Petersburgers, Russian and foreign guests of the city.

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Historical Articles

The Revolution in Science in America, 1900-1950

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Abstract. The US lagged behind the European powers, Germany, Britain and France, in scientific research and development at the beginning of the 20th century. Why this occurred and how Germany and Britain supported their flourishing scientific research cultures are discussed. The first serious expansion in basic scientific research in the US occurred with the influx of European Jewish scientists fleeing Nazism in the 1930's. They specifically brought with them knowledge of atomic physics. The influence of Vannevar Bush, who was Director of the Office of Scientific Research and Development during World War Two proved crucial for the expansion of civilian research and development after the War, supported by the Federal Government. Also after the War, Operation Paperclip brought German scientists to the US and they had significant influence on developments in aeronautics, rocketry and space exploration.

Keywords: History of science, American science, European science, Nobel prizes, Basic research.

1. INTRODUCTION

Americans are used to thinking of their country as the greatest in the world, both in terms of economic clout and military strength. But few know how it got that way. The fact is that the US became the greatest industrial power, out-performing the UK, its parent country, in industrial output (measured as GDP per capita, to correct for different sized populations) around 1890,[1] and has been estimated to have out-produced all of Europe around 1917, during World War One.[2]

But in military terms the US had no "regular" Army as generally understood until 1913, when Secretary of War Henry L. Stimson organized one, in the form of four divisions assigned to protect each geographical region of the USA.[3] At this time, the UK had a large military force both fighting in and occupying colonies throughout the world. For example, at the Battle of Waterloo in 1813, the British Army, consisting of regular and conscripted forces, numbered around 250,000 men.

But, at least until World War One, and more generally until World War Two, the US was still a secondary power, especially in scientific terms. Most of the great discoveries and basic research that revolutionized Western society were made in Europe, in the UK, Germany and France. But eventually the US out-stripped its European rivals in science too. How this happened is a unique and intriguing story.

The first organized attempt to improve US scientific standing was made in 1903 with the formation of the Carnegie Institute of Washington (CIW), founded by Andrew Carnegie, the Scottish immigrant steel magnate.[4] He specifically envisaged that the CIW would engage in basic research (without specific applications) in all areas of science. But, over time, the CIW's impact was limited.

The next great attempt to expand American science was made during and after World War Two by Vannevar Bush, an extraordinary intellect, who envisaged an early version of the internet, and who was appointed Adviser for Science and Development by President Roosevelt.[5] His influence caused a revolution in how science was thought of in America, both by the Government and its people.

Most people would be shocked to discover that the US became the great scientific and technological power it is today by ironically exploiting two groups of Germans, first German (and other European) Jewish émigré scientists before World War Two and then German scientists, particularly German rocket and aeronautical engineers, after World War Two.

I endeavor to tell the story of how America became the world's scientific superpower through these developments in science and technology.

2. AMERICA LAGS BEHIND EUROPE IN SCIENCE AT THE BEGINNING OF THE 20TH CENTURY

It was the end of one century and the beginning of another. At City Hall in New York City, electric lights formed giant letters that spelled out "Welcome 20th Century." Thousands of smaller lights studded the exterior of the building, forming delicate strands of red, white and blue. Thousands of US flags hung everywhere, and the entire city was ablaze with lights. If anything could be gauged from this display it was that electricity that had only recently been invented, was here to stay.[6]

As the hands of the big clock on City Hall reached midnight, all the lights suddenly went out. The City was plunged into darkness. It was a moment's silence that signified the ending of the old century, and when the lights returned, it was the signal that the new century had begun. The crowds began to sing again, bells pealed, and fireworks exploded in the sky. It was the beginning of a new century, 1900 had begun. No-one could have imagined what incredible and amazing discoveries lay ahead that would revolutionize society and everyone's life.

Already, the telegraph that had been invented by Samuel Morse in 1844 had revolutionized long-distance communication. Thomas Edison invented an improved carbon telephone transmitter for telephones in 1877 and the phonograph in 1878. But, it was the development of the first successful light bulb in 1879 that ensured he would be famous.[7] In search of a way to light up the city he formed the Edison electric light company in NY City and he said "We will make electricity so cheap that only the rich will burn candles."[8] To do this he invested in what became known as Direct Current (DC) electricity, ignoring the invention of one of his assistants, Nicola Tesla, an immigrant from Croatia, of Alternating Current (AC), a decision he would later regret. The competition between DC and AC is a well-known story,[9] but AC was found to be by far the best for transmission over long distances and the less dangerous, and when it was chosen to light the Pan-American Exposition in Chicago in 1895,[10] the stage was set for the electrification of America and the world. The future looked bright.

But, notwithstanding these developments pioneered by Edison and a few other inventors, there was a problem in America that few people foresaw. As scientific developments proceeded at a rapid pace in the early years of the 20th century, the US fell behind. Notwithstanding the development of heavy industry, including steel production and extensive railway systems, there was no organized attempt to foster basic research in America.

By contrast, in Europe, Germany and the UK had active and already traditional frameworks of fostering basic research at many famous universities and industrial laboratories. One can see from the ratio of Nobel Prizes that America lagged behind the European nations.[11] Nobel Prizes for such important work in physics as the discovery of radioactivity, the nature of the electron and the atom, in chemistry the development of dyes and drugs, in physiology the understanding of hemoglobin and the function of proteins and enzymes. In all these areas the research level and competition were much more intense in Europe than in America at that time (Figure 1).[12]

Here is a partial list of some early German Nobel Prize winners: In Physics; Roentgen (1901), Lenard (1905), von Laue (1914), Planck (1918), Stark (1919), Einstein (1921), Hertz (1925), Franck (1925), Heisenberg (1932). In Chemistry; Fischer (1902), von Baeyer (1905), Buchner (1907), Ostwald (1909), Wallach (1910), Willstatter (1915), Nernst (1920), Wieland (1927), Fischer

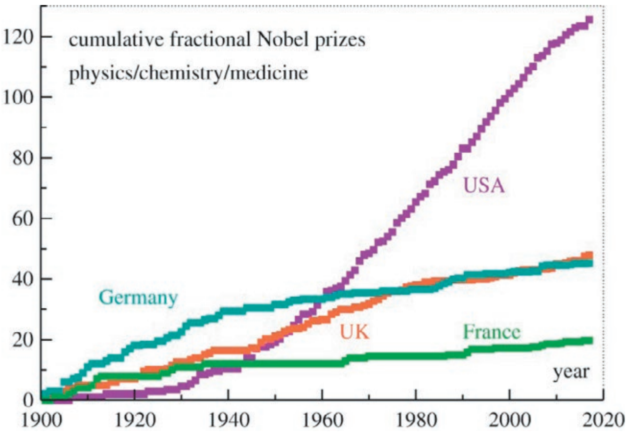

Figure 1. The cumulative number of physics, chemistry and medicine Nobel prizes per country. Prizes are attributed to the respective country according to the nationality of the recipients at the time of the announcement, with prizes obtained by more than one recipient accordingly divided. Note that the US population increased from 76 to 327 million during 1901–2017.[12]

(1930), Bosch (1931). These names are of the highest possible caliber and were responsible for establishing the highest level of these scientific subjects at the time. By comparison during this period the US had the following Nobel Prize winners: Physics; Michelson (German Jewish immigrant, 1907), Millikan (1923), Compton (1927), Davisson (1937), Lawrence (1939); Chemistry, Richards (1914), Langmuir (1932), Urey (1934). Frankly, there is no comparison. The same could be said of comparison of UK and US Nobel Prize winners during the same period 1901-1939.

What is the origin of these differences? In the UK, Government funding of science started in 1675 when the Royal Observatory was established in Greenwich. This was continued in the 19th century with the creation of the British Geological Survey in 1832, and the allocation of funds in 1850 to the Royal Society to award individual grants.[13]

By the First World War in 1915, claims about the poor state of British manufacturing compared to Germany, led to the Department of Scientific and Industrial Research (DSIR) being founded. It was a part of the UK government, staffed by civil servants who distributed grants, operated laboratories, and made policy. Examples included the Radio Research Station, established in Ditton Park in 1924.

In 1918, Richard Haldane produced an official report on the machinery of government that recommended that government departments undertake more research before making policy. It was recommended that they should oversee that specific, policy-minded research was carried out, governed by autonomous councils free from political pressure.

Following the Haldane Report's recommendations, the Medical Research Council (MRC) was created in 1920 from a previous body called the Medical Research Committee that had been established in 1913 to distribute funds collected under the National Insurance Act of 1911. In contrast to DSIR, the MRC was not a government department, its staff were not civil servants, and its resources were concentrated in a small number of central laboratories and a large number of research units associated with universities and hospitals.[13] This is still the pattern today.

In Berlin in 1909, Professor Adolf von Harnack, a close adviser to the Kaiser and a member of the Academy of Sciences, wrote a memorandum to Kaiser Wilhelm II in which he outlined a reform of the German science system. He proposed the establishment of independent research institutes conducting specialized basic research. He wrote that the rapid pace of industrialization had demonstrated the need for greater knowledge of basic sciences. Harnack proposed the foundation of a new type of research association for the advancement of science to be known as The Kaiser Wilhelm Society. Harnack's memorandum paved the way for a reorganization and the establishment of research Institutes that still characterize the German science system today.[14]

The Kaiser Wilhelm Gesellschaft (KWG) was founded in 1911 for the advancement of science and was formally independent of the German state. Some 30 Research Institutes and testing stations were founded all over Germany in specific areas of science. The KWG had Presidents such as Adolf von Harnack, Fritz Haber, Otto Hahn and Max Planck, and each Institute had its own Scientific Director. Funding was obtained from inside and outside Germany. After WWII the KWG became the Max Planck Geselleschaft. [15]

After the First World War the financial situation of the universities and scientific institutions was dire. Their budgets had not been increased since before the War and inflation was rapidly increasing. However, it was precisely in this period following the War that an increase in funding was most needed. The War had been responsible for the interruption of scientific and research activities, young researchers had been called up for military service and research projects had been interrupted. In addition, basic research had been almost completely discontinued in favor of research critical to the war. This situation was further exacerbated by the international isolation of German research, as a result of the Treaty of Versailles, which ascribed sole guilt to Germany for the First World War.

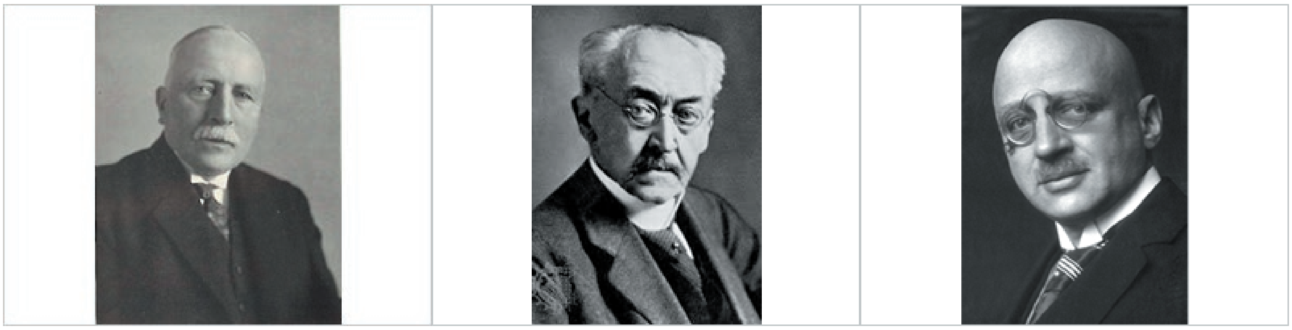

Figure 2. *Left*, Friedrich Schmidt-Ott, President of the Notgemeinschaft from 1920 to 1934; *Middle*, Adolf von Harnack; *Right*, Fritz Haber.

In 1920, leading representatives of science and scholarship in Germany established a working committee, which subsequently adopted the name Notgemeinschaft ("emergency foundation"). Its task was to coordinate joint action and proposals to the parliaments, governments and also potential sponsors in industry, in order to secure the provision of the necessary financial resources to continue basic research. Friedrich Schmidt-Ott, Adolf von Harnack and Fritz Haber played leading roles in this working committee, and also in lobbying the government for funding. [16, 17]

Friedrich Schmidt-Ott (Figure 2) was elected president of the Notgemeinschaft at the inaugural meeting in 1920. Adolf von Harnack was the President of the Kaiser Wilhelm Society (KWG, later the Max Planck Institutes) founded in 1911. Fritz Haber was director of the Kaiser Wilhelm Institute of Physical Chemistry and Electrochemistry in Dahlem. He was awarded the Nobel Prize for Chemistry in 1919 for the fixation of nitrogen from the air. He and Adolf von Harnack became members of the Executive Committee of the Notgemeinschaft in 1920.

The concerns of the Notgemeinschaft fell on sympathetic ears in government and in society; a decline in the standard of German research compared with other nations was seen as a loss of national honor. In addition, there were concerns about a negative impact on Germany's future economic development. In an application by the Notgemeinschaft for financial support from the Reich Government in 1920, Adolf von Harnack stressed the importance of science and research for Germany's overall development:

> The vital necessities of the nation include the preservation of the few assets that it still possesses. Among these assets, German science and research occupy a prominent position. They are the most important prerequisite not only for the preservation of education in the nation and for Germany's technology and industry, but also for Germany's reputation and its position in the world, on which in turn prestige and credit rely.

Following debates on the allocation of Reich funds to the nascent Notgemeinschaft in the Reichstag,[18] in October 1920 the Reich Ministry of the Interior made 20 million marks available in the 1921 budget year "for the advancement of the goals pursued by the Notgemeinschaft der Deutschen Wissenschaft." Funding continued in this manner until 1934, when the Committee of the Notgemeinschaft were forced to resign and were replaced by Nazi Party control. Haber who was born Jewish, had converted to Christianity and was a German nationalist, was nevertheless dismissed from all his positions and left Germany and died in poverty in Basle, Switzerland in 1934.

The Notgemeinschaft was the precursor of the Deutsch Forschungsgemeinschaft (DFG) the German Research Foundation after World War Two, that was founded officially in 1951 and became the Federal organization for the support of basic research in the Federal Republic of Germany.

By comparison with the European powers, the fact is that in the US at the beginning of the 20th century there was no Federal Government support for basic research, there were no institutions that were funded to carry out basic research and no Committees existed to foster such research. It is no wonder then that the US fell behind Europe in the early period in the advancement of science and the advantages that could bring for industry and society.

In the US at the turn of the century, many so-called "robber barons" had made huge fortunes in such industries as iron, steel, coal, railways and automobiles. Several of them in later life turned to philanthropy and established Institutes in their name. Thus there is the Frick Institute on the Mall in Washington DC, established by Henry Clay Frick, who made his fortune in steel and railroads, that holds a wonderful art collection. Leland

Stanford in California, who made his fortune in railroads, chose to establish a famous University.

Two of these luminaries chose to establish Institutions that support the concept of basic research, John D. Rockefeller, who made his fortune in oil refining and was reputed to be the wealthiest American, established the Rockefeller Institute in New York City in 1901 for biomedical research.[19] Andrew Carnegie, who had made his fortune in iron and steel production, realized the need for basic research in America and founded the Carnegie Institute of Washington (CIW).[20] His initial donation of m$10 for this purpose was given with the stipulation that only research without any applied objectives should be conducted there. He hoped that this would engender a commitment to basic research throughout America.

Once established in 1903, the CIW engaged in many areas of research, including physics, chemistry, genetics and astronomy. This included Edwin Hubble who revolutionized astronomy in 1929 with his discovery that the universe is expanding, and Barbara McClintock, who won the Nobel Prize in 1983 for her work on genetics in maize. Although the CIW did make important contributions in all these areas it is interesting to note that while the Director of the CIW, Robert S. Woodward, was himself a physicist, the major project in physics that the CIW undertook to pursue was the construction of a wooden-copper boat *The Carnegie*, to sail the seas of the world and establish the earth's magnetic field.[21, 22] This could not be done obviously in a regular iron ship. But the CIW missed the boat as it were in physics, they chose not to work on the frontline in physics research that was taking place in Europe, where such notables as Rutherford in Britain, Neils Bohr in Denmark, Werner Heisenberg and Albert Einstein in Germany, were grappling with the structure of the atom and its properties. If they had initiated a program of research into the atom, the US might not have had to depend on the immigration of European Jewish scientists in the 1930's to initiate the Manhatten Project to build an A-bomb.

Although the CIW did some notable basic research, its influence was not so great as to bring America in line with its European competitors. During the early part of the 20th Century it was expected that any PhD candidate in science in the US would spend at least some time in post-doctoral studies at one of the great European universities. Also, at the time German was considered the scientific language. Andrew Carnegie's hope that CIW would bring about a revolution in support for basic science in America was not realized at that time.

3. DEVELOPMENT OF MILITARY TECHNOLOGY DURING WWI AND THE INTER-WAR YEARS

It is a well-known truism that warfare results in advances in science and technology that have tremendous consequences. This is certainly true of the main development in military technology that resulted from WWI, namely the tank. Originally ideas of a mobile armored vehicle were conceived by Leonardo da Vinci and H. G. Wells. Wells called them "Land Ironclads" and described their successful use in his story of that name published originally in 1903.[23] But, in reality it took a lot longer to develop them.

At first an American company named Holt of Stockton CA developed caterpillar tractors, that were used to tow heavy equipment around behind the lines of the UK forces in WWI. Their potential as actual fighting vehicles was foreseen by the British who developed a version called the Mark-1 tank that was mainly seen as a means to cross trenches to overcome the stagnant warfare of WWI. Many subsequent versions were produced by many countries and rejected, but tanks were first used effectively by Col. George Patton, in the Battle of Amiens under the command of US General Pershing, that effectively was the last major battle of WWI.[24]

During the 1920's many improvements were proposed, but mostly rejected by traditionally thinking military commands. However, one innovation that proved significant was that of independent suspension of all wheels of the track proposed by an American transportation engineer named J. Walter Christie in 1928.[25] This allowed the tank to move much faster over rough terrain, precisely what a tank was needed to do. This idea too was rejected by US and British Army ordnance officials. But, the Germans, who had been defeated at Amiens by tanks, realized their military significance and took up this idea and incorporated it into their Panzer tanks.

This was one of the main reasons for the defeat of the French and the British Expeditionary Force at Dunkirk at the beginning of World War Two. They were stunned by the speed with which the German tank corps raced ahead and overpowered them. The Russians too took this idea and incorporated it into their tanks and eventually the Americans and British followed suit. Incidentally, one reason that Germany lost World War Two was that although they produced the "best" tank, the famed Tiger tank, they were over-engineered and were so heavy that they had to stop to fire, and Germany produced only 1,350 of these, while the US produced 49,324 Sherman tanks, that were more mobile, more easily repaired and cheaper.[26]

As well as the development of the tank, parallel advances were made in the areas of automobile technology and in airplanes, from the Wright Brothers first flight in 1903 in North Carolina. WWI catapulted the airplane into prominence, first for reconnaissance of enemy positions and then as fighters facing each other. Detailed analysis of the developments in car engine technology and aeronautics is considered beyond the scope of this work.

4. THE INFLUENCE OF EUROPEAN JEWISH EMIGRES

In the period 1930-39 before World War Two, as the wave of anti-Semitism engulfing Europe developed, there was a positive tsunami of Jewish scientists of German, Austrian, Hungarian and other nationalities emigrating from Europe to the US. Their estimated number by 1944 was 133,000, and they contributed enormously to the development of basic sciences in the US, including increases in patents and expansion of scientific networks.[27] Among them was a large proportion of high-level scientists, particularly physicists and chemists, some of whom were helped in various ways by US officials, such a Varian Fry[28] and Hiram Bingham III.[29] While the majority of Jews were denied visas and prevented from entering the US, due largely to anti-Semitism among State Department officials,[30] the cream of the crop of the scientists were facilitated. Among them were the physicists, Albert Einstein from Germany, Leo Szilard from Hungary, Enrico Fermi from Italy, and many others whose names would become synonymous with the leap in American ability in the crucial area for the future war effort of nuclear physics.

Many of these physicists were familiar with the developments being made in nuclear physics in Europe during the period 1900-1930. They knew of the work of Ernest Rutherford in England on the splitting of the atom, of Hans Bethe and Lise Meitner in Germany on the energy produced when splitting the atom, and of Neils Bohr in Denmark on the structure of the atom and his German student Werner Heisenberg, who enunciated the famous "uncertainty principle" and who was later to become the Director of the German nuclear program during World War Two. Each of these individuals contributed significantly to the knowledge and understanding of the atom and of its potential to produce enormous amounts of energy.

However, this culture of scientific achievement in the area of nuclear physics was not present in the US. In fact, the most famous American physicist, Robert Millikan, who had won the Nobel prize in 1923 for measurement of the electron, was quoted as saying in 1929, "There is no likelihood to me that man can ever tap the power of the atom, there is no appreciable energy available to man through atomic disintegration."[31] However, Ernest Rutherford himself also was skeptical that splitting the atom would result in large amounts of available energy.

Following their arrival in the US, several of these German Jewish emigres played very important roles in atomic research in America. Einstein was accommodated at Princeton, where he played a role in the Institute for Advanced Studies in expanding knowledge of atomic theory. Fermi went to the University of Chicago, where he famously built the first nuclear reactor core Pile-1 under the stadium of the Chicago University and Szilard worked with Fermi.

Szilard authored the famous letter which Einstein sent under his signature to Pres. Roosevelt warning him of the possibility of the development of an atomic bomb with enormous potential.[32] This led to the establishment of the Manhattan Project in New Mexico, which was under the scientific direction of Robert Oppenheimer, an American-born Jew.

It is well-known that they did indeed develop the atomic fission bomb and contrary to the original intentions of some of the scientists, two were dropped on the cities of Hiroshima and Nagasaki in order to force the surrender of the Japanese without needing to carry out an invasion of the Japanese Home islands.

What would have happened if these Jewish scientific immigrants had not arrived in the US before World War Two, had they not pursued their research on the atom and had not directly persuaded President Roosevelt to initiate a major and huge commitment to study atomic fission that resulted in the Manhattan project that led to the Atomic Bomb? There would never have been the A-bombs that were dropped on Hiroshima and Nagasaki by order of Pres. Truman and the war would *not* have ended in August 1945 (VJ Day was Aug 15, 1945), but the US would have had to mount an invasion of Japan itself and there would have been an estimated 1 million US casualties.[33]

It is not generally known that an attempt at a coup against the Emperor was tried by elements of the Japanese Army in order to prevent him broadcasting his message of surrender to the Japanese people.[34] Although some 120,000 people were killed by the bombing of Hiroshima and another 65, 000 in Nagasaki, given the amount of resistance encountered in the invasion of Okinawa, and the suicides carried out by large numbers of Japanese, particularly women, it can be estimated that there would have been millions of Japanese casualties resulting from an invasion of the Home islands. So ironically in effect the dropping of the Atomic bombs saved lives, both American and Japanese, although there is some controversy about whether or not the second bomb on Nagasaki was indeed necessary.

5. VANNEVAR BUSH, AND THE OFFICE OF SCIENTIFIC RESEARCH AND DEVELOPMENT

If any one man could be regarded as instrumental as the initiator and proponent of support for basic research in the USA, that man would be Vannevar Bush (Figure 3). He was born in Everett, Massachusetts, in 1890 and went to Tufts University and MIT. Bush played a role in many engineering developments in circuit design and radio technology that led to the development of the Raytheon Company in 1922 that became a large electronics company and defense contractor. At MIT in 1932 he became Vice-President and Dean of Engineering. In 1938 he was appointed President of the Carnegie Institute of Washington, which brough him in close contact with the Government of the USA. He was an engineer, inventor and science administrator, who from its inception in 1941 and during World War Two was Director of the US Office of Scientific Research and Development, and was the first Science Adviser to a US President, President Roosevelt. Although many scientists made contributions towards the development of scientific research in the USA, Vannevar Bush was pre-eminent among them.[5]

In 1940, prior to the US joining the War, the British revealed to the US that they had made significant strides in developing radar to detect approaching German airplanes. Realizing the significance of this technology Bush arranged for MIT to develop airborne radar that was available by 1941.

Figure 3. Vannevar Bush seated at his desk (Library of Congress).

Bush's developments in circuit design had enabled him to effectively develop an analog computer. In 1940, Norbert Weiner approached Bush with a proposal to develop an electronic computer. Bush declined to provide funding because he thought it could not be completed before the end of the war. In this he was correct, but nevertheless, Weiner approached the Army and they provided funding to build what would be known as ENIAC, the world's first electronic computer. Bush was considered short-sighted by many, he refused to provide support for social sciences and also refused to support the development of rockets or missiles. For this he was later criticized.

One of the first applications of science to military technology that Bush oversaw was the proximity fuse, that was developed by Merle Tuve and James Van Allen. This was designed to ensure that bombs would explode even if they did not directly hit their target, they only had to be in the proximity of their target. This was not only advantageous because it increased the likelihood of an effective explosion, but also the damage caused by blast was also very significant. When these proximity fuses were used in American ordnance in the first involvement of American forces in North Africa in 1942, Sir Solly Zuckerman, who was to become the British equivalent to Bush, who was an expert in the effects of bombing, discovered that the American bombs were more efficient at taking out German emplacements than the British ones. When he discovered why, he immediately recommended that the British adopt a similar proximity fuse.[35]

Perhaps Bush's most significant initiative was his role in persuading the US Government to undertake a program to create an atomic bomb that would become the Manhattan Project. Bush met with Pres. Roosevelt in 1941, and following the initiative of the German Jewish émigré nuclear scientists Szilard and Einstein in 1939 and the British program in atomic development, Roosevelt gave his go-ahead for a crash program. The Manhattan Project was to be run by the US army under the direction of Secretary of War Henry Stimson and of Brigadier Gen. Leslie Groves and under the scientific direction of Robert Oppenheimer. He had carried out calculations that estimated that for a Uranium-235 bomb to achieve criticality would require 2.5-5 kg. If we are to believe the evidence of Werner Heisenberg, who was in charge of the German nuclear program, the Germans made mistakes in their calculations and thought that it would require much more, as portrayed in the historical drama "Copenhagen," involving Niels Bohr and Heisenberg.[36]

6. THE AMERICAN REVOLUTION IN SCIENCE AFTER WORLD WAR TWO

After the War, the Office of Scientific Research and Development was no longer needed and was disbanded. But Vannevar Bush realized that there was a great need for a peacetime agency to replace the function of OSRD in promoting science and technology for the national interest. He wrote an essay in 1945 that is considered the most influential paper relating to science and technology every produced in the USA. It was entitled "Science, The Endless Frontier," that was a Report to Pres. Roosevelt,[37] urging the establishment and funding of such a peacetime organization. Note there was 36 years between Vannevar Bush's Report to Pres. Roosevelt and the similar memorandum of Adolf von Harnack to Kaiser Wilhelm II, a measure of the lag in US understanding of the significance of basic scientific research. The change from President Roosevelt, who died in 1945, to President Truman, resulted in a significant loss of influence for Vannevar Bush. Through many political changes and compromises Bush's Report finally resulted in Congress establishing the National Science Foundation (NSF) in 1950 that funds basic research in the USA.

One other significant influence that Vannevar Bush exerted on science in the US after World War Two was his concept of large-scale data manipulation needed for the pursuit of science, something that he called Memex. He had thought about this since the 1930's and he crystallized his ideas in an article entitled "As We May Think," that was published in *The Atlantic* magazine in 1945. It consisted of a data storage device in the form of microfilm that could be rapidly switched to enable rapid access to different information. This paper was a forerunner of what we call "the information age," and was extremely influential in the thinking of people who set about using electronic means to develop the mouse, the computer and the internet.[38]

Apart from their singular influence on the developments in nuclear physics which resulted in the atomic bomb, European Jewish immigrant scientists had a widespread salutary effect on American science. This is attested to by the general increase in scientifically based patents produced in subsequent years following their immigration and the development of a much wider range of research on basic scientific subjects.[27]

Note that Jews have won 26% of Nobels in physics, 20% in chemistry, 27% in physiology or medicine and 41% in economics. Although Jews are only 0.25% of the world's population they have won a staggering 24% of all Nobel Prizes in science (physics, chemistry and physiology or medicine). If we take the period 1901-1939 Jews won 15% of German Nobel prizes while being less than 1% of the German population. From 1939 onwards, when there were no longer any Jews in Germany, the number of Nobels won by Germans did not increase significantly for some time (Figure 1), but this is not surprising since Germany had lost the War and was devastated. Similarly after World War Two the increase in number of Nobels in the UK, which had won the War but was similarly devastated, grew only very slowly. But the US experienced a sharp increase in Nobels following World War Two and surpassed the individual European nations after 1960 (Figure 1), as both its population and expenditure on Research and Development significantly increased.

Countries with increased Research and Development expenditures demonstrate higher growth performance with higher levels of GDP per capita than other countries.[39-41] This salient fact indicates that apart from the influence of the European émigré scientists and the subsequent influence after World War Two of German scientists transferred to the US, particularly in the area of rockets and aeronautics, it was the decision of the US to expend a large amount of funding on research and development after the War that led to its accumulating wealth in that period.

After World War Two, it was perhaps a shock to the Western allies to find that the Germans had been so far ahead in various areas relating to military technology. For example, in the development of rockets, such as the V2, that could be fired into the stratosphere and then crash into a city far away and cause enormous damage. The Allies had no such weapons. Also, the Germans developed the first functioning jet airplane, the Me 262 (called the Schwalbe or swallow), that was used in combat at the end of the War. It could easily outfly the propellor planes of the Allies, although it was developed in 1942, not enough of them were produced to affect the outcome of the War.

To obtain the secrets of German research on these and other technologies, there was a race between the US and the USSR as the War came to an end to capture and use the expertise of the German scientists. Those who were caught and transferred to the US were, of course, quite happy not to share the fate of the rest of the Nazi apparatus they had served. This US operation was called Operation Paperclip and resulted in ca. 1,600 German scientists and engineers being transferred to the US.[42] Werner von Braun, the Head of the German rocket program under the Nazis, whose products, including the V2, that killed tens of thousands of slave laborers in their construction and Londoners as their targets, was never charged with any war crime. Instead, he was appointed Head of the US Army's ballistic missile program and then Head of The National Aeronautics and Space Administration (NASA) space program. The reason was, of course, to try to beat the USSR in the development of rockets and in space exploration. He received the US National Medal of Science in 1975.

The origin of the National Institutes of Health (NIH) can be traced to the Marine Hospital Service started in the late 1790s that provided medical relief to sick and disabled men in the U.S. Navy. By the 1870's a network of Marine Hospitals was developed and Congress allocated funds to investigate the causes of epidemics like cholera and yellow fever. The National Board of Health was also created, making medical research an official government initiative.

In 1887 the Hygienic Laboratory was established at the Marine Hospital in New York for the study of bacteria. In the early 1900s Congress began appropriating funds for the Marine Hospital Service. In 1922, this organization changed its name to Public Health Services and established a Special Cancer Investigations laboratory at Harvard Medical School. In 1930, the Hygienic Laboratory was re-designated as the National Institute of Health by the Ransdell Act, and was given $750,000 to construct two NIH buildings in Bethesda MD.[43]

Over the next decades Congress would markedly increase funding of the NIH until today it is in the billions of dollars, and various institutes and centers within the NIH were created for specific research programs. In 1944, the Public Health Service Act was approved, and the National Cancer Institute became a division of NIH. In 1948, the name changed from singular National Institute of Health to plural National Institute**s** of Health.

The NIH's functions were divided into two, the intramural research program, and the extramural grant program. Each Institute has its own separate intramural and extramural programs designed to advance knowledge and understanding of disease and therapy in each of the major disease categories and to support research through competitive grants at Universities and Medical Schools throughout the USA and the world.

In the period up to the end of World War Two the US relied primarily upon a laissez-faire approach to scientific research and development. In 1950 President Harry S. Truman signed Public Law 507 creating the National Science Foundation (NSF), which provided for a National Science Board of twenty-four part-time members. The NSF began its first full year of operations with an appropriation from Congress of $3.5 million, with which 28 research grants were awarded. After the 1957 Soviet Union orbited Sputnik 1, the first ever man-made satellite, national self-appraisal questioned American education, scientific, technical and industrial strength and Congress increased the NSF appropriation for 1958 to $40 million.[44]

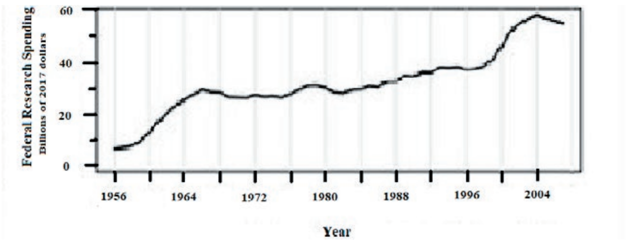

Figure 4. US Federal Government spending on research (in billions of 2017 dollars).[45]

Between them NIH and NSF funding account for most of the biomedical and scientific research carried out in the USA, and constitute the largest commitment of any country around the world to the funding of basic research (Figure 4).[45] The significant increase in scientific research in the US after World War Two parallels the increase in the number of Nobel Prizes won (Figure 1).

7. AMERICA BECOMES WORLD LEADER IN SCIENCE AND TECHNOLOGY

The tremendous increases in expenditures in support for basic scientific research that occurred in the US after World War Two resulted in a veritable explosion of notable accomplishments. The NIH and NSF that fronted the support for research in the health-related medical sciences and the basic sciences respectively, brought extensive advances in understanding of both the biological and the physical world. These advances in knowledge and understanding also resulted in inventions and applications that have revolutionized our world.

These include the transistor that was developed by William Shockley and his team at Bell Labs in 1947, that triggered the development of electronics; the printed circuit that was developed by the US Army during the War and released for commercial use in 1948, key to miniaturization of electronics; the key development of the computer, both hardware by Steve Jobs and Steve Wozniak and DOS software by Bill Gates; the internet, that was first developed as the ARPANET in California in the 1960's; and then of course there was the smartphone In biology, advances in genetics resulted mainly from the ability to sequence large segments of DNA, including the human genome. and this led to the understanding of genetic function.

It is tempting to conclude that all these developments could only have occurred in the US at that time. Clearly the European nations were not only devastated by the War, but also lacked the necessary funds and expertise to continue along the path that could have been projected from before the War. The other victorious Allies, Britain and Russia, were both forced into a long period of recovery. Only the US had the largesse and the industrial potential of exploit the commercial possibilities brought about by this revolution in thinking about science in the US.

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Historical Articles

Capillary Electrophoresis and its Basic Principles in Historical Retrospect. Part 2. Electrophoresis of Ions: the Period from its Discovery in 1800 till Faraday's Lines of Electric Force in the 1840s.

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Abstract. This review is the first in a series that deals exclusively with electrophoresis of ions. Since in modern terminology "*electrophoresis is the movement of dispersed particles relative to a fluid under the influence of a spatially uniform electric field*", electrophoresis is not limited to colloidal particles, it includes ions as well. The history of electrophoresis of ions therefore begins in 1800 at the same time as that of electrolysis, because the two phenomena are so inextricably linked "*that one cannot happen without the other*" (Faraday, 1834). Between 1800 and 1805 about half a dozen different theories of electrolytic decomposition and the movement of the particles – for which we coin the term electrophoretic current – were formulated, all contributing to the discourse, but lacking consistency and none fully convincing. They are discussed nonetheless because most of them fell into oblivion, even though they are interesting for historical reasons. However, from 1805/1806 the predominant theory, formulated by Theodor von Grotthuß and independently by Humphry Davy assumed that polarized molecules of water or dissolved ions form chains between the two electrodes. Only the terminal atoms of these chains were in direct contact with the electrodes and were liberated by galvanic action, but are immediately replaced by neighboring atoms of the same type. This decomposition and recombination of the molecules driven by electric forces which follow the "action at a distance" principle like in Coulomb´s law takes place over the entire chains; they represent the electrophoretic current. However, in 1833 Michael Faraday refuted all previous theories. Two of his groundbreaking findings were of particular importance for the electrophoresis of ions: one was that electricity consists of elementary units of charge. The ions thus carry one or integer multiples of these units. The other was the revolutionary theory of the electric lines of force in early 1840s, and of what was later called the electric field. With these findings Faraday fundamentally changed the previously prevailing view of the electrophoresis of ions.

Keywords: Ion electrophoresis, history, action at a distance, lines of electric force.

1. INTRODUCTION

While the discovery of three phenomena - electrolysis, electrophoresis of colloids and electroosmosis - was discussed in Part 1 of our historical review about capillary electrophoresis[1] the present Part 2 will focus on the ensuing studies of the electrophoresis of *ions*, along with the inextricably linked electrolysis.

Historic sources reveal that electrophoresis was discovered by Nicolas Gautherot in 1801[2] and independently by Ferdinand Friedrich von Reuß in 1807.[3, 4] However, both discoveries have in common that the experimenters observed the motion of colloids and coarse granular particles, dispersed in water, when the electrodes of a voltaic pile were dipped into the dispersion and the electric circuit was closed. The large size of the particles enabled the observation of the particle´s movement by naked eye. Yet, this was one of the reasons why electrophoresis has been attributed to particles of this relatively large size over more than a century after its discovery. It is to note that IUPAC also shares this view and recommends that electrophoresis is "*the motion of colloidal particles in an electric* field".[5] But this view fell short and was for good reasons expanded since nearly one century to ions, small charged particles of atomic or molecular size. At this point it is emphasized that colloids do not differ from ions only by their size, but also by their structure.[1]

Notwithstanding this difference, the updated and more generalized definition of electrophoresis currently agreed by the majority of the scientific community reads that "*electrophoresis is the movement of dispersed particles relative to a fluid under the influence of a spatially uniform electric field".*[2] According to this definition, electrophoresis encompasses a general principle.[3] With regard to this broader view at electrophoresis, reference is made to the more detailed discussion in Part 1 of this series.

Does this generalizing definition of electrophoresis lead to a dilemma concerning the date of its discovery? It was already inferred on the occasion of electrolysis in 1800 that dissolved ions migrate in their solutions under the influence of an electric field. This finding clearly corresponds to the criterion of electrophoresis. In contrast to colloids or coarse granular particles the motion of ions could not be directly followed visually due to their small size, but their migration and the direction in which they move had been proven indirectly from their concentrations close to the electrodes and their decomposition products which were formed by the simultaneous electrolysis process. Contemporary researchers therefore concluded that ions undoubtedly also move by what we call electrophoresis, at the same time when electrolysis occurs.

We therefore consider the commencement of electrophoresis, strictly speaking the electrophoresis of *ions*, to be the day when William Nicholson and Sir Antony Carlisle split water into gaseous hydrogen and oxygen by electrolysis[8, 9] with the newly discovered galvanic electricity.[4] For William Cruickshank the migration of the parts of the decomposable "body" and their perplexing occurrence at the separate poles was a "*mysterious*" phenomenon, for Humphry Davy "*the agency of galvanism is at present involved in obscurity*", and this unintelligible effect provoked an intense research of its causes.

The entire first series of our historical retrospect focuses exclusively on *ions* in solutions. This series about ions consists of this and of following articles and covers the period between 1800 and the end of the *Long 19th Century* in 1914,[5] or what we termed in Part 1 the *1st*

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[1] Electrophoresis of colloids, as well as electroosmosis, belong to the class of electrokinetic phenomena. Colloids, to be precise, colloidal particles, are an own phase in a second phase, they form heterogeneous dispersions, in which the two phases form an electric double layer at their interphase. Ions, in contrast, form homogeneous solution with the continuous medium in which they are dissolved.

[2] In our text, we usually added the adjective "*charged*" to the term "*particle*" as it facilitates its reading. However, this is not required and the adjective "*charged*" can be omitted. The reason is that an uncharged particle can move under the influence of a field by electroosmosis, but in this case it does not move relative to the fluid but just like the fluid. When the motion of an uncharged particle is caused by diffusion or convection, it does move relative to the fluid, but not caused by the electric field. Only a charged particle will definitely move in the field relative to the fluid due to the electrical force acting on it; therefore, the addition of the adjective is needless.

[3] We think that it is necessary to account for this wider view of electrophoresis, since it is at present mainly considered as a separation method only. In contrast, we endorse the above cited general definition (see. e.g. refs. [6] and [7.]). It should be noted that this definition applies to all dispersed particles, from the smallest inorganic ions up to viruses, bacteria and cells. Moreover, in none of the definitions or recommendations electrophoresis is limited to separation methods. Note that neither Gautherot nor von Reuß, the classical discoverers of electrophoresis, carried out separations. So we find no sound reason not to base the view on electrophoresis on the general principle outlined above. In this sense electrophoresis is not a separation method, but can be utilized as such.

[4] We briefly mention that a different terminology was used in the original documents compared to the current ones. Even the term *electrophoresis* was unknown until the *Short 20th Century.* In the present article we use – ahistorically – the modern terminology, but occasionally also the contemporary one of the original works, for instance when we quote verbatim. "*Pole*", i.e., was substituted by "*electrode*" not until 1833.

[5] We borrowed the term *Long 19th Century* from Eric Hobsbawm's trilogy on European history between the French Revolution in 1879 and the begin of World War I in 1914. It is the same period of time, in which all the main principles and theories of electrophoresis were already known, but – surprisingly – no attempts were made in this "*1st epoch*" to use them for a separation method; see Part 1.[1]

epoch of electrophoresis. We repeat that the electrophoresis of colloidal particles is not included, since its history cannot be told without that of the ions. A historical retrospect of electrophoresis of colloids, together with that of electroosmosis, will be the topic of a future separate series of articles.

The narrative in the present Part 2 of this series about *ions* spans the period from the discovery of electrolysis in year 1800 to the 1840s. In those 1840s, Michael Faraday overthrew the hitherto established concept of the *action at a distance* by the introduction of the groundbreaking theory of the *lines of electric force* or *lines of action* (later called *field lines* of the *electric field*).

One would expect this Part 2 to continue with electrophoresis only. However, it is inevitable to consider that the theories of electrophoresis would have remained in the dark without the results obtained by electrolysis. Indeed, one can argue that the theories about electrophoresis had their roots in the conclusions drawn from the experimental results of electrolysis.

Before we begin the historical review of the development of electrophoresis, we would like to mention briefly that almost all technical terms, with the exception of galvanic electricity, which have been used so far in this text, were unknown at this point in time. Moreover, the term *electrophoresis* remained unknown even during the *Long 19th Century*. Still, we find it useful to coin a new term in the present part. Our motivation is that in the early literature the complete electrical current flowing during electrolysis was expressed by many different and ambiguous phrases such as "*the flow …, the transmittance …, the transfer …, the transmission of electricity, ... the transport of galvanic electricity*" and several others. However, this complete current consists in two different forms. The *galvanic current* is the current of electrons in the metallic conductors of the circuit, and differs principally from the flow of charges which are carried by the dissolved ions. Hence, we think we have every reason to merge the various historical and confusing expressions for the flow of the charges by ions in solutions into the single and unambiguous term *electrophoretic current* .[6] This term is not usual, but it is to the point, and is full in line with the definition of electrophoresis.

2. HOW DOES ELECTRICITY FLOW THROUGH WATER OR THROUGH SOLUTIONS OF COMPOUNDS DISSOLVED THEREIN DURING THEIR DECOMPOSITION?

In the beginning of research in the effect of galvanic electricity on water[7] and its electrolyte solutions, researchers in Britain dominated this area for the first two years after its discovery. Admittedly, their investigations were rather directed on the chemical transformation of the constituents of the liquid at the electrodes by electrolysis than on the flow of the electric current through the liquid. Their findings were published mainly in Nicholson´s Journal,[8] which served them as a kind of "Central Organ". This can be said considering the remarkable large number of the appropriate papers in Volume IV from 1801, which was the first to publish articles on this subject. The title page of this volume of historic merit is shown in Figure 1.

It was the volume where William Nicholson reported the discovery of the decomposition of water by galvanic electricity.[9] In addition, in the same volume William Cruickshank proposed a first theory of electrolysis and – please note – the inextricable linked transport of electrified particles of atomic size in solution between the poles.[11]

2.1 September 1800: The first theories by William Cruickshank and by Johann Wilhelm Ritter

2.1.1 W. Cruickshank´s theory of the oxygenated and the deoxygenated electric fluid

William Cruickshank, a friend of Nicholson,[9] was the first who reported his investigations on the present

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[6] We coin the term *electrophoretic current* analogue to the term *galvanic current*. We mention, however, that we are not consistently replacing the various terms used at that time by *electrophoretic current*. We replace them when it is appropriate in the context.

[7] It is important to realize that through the period under consideration water that was used for the experiments was never pure, but was always contaminated with impurities. Even when it was distilled, it certainly contained electrolytes. Water with highest purity was first obtained around 1890 by Adolf Heydweiller, a coworker of Friedrich Kohlrausch, after fiftyfold distillation under vacuum in a quartz apparatus. We mention this fact because the detailed process of the electrolytic decomposition of water depends on its purity, and on the kind of the contaminants or on the intentionally added compounds such as acids, bases or salts. Acidulation, for instance, increases the speed of the generation of the gases. In this context, Faraday stated in 1834 that "*even water itself, which so easily yields up its elements when the current passes, if rendered quite pure, scarcely suffers change, because it then becomes a very bad conductor*".[10]

[8] This periodical journal was founded in 1797 and published by William Nicholson entitled *Journal of Natural Philosophy, Chemistry & the Arts*. It was commonly called *Nicholson´s Journal*, and merged in 1814 with the *Philosophical Magazine* to *The Philosophical Magazine and Journal*, later named *The Philosophical Magazine*. Please note the combination of natural philosophy, chemistry and arts at the time.

[9] There is not a very detailed record of William Cruickshank`s life. He was born in north-east Scotland in the 1740s or 1750s. Known is that in

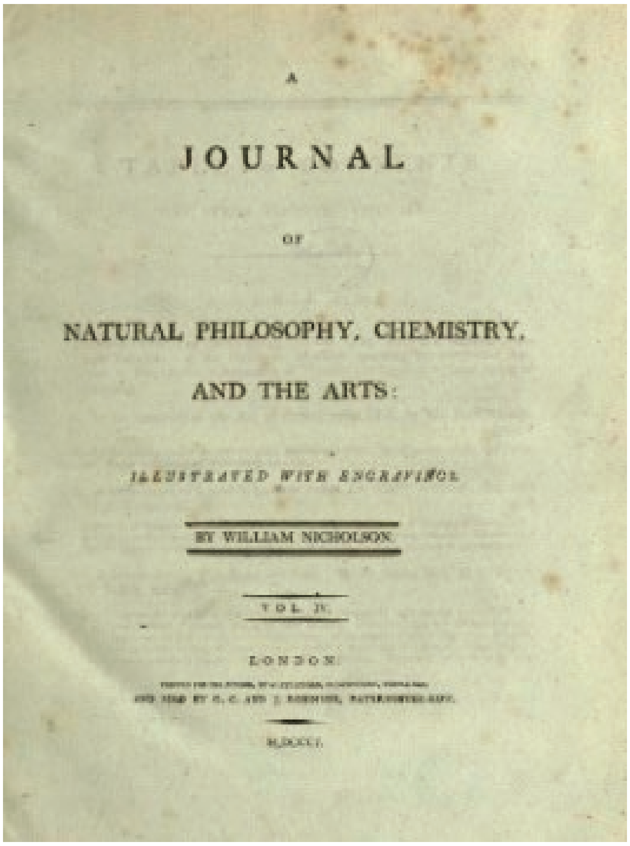

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Figure 1. Title page of the remarkable Volume IV of *Journal of Natural Philosophy, Chemistry and the Arts*, called *Nicholson's Journal*. In this Volume from 1801, in the six issues from July to December 1800 the notable number of 13 papers (out of a total of 58) were published which exclusively dealt with galvanic action.

topic, remarkably as early as July 1800 in Nicholson´s Journal.[11] Cruickshank began his experiments by repeating those of Nicholson and Carlisle, albeit with another device. Briefly, he used a horizontally placed glass tube, completely filled with water, with both openings closed with cork stoppers.[10] Then he inserted wires made from silver through the corks at each end into the water and connected them with a voltaic pile composed from plates of silver and zinc. After completing the circuit, he observed that gases were evolved at the two poles, with hydrogen at the *silver wire* and oxygen at the *zinc wire*.[11] In addition, he observed corrosion of the *zinc wire*. Upon adding a tincture of litmus or Brazil wood, and carrying out the experiment again, he observed that at the *zinc wire* the water became acidic, at the *silver wire* alkaline, effects that were noted also by others. He decomposed also "metallic" solutions, that are solutions of salts of metals. With silver dissolved in nitrous acid he got a precipitate of needle-like crystals in the form of *arbor Dianae*.[12]

In the same paper he tried to find out how far the influence of galvanic electricity is reaching. To this end, he connected two tubes described above for their communication by a silver wire, a 1st class conductor, that was passed through a cork of each tube. After closing the circuit, he observed the usual corrosion or disengagement of gases at the poles, what convinced him that an even greater number of tubes connected in series would give a similar result.

In the subsequent article in the issue of September 1800,[14] Cruickshank addressed that significant problem which was incomprehensible since its discovery: the occurrence of the individual gases in the water at the two different poles when galvanic current is applied. To attempt to solve this, Cruickshank used single tubes as described above, and carried out a series of quantitative measurements of the gases which evolved under various conditions. Based on his findings he formulated the first theory of the transport of the particles which were decomposed during electrolysis (ref. [14], pp. 257, 258). For water as liquid, Cruickshank hypothesized that the "*galvanic influence (whatever it may be) is capable of existing in two states, that is, in an oxygenated and deoxygenated state*". Since its affinity for oxygen is weaker than for solid metals, Cruickshank assumed that upon

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1765 he received his master from King's College in Aberdeen and later a diploma from the Royal College of Surgeons of England. In 1788 he got a position as assistant at the Royal Military Academy, and as lecturer in 1796 until 1804. He died in 1810 or in 1811 in Scotland. In addition to his first theory of the decomposition of water, he invented the trough battery.[12]

[10] Unfortunately, in the original paper in Nicholson´s Journal the drawings of the devices were not printed, because Cruickshank missed the deadline to submit them. Their schematic reproductions are found in the comprehensive and detailed study about electricity from 1751 till 1807 by Amy Alice Fisher.[13]

[11] One has to differentiate Cruickshank´s designation of the metals of the wires inserted into the liquid in which decomposition occurs, on the one hand, and of the plates of the voltaic pile, on the other hand. This terminology was later used by others, but not by everyone. Cruickshank, who applied the common configuration of the pile, which was made from plates of silver and of zinc, did not define the poles as positive or negative. He stated instead; "*In future, to avoid circumlocution, I shall call the wire attached to the silver plate, the silver wire, and the other the zinc wire*." This terminology did not define the metal of the wire (e.g. gold, silver, platinum, iron, etc.), which was occasionally used as pole immersed into the liquid under study, it refers to the metals of the pile`s plates onto which the wires were attached. We will italicize these wires regardless of their metal. In the present example, it could be confusing because both wires consist of silver.

[12] *arbor Dianae*, Lat. tree of Diana, also philosopher's tree, Lat. *arbor philosophica*, the silver tree, is formed when silver is precipitated from a silver salt solution by reduction. It has a shape like a tree, and consists of crystals of silver or silver amalgam. These trees were named by alchemists relating to the name for silver, Diana.

the deoxygenated "*galvanic influence*" (probably somewhat like a galvanic electric fluid) from the *silver wire* enters the water, disrupts it into its components and seizes the free oxygen, whereby hydrogen gas is segregated. Then, the electric fluid, together with the oxygen, passes the water to the opposite pole, where the oxygen is transferred to the *zinc wire*, and is released as a gas. Eventually, after transmission of the oxygen, the deoxygenated electric fluid flows back to the pile. Note that Cruickshank believed that the two evolving elements came from the same water molecule.

In case that the interposed liquid is a solution of a salt from a metal, the deoxygenated electric fluid passes from the *silver wire*, seizes the oxygen of the metal calx, transports it to the *zinc wire*, where oxygen is released and the deoxygenated electric fluid enters the metallic pole.

Yet, Cruickshank recognized the somewhat inconsistent suppositions of his theory, and finally conceded:

> "In reflecting on these experiments it would appear, that (….) the water must be decomposed; but how this can be effected, is by no means so easily explained. For example, it seems extremely mysterious how the oxygen should pass silently from the extremity of the silver wire to that of the zinc wire, and there make its appearance in the form of a gas." (ref. [14], p. 257; note the attribution "extremely mysterious.")

In the aforementioned Vol. IV of Nicholson´s Journal also other researchers, e.g. William Henry, Col. Henry Haldane and Humphry Davy reported the electrolysis of water, and all agreed that water is a compounded body, composed from about two parts of hydrogen and one part of oxygen. However, one researcher, Johann Wilhelm Ritter from Jena in Germany, one of the most passionate followers of the *Romantische Naturphilosophie* (*Romantic Nature Philosophy)*,[13] was strictly convinced that water was an undecompounded body, a chemical element.

2.1.2 September 1800: J. W. Ritter's theory of the metamorphosis of water by galvanic action

Johann Wilhelm Ritter was the opponent of the current hypothesis of the electrolysis of water (please pay heed to footnote [14]) He believed that water does not decompose under galvanic action and therefore formation and migration of ions do not occur. That may sound like a paradox, taking into account that he was the first researcher in Germany who experimentally fractionated water into gaseous hydrogen and oxygen using galvanic electricity. We find him noteworthy in the present historical retrospect not only because he pioneered the research in galvanism in Germany (together with Theodor von Grotthuß, see below), but also, due to his outstanding and unusual personality in the scientific community. He was a somewhat strange person of vivid imagination, unusual mental agility and seemingly borderless inventive creativity.[15] Humphry Davy, for example, characterized Ritter´s person and activities in his Bakerian lecture in 1826 (ref. [21], p. 385) as follows:

"Ritter's work contains some very ingenious and original experiments on the formation and powers of single galvanic circles; (….) : and in the obscurity of the language and metaphysics (…..) , it is difficult to say what may not be found. In the ingenious, though wild views, and often inexact experiments of Ritter, there are more hints which may be considered as applying to electro-magnetism than to electro-chemistry, … ".

Without having a regular income, Ritter began his research, notwithstanding the problems of getting access to the current literature sources in Jena[16] where he conducted his scientific and philosophical studies.[24] He carried out his experiments knowing only how to put a voltaic pile together, but without having knowledge of comparable experiments that were already done. Nonetheless, he was able to complete his investigations and to publish his results as early as in September 1800,[25] remarkably just two months after Nicholson and Carlisle, and at the same date when Davy had completed his first experiments on this subject - albeit under relevantly better conditions. In his first experiments he subjected water to galvanic action with a simple, self-made device, and measured quantitatively the volumes of the two gas-

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[13] Ritter was strongly influenced by Friedrich Wilhelm Joseph Schelling, the main philosopher of the *Romantischen Naturphilosophie* "*The Romantic Nature Philosophy considered the human being as a whole in the system of nature. Philosophy provided a system of thought from which the events of nature observation can be read*." Transl. from ref. [15], p. 23.

[14] Johann Wilhelm Ritter (1776, (Samitz (Zamienice) near Haynau (Chojnów), Silesia - 1810, Munich) was a German physicist (initially he was an apothecary), philosopher and an extraordinarily multifaceted personality. He can be considered as an outstanding scientist, but till at present time he is quite underestimated. Without never getting a position at a university (he only became member of the Bavarian Academy of Science in 1804, see his portrait in Figure 2) he contributed as autodidact to galvanism, e.g. by the independent discovery of the electrolysis of water in September 1800. In the course of these experiments, he invented electroplating. He discovered UV-radiation in 1801,[16]. and invented the dry cell battery in 1802. Ritter built the battery from 600 zinc-copper plates. It reached a potential of more than 700 Volt. In the last years of his live his interest turned, influenced by the German theosophist Franz Xaver von Baader, to siderism and radiesthesia.[17],[18],[19]. He died in poverty at the age of 33 by tuberculosis.

[15] The character of the protagonist is borrowed from the real person Johann Wilhelm Ritter in the novel "*Die Unglückseligen*" (*The Unfortunate Ones*) by the German woman writer Thea Dorn.[20]

[16] See e.g. his letter to Horkel.[23]

Figure 2. Portrait of Johann Wilhelm Ritter, wearing the uniform of the Bavarian Academy of Sciences. About 1804. Unknown artist. Taken from ref. [22].

es which were separately generated at the electrodes by collecting them in two tubes after closing the circuit.[17] Although Ritter identified the two gases as oxygen and hydrogen in roughly the correct proportions of one to two and a half volumes, he asked himself the same question that British researchers did, namely

> "Kann sich aber das nemliche Atom Wasser in einem und dem nemlichen Augenblicke zugleich an diesem und wieder an jenem Drathe befinden ? – Und doch müßte das der Fall seyn , wenn beyde Gasarten , beyde Stoffe, das Oxygen und Hydrogen , von einer wirklichen Zersetzung des Wassers herrührten." (But can the same atom of water be on this and on that wire at the same moment? – And yet this would have to be the case if both types of gas, both substances, oxygen and hydrogen, resulted from a real decomposition of water.)

Ritter could ignore this problem because he believed that water was an element and not a molecule. He was convinced that the collected hydrogen and oxygen were not decomposition products of water, but they were still water which was transmuted into other forms. As a proof for his conviction he filled a V-shaped glass tube (depicted in Figure 3) halfway with concentrated sulphuric acid, and covered the acid meticulously on both side pieces with distilled water, taking care to avoid any mixing of the two liquids.[25] The acid was intended to act as a barrier to prevent the transfer of water or of its components through the acid and thus to the opposite side piece. To this end he selected concentrated and rectified sulfuric acid after testing that it did conduct electricity,[18] but did not evolve even a trace of gas under the action of galvanic electricity.

Figure 3. The V-shaped glass tube with side pieces of 2 German inches (i.e. about 3 cm) in length was first filled halfway with pure concentrated sulphuric acid. The acid was then overlaid with distilled water, into which the two poles *a* and *b* were dipped. The poles, made from gold, were connected with the voltaic pile. Taken from ref. [26], after p. 326, Taf. 1, Fig. 15.

Ritter dipped one pole through the one, the other pole through the other opening of the tube into the water, completed the electric circuit, and observed the immediate and separate formation of gaseous hydrogen and oxygen at the individual poles (*a* and *b* in the original "*Fig. 15*") without any gas showing anywhere else in the tube between *a* and *b*.

After he had executed several similar experiments and obtained the same results; he concluded (p. 390)

> "So ist es also durch Versuche nun nicht bloß auf das Vollständigste erwiesen: daß die bey der Einwirkung des

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[17] A drawing of this device is depicted on p. 372, (Fig.3, Tab.V) of Voigt´s Magazin, ref. [25]. The complete name of this little-known journal was *Magazin für den neuesten Zustand der Naturkunde mit Rücksicht auf diedazu gehörigen Hilfswissenschaften, herausgg. von Johann Heinrich Voigt.*

[18] The conscientious experimenter Michael Faraday found the very reverse and explained "*681. On experimenting with sulphuric acid, I found no reason to believe that it was by itself a conductor of, or decomposable by, electricity*" and continued "*When very strong it is a much worse conductor than if diluted*".[10]. This comment suggests that Ritter's sulphuric acid still contained traces of water.

> verstärkten Galvanismus auf Wasser erzeugten beyden Gasarten, das Hydrogen wie das Oxygen, keinesweges von einer sogenannten Zersetzung des Wassers herrühren können, sondern überdies noch: daß auch die Erzeugung jeder einen Gasart ein Proceß sey, der ganz und gar nicht mit dem der Erzeugung des anderen zusammenhänge, sondern daß, beyde durchaus unabhängig voneienader, und einzeln, Statt haben können." (Thus, it is not only proved to the most complete extent by experiments: that the two types of gas, hydrogen and oxygen, produced by the action of the amplified galvanism on water can´t at all result from a so-called decomposition of water, but, moreover, that the generation of each type of gas is also a process which is in no way connected with that of the generation of the other, but that both can take place entirely independently of one another and individually.)

These results convinced Ritter once and for all to have demonstrated that water on both sides was in fact independently transmuted by a kind of metamorphosis into another modification by electricity, but not decomposed.[19] He took this result as evidence that oxygen is water minus electric fluid, and hydrogen is water plus the electric fluid, but they still remain elemental water.

A severe disadvantage to follow Ritter's argumentation was his circuitous and protracted style of writing, which was very difficult to understand - even for native speakers. This peculiarity was communicated by the Anglo-Irish physician and mineralogist William Babington[20] in a letter dated December 1800, entitled "*On the State of Galvanism and other Scientific Pursuits in Germany*" and printed in Nicholson´s journal.[27] Nevertheless, von Grotthuß acknowledged Ritter (ref. [28], p. 113) that he – although he never graduated from university – possessed the ability and acumen to refute all theories proposed prior to 1805 about the flow of electricity during the electrolysis of water (see ref. [29]).

Ritter published his theory in September 1800, at exactly the same date as Cruickshank. So there are two *philosophers* who could have claimed priority, although their theories could not be more different, but the credit goes to only Cruickshank. Only his theory deals with the motion of particles, a criterion of electrophoresis. However, in the end, Cruickshank's theory as well as Ritter´s theory of the "*Einfachheit des Wassers*" ("*elementariness of water*")[24, 30] soon failed due the investigations of Davy, von Grotthuß, and others.

2.2 Other theories from 1800 till 1805

In autumn 1800 Humphry Davy, too, wondered whether the formation of oxygen or hydrogen gas took place when the water is filled into separate vessels (each connected to the pile with a wire). The water was not in direct contact in Davy´s experiments either, but in contrast to one of Cruickshank´s devices (in which the two tubes were connected by a silver wire), it communicated through 2nd class conductors.[31] First, Davy closed the electric circuit by dipping the fingers of his right and his left hand into the water in the separate vessels, and observed the disengagement of gases at the poles. The gases were also generated when communication was through three persons, or by connecting the two vessels with muscular or living plant fibers, respectively, or with moistened thread, all acting as 2nd class conductors. This result led him to conclude that not only galvanic current in the metallic wires, but also the flow of the current by electrified bodies in the connecting wet organic matter enabled the communication of the water in the separate vessels.

Davy investigated, in addition to that of water, the electrolysis of aqueous solutions of various acids and bases. He found, among other effects, that pure hydrogen was always generated at the one pole, but at the other pole oxygen was either released as gas or it oxidized the metal of the wire. He published his results between September and December 1800 in three papers in the notable Vol. IV of Nicholson´s Journal mentioned above.[31-33]

Nevertheless, after having executed numerous experiments Davy restrainedly summarized in December 1800 his attempts to clarify these difficult to understand invisible motion through water and other menstrua. He stated (ref. [33], p.400)

> "Many new observations must be collected, probably before we shall be able to ascertain whether water is decomposed in galvanic processes. Supposing its decomposition, we must assume, that at least one of its elements is capable of rapidly passing in an invisible form through

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[19] Ritter carried out all these experiments in Jena within days, namely from September 28 to 30, 1800.

[20] William Babington (1756, Portglenone near Coleraine, Irland - 1833) reported, for instance, in his letter to the editor: "*…The principal galvanic discoverer here is a young man, called Ritter, at Jena, in Saxony: about two years since he published the result of his almost innumerable experiments, in which he established all its laws, and anticipated almost all the newer experiments. Unfortunately the book was written very obscurely, and was still more obscured by the language of the newer philosophy. ….. this suggested to him to interpose some substance between the extremities of the wires, which was at the same time capable of conducing the galvanic influence, and of remaining perfectly unaltered by it. …. thus it is proved, that water under certain circumstances, may be wholly converted into oxygen gas, and under others, into hydrogen-gas; the rationale of this phaenomenon is as yet in obscurity*". The present author illustrates his intricate and circuitous style by one example taken from pages XXI and XXII of his book about Siderism: one single sentence, which is composed of many subordinate clauses and nested sentences, consists of the remarkable number of 297 words.[17]

> metallic substances, or through water and many connected organic bodies; and such an assumption is incommensurable with all known facts."

It is worth noting that at the turn of 1800 to 1801 in Germany four researchers independently realized that the order of the metal plates on the voltaic pole built by earlier philosophers was misleading. In the past, the pile was composed of plates of zinc (Z) and silver (A) with an interposed wetted layer (w) in the sequence [-SZwSZw… SZwSZ+]**.** But K. W. Böckmann,[34] A. von Arnim, who entitled his paper "*Über die Benennung der Endpole der Voltaische Säule*" (*On the designation of the end poles of the Voltaic pile*),[35] P. Erman[36] and W. Gruner[37] discovered that the proper sequence of the pile should be [-ZwSZwS...ZwS+], which is obtained by omitting the zinc and the silver plate, respectively, at the two extremities of the earlier pile.[21] We can especially recommend reading the expounded and informative comments of the highly competent editor of *Ann. Phys.*, Ludwig Wilhelm Gilbert, on Erman´s[38] and on von Arnim´s[39] contributions.[22]

However, at the European Continent several other theories of electrolysis and the electrophoretic current were formulated in these years. This happened for the most part in Germany, France, Italy, and in Sweden. In Germany, among others, Paul Ludwig Simon (1771 - 1815, Berlin), professor at the Building Academy in the faculty of architectural physics in Berlin,[40, 41] and Christian Heinrich Pfaff, professor of medicine, physics and chemistry in Kiel,[42] stepped forward with theories of the action of electricity on water which are not going to be discussed further.[23]

In France A. F. Fourcroy, L.- N. Vauquelin and L. J. Thénard[24] published a number of papers in *Magasin Encyclopédique, ou Journal des Sciences, des Lettres et des Arts*. In 1800 and 1801. In 1801 *Citoyens* Fourcroy and Vauquelin hypothesized the circulation of the electric fluid from the positive to the negative pole. They assumed that this fluid decomposes water at the positive wire, where oxygen is released as gaseous bubbles. There, the positive fluid combines with hydrogen, and the combined hydrogen is transported unseen by an assumed *fluidum deferens*, the *galvanique*, to the negative wire. The *galvanique* enters this wire, whereupon the hydrogen is evolved as gas bubbles.[25]

An "*electric acid*" ("*l´ossielettrica*"), an expansive liquid with fineness like heat and light, smelling similar to phosphorus, and tasting pungently was conjectured in 1800 by Luigi Valentino Brugnatelli (1761 - 1818, Pavia), professor of chemistry in Pavia, Italy, and friend of Volta.[44, 45] According to his theory, the electric acid easily enters the metals, and dissolves them – such as water dissolves a salt – as soon as it is set in motion ("*quando l´osielletrico é in moto*"*)*. It is soluble in water, and in such a dissolution most metals are oxidized at the expense of water, whereupon hydrogen is formed through decomposition. The metal oxides formed by this reaction combine with the electric acid under formation of metal *électrates (*"*osielettrati*"*)*. For example, the électrate of copper is green, that of silver is white, both are transparent and insoluble in water. Their most pronounced capability is that they can be carried away through the water by the electric acid over comparably long distances. Finally, the électrates are precipitated at the metal of the pole as salt-like crusts.[26]

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[21] Karl Wilhelm Böckmann (also Boeckmann) (1773 - 1821, Karlsruhe), physicist and chemist, professor for physics. (Carl Joachim Friedrich Ludwig) "Achim" von Arnim (1781, Berlin – 1831, Wiepersdorf), Göttingen. Paul Erman (1764 - 1851, Berlin), professor for physics in Berlin. Johann Ludwig) Wilhelm Gruner (1771, Halle on Saale – 1849), court apothecary in Celle.

[22] In von Arnim´s paper Gilbert (1769, Berlin – 1824, Leipzig) wrote as a part of a comprehensive comment somewhat caustically: "… *Wenn also Nicholson seine Voltaischen Säulen auf folgende Weise errichtet:* S., Z., fL., S., Z., fL., S....Z., fL., S., Z., *so sind die erste Silber- und die letzte Zinkplatte der Säule offenbar überflüssig und nicht als Glieder der galvanischen Ketten, sondern bloß als ein willkürlich hinzugefügter Metallleiter zu betrachten, der, ohne etwas zu ändern, so gut fehlen als da seyn kann. Nach ihnen den ersten Pol den Silberpol, und den letzten den Zinkpol zu nennen, wie man es bisher gethan hat, ist daher gewiß unschicklich und verwirrend, ...* " (*So if Nicholson builds his voltaic pile in the following way:* S., Z., fL., S., Z., fL., S....Z., fL., S., Z., *the first silver- and the last zinc plate of the pile is evidently superfluous but to be considered merely as an arbitrarily added metal conductor, which can be lacking as well as be present, without changing anything. Terming the first pole the silver pole and the last the zinc pole, as has been done thus far, is therefore certainly improper and confusing. ...*). [fL. stands for the wetted layer; the author].

[23] Paul Ludwig (also Paul Louis) Simon (1771, Berlin – 1815, Berlin); Christoph Heinrich Pfaff (1773, Stuttgart - 1852, Kiel).

[24] Antoine François, comte de Fourcroy (1755 - 1809, Paris); Louis-Nicolas Vauquelin (1763 – 1829, Saint-André-d'Hébertot, Normandy); Louis Jacques de Thénard (1777, La Louptière, near Nogent-sur-Seine (Aube) - 1857, Paris).

[25] Their hypothesis is published in *Séance publique de l´Ecole de mêdicine de Paris, du 24 vendèmiaire an 10,* [Sept. 24,1801; the author] *in-4°., page 67*. and reads: "*Les CC. Fourcroy et Vauquelin, …, admettent l´existance d´un fluide particulier, qu´ils nomment galvanique, et qui circleroit du côté positif de la pile, vers le côté négatif. Selon eux, ce fluide décompose l´eau en sortant du côté positif: il laisse échaper l´oxygène en bulles; mais il se combine avec l´hydrogène pour former un liquid, lequel traverse l´eau, …. , pour aller gagner l´extrémité du fil négatif. Là le galvanique abandonne son hydrogène, et le laisse échapper à son tour sous forme de gaz, tandis que lui-même pénètre dans le fil.*" (ref. [43], p. 157.)

[26] Alessandro Volta explicitly distanced himself from Brugnatelli´s theory and stated in ref. [46]., p. 264, "*Ich habe keinen Antheil an seinen Meinungen oder Ideen über die electrische Säure, die electrisch-sauren Metalle, u.d. m.*" [Ann. Phys. (Gilbert ed.) XIV (7), p. 264.] *("I have no share in his opinions or ideas about the electric acid, the electric-acidic metals, etc).*"

To his surprise, when he visited Paris with Volta, Brugnatelli found a paper in the issue of August, 1801 (*le 11 fructidor an 8*) of *Ann. Chim.*, authored by the Belgian Étienne-Gaspard Robert. Around 1800 Robert executed experiments with galvanism, and read one of his works before *l'Institut National de France* in August 1801, which was published in the aforementioned *Ann. Chim.*, entitled "*Expériances nouvelles sur le fluide galvanique*".[47] He proposed a theory which was very similar to Brugnatelli´s,[27] and in which he termed Brugnatelli´s electric acid "*l´acide galvanique*".

Robert was well-known by his stage name Stephan Kaspar Robertson, also Robert-son,[28] whereby it was peculiar back then as it is today, why ask a professor of physics would choose a stage name.[29]

Due to his interest in many various areas. it was not surprising that the German physician Johann Friedrich Erdmann was fascinated by the recently discovered galvanic electricity, and in its applications to medical issues.[30] He decomposed water by electrolysis and obtained hydrogen and oxygen in right proportions as usual. In 1802 Erdmann put forward the hypothesis that galvanic electricity flows into the water at the + pole, and leaves it at the - pole.[56] By entering water at the + pole, it binds hydrogen, since the latter has a larger affinity to electricity than to oxygen, and thus oxygen is liberated. Hydrogen unites to hydrogenated electricity, which traverses the liquid towards the - pole, where the electric matter intrudes the metal of the pole and hydrogen is released as gas.[31]

Since in the first years after 1800 the subject of most of the works was the decomposition of solutions of arbitrarily chosen salts, acids and bases by galvanic electricity, it was quite difficult to find a coherent structure in the results obtained under these widely varying conditions. This gap motivated the Swedes Wilhelm Hisinger and Jöns Jacob Berzelius *"to search for as many as possible general results from the experiments we and others have performed, so that the phenomena"* of the electric decomposition and the motion of the ions could be better understood and even foreseen (ref. [57], p. 115 - 116). They published a systematic study of nearly thirty selected electrolytes in 1803 in German translation[57] from Swedish and in 1804 in a condensed version in French.[58] It can be said that this work did not contain really new aspects, but the categorization of the experimental outcomes enabled them to formulate certain valuable rules, which they summarized in seven points. We cite those rules which have a direct context to the motion of decomposed particles. They read[32]

> "Versuch, aus den obigen sowohl, als aus anderen bekannten galvanischen Versuchen, einige allgemeine Folgerungen herzuleiten. 1. Wenn sich die electrische Säule durch eine Flüssigkeit entladet, so sondern sich die Bestandtheile dieser Flüssigkeit dergestalt von einander ab, daß sich einige von ihnen um den negative Pol, andere um den positiven ansammeln. 2. Diejenigen Stoffe, die sich zum Drahte eines und desselben Poles hin begeben, stehen unter sich in einer gewissen Analogie. Zum negativen Pol gehen alle brennbaren Körper, Alkalien und Erdarten; zum positiven hingegen Sauerstoff, Säuren und oxydierte Körper. 7. Wasser wird in Wasserstoff und Sauerstoff zerlegt, die aber in unzerlegtem Wasser unauflöslich sind, daher ersteres vom negativen, letzteres vom positiven Draht, gasförmig entwickelt wird." (Attempt to draw some general conclusions from the above, as well as from other known galvanic experiments. 1. If the electric column is discharged through a liquid, the components of this liquid separate from one another that some of them collect around the negative pole, others around the positive. 2. Those substances which move to the wire of one and the same pole stand in a certain analogy among themselves. All combustible bodies, alkalis and earths go to the negative pole; to the positive, on the other hand, oxygen, acids and oxidized bodies 7. Water is fragmented

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[27] Chapitre X. *Expériences et observations sur le galvanism, par MM. Nicholson, Carlisle, Robertson, Cruickshank, Henry and Davy*; ref. [48]., p. 282 ff., §. II. *Expériences et observations de M. Robertson*, see p. 294.

[28] The hyphen in Robert-son is not a printing error.

[29] Robert had a remarkably eventful biography (see his *Mémoires*).[49],50]. Born in 1763 as Étienne-Gaspard Robert in Liège, Belgium, he studied at Leuven, and became professor of physics, specialized in optics, at *l'école centrale du département de l'Ourthe.* In 1791 he moved to Paris to strive for a career in art as a painter. There, he attended in 1792 and 1793 the scary ghost-raising show *Phantasmagorie*, and easily figured out that the ghosts were created by the use of a *Laterna Magica*. He premiered his own show (under the stage name Robertson) in Paris in 1798 which he later performed with great success around the world. During these trips he became fascinated by ballooning and flew balloon shows in Vienna, Dresden, Leipzig, Moscow and other cities. He considered some flights by himself as being scientific, because he connected them with meteorological investigations. He managed to publish three of his flights in *Ann. Phys.* in 1804 as communications to the editor Ludwig Wilhelm Gilbert.[51],[52],[53]. It is interesting to read Gilbert´s critical comments and references to errors in Robertson´s reports, which make up a large part of the papers. Robert died in 1837 in Paris.

[30] Erdmann (1778, Wittenberg - 1846, Wiesbaden) published, for instance, in 1803, one year after his doctorate in medicine, a paper entitled "*Beschreibung zweier von Dr. Brunner in Wien erfundenen voltaisch-elektrischen Apparate zur Entdeckung des Scheintodts und zur Wiederbelebung der Scheintodten*" (*Description of two by Dr. Brunner in Vienna invented voltaic-electrical apparatus to discover the apparent death and to revive the apparent dead*),[54] and in 1804 one about "*Galvanische Versuche, angestellt im Wiener Irrenhaus*"(*Galvanic experiments, employed in the Vienna madhouse*).[55]

[31] This paper was an extract of his doctoral thesis entitled "*Utrum aqua per electricitatem columnae a cel. Volta inventae in elementa sua dissolvatur?*", which he defended on May 2, 1802, at the Medical Faculty of the famous Alma mater Wittenbergensis.

[32] Points 3, 4, 5 and 6 are not directly relevant for the topic at hand, therefore we leave them out.

> into hydrogen and oxygen, which, however, are insoluble in undecomposed water, so the former is developed in gaseous form from the negative, the latter from the positive wire.).

Hisinger and Berzelius interpreted their findings as the result of the electrostatic attraction and repulsion of the ions to and from the respective charged poles.[57] They assumed these electric forces to follow the principle of the *action at a distance*. In the concept of the action at a distance[33] the forces are strongest at their poles and diverge then in the inverse ratio of the square of their distance. The two forces cross in the middle between the poles and compensate each other at the point of neutrality or indifference point. Decomposition happens not at the poles, but near or at this point. This concept was later a key part of Humphry Davy´s theory of the electrolysis and the motion of the decomposed particles.[62]

Hisinger and Berzelius were not really convinced of this hypothesis. They doubted the assumption of decomposition at the point of indifference, as this contradicted what was observed in practice (ref. [57], p.148) Therefore, skeptical about their still unsatisfactory results, they concluded

> "Wir wagen kein Raisonnement über das Wie der obigen Zerlegungen. Doch scheint uns am meisten natürlich, dieselben durch Attraction der Electricität, die sie auf gewisse Stoffe, und Repulsion,[34] die sie gegen andere äußert, zu erklären, ob uns gleich diese Erklärung wenig genügend scheint." (We do not dare upon making any reasoning about how the above decompositions are made. Yet it seems to us most natural to explain them by the attraction of electricity, which it expresses for certain substances, and repulsion, which it expresses against others, although this explanation seems little sufficing to us.)

However, none of the theories proposed thus far had been considered as generally valid due to contradictions and inconsistencies, and the confusion about the transport of hydrogen and oxygen. The question of the flow of the electric current through water during its decomposition remained. But in 1805, this patchwork of disorientating theories was resolved by the - surprisingly - only twenty years old German student Theodor von Grotthuß.

Figure 4. Portrait of baron Christian Johann Dietrich Theodor von Grotthuß (C. J. Théodore de Grotthuss). Photogravure by Meisenbach and Riffart & Co. in Leipzig, produced prior to 1894, undated.

2.3 1805: C. J. T. von Grotthuß´ theory of the electrophoretic current during the electrolysis of water and of the bodies which it holds in solution

During his stay as a student of natural sciences in Italy from 1804, baron Christian Johann Dietrich Theodor von Grotthuss (also C. J. Théodore de Grotthuss)[35] formulated a theory that made him highly recognized, in particular that of the flow of electricity during the decomposition of water. His theory was so plausible to his contemporaries that, unlike the ones discussed above, it found general acceptance. It was compelling

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[33] The concept of the action of a distance, expressed also as the inverse square law, applied to Newton's law of universal gravitation,[59],[60] and to Coulomb´s laws for the electrostatic repulsion of equally charged and the attraction of oppositely charged points.[61]

[34] They relativized on p. 148, footnote 3: "*Daß unter Repulsion richtiger eine geringere Verwandschaft als eine wirkliche Zurückstoßung zu verstehen sey, wird man leicht einsehen*". (*It will be easy to see that by rejection it is more correct to mean a lesser relationship than an actual rejection.)*

[35] Christian Johann Dietrich Theodor von Grotthuß (1785, Leipzig, Germany - 1822, Geddutz (at present day Gedučiai), Lithuania. See his portrait in Figure 4), member of a German-Baltic noble lineage, began his university studies in Leipzig in 1803, and continued six months later at *École Polytechnique* in Paris, then from 1804 in Italy. He left Italy in 1806 and returned via Paris, Munich and Vienna in 1898 to his manor Geddutz in Courland. Since his return to his manor von Grotthuß tended to live secluded from the scientific community. There he continued his electrochemical research, and investigated the chemical effect of light.[63]. In 1819 he formulated the photochemical absorption law (named Grothuss-Draper law, or the Principle of Photochemical Activation; this law was independently formulated in 1842 by the English-born American scientist John William Draper). (for details, see *e.g.* ref. [64]).

because it could provide an answer to the previous question how hydrogen or oxygen can traverse water in the form of a gas from one pole to the other.[65-67]

In Chapter II of "*Mémoire sur la decomposition de l'eau et des corps qu'elle tient en dissolution à l'aide de l'électricité galvanique*" which Grotthuß published in 1805 in Rome,[65] and in 1806 in *Ann. Chim.* in Paris,[67] he postulated that in each water molecule – he assumed that it was made of (HO) – the hydrogen and the oxygen atom are positively and negatively polarized, respectively.[36] Upon application of an electric potential the molecules orient themselves with their polarized atoms in direction of the oppositely electrified poles, forming a chain in the liquid in this way, schematically depicted by $(^{(+)}H\text{-}O^{(-)})(^{(+)}H\text{-}O^{(-)})$. In §. 20. of his treatise, he formulated his basic idea as follows

> "Il est clair que, dans toute cette opération, les molécules d`eau situeés aux extrêmités des fils conducteurs, seront seules décomposées, tandisque toutes celles placées intermédiairement, échangeront réciproquement et alternativement leurs principes composans , san changer de nature. J`en déduis que, s`il était possible d`établir un courant d`électricité galvanique dans de l`eau, de façon qu`il décrivit dans celle-ci une ligne parfaitement circulaire, toutes les molécules du liquide situées dans ce cercle, seraient decomposées, et a l`instant recomposées: d`où il suit que cette eau , quoique subissant l`effet de l`action galvanique, resterait toujours eau." (It is clear that, throughout this operation, only the water molecules located at the tip of the conducting wires will be decomposed, whereas all those located at intermediate positions will exchange their composing principles reciprocally and alternatively, without changing their nature. From this I deduce that if it were possible to apply a galvanic current in water such that it follows a perfectly circular line, all the water molecules of the liquid located in this circle would be decomposed and instantly recomposed: whence it follows that this water, although subjected to the effect of galvanic action, will always remain water.)[37]

In Figure 5 the scheme of the mechanism of the flow of the electrophoretic current during the decomposition of water is depicted.

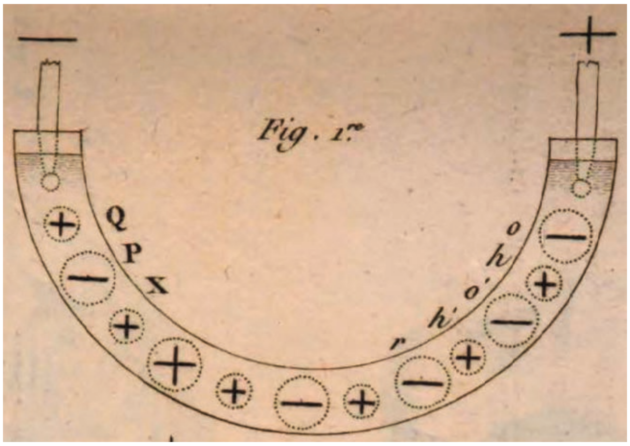

Figure 5. Schematic drawing illustrating Grotthuß´ concept of the flow of the electric current during the electrolysis of water. "*Fig.1re*" shows a U-tube filled with water, which forms of a chain of positively polarized hydrogen and negatively polarized oxygen atoms. It is important to realize that the circles with + and – signs are *not* ions, they are schematic depictions of the polarized atoms of the intact, neutral water molecules (which consist here from one hydrogen and one oxygen). During the complete process, free ions are not present in water.[38] For a more detailed explanation see text. Taken from ref. [67].

The U-shaped tube ("*Fig.1er*") is filled with water into which two poles connected to a voltaic pile are dipped. The water molecules are pictured as a series of circles with positive and negative charges, which is the stylized way of depicting von Grotthuß´ real conception of a chain or row of polarized $(^{(+)}H\text{-}O^{(-)})$ molecules but does not display a sequence of ions since Grotthuß refused the presence of free ions from water. He believed that an ion is always associated with its oppositely charged ion. According to his theory, each of the elements of a molecule is subject to an attractive and a repulsive force, acting in contrary directions. The negative pole attracts the positively polarized hydrogen atom and repels the negatively polarized oxygen of the water molecules, the positive pole accordingly attracts oxygen and repels hydrogen.[39] These electric forces are sufficiently energetic to overcome the chemical affinity in the terminal water molecules (that is to say, only in those at the ends of the chain). Considering for example hydrogen *Q* at the end of the circular line (positive *Q* of the water molecule *QP* at the negative pole in Figure 5), decomposition of molecule *QP* occurs, because it gives up its hydrogen *Q*, which is in direct contact with the pole, to the electricity of the negative wire. But at the same time as hydrogen atom *Q* is liberated to hydrogen gas, the chain is *instantaneously* ("*à l`instant*") re-hydrogenated by hydrogen

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[36] In his next paper dated 1807[68]. he depicted the water molecule as composed of one hydrogen and two oxygen, what he repeated in his work from 1811,[69]. and from 1818.[70]

[37] The English version is published in ref. [71].

[38] Comment of the author: In the fourth circle .after the minus pole of the tube in "*Fig. 1*" a *minus* should be inserted, not a *plus*; In the English translation of this paper in *Phil. Mag.* from 1806 this error was corrected, see *Plate IX*, *Fig. 1* in ref. [66].

[39] Although Grotthuß initially assumed that the forces follow the inverse square law according to the action at a distance, he nevertheless believed that the atoms move with constant velocity, what is a contradiction in itself.

X of the adjacent molecule, a transfer which occurs in the same moment. Oxygen reacts analogue at the positive pole. It is decisive that only those atoms of the water molecules are segregated which are in direct contact with the poles. All other water molecules, which are between the poles, only exchange their atoms reciprocally, but do not change their nature. On these grounds, the flow of the electric current is caused by both kinds of atoms which continuously travel in opposite direction within the aligned chain of water molecules between the terminal atoms, forming an electrophoretic current in this way. The crucial fact of the matter is that ions are never present in their free form, because upon disintegration of the molecules the atoms bind immediately to the partner atoms of the next following molecules. Hence, all molecules in the solution are subject to the permanent and instantaneous process of decomposition and recomposition.[40]

It must be noted that Grotthuß initially assumed, but later withdrew, that the force of attraction or repulsion follows the action at a distance as Davy and Berzelius did. Yet, it is of paramount importance that Grotthuss' theory gave an answer to the apparently paradox effect of the evolvement of hydrogen and oxygen at the separate poles, because in his theory the evolved gaseous elements of water do not originate from the same water molecule and therefore do not travers the liquid. Grotthuß´ theory was widely accepted[41] but - to his annoyance - was initially attributed to the famous scientists Davy and Berzelius, and not to the unknown young German student. It took about fifteen years until Grotthuß asserted his priority on the theory in Volume 1 of his book entitled "*Physisch-chemische Forschungen*",[28] which he published in 1820, and in which he had collected his main scientific papers (Volume 2 did not appear anymore). This book can be regarded as his scientific testament, since two years later he committed suicide.

In the introductory commentary of his article from 1805 which he translated into German by himself in "*Physisch-chemische Forschungen*" Grotthuß wrote somewhat embittered (ref. [75], pp. 113-115):

> "Meine (…) Theorie ist später von Davy (…). und von Berzelius (…) ohne meiner zu gedenken, weiter verbreitet und (…) jetzt von allen Chemikern (…) angenommen worden; nur muß ich bedauern, daß viele von ihnen, wiewohl fälschlich, nicht mir, sondern den beiden letztgenannten Chemikern diese Theorie zuschreiben die ich jedoch weit früher aufgestellt (…) habe[42], (…) Nachfolgender Aufsatz wurde von mir 1805 in Neapel entworfen, und noch in demselben Jahre in Rom gedruckt. (…) daß diese Grundidee von mir ein ganzes Jahr (…) früher als Davy (…) aufgestellt worden ist, brauch ich wohl kaum noch hinzuzufügen. Diesen 1805 in Rom in französischer Sprache gedruckten Aufsatz[43] sandte ich an Fourcroy nach Paris und dieser ließ ihn einige Monate später nämlich im April 1806 in den Annales de Chimie aufs neue abdrucken,[44] Davys obenangeführte Abhandlung betreffend, über einige chemische Wirkungen der Electricität wurde erst am 20. November 1806 von ihm in der königl. Gesellschaft zu London vorgelesen und erschien erst 1807 in den Transact. philos.[45] gedruckt." (My (…) theory was later disseminated by Davy (…) and Berzelius (…) without further commemorating me, and is now accepted (…) by all chemists; but I must regret that many of them, albeit falsely, attribute this theory not to me, but to the latter two chemists, though I have it established much earlier, (…) The following essay was drafted by me in Naples in 1805, and printed in Rome the same year (…). I hardly need to add that this basic idea was put forward by me a whole year (…) earlier than Davy. I sent this essay, printed in French in 1805 in Rome, (…) to Fourcroy in Paris, and a few months later, in April 1806, he reprinted it anew in the Annales de Chimie. Davy's above-mentioned essay about some chemical effects of electricity was read only on November 20, 1806 by him at the Royal Society in London and appeared printed not until 1807 in the Transact. philos.). [Citations added by the author].

In this complaint Grotthuß referred to Davy´s celebrated Bakerian lecture,[46] read on November 20, 1806, entitled "*On Some Chemical Agencies of Electricity*" (ref. [62], p.29).

Yet in Chapter I of Grotthuss´ aforementioned paper[67] the subject was the "*Action of Galvanic Electricity upon certain Bodies dissolved in Water*", p. 330-334 in the English version[66]). In this theory, "metallic" solutions[47]

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[40] The German translation and comments were published in 1808 by Johann Salomo Christoph Schweigger, professor of philosophy, physics and chemistry, and editor of *Journal für Chemie und Physik*.[72]

[41] The author points out the following inconsistency in Grotthuß´ description of his theory: according to this theory, negative oxygen *P* combines after the release of positive hydrogen *Q* with neighboring positive hydrogen *X* under formation of the new molecule ($^{(+)}P$-$X^{(-)}$). In this configuration, the negative oxygen *P* is that atom which is closest to the surface of the – pole. To get into the proper position the molecule has to rotate by 180° to ($^{(+)}X$-$P^{(-)}$) in order to re-position hydrogen *X* onto the surface of the – pole. These rotations apply to all molecules in the chain. Grotthuß´ did not mention this necessity. Faraday pointed to this fact when he explained that ice as ordinary insulating dielectric cannot be electrolyzed, whereas liquid water can (*Experimental Researches in Electricity - Fourteenth Series*, 1839; 1705.)[73],[74]

[42] See *e.g.* ref. [76], p. 691.

[43] See ref. [65].

[44] See ref. [67].

[45] Ref. [62].

[46] The Bakerian Medal and Lecture is awarded annually by the Royal Society and was established in 1775 by Henry Baker. Humphry Davy was awarded the medal every year between 1806 and 1811, and then in 1826.

[47] Meant were solutions of metal salts or metal oxides.

form a chain of charged particles in the same way as water, which move electrophoretically towards their respective electrodes. Grotthuß wrote (on p. 338 of ref. [66])

> "XXIV. The polar arrangement, such as exists in the elementary molecules of water traversed by the Galvanic current, ought to be established equally among the elementary molecules of every other liquid body, provided they are solicited by the same forces. In the metallic solutions the electric polarity takes place among the elements of the oxide, the oxygen of which passes to the positive pole, and the metal of it is deposited at the negative pole."

Grotthuß observed that with certain salts "*the molecules of the metal in solution are revived, assuming a symmetrical arrangement, which extends in the direction of the galvanic current*." This symmetrical arrangement mimicked the shape of leaves of ferns, or of trees with limbs and twigs; its generation was therefore named arborisation.[48] The metal trees grew continuously larger at the negative pole, but hydrogen was never formed as gas there during the galvanic action. Quite remarkably, Grotthuß stated that the arboreal growth from the negative toward the positive pole was always in the direction of the current. He took this fact as evidence of the correctness of his theory regarding water which he described in Chapter II of his paper.

2.4 November 1806: Humphry Davy´s Bakerian Lectures, catalysts for resurgence of research in galvanic electricity in Britain after a four-years hiatus

After a gap of four years since his last publications on galvanic electricity in 1802, Humphry Davy presented the results of his recent investigations in his celebrated Bakerian lectures, read November, 1806,[49][62] and November, 1807.[78] Davy reported the results of his numerous elaborate experiments with galvanic electricity under various experimental conditions, and with a large number of compounds. With respect to the action of the galvanic electricity on water Davy presumed (in the same manner as Grotthuß) that the constituents of water, hydrogen and oxygen, are positively and negatively polarized (electropositive and electronegative), and form a conducting chain. Davy assumed that upon completing the electric circuit oxygen and hydrogen are attracted by or repelled from the electrified metallic surfaces of the oppositely charged poles, and the electric forces follow the action at a distance. Water is split into its elements when its chemical affinity in the molecule is overcome by electrical forces. The energies of the particles which are electrophoretically moving are transferred from one particle to the "immediate neighboring particle of the same kind", which causes the rows of both elements to move towards their respective poles. At this point, note that each relocated particle is immediately substituted by that behind, and the water remains unchanged within the internal volume. This brings Davy to the point to state

> "In the cases of the separation of the constituents of water, (…..) forming the whole of the chain, there may possibly be a succession of decompositions and recompositions throughout the fluid."

and he continued, referring to a neutral point, which is characteristic for the action at a distance

> "It is easy to explain, from the general phenomena of decomposition and transfer, the mode in which oxygene and hydrogene are separately evolved from water. The oxygene of a portion of water is attracted by the positive surface, at the same time that the other constituent part, the hydrogene is repelled by it; and the opposite process takes place at the negative surface; and in the middle or neutral point of the circuit, whether there be a series of decompositions and recompositions, or whether the particles from the extreme points only are active, there must be a new combination of the repelled matter."

Davy also wondered whether the particles of the salts can pass from the one to the opposite pole through different "menstrua", even when they possess a stronger attraction to them. An example of an experimental arrangement for this question is shown in Figure 6.

In one of these experiments Davy filled dissolved muriate of barytes[50] into tube *A* with the positive, and distilled water into tube *B* with the negative pole. First he poured muriatic and nitric acid, respectively, into the middle tube. Once the circuit was closed, the barytes, like most other alkaline substances, passed through the acids without any problems, and were transmitted to tube *B* with the negative wire. Vice versa, these acids

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[48] Arborisation of metals without electricity had already been executed by alchemists. By galvanic electricity it was described first in 1800 by Cruickshank with silver trees (*arbor Dianae*),[11]. in 1800 by Brugnatelli (published in Annali di Chimica, 1800, T. XVIII, p. 136; excerpt in ref. [45]., in 1801 by Gruner as dendrites of silver from silver salt solutions (ref. [37], pp. 216-227.) and in 1805 by Ritter as tree of lead dendrites.[77]

[49] It was the same Bakerian lecture that was discussed in the previous Section, which dealt with the decomposition of water; now the focus is to that of salts, acids and bases.[62]

[50] Barytes, a term which dates back to late 18th century, is a mineral which consists of barium sulphate. In the main text muriate of barytes means barium chloride. Muriatic acid is hydrochloric acid.

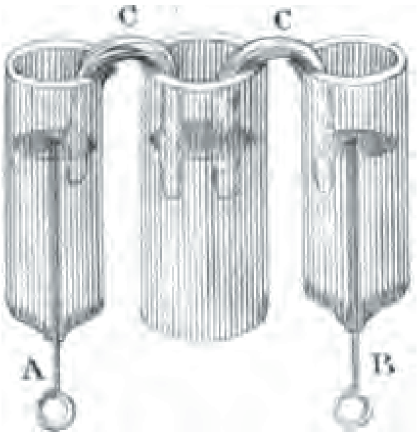

Figure 6. Drawing of Davy´s experimental arrangement for the study "*On the Passage of Acids, Alkalies, and other Substances through various attracting chemical Menstrua, by Means of Electricity*". It shows three glass tubes with platinum wires as poles in the two outer tubes *A* and *B*, which communicate with the middle tube by strips of amianthus *C* (i.e. a fine silky asbestos), wetted with distilled water. The experiments are described in the text. It clearly confirms the migration of ions by electrophoresis. Taken from ref. [79].

passed trouble-free electrophoretically through aqueous solutions of barytes.[51] However, attempts to pass barytes when sulphuric acid was inserted into the middle tube gave a completely different result: after closing the circuit, barytes could not be found in the distilled water in tube *B*, but sulphate of baryte precipitated in the middle tube. The same effect was observed when a solution of sulphate of potash[52] was in tube *B* with the negative pole of the circuit, a saturated solution of barytes in the middle tube, and distilled water in that with the positive pole. In this case sulphuric acid could not be found in distilled water in tube *A* after closing the circuit, but again sulphate of baryte precipitated in the intermediate tube. Due to its insolubility, in both cases this salt became excluded from the galvanic action, inhibiting the further transmission of baryte to the negative, and of sulphate to the positive pole as consequence. This result was clear evidence that the electrophoretic current is due to the migration of ions through the solution, and is an important finding for the subject at hand.

Davy summarized his observations in section "*vi. Some general Observations on these Phenomena, and on the Mode of Decomposition and Transition*" commencing with the repetition of the known facts (pp. 28, 29)

> "…that hydrogene, the alkaline substances, the metals, and certain metallic oxides, are attracted by negatively electrified metallic surfaces, and repelled by positively electrified metallic surfaces; and contrariwise, that oxygene and acid substances are attracted by positively electrified metallic surfaces, and repelled by negatively electrified metallic surfaces; and these attractive and repulsive forces are sufficiently energetic to destroy or suspend the usual operation of elective affinity."

In an attempt to generalize the theory that he had put forward about the electrolysis of water and the simultaneous electrophoresis of the ions he continued

> "It is very natural to suppose, that the repellent and attractive energies are communicated from one particle to another particle of the same kind, so as to establish a conducting chain in the fluid; and that the locomotion takes place in consequence; …"

and he expressed (see Figure 7 and its Legend) that

> "solutions of neutral salts forming the whole of the chain, there may possibly be a succession of decompositions and recompositions throughout the fluid."

2.5 Theories as of 1807 at the European Continent

In France the chemist Jean René Denis Riffault (1752 – 1826) and the physicist and mathematician Nicolas Maurice Chompré (1750 - 1825) published in 1807, too, a theory about the transition of electricity in solutions of acids or bases. They hypothesized that two simultaneous currents fragment the bodies into their elements throughout the solution and not only at the poles. They assumed that the flow of the negative electricity collects the acids and transports them to the positive pole, and the same happens vice versa with the bases. In their opinion the currents were the stronger the closer they were to their respective poles.[82, 83]

Jean-Baptiste Biot, the French physician, mathematician, and astronomer, described his somewhat complex theory in 1824 in Chapitre XVII. *Effets chimiques de l'Appareil voltaïque*. pp. 628-651 of his book *Précis Élémentaire de Physique Expérimentale*.[84] Biot assumed that the decomposable substance possesses opposite electrical states close to the two poles. The fluid is most positive at the positive pole, from where its positive polarity decreases with increasing distance, and reaches neutrality at the indifference point in the middle between the poles. From here on, it approaches the neg-

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[51] Note that barium chloride and nitrate are well soluble in water, in contrast to the sparingly soluble sulphate.

[52] Potash is a mixture of water soluble potassium compounds and potassium-containing materials; its main component is potassium carbonate. In the present context sulphate of potash stands for potassium sulphate.

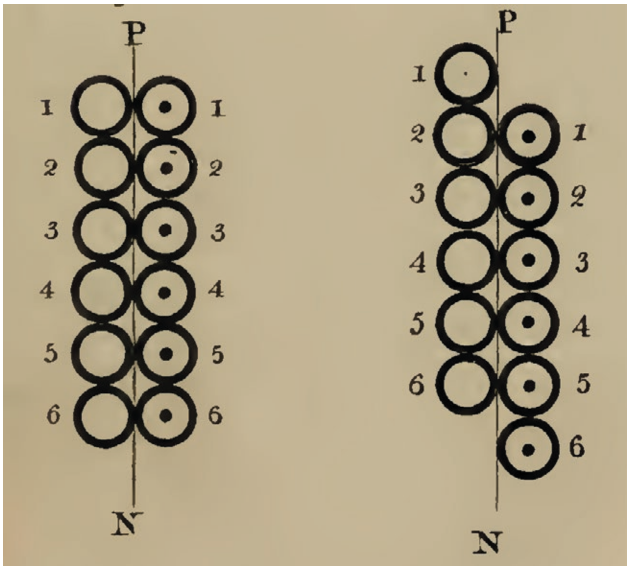

Figure 7. Illustration of Davy´s theory of the electrophoretic migration of the oppositely charged particles of a neutral salt during electrolysis. P, N: positive and negative poles. ⊙, ○: positiv and negativ particles of the neutral salt ○⊙, which forms a conducting chain in the solution. Left and right pictures: arrangement prior and after closing the circuit. See the main text for details and footnote[53] for author's comment. Taken from ref. [80]. Nearly the same scheme is depicted by Berzelius to illustrate his similar theory in ref. [81], p. 278.

ative pole and becomes increasingly negative. When a salt particle is disassembled at the negative pole, its acid part becomes more negative than the undecomposed ones. It is thereby repelled from the pole and increasingly attracted by the positive pole and by the particles of the undecomposed positive fluid around this pole. In contrast to Davy, Biot assumed that the particle is attached to electricity for the duration of the transition and is therefore drawn to the pole with the opposite charge. Thus, decomposition of the particles happens in the portions of the solution close to the poles, but not between them.

The Swiss chemist Auguste Arthur de la Rive (1801, Geneva - 1873, Marseille) published in 1825 a theory that dismissed Grotthuß´ and Davy's concepts of electrophoretic motion through decomposition and recombination.[85] de la Rive assumed a combination of the decomposed bodies with the electricity which is released from respective poles. Concerning water, the electricity from the positive pole unites accordingly with the hydrogen, moves to the negative pole where it is decomposed into electricity and hydrogen, which is set free as gas. An analogue process takes place with the electrified oxygen, which travels from the negative pole to the positive one. In contrast to Grotthuß´ and Davy´s theories, in that of de la Rive the successive decomposition and recompositions in the course of the current does not occur. Decomposition of the particles happens only at the poles, but no recomposition follows.

For completeness we mention the French mathematician Jean Nicolas Pierre Hachette (1769, Mézières - 1834, Paris). In 1832, in the same year Michael Faraday presented his *First Series of Experimental Researches in Electricity*,[86] Hachette assumed the successive decomposition of water by a magneto-electric current.[87, 88]. However, he did not discuss the migration of the decomposed parts. He concluded (ref. [87], p. 73)

> "Il résulte de cette experience, 1° qu'il n'est pas nécessaire, comme on le croyait, que l'action des deux électricités positive et négative, soit simultanée pour la décomposition chimique de l'eau; 2° que l'action, dont la discontinuité n'est qu'instantanée, peut aussi produire cette décomposition." (It results from this experiment, 1°, that it is not necessary, as it was believed, that the action of the two electricities, positive and negative, be simultaneous for the chemical decomposition of water; 2° that the action, the discontinuity of which is only instantaneous, can also produce this decomposition.)

In any case, taking the various theories into account, it is remarkable how long Grotthuß´ from 1805 lasted. Notwithstanding its replacement by Rudolf Clausius´ much better-founded theory in 1857,[89-91] Clausius´ theory – which will be discussed in the subsequent Part 3 of this series – was acknowledged, but largely ignored; and that of Grotthuß was accepted almost unchanged for eight decades.

Although Grotthuß´ theory is rather a subject of the history of electrochemistry, his name is still connected at present time to the special mechanism of the electrophoretic transport of H^+ in aqueous solutions (named proton-jumping or proton-hopping). This Grotthuß-mechanism explains the extraordinarily high ion conductivity and ionic mobility of H^+ due to the presence of clusters of water molecules and their involvement in H^+ transfer (see e.g. ref. [92]).

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[53] Comment of the author: This configuration will most likely not form a stable chain because the particles ⊙ and ○ in the vertical rows are in direct contact with those of like charge. In addition, the molecules would not be arranged parallel in the chain and thus not perpendicular to the current, but would rotate alternately by 90° and form a chain that is arranged as … ⊙○⊙○⊙○ … . The same applies for Berzelius´ theory, but not for Grotthuß´.

3. AS OF 1832: MICHAEL FARADAY´S POINEERING CONTRIBUTIONS IN ELECTRICITY

Michael Faraday[54], having attended only elementary school was given by a fortunate coincidence and on his own initiative the position as Sir Humphry Davy´s laboratory assistant in March 1813. This was the beginning of his outstanding career.

At first he assisted Davy with chemical experiments, and was allowed to carry out some by himself.[55] In 1820 he was fascinated by the discovery of electromagnetism by Hans Christian Ørsted [56,][99] and began research in this new field, concurrently to his chemical work on organic compounds. In autumn of 1821 he discovered the electro-magnetic rotation.[100] During 1824 and 1826 he attempted, to "*convert magnetism into electricity*", but without success.[101] After a break until 1831 he returned to investigate electromagnetic phenomena and to electricity. In this year he made the important discovery of the electromagnetic induction.[86]

3.1 Faraday´s Series of "Experimental Researches in Electricity"

From 1832 to 1834 Faraday published eight comprehensive papers of the series entitled "*Experimental Researches in Electricity*". In this series Faraday communicated the results of his pioneering research on electromagnetism, magneto-electric induction, electricity and electrolysis in *Phil. Trans.*[10, 86, 102-107] After his investigations of electromagnetism in 1831 and 1832 he focused his research on electrical and electrochemical topics. The "*new law of electric conduction*" was published in 1833 in the *Fourth Series of Experimental Researches in Electricity*,[104, 108] and aroused his interest in electrochemical decomposition. Although Faraday is better known for his work on electrolysis - where he derived the laws named after him - his theories about the motion of ions, which superseded those put forward so far, cannot be emphasized enough. Hence, Faraday evaluated and criticized these theories in the *Fifth Series,*[105, 109] § 11. *On Electro-chemical Decomposition*, read June 20, 1833, 481. - 491.)[57], and presented his own conclusions.

That being said, Faraday published numerous important contributions in many scientific fields, but in this review only those will be discussed which had a closer connection to the present topic. It is mentioned that these contributions do not necessarily follow a chronologic order in this text. They are, nevertheless, dealing with the migration of *ions* in solution in direction of lines of electric force, in accordance with the definition of electrophoresis given above. Note that Faraday coined two new key terms (in the previous sentence marked in Italic): *ion* and lines of electric force. We take thus the occasion to begin with Faraday's proposal of a new, unified terminology, which replaced the earlier less systematic one, und will end this review with Faraday`s groundbreaking theory of the lines of electric force, also the electric lines of force, the basis of James Clerk Maxwell´s field theory.

3.1.1 Faraday`s recommendation for a defined terminology

In the preliminary of his Bakerian lecture in which Faraday summarized his results in the *Seventh Series*[10] he pointed to the confusing and arbitrary denotations applied thus far in electro-decomposition issues and recommended their replacement by a consistent and well-defined terminology.[58] For this purpose, he suggested to use artificial words, constructs of ancient Greece words, *viz.* by replacing the term *pole* by *electrode*, and to distinguish between *anode* and *cathode*. He also suggested the terms *ion, anion*, *cation*, *electrolyte*, *electrode*, and *electrolyze*.[59]

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[54] Michael Faraday was born in 1791 in Newington Butts, now part of London, and died in 1867. Instead of going into details of Faraday´s biography, We refer to a recently published paper by F. Bagnoli and R. Livi in this journal.[93]. In their publication the scientific focus is not on the migration of ions by electrophoresis. We have avoided duplicating information, although in some cases it was is inevitable, for example in definitions or in verbatim reproductions of Faraday's statements.

[55] Faraday's first scientific publication which he was allowed to publish as laboratory assistant by his own name was about "*Analysis of the native caustic Lime*" and appeared in 1816 in Vol. I of *The Journal of the Science and of the Arts*, later named *The Quarterly Journal of Science, Literature, and the Arts*.[94]. The subsequent experiments dealt especially with compounds from chlorine and carbon, and the isolation of "*bi-carburate of hydogen*" (i.e. benzene) and other arenes (see e.g. refs. [95],[96],[97],[98]).

[56] Hans Christian Ørsted (in German Hans Christian Oersted; 1777, Rodkøbing – 1851, Copenhagen) was a Danish physicist, chemist and nature-philosopher. He was a friend of Johann Wilhelm Ritter.

[57] The numbers, here 481. and 491., are those of the sub-sections of the paragraphs which subdivide the entire Series.

[58] Although Berzelius opposed against it, meaning: "*Faraday glaubt, … daß unsere gewöhnlichen Wissenschafts – Benennungen … unzureichend werden; daher hat er andere eingeführt, von denen ich aber nicht glaube, weder daß sie in irgend einer Hinsicht nothwendig waren, noch daß sie befolgt zu werden verdienen.*" (ref. [110], pp. 37,38) (*Faraday believes … that our common scientific designations … are becoming inadequate; hence he introduced others, but I do not believe that they were necessary in any way or that they deserve to be obeyed.*)

[59] One might wonder about the reason why Faraday did not introduce the term *electrophoresis* (greek ἤλεκτρον and φόρεσις (phóresis) "the act of bearing", means thus "the act of bearing electricity"). Probably he avoided its use because the simple and common device for the generation of electricity, the "*electrophorus*" was still widely known since Volt´s time (see Part 1 of this series).[1]. But the author must confess that he did not search for an according text passage, neither in the six

Since the historical background of the creation of this new terms was already briefly discussed in a previous issue of this journal,[93] we will not go further into the details of their origin. Yet, it is remarkable that it is still standard nomenclature even today, about two centuries after Faraday´s recommendation.

3.1.2 The inextricable connection of electrolysis and the electrophoretic current

A central point in Faraday´s theories was the co-occurrence of electrolysis and the electrophoretic current. He considered the two phenomena as being so inseparable, "*that one cannot happen without the other*". The importance of this connection for Faraday becomes clear as he repeated his conviction in various formulations (see § 13 of the *Seventh Series,*[10] and the *Eighth Series*[107], p. 436), which read, for example

> "854. On the other hand, the relation between the conduction of the electricity and the decomposition of the water is so close, that one cannot take place without the other. …
> 855. Considering this close and twofold relation, namely, that without decomposition transmission of electricity does not occur......
> 858. Those bodies which, being interposed between the metals of the voltaic pile, render it active, are all of them electrolytes (476.); and it cannot but press upon the attention of every one engaged in considering this subject, that in those bodies (so essential to the pile) decomposition and the transmission of a current are so intimately connected, that one cannot happen without the other. …
> 923. … An electrolyte is always a compound body: it can conduct, but only whilst decomposing. Its conduction depends upon its decomposition and the transmission of its particles in directions parallel to the current; and so intimate is this connexion, that if their transition be stopped, the current is stopped also; if their course be changed, its course and direction changes with them; …"

In these statements the flow of charge carried by ions is phrased as "*conduction of electricity, transmission of electricity, transmission of a current, transmission of its particles, transition [of particles]*", all of which express what we name the electrophoretic current.

3.1.3 1833/1834: Faraday´s theory of the electrophoretic migration of the ions during electrolysis, and his seminal concept of the lines of force

The part following the preliminary in the aforesaid *Seventh Series* in 1834[10] can be seen as the focus of his point of view at the motion of ions in solution during electrolysis. In this part Faraday reported his experiments of the relation between current and electrochemically decomposed matter, what he already did in the *Fifth Series* in 1833.[105] One might ask how this relation can contribute to the problem of the migration velocity of an ion; we detail it as follows.

With reference to the previous theories, the velocity of migration is determined by the electrical forces that act on the ion by the action at a distance. In this case, the electric forces and therefore the migration velocity are not constant but vary with the distance between ion and electrodes. We recall that electricity was throughout considered as a fluid. Over the course of his research, Faraday began to doubt these previous theories about the continuous character of electricity and the action at a distance. It was his unparalleled merit, thanks to his studies of electricity and magnetism, to open the window for a new look at the migration velocity of ions.

3.1.4 The absolute quantity of electricity, a consequence of the law of definite electrochemical action

In the *Fifth Series* Faraday argued "*505. That for a constant quantity of electricity, whatever the decomposing conductor may be, … the amount of electro-chemical action is also a constant quantity, i.e. would always be equivalent to a standard chemical effect founded upon ordinary chemical affinity*". In the *Seventh Series*[10] in 1834 he presented as conclusion which he derived from the quantitative measurements of numerous electrolytically decomposed electrolytes the "*law of definite electrochemical action*", or the "*law of the definite chemical action of electricity*" (807.) which he expressed in different phrasing, for example as

> "732. … with respect to water, that when subjected to the influence of the electric current, a quantity of it is decomposed exactly proportionate to the quantity of electricity which has passed, …
> 783. The law was expressed thus: The chemical power of a current of electricity is in direct proportion to the absolute quantity of electricity which passes.
> 810. …the results prove that the quantities so decomposed are perfectly definite and proportionate to the quantity of electricity which has passed.
> 836. Electro-chemical equivalents coincide, and are the same, with ordinary chemical equivalents."

Note that Faraday accentuated the quantity of electricity, not its intensity, what he already did in the *Third Series* (ref. [103], 329.).

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volumes of Faraday´s correspondence,[111]. nor in the seven volumes of his diary (the "*Experimental Notes*").[112]

The forecited extension to quantitative experiments enabled Faraday to show that the law of definite electrochemical action is generally valid. The *electrochemical equivalent* is a property of a particular ionic species (see section vii of the *Seventh Series*, *"On the definite nature and extent of Electrochemical Decomposition"*).[10] He explained that the anions and the cations of an electrolyte decompose in portions of electrochemical equivalents, that is to say, in quantities which are given by their atomic weigh divided by their charge number. Thus, the electrochemical equivalent weight of hydrogen is 1, that of oxygen is 16/2 = 8, etc. (p. 111).

Because of the law of definite electrochemical action Faraday came to his fundamental conclusion that "*an absolute quantity of electricity associated with the particles or atoms of matter*" exists (§13). He wrote

> "852. The theory of definite electrolytical or electro-chemical action appears to me to touch immediately upon the absolute quantity of electricity or electric power belonging to different bodies. …, yet there is an immensity of facts which justify us in believing that the atoms of matter are in someway endowed or associated with electrical powers, to which they owe their most striking qualities, and amongst them their mutual chemical affinity."

From this insight Faraday derived that electricity consists of fundamental quantities. Ions are therefore always charged by one or integer multiples of this charge unit.[60]

3.1.5 Faraday`s rejection of the action at a distance

Faraday contradicted especially the established concept of the action at a distance, the inverse square law. One might remember that Grotthuß formulated in §. 18. of his original paper from 1805[65] this *a*ction at a distance concept in regard of the transport of the charged particles in water as follows:

> "§. 18. L'action de chaque force par rapport à une molécule d'eau située sur la route du courant galvanque, est en raison inverse du quarré de la distance à laquelle elle s' exerce."[61]

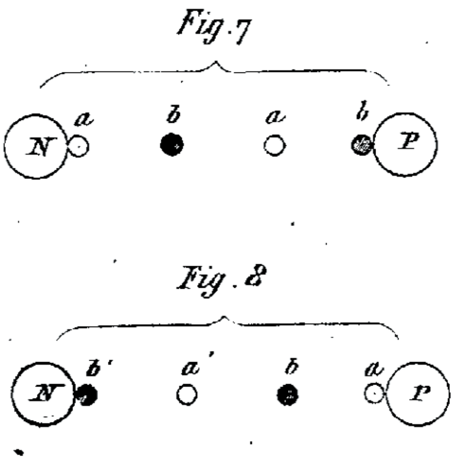

Figure 8. Drawing which illustrates Michael Faraday´s concept of the electrophoretic migration of the ions during electrolysis. In the upper scheme anions *a* and *a´* migrate towards the anode, *P*, cations *b* and *b´* to the cathode, *N*. They are moving parallel to the lines of forces, which fill the space between the two electrodes. For details, see main text, quoted sub-section 519. in Faraday´s *Fifth Series*. Taken from ref .[109].

From his magneto-electric investigations Faraday realized that this action at a distance does not apply, and this previous concept was false. Fortuitously, this part of Grotthuß´ theory was already withdrawn by himself in 1820, about one decade prior to Faraday's criticism. Most probably Faraday did not have knowledge of Grotthuß´ comments in the German translation of his article, which he published in his book "*Physisch-chemische Forschungen*" (this book is quoted above)[28]**.** Grotthuß added (in §. 18, p.122)

> "Die Annahme daß die Polarelectricität (Galvanismus) umgekehrt wie das Quadrat der Entfemung wirke, ist grundlos und nicht einmal ganz zuverlässig für die gewöhnliche Electricität erwiesen (M, s. Simon im 28sten Bde. von Gilberts Annalen[62]). Daher hätte dieser Paragraph füglich wegbleiben können." (The assumption that the polar electricity (galvanism) is inverse of the square of the distance is proved groundless and not even completely reliable for the ordinary electricity (M, see Simon in the 28th volume of Gilbert's Annals). Therefore, this paragraph could have stayed off.)

3.1.6 The migration of ions and the electric lines of force

Already in the *Fifth Series,* § 11, iii., "*Theory of Electrochemical Decomposition*",[105] read a few months prior

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[60] It may appear questionable to the reader that we are discussing properties that seem to be only relevant in electrolysis. However, since the migration velocity of an ion depends on its charge, the findings just discussed are of outmost importance for electrophoresis.

[61] Grotthuß` own translation into German in his book from 1820 *reads: "§. 18. Der Einfluß einer jeden Kraft hinsichtlich auf ein Teilchen Wassers, welches in der Richtung des galvanischen Stromes liegt; wirkt umgekehrt wie das Quadrat der Entfernung in welcher sie sich äussert"* (ref. [28]., p. 122). In the English version published in *Phil. Mag.* it was translated as: *"XVIII. The action of each force, in respect to a molecule of water situated in the direction of the Galvanic current, is in the inverse ratio of the square of the distance to which it exercises its influence."* (ref. [66], p. 335).

[62] Ref. [113], specified by the author.

to the *Seventh Series*,[10] Faraday described his view at the migration of ions. In his opinion, "*the two elementary electric currents, moving in opposite directions, from pole to pole, constitute the ordinary voltaic current*."[63] He stated that the influence that is present in the electric current has to be strictly devised as "*an axis of power having contrary forces, exactly equal in amount, in contrary directions.*" (517.). This theory was in clear contradiction to the earlier established concept of the action at a distance and the point of indifference or neutrality and marked a fundamental change in the principles of ion migration.

Faraday considered the decomposing bodies as a mass of particles, which contribute to the final effect given that they are in the course of the electric current. The effect of the electrochemical decomposition is based on an internal corpuscular action, which originates from a force, that either adds to the common chemical affinity, or determines its direction. The combining particles pass in opposite directions because the usual chemical affinity is reduced, weakened or partially neutralized by the influence of the electric current in one direction parallel to its course, and reinforced or supplemented in the opposite direction. The author comments that this is in fact the description of the electrophoretic motion.

Faraday expounded his theory again in section 519. of the *Fifth Series* (ref.[105], p. 696¸ German translation ref. [109]) explaining (see Figure 8).[64]

> "519. In this view the effect is considered as essentially dependent upon the mutual chemical affinity of the particles of opposite kinds. Particles *a a,* fig. 7, could not be transferred or travel from one pole *N* towards the other *P,* unless they found particles of the opposite kind *b b,* ready to pass in the contrary direction: for it is by virtue of their increased affinity for those particles, combined with their diminished affinity for such as are behind them in their course, that they are urged forward: and when any one particle *a,* fig. 8, arrives at the pole, it is excluded or set free, because the particle *b* of the opposite kind, with which it was the moment before in combination, has, under the superinducing influence of the current, a greater attraction for the particle *a´,* which is before it in its course, than for the particle *a,* towards which its affinity has been weakened."

Consequently, all composite particles in the course of the current act conjointly, except those which are in contact with the poles. They "*consist of elementary particles, which, whilst they are in one direction expelling, are in the other being expelled*". The acting particles (i.e. the ions) which represent the electric current move in direction of the electric lines of action or lines of electric force. Like the lines of magnetic force[65] the electric lines do not necessarily form a straight line between the electrodes, neither must they be parallel, but they do not cross.[66]

Due to its importance, we repeat the explanation of the line of force which Faraday gave about one decade later, viz. in the *Nineteenth Series*, read in November 1845.[114] He stated

> ":—thus, by line of magnetic force, or magnetic line of force, or magnetic curve, I mean that exercise of magnetic force which is exerted in the lines usually called magnetic curves, and which equally exist as passing from or to magnetic poles, or forming concentric circles round an electric current. By line of electric force, I mean the force exerted in the lines joining two bodies, acting on each other according to the principles of static electric induction, which may also be either in curved or straight lines."

3.1.7 The migration velocity of the ions and its assumed context with the decomposition of equal chemical equivalents of anions and cations

Faraday's replacement of the earlier theory of the action at a distance by that of the electric lines of force[67] and the conclusion of an elementary charge unit had far-reaching consequences for the question of the migration velocity of the ions. In the earlier concept of the action at a distance this electric force acting on an ion varied with the in the inverse ratio of the square of the distance from the electrodes, and consequently its drift velocity varied as well. In Faraday´s theory, the velocity in the electric field, in contrast, is constant during the motion of the ion along a field line.[68] That is to say, in a homo-

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[63] This attribution deviates from ours, because the ordinary voltaic current is the flow of electrons (electrons were unknown at the time). In contrast, "*the two elementary electrical currents that move from pole to pole in opposite directions*" is the flow of charge carried by ions in solution. It is the current for which we coined the term *electrophoretic current*.

[64] The collection of all 14 Series of the *Experimental Researches in Electricity*, reprinted from the *Phil. Trans.* of 1831 – 1838 is published in ref. [73].

[65] In the *First Series of Experimental Researches in Electricity*, read November 1831, Faraday reported the induction of electric currents and the generation of electricity from magnetism. In this paper, Faraday defined for the first time the *lines of force* as "*By magnetic curves, I mean the lines of magnetic forces, however modified by the juxtaposition of poles, which would be depicted by iron filings; or those to which a very small magnetic needle would form a tangent*."(ref. [86],114.; footnote at p. 154). These magnetic field lines can be visualized by iron files poured onto a sheet of paper with a magnet underneath.

[66] All these properties apply for all configurations. In a homogeneous electric field, for example in the field between two plate electrodes, nearly all lines are straight and parallel, and, as all others in all configurations, are perpendicular to the surfaces of the plates.

[67] Ref. [114], 2149., and ref. [115],1662.

[68] To emphasize the importance of Faraday´s theory of the lines of electric force for electrophoresis, and his conclusion that ions carry elementary charge units, we skip a period in the development of the theory of

geneous field ions migrate with an equal and constant velocity along the field lines that run parallel to one another. Faraday brought forward this argument in the *Eighth Series* read June 1834,[107] p. 448, that

> "964. … If any number of them [anions and cations] enter as ions into the constitution of electrolytes, and, forming one circuit, are simultaneously subject to one common current, the anions must move in accordance with each other in one direction, and the cations in the other. Nay, more than that, equivalent portions of these bodies must so advance in opposite directions; for the advance of every 32*5 parts of the zinc … must be accompanied by a motion in the opposite direction of 8 parts of oxygen … of 36 parts of chlorine … , of 126 parts of iodine … ; and in the same direction by electro-chemical equivalents of hydrogen, … lead, copper and tin, …"

It can be seen that Faraday based his conclusion on the opposite movement of equal electrochemical equivalents of cations and anions of an electrolyte to their respective electrodes during electrolysis. In the simplest case the electrolyte consists of two ions with a single charge each. Then, an anion cannot be oxidized on the anode unless a cation is reduced at the same time on the cathode. Due to the requirement to reach their electrodes at the same time Faraday concluded that the migration velocities of cations and anions must also be equal. Faraday did not provide any values for this velocity. On the top of that, it will be seen later that his hypothesis was based on a mistake in reasoning.

The first systematic attempts to measure the values of the drift velocity were made by Wilhelm Hittorf in the 1850s. Yet, Hittorf did not determine the absolute, but the relative velocities of the various ion species to one another, referred to as transference or transport numbers. This topic, and the subsequent studies to determine the actual migration velocity of an ion will be the subject of the following Part 3 of this historical retrospect.

4. SUMMARY

By following the general definition that "*electrophoresis is the motion of dispersed particles relative to a fluid under the influence of a spatially uniform electric field*" we have chosen a probably unusual view at electrophoresis in this Part 2, since the focus is aimed exclusively at ions. This view is justified because, as defined above, ions of atomic or molecular size are also the subject of electrophoresis, not just colloidal particles as is conventionally considered.

Due to the inextricable linkage between ion migration and electrolysis the histories of these two phenomena are also intrinsically related. It is for this reason that this review begins with the year 1800 when electrolysis by galvanic electricity - which was considered as a fluid at that time - was discovered. It extends over the time until the 1830s and early 1840s when Michael Faraday superseded the previously established concept of action at a distance by that of the electric lines of force, which were later referred to as field lines of the electric field.

It is pointed out that during the electrolysis of decomposable compounds by galvanic electricity two kinds of currents can be differentiated in the closed electric circuit. The galvanic or voltaic current is the flow of charges carried by electrons in the metallic parts (electrons were not known at the time). But decomposition can only take place if an electric current flows through the liquid from one pole to the other. Although this process is obviously invisible to the naked eye, the several observations provided evidence that electricity was actually being transported through the liquid, e.g. due to the increased speed of electrolysis at higher concentrations of decomposable bodies, the analytic determination of parts of the decomposed molecules close to one pole, e.g. of potassium at the negatively charged electrode after electrolysis of muriate of potash, or by the kind of the decomposition products formed at the poles by electrolysis For this flow of these charged particles, later named ions, between the poles, which is an electric, but not a galvanic current, we coin the term *electrophoretic current*. While not common, it fully conforms to the definition of electrophoresis quoted above.

Taking these facts into account, the history of electrophoresis begins in 1800 with W. Nicholson´s and A. Carlisle´s experiments of decomposing water by the aid of a voltaic pile. Remarkably, just two months after their publication, as early as in September 1800, the first theories of the action of galvanic electricity on water were presented by W. Cruickshank in Britain and by J. W. Ritter in Germany. Both researchers hypothesized that gaseous hydrogen and oxygen, evolving at the separate poles,

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ion migration. Today it is well-known that the electrical force acting on an ion is proportional to its charge, $z.e$, and the strength of the electric field, $E = U/d$. Here z is the number of charges, e the electron charge, U the potential difference and d the distance between the electrodes. That is, on ions with the same number of charges an equal electrical force is acting, independent of its distance from the electrodes. This is in clear contradiction to the action at a distance. This force accelerates the ion, but the oppositely directed frictional force of the medium increases with increasing speed. The frictional force depends on the size and shape of the ion and is thus different for different ions. When both forces are equal, the ion moves with a constant migration velocity (for the sake of simplicity, we have considered an ion at infinite dilution).

came from the same water molecule. In the following years, not surprising due to the novelty of the phenomena, experiments were carried out mainly for the acquirement of the results of galvanic action on solutions of arbitrarily chosen compounds and different experimental set-ups. In all cases the researchers were convinced that the two ions that assemble the decomposable molecule are tightly bound to each other, and could only be separated by the action of galvanic electricity, when the electric force from the connected voltaic pile overcame their chemical affinity. Davy and Berzelius assumed that the ions migrated because they were attracted or repelled by the charged poles, whereby the electric forces obeyed the action at a distance. That is, the forces decrease in the inverse ratio of to the square of the distance from the poles and cross at the point of indifference or neutrality. The compounds are decomposed near or at this point, but the decomposed particles appear at the poles, which makes this hypothesis quite difficult to comprehend. The action at a distance brought forth that the ions moved with varying, but not with constant velocity.

In 1803 Berzelius and W. Hisinger were able to create a classification based on the properties of the ions involved in electrolytic decomposition and the direction of their electrophoretic migration towards their respective poles. It was a first step to systematically categorize compounds into electropositive and electronegative classes.

Back in 1800, beginning with Cruickshank and Ritter, several other theories about the electrolytic decomposition and the electrophoretic current were developed. Works up to 1805 include the theory of the Italian L. V. Brugnatelli from 1800, who, to his surprise, found that the Belgian E.G. Robert (also Robertson and Robert-son) had already published almost the same theory before him; they report the theories of the French A. F. Fourcroy, L.-N. Vauquelin and L. J. Thénard in 1800 and 1801, of the German J. F. Erdmann in 1802, of H. Davy, who paused after 1802 for four years, and of the Swedes W. Hisinger and J. J. Berzelius in 1803.

However, one of the most plausible theories at that time, which surprisingly outlasted almost eight decades, was presented in 1805 by Theodor von Grotthuß (also C.J.T. de Grotthuss). He hypothesized that water or dissolved salts form a chain of polarized molecules, and only the terminal atoms of the chain, which were in direct contact with the surfaces of the oppositely charged electrodes were set free by galvanic electricity. However, important for electrophoresis is Grotthuß´ hypothesis how the current flows through water or salt solutions. He assumed that the liberated terminal atoms are instantaneously replaced by the neighboring atoms of the same species, which led to a permanent decomposition and recombination of the molecules in the chain, and to the electric current in this way.

It was thus believed that free ions were never present in the fluid. To his disappointment, the priority of his theory was initially assigned to the widely recognized scientist Davy, who published a similar theory about one year later.

Indeed, in December, 1806 Davy read a celebrated Bakerian lecture with a theory in which he also assumed a chain of molecules, and a similar process of decomposition and recombination as Grotthuß. After Grotthuß and Davy, fewer theories were formulated, e.g. by the French J. R. D. Riffault and N. M. Chompré in 1807, and after a break of about fifteen years, by the French J.-B. Biot in 1824, then by the Swiss A. A. de la Rive in 1825, and the French J. N. P. Hachette in 1832.

However, all these theories were dismissed in 1833 by Michael Faraday, who unambiguously rejected the concept of action at a distance. Based on his experience, which he had gained from his previous studies of magnetism and electromagnetism, Faraday developed the theory of lines of magnetic and electric force, which served James Clerk Maxwell for the mathematical formulation of the field theory. This was one of Faraday's groundbreaking contributions to the further development of electricity and electromagnetism and thus to electrophoresis as well and opened a new era in these topics. Another major contribution, which he deduced from his *law of definite electrochemical action*, was his proof that electricity consists of individual elementary charge units. The consequence of Faraday's seminal theories was that ions move at constant velocities parallel to the lines of the electric force that fill the space between the electrodes. Thus, after more than three decades the concept of the action at a distance and its consequences were superseded. What remained was the conviction that electrolyte molecules consist of tightly bound ions of opposite charge, which can only be separated by electrical forces, whereupon they are permanently and instantaneously decomposed and recombined forming in this way the electrophoretic current. Accordingly, free ions are not present in solutions in the absence of an electric field.

However, none of these theories dealt with the magnitudes of the velocities of ion migration, and the questions whether these speeds are actually equal, how high they are and on what conditions they depend, remained open.

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Historical Articles

Disinfectants: Use of Different Types of Sanitization Techniques in 18th and 19th Centuries Britain and India

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Abstract. The article focuses on the use of different kinds of disinfectants used for sanitization and cleaning of public and private places for curbing the spread of diseases from one place to another. Multiple methods were employed for disinfection; some of which are easily accessible to the common people while others were particularly used in infirmaries and hospitals at the time of treatment. The article also shows that disinfectants were supplement to medicine and they were used to limit the contagion to a space whereas medicines were not accessible for the treatment of patients. Historically, the eighteenth and nineteenth centuries witnessed an unprecedented development in the field of chemistry which led to the discoveries of different types of antiseptic solutions and disinfectants apparently endorsed by the germ theory.

Keywords: Disinfection, Sanitization, Detoxification, Public Health, Medicine, Chemical Compound, Metal.

Amidst the rising number of Covid19 cases across the globe, the health ministries and disease control agencies of different countries have been periodically issuing guidelines and protocols for people to safeguard themselves from the contagion. These guidelines give people psychological satisfaction that if they bring change in their lifestyle and live disciplined public life, then they would soon resume their daily choruses. Medical researchers and health experts have revealed that people are required to be more conscious towards their personal hygiene and use disinfectants/sanitizers frequently in their homes and offices. In this context, the World Health Organization (WHO) and the US Environmental Protection Agency (EPA) have recommended a list of disinfectants, such as hydrogen peroxide, hypocholorus acid, sodium hypochlorite, sodium chlorite, calcium hypochlorite (bleaching powder)[1] detergent powder and soap, to disinfect places. The Indian Ministry of Health and Family Welfare also issued a brochure titled "Covid19: Guidelines on Disinfection of Common Places Including Offices"[2] to explain people what kinds of disinfectants to be used for cleaning indoor and outdoor spaces. The brochure also incorporated the list of cleaning agents (chemical compositions), details of hand hygiene and use of mask to encourage people for adopting clean ways of living.

This article is a chronological study of disinfectants with an objective to trace and analyse how these sanitization methods were employed by administrative authorities and medical institutions in Europe and India during the eighteenth and nineteenth centuries for confining diseases to specific locations. The article also gives an insight into four broad categories of disinfectants that were used in both civil and military firmaments against diseases and to provide clean and hygienic environment to patients in hospitals. It also studies the reasons for the recurring breakout of epidemics in slums of European cities in the nineteenth century despite persistent advocacy for disinfectants. The article also analyses the problem of frequent emergence of diseases in colonies and how they pressurized the colonial administration for pro-active steps to curb contagions.

GERM THEORY

While people associated with different fields of science had been conducting experiments and analysing data to approve their theories of the existence of diseases causing agents in the air, it was in the nineteenth century that the 'germ theory' got recognition owing to the efforts of scientists and physicians like Ignaz Philip Semmelweis, Louis Pasteur, Robert Koch and Joseph Lister. In this list, Ignaz Philip Semmelweis, the Hungary born physician and scientist, deserves special mention for his astonishing contribution in finding the causes for the death of labouring women in obstetrical and midwifery wards.[3] In 1844, Semmelweis took master's degree in midwifery and applied for the position of assistant to the Clinic of Obstetrics in Vienna General Hospital. While working in the midwifery section of the hospital, Semmelweis observed that "the disease from which Prof. Kolletschka (his friend) had died was identical with that from which I had seen so many lying-in women die."[4] His pathological discovery produced astonishing results as "the mortality of parturient women in the first clinic (where the entry of physicians and students working in mortuary and post mortem restricted) fell from 12% to 3% in the course of two months."[5] This plunge in mortality rate Semmelweis attributed to following a simple practice of hand hygiene before entering the obstetrics wards but his inference was discarded by his colleagues and other physicians.

Although Semmelweis's discovery of pathological agent that cause puerperal fever in lying-in women was received with indifference, Louis Pasteur, Robert Koch and Joseph Lister consistently worked in this field and transformed the perception of people towards pathology and diseases with their revolutionary ideas and findings. Sterilization of surgical instruments and cleaning the space with disinfectants considerably reduced in-hospitalization and post-operative deaths apparent from an article by a physician George F. Elliott on 'Germ Theory'[6] wherein he credited Professor Lister for his experiment with carbolic acid (phenol) in surgical theatre. Not only this, Prof. Elliott argued that the rooms where patients were taken post-surgery ought to be free from germs and therefore disinfected by means like fumigation, chemical solutions and spraying of germs killing deodorants.

With the progress in healthcare procedures and medicines, the use of disinfectants was voraciously advocated by physicians, microbiologists, biologists and pharmacists to clean laboratories, dormitories, infirmaries, clinics, and areas ravaged by diseases.[7] Hence, disinfectants were used as supplementary chemical compounds that would help in killing germs and curbing the spread of diseases like cholera, smallpox and plague.

TYPES OF DISINFECTANTS

In the eighteenth and nineteenth centuries, disinfection was carried out in four distinctive ways – a) use of physical agents, b) use of chemical compositions, c) use of biological agents, and d) deodorants. Physical agents were profoundly used for disinfection in the ancient time and remained the prime and easily accessible for the common people in the latter centuries. Some of the common physical agents were -

i) **Boiled Water** –Boiled water was the most common disinfecting agent in the ancient time. The Greek philosopher Aristotle suggested soldiers and army heads to boil water before drinking while fighting in areas unknown to them. He believed, "everything that may abide by fire had to be put into the fire and the rest had to be immersed in boiling water. He understood the need to avoid disease and instructed Alexander the Great that his armies boil drinking water and bury dung."[8] Not only this, objects and clothes of medical professionals were disinfected by placing them in boiled water for a specific time period and then let them dry in the sunlight. The prevalence of this practice could be assessed from the fact that "in 1797, Viborg recommended heating up to 64-65°C objects which had been in contact with the 'contagious poison' responsible for equine glanders"[9] With the increasing level of contamination of rivers water, it became necessary to employ water filtration techniques for clean water in the nineteenth century Britain. On the one hand, the industrial waste was released in the rivers and on the other hand, water closets were connected with the main sewers. For instance – after the uplifting of ban on connecting the household water closets to the main sewer in 1815, the city of London faced the problem of clean water because household discharge was directly released in the Thames. Thereafter, the pressure was built on the local administration to supply clean drinking water to people particularly in wake of frequent outbreaks of cholera in sullied, congested pockets of cities in the first half of the nineteenth century. The local authorities took steps in this direction and provided clean drinking water for which investments were made in filters and water treatment technologies. Those areas of the city where pipe water could not be reached, people were encouraged to boil water before drinking.

In India, the practice of boiling water for drinking was quite old and diligently followed in many communities. Health conscious people continued this ancient practice in the eighteen and nineteenth centuries for which they heat water under the sun and then filter it with gravel and charcoal. Boiled water was a necessary component of medicine and dietary chart especially to those who fall sick from critical ailments. In the city of Puri (princely state of Keonjhar), victims of leprosy were given herbal medicine with boiled water and emphasis was laid on incorporating boiled water in diet.

The dietary prescription with their stress on vegetarianism, demonstrate a significant level of Hinduization. The stress on warm and boiled water seems particularly striking perhaps reflects interaction with the colonial medical system.[10]

ii) **Fire** – In the middle ages, people were scared of dead bodies afflicted from diseases. Incineration of corpses, both human and animals, was perceived as the only way to avert contagion from spreading to others. The belongings of people died from diseases were immolated with the body and the premises where the death occurred sanitized and left unoccupied for nearly three months. Additionally, the family members and the ones who came in contact with the person died of disease (like plague) were forced to burn their clothes else severe punishment was given on failing to comply with the social and cultural norms. Another example of burning clothes came from the eighteenth century when families of those who died from tuberculosis were mandatorily placed everything in fire.

iii) **Fumigation** – Sanitization of a place where a person died of contagion was a compulsory practice for which fumigation through herbs was aggressively promoted in the eighteenth century. Burning of odoriferous herbs was a widely accepted practice to chase away insects in the streets and to disinfect clothes and objects of those suffered from mild diseases. The popularity of fumigation for sanitization could be understood from the advisory of English Physician Daniel Layard issued in 1752 during the epidemic of cattle plague ('contagious distemper') – "the fumigation of stables using the following mixture: Wet gunpowder, pitch, tar, brim-stone, tobacco, frankincense, juniper and bay-berries, [...] should be burnt, and the smoke confined in these stables, more than once"[11] Sulphur and Mercury were two chemicals frequently used for fumigation of spaces and to detoxify objects that could not be immersed in boiled water. In India, Susruta wrote in his book *Susruta Tantra* that the fumes of sulphur should be released in rooms used for surgical purposes to purify them from all kinds of impurities.

Disinfection through chemical compounds

Although there are several literary and non-literary records from the ancient times[12] to testify the use of chemicals for detoxification and purification of spaces and objects, the pre-modern era (around renaissance movement) witnessed extensive research and application of chemicals like sulphur, mercury, sodium, calcium and others for sanitization purposes. In the last phase of the middle ages, Europe became the centre of knowledge with endorsement to the classification of data and emphasis on empirical approach. Practical chemistry received extensive attention along with the documentation and translation of books in many European languages. Georg Pawer, a German thinker, studied chemistry, physics and medicine in the 16th century and spent his entire life in understanding of mining and metal production. Similarly, John Pettus, an English scientist, had deep interest in metallurgy and mining that made him the member of Society of Mines Royal and Battery Works in 1651. The impact of these developments could also be seen on chemical disinfectants and their uses -

i) **Sulphur** - Sulphur and its derivatives were the main disinfectants used for sanitization of not only places but also objects used for the treatment of patients.

Owing to its awful smell and lethal impact on small plants and insects, sulphur dioxide was produced through chemical reaction or by burning the metal in fire. The fumes of sulphur dioxide easily spread in streets, houses and closed spaces. In the last quarter of eighteenth century, fumes of sulphur dioxide were used to disinfect spaces in England where the cattle plague wreaked havoc. The fear of infection was so deeply rooted in the minds of people that many European countries in the nineteenth century passed "rules not to take correspondences or letters from Asian countries like India until they were sanitized in ships before unloading and then dispatched to the addresses after twenty four hours."[13] Parcels shipped from the disease ridden colonies were first placed in a room and fumes of sulphur dioxide were released and then left them unattended for some-time before starting their deliveries.

ii) **Mercury** - From the ancient time till the late nineteenth century, chemists and metallurgists observed corrosive properties of mercury that encouraged people to use the metal in medicines for treatments of diseases in both humans and animals. Compounds of mercury were abundantly used for treatments of diseases like leprosy, syphilis, tuberculosis and other kinds of contagious diseases. Robert Koch, the nineteenth century German physician and microbiologist, demonstrated with his experiments that due to corrosive effect of mercury, it can sublimate the multiplication of microorganisms. Although mercury was used in India prior to the British intervention in indigenous cures, the metal was aggressively endorsed by the British Indian government for the treatment of syphilis in European soldiers. In the article "Sexually Transmitted Diseases and the Raj," R. Basu Roy writes

> The mainstay of the treatment of syphilis in the 19th century was mercury. In India, mercurial preparations had been in use for years for the treatment of many non-venereal complaints, and its side effects were well known. In the case of syphilis, the army authorities did not like oral treatment with mercury compounds because of gastrointestinal side effects and the difficulty of securing compliance… In 1903 the expert adviser to the army at the time proposed repeated injections of "mercurial cream", also known as "grey oil", a suspension of metallic mercury in oil and fat which had been devised by Lange in Vienna in 1887 The metal was applied to the skin of patients.[14]

iii) **Copper** – Unlike mercury and sulphur, this metal was primarily used for manufacturing utensils and objects. People were familiar with corrosive property of copper apparent from its hostility to the growth of algae and fungi. In India, copper utensils were extensively used to store drinking water. In the eighteenth and nineteenth centuries, cholera ravaged several parts of India. *Hakims* and *Veds* recommended to their patients and their family members to store drinking water in copper utensils because the metal was known for its anti-microbial properties.

iv) **Potassium Permanganate (Condy's Fluid)** – Crystals of Potassium Permanganate were dissolved in water to prepare a solution called Condy's Fluid in which saucer and utensils of patients were dipped for some-time before placing them in running clean water. The solution was used to soak in the clothes of sick people and to spray on furniture kept in the rooms of patients. Besides, the solution was used to disinfect rooms, halls, galleries and compounds of hospitals and even kept in hospital toilets to sanitize the hands of doctors. Henry Bollmann Condy, an Englishman chemist and industrialist, prepared Condy's fluid in 1857 to be used externally as well as internally. Condy recommended not to use this fluid with carbolic acid because of their opposite properties. The fluid was purchased in abundance by cargo companies in the nineteenth century for the purification of ships. The British government released advisories for the cargo shipping companies to disinfect their coolie ships coming from cities like Calcutta and Bombay in the wake of frequent outbreaks of epidemics like cholera and plague. Consequently, the manufacturers exploited the growing concerns of epidemics in Britain and advertised their disinfectant products in newspapers - Advertisements that appeared in the Kingston newspaper – *The Gleaner* – during 1860s and 1870s proclaimed that Condy's fluid was strong enough to be used 'To purify Bilge Water in Ship's Well To parity with the Interior or Hold of a Ship.[15]

v) **Carbolic Acid (Phenol)** – Carbolic acid gained popularity for its qualities of disinfection and antiseptic to treat wounds and other kinds of injuries. Joseph Lister, the British surgeon, acknowledged Louis Pasteur's contribution of microbes and introduced carbolic acid as an antiseptic solution for sterilizing of surgical instruments. Lister widely used carbolic acid to minimize post-surgical infections. Owing to its highly inflammable qualities, carbolic acid was given to people in crystalline solid form. Crystals were dissolved in water to prepare a solution used for washing clothes, furniture, utensils, and to clean hands of attendants, sick and children. During the Bombay Epidemic 1896-97, the British Indian government made steam disinfection mandatory near the quarantine centre and people coming to these centres were bound to take bath. Besides, they were given douche of 2 per-cent solution of carbolic acid. Clothes of patients and suspected people were immersed in 1-1000 solution of perchloride of mercury for ten minutes."[16]

The pure form of carbolic acid was used for surgical purposes and its lotion was applied on ordinary sores and ulcers. The significance of carbolic acid at the breakout of cholera could be assessed from the report – 'Cholera: Its Nature, Detection and Prevention' published in *Public Health Reports* in 1910. The report highlights multiple uses of the acid including

> In the room with the patient, there should be a tub or other large vessel containing five per cent solution of carbolic acid crystals for the immediate reception of soiled linen… the stools and vomit of the patient should be disinfected at once by adding an equal volume of five per cent carbolic acid solution, five per cent formaldehyde solution, or milk of lime.[17]

vi) **Chlorine gas** – Carl Wilhelm Scheele discovered chlorine in 1774 and studied its properties that resulted in its massive industrial use like bleaching agent in paper and textile mills. Considering the exclusive quality to disinfect, chlorine was used to clean portable water and to disinfect sewages but it did not find much use in hospitals and infirmaries since it caused irritation in eyes and lungs. Chlorine gas was obtained through several methods but the one most often used was adding water to chloride of lime (bleaching powder) in small quantities. For the purpose of disinfecting rooms occupied by sick people, chlorine gas was obtained in large quantities using several chemical agents.

vii) **Different kinds of Acids** – Due to corrosive properties of different types of acids on some metals and stones, the use of such chemical liquids was aggressively adopted in the ancient times. Among them, wine, alcohol, ink, lemon, sodium tartrate, sulphuric acid and vinegar were commonly used as medicines and disinfectants. For instance – vinegar was given to people having complaints of abdominal pain and wounds. Lemon was advised to people for the treatment of many skin problems excluding leprosy and other deadly contagions.

Disinfection through biological agents

This is one of the oldest techniques of disinfection in which decomposable and disintegrable matter is buried in soil to suppress the foul odour. Human bodies, carcasses of animals and excreta are buried deep to expedite enzymatic degradation and to cut off oxygen supply that was assumed to activate chemical reaction and release unpleasant smell in the atmosphere. This practice apparently discards the concept of disinfection through fire owing to the acceptance of some unscientific explanations. For instance - in many cultures, it was believed that bodies of people died from contagious diseases ought to be buried instead of burning them in woods as the smoke emerged out of pyre had pathogens that spread rapidly in the air. These pathogens reach to human beings through air and cause infection.

Disinfection through Deodorants

This kind of practice for disinfection was perceived essential to counter the spreading of diseases that might be caused by unattended carcasses of animals that release unpleasant odour. Deodorants have the capability to subsume filthy smell with fragrance but lose their potentiality to remain effective disinfectants. Some examples of deodorants were brown paper, tar fumes, acetic acid, ammonia, roasted coffee and pastilles.

DISINFECTANTS, SLUMS AND PERSONAL HYGIENE IN BRITAIN

These methods of cleanliness and decontamination had profound impact on exterminating diseases and to reduce the circumference of epidemics to certain pockets or cities. However, it is equally important to take into account that the use of chemical agents for sanitization in the nineteenth century worked well in major metropolitan cities of Europe like London, Manchester, Bristol, Paris and others. Since these cities witnessed the mushrooming of dark and filthy slums infested with pathogens at the time of industrial revolution, the disinfectant solutions emerged as potent tools for the government authorities to curtail the spreading of diseases and to safeguard the premises of upper class people. In the article "The Public's View of Public Health in mid-Victorian Britain," the authors argued the sanitary reforms in the 1830s, 40s, 50s and 60s bounded authorities for providing better hygienic conditions to the city dwellers and induced perceptual change among them for living healthy life. For example – in the cholera epidemic of 1848-49, people did not resist against cleanliness drive as they had objected to in the cholera outbreak of 1831-32. In 1848-49, people "allowed cholera victims to be removed to Houses of Recovery or special hospitals. These institutions were operated, on official anti-contagionist lines, not to isolate victims as such, but to remove them from the poisonous conditions which had produced their disease."[18] With regard to personal hygiene and home cleanliness in the slum, it was found that "certain families were clean and wholesome while their immediate neighbors were filthy and verminous."[19]

This aspect of personal and social hygiene opens up the seamy side of institutional and governmental negligence. Instead of putting onus on individuals for their inability to adopt clean ways of living owing to poverty, it criticized utilitarian approach for affixing people's habits with their birth. To highlight the administrative failure in providing better facilities, examples of local governments and their indifference towards improving the constantly increasing slums ought to be cited. For instance – during the outbreak of cholera in 1831-32, Liverpool was one of the worst overcrowded cities with extremely poor amenities and a large section of the population living in slums. More than half a million people migrated to Liverpool from Ireland in the first half of the nineteenth century that put a lot of pressure on the city's infrastructure. Since the population density was very high in slums and basic amenities like disposal of waste and supply water were almost absent, cholera spread at a rapid pace in which 1523 people died out of 4977 cases in the city.[20] One of the main reasons for such pitiable conditions of industrial towns was the corruption and strong class biasness apparent from the sanitary works undertaken in the nineteenth century. While Chadwick's Sanitary Report (1842) recommended providing, better amenities to people living in filthy slums where atmospheric impurities accelerated diseases, the local governments worked on "piped water, glazed sewers, street widening, drainage and paving were to be found first in the areas where rate payers, local councillors traded or lived."[21]

DISINFECTANTS, INDIGENOUS MEDICINES AND COLONIAL INDIA

British colonies offered more complex conditions with limited access to medicine and sanitization products. Britishers were dependent on natives for various kinds of menial works including cleaning of toilets, disposable of sewages, fetching water from wells and domestic choruses. In the absence of modern disinfectants, British administrators and soldiers were vulnerable to native diseases even in their cantonments. J. R. Martin, Presidency Surgeon of Bengal and later President of the EIC's Medical Board, argued that the natives lack habits of personal hygiene owing to their deep rooted belief in religion. On the one hand, Martin admired the efforts of William Bentinck for his utilitarian approach to introduce social and cultural reforms in India; on the other hand, he vehemently criticized the Bengalis for their poor hygiene habits and wrote

> The natives have yet to learn that the sweet sensations connected with cleanly habits, and pure air, are some of the most precious gifts of civilization. Neither did they seem to be impressed by the importance of pure water. Everywhere one finds the tanks in an impure and neglected condition.[22]

The concerns of Surgeon Martin did not vanish even after lapsing of several decades and investments in healthcare with the opening of hospitals and dispensaries. E Carrick Freeman captures the fear of British people and challenges they have to face in India

> Owing to the primitive habits of natives, the face of the country, wherever the population is at all dense, as little may be regarded as little better than one huge latrine. The purifying and germicidal agencies which tend to counteract the evils of this state of affairs
> are the intense heat and light of the sun, extreme dryness of the air in many parts and length, volume, and rapid flow of the great rivers.[23]

In this regard, Sir William Moore, Surgeon General with the Bombay government, prepared a comprehensive manual titled *A Manual of Family Medicine and Hygiene for India*, published in 1889 to educate British men and women in domestic (indigenous) medicine and their preparations. He also elaborately discussed the management of room occupied by sick, application of local disinfectants, preparing medicines from indigenous items in emergency and instructions on protecting oneself during epidemic. On the non-availability of modern medicines and sanitary products, Surgeon Moore prepared a list of medicines with their Hindustani names that could be easily purchased from local bazars –

English Names	Hindustani Names
Alum	*Phitkarree*
Camphor	*Kafoor*
Sulphur	*Ghundak*
Potash, Nitrate of, Salt Petre	*Shora*

Source - *A Manual of Family Medicine and Hygiene for India.*

The manual comprehensively explained the need to dispose discharge of sick like vomit, urine, and bowels during epidemic outbreak, disinfection of rooms with proper ventilation and charcoal; disinfecting clothes, utensils and furniture with chemical compounds like carbolic acid or Condy's fluid (if available) or with boiled water to kill germs. Moore also emphasized on personal hygiene especially in tropical climate.

The complexity could also be understood from the fact that on January 18, 1924, E. H. Hankin[24] wrote a letter highlighting the major challenges for British troops and officers owing to the lack of awareness for sanitization among Indians. Based on his personal experiences, Hankin pointed to the autocratic and hierarchical system as obstacle in providing safe environment during cholera outbreak. Hankin discovered that filters used for cleaning drinking water could not kill germs that cause cholera. Hence, military officers, administrators, soldiers, engineers and others, who came alone or with their families to colonies to serve the British Empire, had to be trained in indigenous items that could be used as alternatives of western products.

Although the British administered Indian cities witnessed infrastructure development, they were still far behind to their counterpart cities in England especially in terms of decongestion plans, sanitary works, drinking water supply and drainage system. Owing to the poor infrastructure in the Indian cities, British families were taking necessary precautions to stop the incursion of diseases in their residences for which they exclusively invested in disinfectants. Dining tables, cutlery and crockery were cleaned with dish bar and detergents. In case any family member was ill, tableware were not only cleaned with dish bar but also shown to steam heat or immersed in boiling water. These conditions provided favourable environment to druggists and chemists to exploit the demand of English medicines and chemicals compounds in India.

Consequently, British pharmacies selling western medicine started to sprout in major Indian cities to meet the requirements of British officers who gave preference to modern methods of treatments over indigenous techniques of cure and prevention. On tracing the history of pharmacies in India, it is found that the first chemist shop named Bathgate was opened in 1811 at Lal Bazar in Calcutta followed by opening of a pharmaceutical company in 1812 by the two British surgeons John Robinson and James Williamson who primarily dealt in apothecary and surgical instruments. Assessing the drug list of pharmaceutical company Thomson and Taylor, it is found they dealt in more than "three thousand items which included surgical instruments, chemical, physical and pharmaceutical apparatus, dental goods, electrical apparatus, microscopes, bacteriological goods, spectacles, photographic goods, medicine chests, foods and dietary preparations, aerated waters, proprietary preparations, toilet and nursery requisites, patent medicines, wines and spirits, and hospital requisites."[25] These items were promoted through catalogues that were circulated with newspapers. Medical journals like *Chemist and Druggist* regularly published advertisements of those products that might see huge sales in the Indian market considering the country's climate and paucity of resources. Products used for sanitization had good demand in the market owing to perpetual fear of contamination and frequent outbreaks of epidemics.

CONCLUSION

Disinfectants remain integral to the activities of people knowingly or unknowingly inherited from their ancestors. As and when new compounds hit the market, people resist to their adoption but gradually homogenize them in their lives considering their benefits. Analysing the history of disinfectants, it is not wrong to say that these compounds and techniques of disinfection in the past were primarily targeted at controlling diseases from spreading to others but their utility has changed in the contemporary times as precautionary items to protect people and to maintain personal hygiene. Families, in metro cities, use disinfectants on daily basis to clean floors, toilets and bathrooms that ensure healthy and illness free lives. Demand of disinfecting products spirals with the rapid circulation of information and the onslaught of seasonal diseases. In the present times, it becomes imperative to depend on chemical disinfectants for protection against pathogens.

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Historical Articles

A Brief History of Oil Refining

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Abstract. Since its beginnings in the mid-nineteenth century, oil refining technology has evolved in a continuous process of adaptation to the demands of society, in matters as vital as the supply of energy, lighting, transportation or new materials to improve the quality of life. In that time, this has been one of the greatest examples of how the technological innovation of an industry contributes to the welfare and development of society. The objective of this manuscript is to describe the history of these technological advances and the causes that motivated them.

Keywords: Technology History, Oil Refining, Catalysis, Chemical Engineering, Process Design.

INTRODUCTION

Since its beginnings in the mid-nineteenth century, oil refining technology has evolved in a continuous process of adaptation to the demands of society, in matters as vital as the supply of energy, lighting, transportation and producing chemicals to improve the quality of life. In that time, this has been one of the greatest examples of how the technological innovation of an industry contributes to the welfare and development of society.[1]

The objective of this manuscript is to describe the history of these technological advances and the causes that motivated them. The magnitude of the achievements obtained by the refining industry far exceed the available space, which is why in this manuscript the detailed technical description of the processes has been sacrificed and attempts have been made to expose the causes that have motivated the successive technological advances, establishing a common thread, such as the evolution of the refinery configuration over time.[2, 3]

CHEMICAL ENGINEERING AND OIL REFINING

The purpose of a refinery is to transform crude oil into more valuable products that meet the demands of the market, both in quantity and quality, respecting safety and environmental regulations. Since the production of crude oil began in 1850, the market for petroleum products has been changing continuously and drastically in some cases, forcing the refineries to modify their configurations to meet this demand. Refineries have also adapted to the growing diversity of crude oils with different compositions.

The evolution of the refineries has been deeply linked to the advances of Engineering and vice versa. In the refinery´s process units, term coined by P.H. Groggins in 1928, we can find all the examples of the unit operations as defined by Arthur D. Little in 1912. The concept of unit operations in Chemical Engineering is very much related to the development of refining technology. In 1910, the most important chemical industry in the world was in Germany, where synthetic dye companies such as the IG Farbenindustrie AG or the Haber-Bosch process for the manufacture of ammonia, were milestones in the chemical industry. However, the design of these plants was based on the product to be obtained and their equipment was designed specifically without benefiting from the exchange of experience with the manufacturing technology of other products. On the other hand, Chemical Engineering, founded by Warren K. Lewis from the Massachusetts Institute of Technology (MIT), is based on identifying and grouping common processes or unit operations. Based on this classification, a process unit is designed by choosing several unit operations seeking the highest efficiency, performance and economy. The developments in each of the unit operations are shared between the different technologies and these evolved rapidly benefiting from the common experience. Some authors have cited the use of unit operations in the American chemical industry as one of the causes of their worldwide leadership until the 1970s. In the sequel, we will describe the main milestones that have guided the evolution of the petrochemical industry and the refinery configuration evolution.[5]

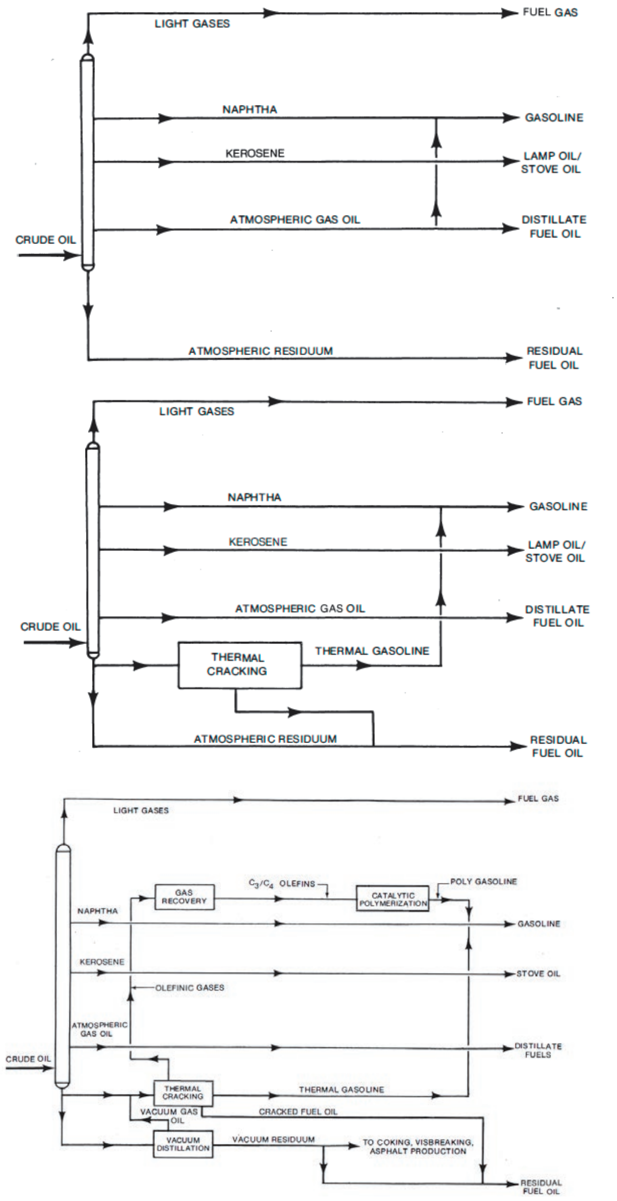


Figure 1. Refinery Configuration Evolution in 1915, 1920 and 1930. Reproduced from *U.S. Petroleum Refining: Meeting Requirements for Cleaner fuels and Refineries. Appendix C. History and Fundamentals of Refining Operations,* National Petroleum Council, **1993**.

THE PIONEERS OF THE INDUSTRY

In the early days of the industry, fuel was the main use of crude oil, even though it had been found that the combustion of crude oil, as an energy source in oil wells, produced toxic fumes and gases that prevented its use. Then, crude oil started to be processed in oil refineries that evolved, as shown in Figures 1 and 6, from discontinuous distillation in foundry vessels that had kerosene as their major product to the highly complex refineries that we have today, which produce a multitude of different fuels and petrochemical products from a variety of different crudes.

Samuel M. Kier was the first person to distill oil. By 1845 in southwestern Pennsylvania, he verified the presence of oil in the salt production facility he owned, when drilling wells to obtain salt water, a liquid with a strong odor mixed with brine appeared. In general, this was considered an inconvenience in the production process and was usually burned or poured into nearby waterways. Kier was an innovative entrepreneur and decided to use oil as fuel for the lamps that illuminated brine wells at night, despite the smoke and its bad smell. This allowed him to use the already expensive whale oil available at the time for other applications. He even bottled it and sold it for 50 cents as a medicine, establishing a commercial network for its distribution. In 1849, Kier shared oil samples with James C. Booth, a chemist in Philadelphia, and both agreed that it could be used as fuel for lighting lamps, but that it could be greatly improved if refined so that its combustion did not produce fumes and odors. In 1850, Kier began to experience different distillation processes and was the pioneer of this use of oil, by obtaining a product called "Carbon Oil" that allowed lighting in oil lamps with little smoke and odors. Kier partnered with John T. Kirpatrick and tested the first oil distillation in Pittsburgh, Pennsylvania.[6]

In 1846, Semyonov and Alekseev had already produced oil in the Baku oil fields (Azerbaijan), then in 1859, Edwin L. Drake began producing oil near Titusville, Pennsylvania and the market was flooded by oil production. The first refineries were built in Europe, in 1854 Ignacy Lukasiewicz built a primitive crude oil refinery near Jasło in southern Poland, distilling kerosene from a tar sand available in the region. The first large refinery was started in 1856 near Ploiești (Romania), one of the best-known and oldest oil fields in Europe and Bucharest was the first city in the world to be lit with kerosene lamps in 1857. Also in 1859, a kerosene refinery was built on Pirallahi Island (Azerbaijan), distilling the so-called "kir" produced in the Baku oil fields near the Caspian Sea and in 1860 already 58 refineries were built in Pennsylvania. There are currently about 700 refineries in the world that can process close to 100 million barrels of oil per day.[7, 8]

In 1860, due to indiscriminate whaling and the near extinction of these species, the use of whale oil as fuel for lighting had become expensive. The price of whale oil was $ 1.77 per gallon and almost doubled that of crude oil, which was sold at $ 0.90 per gallon. This fact, together with the invention and improvement of the kerosene lamp in 1857 by Michael Dietz, further strengthened the supremacy of kerosene for lighting.[9]

In the refineries, crude oil was distilled to produce kerosene that was used for lighting lamps. The advantage of kerosene in this case was that it did not emit smoke when burned due to the paraffinic nature of Pennsylvania crude. The heaviest parts were used as lubricants for steam engines, which were ubiquitous at that time. The lighter distillation fractions such as naphtha, propane and butane were considered to be a residue and were burned in flares since their high vapor pressure and low flash point prevented their safe storage.[10]

The installation was operated in a discontinuous mode and the oil was loaded in a vessel where it was heated with gas or other crude product. This heating generated a residue inside the container and other equipment that required cleaning from time to time. The dephlagmator tower was the precursor of the distillation towers and separated the generated vapors that were sent to a separator where the gaseous fraction and the final kerosene product were separated. This product was redistilled to control its flash point and thus allowed its safe use in the lamps reducing the generation of smoke. The heavy fraction or Tar was re-distilled under vacuum, obtaining a lubricating oil and greases in addition to waxes and paraffin for candle making.

At this time, and as means for transportation were needed, both the oil and the products produced began to be transported in barrels and a standard measure that still survives emerged. A barrel of oil had 42 gallons, about 159 liters. The measure was imported from England, where a law issued by Edward IV in 1482, established 42 gallons as the standard capacity for herring barrels and to prevent scams in the fish trade. In 1866, seven years after the discovery of the first well by Colonel Drake, the Pennsylvanian producers confirmed this measure as the norm in the oil business.

The discontinuous distillation system was limited in terms of capacity. As the size of the vessel increased, the ratio between the heat transfer surface and the volume of oil decreased, and therefore, it was not profitable to increase the process capacity more than a given volume of oil. A long contact time between the oil and a hot surface led to oil decomposition and the deposition of a layer of coke, which further limited direct heat transfer. It was also quite risky to subject large quantities of oil to direct heating. The maneuvers of loading the oil and emptying the residue, in addition to the cleaning of the systems, required a lot of time and effort making the entire process very inefficient. As the demand for kerosene grew, two distillation units began to be used, one for the first separation and the second to refine the quality of the kerosene, paving the road for continuous distillation.[11]

In 1880, continuous distillation was introduced, the process consisted of several vessels connected to each other and heated separately at growing temperature levels. The vessels were installed so that the oil flowed by gravity from the first to the last. The product was subjected to successive distillations, the operation was adjusted by means of the "look box" through which the distilled product could be seen and depending on its color the operating conditions were adjusted to improve the separation by distillation of light and heavy naphtha and kerosene. In the last vessel the temperature was successively increased causing oil cracking to obtain more

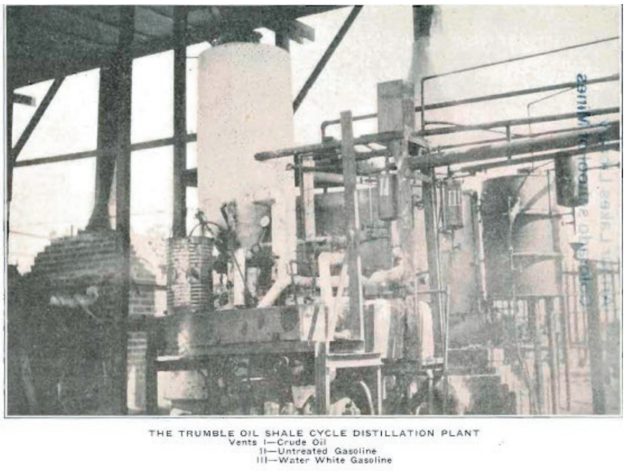


Figure 2. Continuous Distillation Trumble Process. Reproduced from V. Alderson, *Quarterly of the Colorado School of Mines* **1924**, 19 (3), 5-7.

kerosene. The residue from the last vessel was used to obtain lubricants or fuel oil.

One of the drawbacks during the combustion of kerosene related to the variability of the distillation quality, was the emission of noxious odors and gases due to the presence of sulfur compounds in kerosene and gasoline. In 1885, Herman Frasch discovered that copper or lead oxides reacted with the sulfur compounds of petroleum and could be regenerated and reused, thus eliminating the problem of odors and producing sulfur. This technology started the oil treatment industry to eliminate oil contaminants.[12]

In 1900, the partial condensation was introduced, which allowed a better separation of the products. A partial condenser or Dyke tower was installed between the vessel and the water-cooled condenser. The lower part of the tower was filled with stones and insulated with bricks to facilitate the condensation of heavier compounds that were subsequently sent back to the distillation vessel. The light part passed to another section where it condensed in air-cooled tubes to obtain a head product. The rest of the stream continued towards the water-cooled condenser.

Vacuum distillation was developed to solve the need to separate less volatile products, such as lubricating oils without degrading their properties due to high temperatures. The boiling point of the heaviest cut obtained by atmospheric distillation is limited by the temperature and residence time at which it begins to decompose thermally modifying the quality of the cut.

Around 1910, some of those limitations were solved when a continuous distillation process was developed by grouping several connected containers, where the products were flowing from one to another subjected to increasing temperatures to obtain a stepped vaporization of the different cuts. Heat exchange systems with cold feed oil and stirring systems were introduced that improved the process efficiency. Instead of condensers, fractionation columns were installed with internal liquid-vapor exchange systems, which, although rudimentary, improved the quality of the fractionation.

To eliminate the direct heating system of a vessel and improve the capacity and efficiency of the system, it was necessary to find a system with a high surface to volume ratio, which could be heated throughout its entire surface. This would allow faster heating while having smaller volumes of crude oil so that they could flow rapidly through the heating zone and minimize coke formation by increasing heat transfer. In 1910, Milo J. Trumble introduced a distillation process that met these requirements and is shown in Figure 2. The oil was pumped through a pipe into a furnace and the furnace outlet was directed to a tower – the evaporator – where vaporized and liquid products flowed over a series of screens. The vapors were collected in a central pipe and the hot residue transferred its heat to the cold load in a heat exchanger. In the initial design, the vapors were condensed in a single stream, later the system was modified to obtain three or more fractions. The first plant was installed in Santa Fe, California in 1911.[13]

The advantages of the Trumble process meant lower operating costs due to a large increase in the energy efficiency of the process; in addition, the installation cost was also lower compared to existing systems. Furthermore, the design allowed the construction of higher capacity plants. In 1925, the initial design of the condensers was replaced by tray towers, which simplified and improved the process leading to the present distillation unit designs. The separation between the furnace and the distillation tower was the fundamental innovation to achieve efficient distillation units.

THE INTERNAL COMBUSTION ENGINE AND ITS FUELS

The demand for oil remained stable during the second half of the 19th century. In 1878 and thanks to the invention of the electric light bulb by Thomas Edison, the demand for lighting kerosene began to decline, although it remained in many places far from cities or in services such as rail transport. In 1893, Rudolf Diesel developed the Diesel engine, and in 1889 Gottlieb Daimler, Wilhelm Maybach and, independently, Karl Benz developed the internal combustion engine that has been the transportation paradigm since then. In 1901, Ransom E. Olds began the production of affordable price cars under the Oldsmobile brand. Henry Ford built his first gasoline vehicle in 1896 and founded the Ford Motor Company in 1903. In 1908, he started selling the T model for $ 950 and he revolutionized the world transport and also the oil industry. In fact, the demand did not stop growing until the Arab oil embargo of the 70´s. Beetween 1907 and 1917, 15 million Ford Model T vehicles were sold in the US, and the price dropped to $280 thanks to the reduction in the assembly line costs. This technological innovation drastically changed the oil refining industry.[14]

In the first refineries, the most demanded products were kerosene and light distillates. Gasoline was a byproduct until the beginning of the 20th century, when the development of the combustion and automobile engines caused a large increase in the demand for automotive gasoline and other refinery products such as asphalt, lubricants and fuel oil.

Although the history of the asphalt dates back to the time of the Babylonians, paving tests with naturally obtained asphalts were made in the nineteenth century. It was in 1870 when Belgian chemist Edmund J. DeSmedt paved the Avenue of Pennsylvania in Washington DC with a mixture of asphalt. Then, in a short time the first patents for asphalt road blends were filed. In 1901, the Warren brothers built the first modern asphalt factory in Massachusetts. As a result of the success of the car industry, by 1908 all the roads necessary for the circulation of cars were paved with asphalt, thus adding another product of great demand to the oil industry. These technological advances doubled the demand for asphalt every decade from 1880 until the oil crisis in 1973.

Another important milestone was the change from coal to fuel oil as marine fuel. In 1911, Winston Churchill was appointed First Lord of the Admiralty and with the collaboration of Admiral John Fisher decided to change the fuel of British Navy ships from coal to fuel oil, the heaviest and most abundant fraction of oil. This fact was justified by the easier handling due to its liquid state and the greater calorific value of the fuel, which allowed the boats navigate faster. At the time, it was a hotly debated decision because Britain produced large quantities of coal and also due to the complicated logistics of the world's fuel oil supply, but given its technical advantages, fuel oil was quickly adopted as the preferred marine fuel.[15]

THE CONVERSION INCREASE

The rise of transport vehicles based on internal combustion engines created a new challenge for the oil industry. At the beginning of the 20th century, the proportion of products obtained by distillation did not match the market demand. The automobile industry and later on the aviation industry improved their engine designs to increase power, which led to the need for higher quality fuels able to maintain higher compression ratios in the engines.

The introduction of the internal combustion engine and the decrease in vehicle prices increased the demand for oil and especially for gasoline, compared to the traditional kerosene market. Improving the distillation of oil was not enough to meet the demand and in response, the refining industry developed conversion processes to obtain more gasoline and reduce the proportion of heavy products while improving its quality. Adjusting to market demand and producing higher quality fuel and products have been the factors that have guided many of the innovations in oil refining technology, some of these process development dates are shown in Table 1.

Indeed, a key conversion process to meet the demand of gasoline has been oil cracking, first thermal and later catalytic. There are already references in 1850 and since 1860 to using thermal cracking of hydrocarbons for the production of kerosene. Initially, thermal cracking was carried out at atmospheric pressure at which the kerosene yield was high. The process consisted basically on heating a vessel with oil until all the kerosene had been produced and the overhead product had a dark color. At that point, the distillation was stopped and the heating of the vessel was maintained to favor the thermal cracking reactions that produced lighter products of lower molecular weight. After a certain operation time that was empirically fixed, distillation was resumed by extracting cracked light products. This practice increased the kerosene yield, but did not produce gasoline in large quantities. In 1889, two English chemists, J. Dewar and B. Redwood, registered a patent on cracking carried out at pressures greater than atmospheric. When the pressure was raised, the selectivity of the process changed and much more gasoline than kerosene was produced. In pressure cracking, the oil was heated to about 425 °C in specially reinforced vessels to operate at pressures of about 7 kg/cm^2 for 24 hours. Then, the distillation of the cracked product began and low molecular weight compounds were obtained. Those compounds were treated with sulfuric acid to remove the gums and residues formed by the generation of olefins and diolefins and then redistilled to produce gasoline and a residual fuel oil.[16]

The first process that innovated the technology to increase the conversion of the refineries, was the thermal cracking patented in 1912 by William Burton and Rob-

Table 1. Oil Refining Process Timeline.

	Process	Target	Process Type
1862	Atmospheric Distillation	Kerosene Production	Separation
1870	Vaccum Distillation	Lubricants (original) Cracking Feedstock (1930's)	Separation
1913	Thermal Cracking	Gasoline Production	Thermal Cracking
1916	Sweetening	Sulphur and Odor Removal	Chemical Treatment
1930	Thermal Reforming	Gasoline RON Improvement	Reforming
1932	Hidrogenation	Sulphur Removal	Catalytic Treatment
1932	Coking	Gasoline Production	Cracking
1933	Solvent Extraction	Lube Viscosity Index Improvement	Extraction
1935	Dewaxing	Cloud Point Improvement	Extraction and Crystalization
1935	Polimerization	High RON Gasoline Production	Reforming
1937	Catalytic Cracking	High RON Gasoline Production	Cracking
1939	Visbreaking	Fuel Oil Viscosity Reduction	Thermal Cracking
1940	Alkylation	High RON Gasoline Production	Reforming
1940	Isomerization	Feedstock to Alkylation	Reforming
1942	Fluid Catalytic Cracking	High RON Gasoline Production	Cracking
1950	Deasphalting	Lube Quality Improvement	Extraction
1952	Catalytic Reforming	High RON Gasoline Production	Reforming
1954	Hydrodesulfuration	Sulphur Removal	Catalytic Treatment
1956	Mercaptan Oxidation	Mercaptan Removal or Sweetening	Chemical Treatment
1957	Catalytic Isomerization	High RON Gasoline Production	Reforming
1960	Hidrocracking	Light distillates production	Cracking
1974	Catalytic Dewaxing	Cloud Point Improvement	Cracking
1975	Residue Hidrocracking	Residue yield reduction	Cracking
1990	Gasification	Residue Removal	Cracking
2000	FCC naphtha hydrotreatment	Sulphur Removal with no RON loss	Catalytic Treatment
2000	Gasoil Hydrotreatment	Sulphur Removal below 10 ppm	Catalytic Treatment
2005	Petrochemical FCC	Increase Propylene yield	Cracking
2008	Biofuels	Renewable Fuels from Vegetable Oils	Catalytic Treatment, Reforming
2012	Tight Oil	Tight Oil Refining	Metal Removal and Additives
2014	Reside Slurry Hidrocracking	Residue Removal	Cracking, nonocatalysis
2020	"Crude To Chemicals"	Petrochemical Refineries	Cracking, refining

ert Humphreys. The Burton-Humphreys process doubled the gasoline production of a refinery and prevented fuel shortages during World War I. W.M. Burton, who was responsible for one of the Standard Oil Company refineries, had the idea of cracking only the fraction called diesel instead of the whole oil fraction with boiling points higher than kerosene. Depending on the crude oil treated, diesel constitutes 30 to 50% of the total volume. This change together with improvements in the design of the cracking installation made by R.M. Humphreys in 1910, allowed the first thermal cracking unit in Indiana Standard to be successfully launched in 1913.[17]

The Burton process operated discontinuously at a temperature of 425 °C and 5 to 7 kg/cm^2, the cracking vessel had to be stopped every day and the residue was cleaned out. The process was successful but from 1914 to 1922 a series of continuous cracking technologies were developed that significantly improved the process. In these technologies the diesel was pumped and heated to the operating temperature, it was maintained under these conditions and then the cracked products were sent to a distillation unit where they were separated into gases, gasoline, diesel and a residue often known as tar. Gasoline from thermal cracking had a higher octane number so it worked much better in combustion engines than the gasoline produced by direct distillation.

In 1914, Jesse Dubbs and J. Ogden Armor founded the National Hydrocarbon Company, which would later be the Universal Oil Products (UOP). The UOP would grow to be the largest technology licensor for petroleum refining and petrochemicals. In 1919, UOP commercialized the Dubbs process, which solved some of the technical problems of the Burton-Humphreys process. The Dubbs process generated fewer coke deposits, treated heavier crudes and had longer operating cycles. The Dubbs process developed by the UOP, meant an advance in thermal cracking technology and its use was competitively extended until the forties. In this case, the feedstock was crude oil with the light fractions removed. The feedstock was preheated with the reaction products, sent to an oven and from there to a reaction chamber. The biggest advance of the Dubbs process was to recirculate the cracked stream from the fractionation section to the reaction section; this allowed a finer control of the reaction and stabilized the process.[18,19]

The "Tube and Tank" process introduced a significant advance by adding the concept of the cracking reactor. In this process, diesel preheated by heat exchange with the reaction products, was pumped into a furnace where cracking was carried out. The outlet was sent to a reaction chamber (Soaker), where it was kept at the temperature and reaction pressure for a certain time until the cracking reactions were completed. The reaction products then entered a low pressure separator where all the products were vaporized except for the residue. The vapors left the separator at the top and were distilled to obtain gases, gasoline and gas-oil. The residue from the bottom of the separator was extracted for use as asphalt or fuel oil. With the exception of a lower operating temperature, the "Tube and Tank" process can be considered a precursor to the current delayed coking units.[20]

In 1919, the UOP sued the Standard Oil Company for the thermal cracking patent since they considered that Dubbs had preference over the Burton process. Dubbs filed a patent in 1909 on the manufacture of asphalts that included the production of gasoline through an operation similar to thermal cracking. This lawsuit, which ended in 1931 with an adverse result for the UOP, placed the company in a difficult situation and gave rise to a company model of great importance for refining technology. In this way, a licensing company, whose maximum exponent was the UOP itself, had its own research, development and engineering resources to market processes that were sold to those refining companies who did not have R&D departments and were, therefore, at a disadvantage with large companies such as Standard Oil that had their own technologies. Hiram Halle, president of the UOP, created this concept, that has become popular within other companies such as Scientific Design, Axens, Haldor Topsoe, KBR, etc .

The license to operate a process allows a company to acquire the design of a plant and its catalyst. The company builds the plant according to the design of the licensor who collaborates during the engineering and supervises the construction and commissioning until compliance with guarantees of capacity and quality. Apart from the income due to the purchase of the design, catalyst and license, the licensor charges annual fees or royalties depending on the capacity processed by the plant, which allows to continue investigating to improve the process. The licensor also benefits from the experience acquired during the installation of the new plants to improve the technology. The refinery, in turn, benefits from the installation of competitive technologies that allow it to remain profitable without having to wait for the development of the process or incurring research and development expenses.[21,22]

THE SEARCH FOR GASOLINE

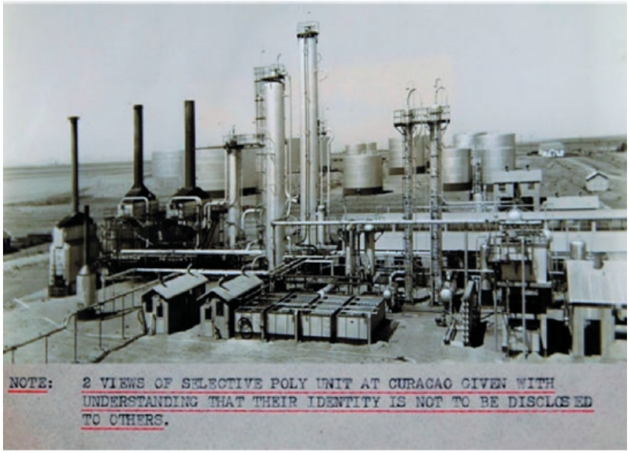
The manufacturers of internal combustion engines complained to the refineries that the quality of the gasoline was not uniform and the engines had disparate performances depending on the origin of the distilled oil. Better gasolines allowed the engines to go at more revolutions by providing more power without affecting the integrity of the engine. Poor quality gasoline, on the other hand, produced a knock on the engine that affected its performance and could cause mechanical damages. The ability of gasoline to avoid engine knocks is expressed as its octane number on a numerical scale. The scale is based on pure chemicals, ranging from n-heptane with an octane number of 0 to isooctane with a value of 100. This scale was proposed by Graham Edgar of the Ethyl Corporation in 1926. A high octane gasoline burns slowly in the engine piston producing a regular movement of the engine. On the other hand, the low octane gasoline burns quickly, generating sudden increases in pressure on the piston that generate the engine knocking and can damage the engine.[23]

A similar parameter is defined in diesel engines, the cetane number, developed in 1930 by the Cooperative Fuel Research (CFR). The cetane number measures the time between fuel injection and the beginning of its combustion. In this case, unlike gasoline engines, the more paraffinic the diesel, the better the cetane number is because the ignition delay in the engine is smaller.

In 1919, Charles F. Kettering and Thomas Midgley from General Motors began studying the phenomenon of knocking and in 1921, they discovered that a mixture of tetraethyl lead and gasoline attenuated this phenomenon. In a few years the process of synthesis of tetraethyl lead (TEL) was industrialized and refineries could manufacture gasoline with a constant octane number from naphtha of different crude oils. The TEL additive added 5 to 7 octane numbers to gasoline, but its toxicity made it very difficult to handle in the refineries. Afterwards, its harmful effects on humans were discovered when lead compounds were emitted in the exhausted gases.[24]

Between 1920 and 1930, gasoline demand growth confirmed the trend of converting heavy residue and distillates into high quality gasoline. Another advance was the consolidation of vacuum distillation as a second stage after atmospheric distillation. It has been indicated that the heavy distillation cut consisted of hydrocarbons that did not vaporize at atmospheric pressure. Subjecting this cut to vacuum distillation allows an additional amount of distillate, known as vacuum diesel, to be vaporized and sent directly to the thermal cracking units, increasing the refinery's gasoline yield. Also in the thirties, the thermal reforming of naphtha was introduced, a seeking an increase in the octane number. In this process the naphtha was subjected to cracking reactions in a reactor after heating in a furnace. The process had a low selectivity and added little performance to high octane gasoline, for these reasons, its use was limited. The solution for further increasing the yield and quality of the gasoline was achieved by means of catalysis. It can be said that the introduction of catalysis in the refining industries opened a new era in this industry. Catalysts allowed to improve yields without the necessity of introducing major modifications in the original design.

As we have seen, the reaction mechanism of thermal cracking is not very selective towards the desired products and generates a large amount of gases rich in unsaturated hydrocarbons or olefins, which are generally burned to provide the necessary energy in the cracking process. Olefins are very reactive compounds and can be combined to form heavier and more useful cuts. The processes of Polymerization and Alkylation were developed in the thirties to valorize this very rich olefin stream converting it into high octane gasoline. In 1935, the Pure Oil and Philips Company developed a thermal polymerization process, although its low yields doomed it to be quickly surpassed by catalyst-based processes. In 1930, the Russian chemist V.N. Ipatieff from UOP, investigating in the Riverside Laboratory (Illinois), introduced the first important catalytic process in refining technology. The catalytic polymerization, shown in Figure 3, employed a catalyst based on phosphoric acid supported on alumina. Light olefins reacted with each other giving rise to heavy olefins of longer chain length and whose boiling points allowed their use in the formulation of high octane gasolines. The efficiency of the process was improved by separating the light olefins in a gas recovery plant for processing in the polymerization unit. This unit increased the value of the gaseous stream produced during cracking and thermal reforming and was included in the schemes of the refineries of the thirties. Since the Ipatieff's discovery, the polymerization has played an important role in the refinery until the development of olefin alkylation.[25, 26]



NOTE: 2 VIEWS OF SELECTIVE POLY UNIT AT CURACAO GIVEN WITH UNDERSTANDING THAT THEIR IDENTITY IS NOT TO BE DISCLOSED TO OTHERS.

Figure 3. First Polymerization Unit in Curaĉao Refinery circa 1939. Reproduced from *ACS Catalysis* **2018**, 8, 8531-8539.

The alkylation of olefins produced either by thermal or catalytic cracking had been a developing field since the thirties. It was mainly used in the alkylation of isobutane and butene or propylene to produce branched paraffins of seven or eight carbon atoms with high octane number. The alkylation of paraffins was discovered by V.N. Ipatieff in 1935. In the search for gasoline with a high octane number, a consortium of refining companies - Anglo-Iranian (future BP), Humble (future Exxon), Shell, Standard Oil and Texaco - developed the alkylation process of butene and isobutane to produce high octane gasoline by means of a strongly acid catalyst. This process was commercialized in 1938 at the Humble refinery in Baytown, Texas. The catalyst used for this reaction was sulfuric acid. The alkylation produced large quantities of aviation gasoline that was particularly important during World War II. In 1940, Phillips Petroleum (future Phillips 66) developed alkylation with hydrofluoric acid, which produced better reaction yields. The alkylation process combines light olefins, mainly butenes, with paraffinic isobutane, to produce a high octane gasoline. This reaction needs, as we have seen, an acid catalyst, hydrofluoric or sulfuric acid, under conditions that maximize the performance and quality of the product. The resulting alkylate has an excellent octane number, as well as a low vapor pressure and does not contain sulfur, olefins or aromatics, all this makes it the ideal component for formulating gasoline.[27]

Research and development in alkylation technology has been aimed at eliminating the use of sulfuric or hydrofluoric acids as catalysts. For a long time, solid catalysts have been sought to replace them and recently, the Alkyclean process of Lummus and Neste Oil has been commercialized, with a zeolitic catalyst from Abermarle. Another option has been to use ionic liquids instead of acids, as in the Chevron and UOP IsoAlky process.[28]

THE CATALYTIC CRACKING

Until 1925, high-boiling petroleum molecules reacted with low-boiling molecules subjected to thermal cracking reactions, mainly through the processes developed by Dubbs and Burton-Humphreys. In 1930, approximately half of the gasoline produced in the world came from thermal cracking processes, the average octane number was 70 versus values between 50 and 60 for direct distillation gasoline. The thermal cracking gasoline was mixed with polymerization or thermal reforming gasoline to produce a base gasoline of octane number 65, which required tetraethyl lead (TEL) for increasing the octane number to 70 and 80 for Regular and Premium gasoline, respectively. The compression ratio demanded by the engines of the increasingly powerful cars created by the industry needed something else and by 1936, a new process opened the way to obtain high octane gasoline. In 1915, the Mcaffe catalytic cracking, process used aluminum trichloride as a catalyst, and operated in a discontinuous mode due to the deposition of sludge formed by hydrocarbons and aluminum chloride residues. Between 1912 and 1926, Gurwitsch and Herbst described the activity of certain activated clays, but it took until 1936 when the French chemist, Eugene Houdry presented a process where the problems of catalyst deactivation, regeneration and stability were solved, in combination with an effective process design. Looking for better quality gasoline, he studied the chemistry of hydrocarbons and the synthesis of branched chains of paraffins and olefins that gave gasoline a higher octane number. Houdry designed a cyclic reaction-regeneration system with activated clays and fixed-bed reactors that maintained the energy balance of the cracking unit and allowed for continuous operation, greatly facilitating the commercialization of the process.

The cyclic operation of these fixed-bed cracking units used the heat of regeneration to obtain high cracking temperatures in the reactors and became a reality when the Houdry Process Corporation together with the Socony Vacuum Oil Company and the Sun Oil Company, built the first industrial units for both companies between 1936 and 1938. The catalyst was loaded in a series of parallel tubes which were kept in a bed of molten salts. The Houdry process was very successful and in World War II it is considered that 90% of the aviation gasoline used, with an octane number of 100, contained products obtained in Houdry units. The war increased the needs for aviation gasoline and accelerated the diffusion of the new process. Between 1938 and 1950 many units were built and despite subsequent developments, some of the units were still operative in 1960.[29,30]

Again, World War II and the demand of large quantities of high octane aviation gasoline was an incentive for the oil industry in the search for technological improvements in refining processes. The industry, especially at the Allied side that had access to large quantities of oil, dedicated its best talents and means to respond to the war needs. Processes such as alkylation, isomerization, toluene production for explosives and, finally, the greatest innovation among the conversion processes of heavy oil fractions, catalytic cracking in fluidized bed, came out from research work at companies and academia.

The production of fuels by catalytic cracking required large investments to install the reactors where the reactions occurred, as well as the associated product separation equipment. In addition, the Houdry Company charged very expensive licenses for the use of its technology. Then, some companies decided to study other technological processes. This group known as Catalytic Research Associates was formed by Standard Oil of New Jersey (Exxon), MG, Kellog, Standard Oil Company of Indiana (Amoco), Anglo-Iranian Oil Company (BP), Royal Dutch Shell, Texaco and Universal Oil Products (UOP).[31]

In an attempt to improve the process and especially to avoid the discontinuous operation of the cracking reactors, designs were created in which the catalyst moved continuously from the reactor through a purge zone to the regenerator, and from there once regenerated it returned to the reactor again. This was achieved in the so-called mobilized bed operation, which was introduced by Socony-Vacuum Oil Company in 1942. The pellet-shaped or extruded catalyst moved by gravity from the reaction zone to the regeneration zone and then was raised from the bottom of the regenerator to the reactor inlet by means of a bucket system. At the beginning of the fifties, this design was improved by replacing the elevator with a pipe where the catalyst circulated mobilized by a high speed gas. The designs were marketed by the Socony Vacuum Oil Company under the name of “Thermofor Catalytic Cracking” (TCC), and by the Houdry Process Corporation under the name of “Houdry Flow”. These units have operated satisfactorily for many years but disappeared due to their limitations in the heat balance that prevented building units of more than 20,000 barrels per day.

In 1942, the Catalytic Research Associates consortium, under the leadership of the Standard Oil of New Jersey introduced the first fluid bed cracking unit, “Fluid Bed Catalytic Cracking” (FCC). A key fact of this technological milestone was the suggestion by Warren K. Lewis and Edwin R. Gillian from the MIT that a low velocity gas could fluidize the powder catalyst making it behave like a liquid. Subsequent tests confirmed this hypothesis and a pilot plant was built that began operating in 1940, from there, the Model I of the Fluid Catalytic Cracking unit was launched in May 1942, being the first FCC unit in the world.[32]

The FCC represents one of the paramount developments in oil refining technology and was based on the idea coming from the academia that the catalyst could behave like a fluid. For this, the catalyst was in the form of very fine particles with sizes smaller than 70 microns and kept in suspension by a stream of reacting vaporized hydrocarbons. In this way, the catalyst crossed the reactor and was collected in cyclones, while reacted hydrocarbons went to the fractionation section. The deactivated catalyst passed from the cyclones of the reactor to the bottom of the regenerator and was fluidized by an air stream that produced coke combustion. Then, once its activity was recovered, it travelled back to the reactor, on a closed loop, as shown in Figure 4. This revolutionary idea changed the refining industry and gave the industry a high conversion cracking process with an unbeatable energy balance, as the heat generated was recovered in the process.

Over the years, improvements have been added to this design, such as the reduction of the contact time between the catalyst and the feedstock jointly introduced into a tubular reactor or riser, where the reaction occurs in a high turbulence regime. The design of the FCC could be easily scaled due to the good control of the reaction temperature provided by the heat exchange between the catalyst and the charge. This fluidized bed reactor design has been used in other processes with exothermic or endothermic reactions.

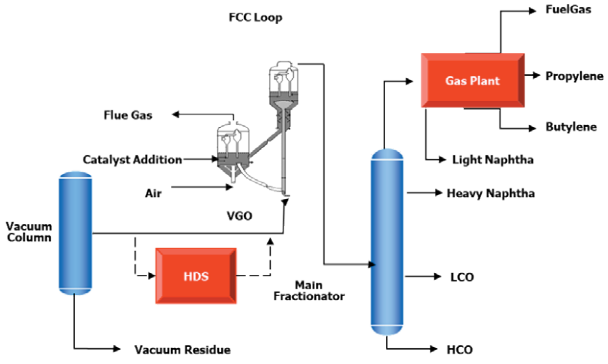


Figure 4. FCC Reactor and Fractionation Scheme.

The FCC converts heavy distillates into high octane gasoline, gases with a high olefin content and distillates known as Light Cycle Oil (LCO) and Heavy Cycle Oil (HCO), finally producing a residue known as Slurry. With a proper design and in the right operating conditions, the FCC’s performance in terms of produced gasoline and distillates can be 75-80% by volume of the unit feedstock.

The stream of light olefin-rich gases could be sent to the polymerization or alkylation units, already described, to produce high octane gasoline. The FCC and alkylation processes are of great importance in the manufacture of gasoline. The gasoline yield of both processes, that is, FCC gasoline and alkylate obtained from FCC light olefins, exceeds 90% of the FCC feedstock volume.[33]

As we have seen, isobutane is consumed in the alkylation process, therefore, the process of isomerization of butanes can be included in the refinery scheme to supplement the natural content of isobutane in the crude. In 1930, V.N. Ipatieff discovered that the butane molecules present in gasoline could be transformed into isobutane using an aluminum trichloride catalyst. In those years, this did not raise much interest because the isobutane content of gasoline was limited by its high volatility. But the need for high octane aviation gasoline revived interest in this process and large quantities were produced during the war to feed the alkylation units that supplied the Allied air forces. Later in the fifties and sixties, coinciding with the development of the catalytic reforming and the demand for high octane streams, the light gasoline composed of pentanes and hexanes with low octane was identified as a potential feedstock for the isomerization process and alumina-supported platinum catalysts were developed to increase the octane number from 60 to 90. In the 1980s, the possibility of using zeolites to isomerize light naphtha was investigated; in that vein, the mordenite-supported platinum catalysts were shown to be excellent for isomerization.

After the emergence of the FCC, thermal cracking processes were progressively abandoned due to their lower yields and selectivity to gasoline and distillates, and thermal cracking technology evolved towards an increase in cracking severity and the use of vacuum residue as feedstock. This process, known as Delayed

Coking or Coker, was introduced in 1929 by Indiana Standard Oil, based on the facilities of a Tube and Tank unit in Whithing (Indiana). In the Coker the feedstock is heated and maintained at high temperature until the long chain hydrocarbon molecules are cracked into light hydrocarbons and also decomposed to a carbonaceous residue known as coke. Periodically the reactors, typically from two to six, or Coke Drums are filled with this coke and must be switched off to eliminate the accumulated coke, in a reaction-decoking cycle of the reactors. The products of the coker are light olefins, as well as naphtha and diesel with low quality that must be hydrotreated prior to marketing. The coke that is extracted from the reactors, depending on its quality, is used as fuel or other uses such as the manufacture of anodes.[34]

THE ZEOLITES

As changes in the mechanical design of the FCC were introduced, the catalyst itself saw great improvements. The original catalysts were acidic clays of the montmorillonite type. With them, good yields were obtained of high-octane gasoline. These clays were progressively replaced by synthetic amorphous silica-alumina catalysts, which were more stable under regeneration conditions and gave a good product distribution. Gasoline yields increased from 20% in thermal cracking to 40% with silica-alumina catalysts. In 1945, after three years of operation, the importance of the shape of the catalyst, its pore distribution and also the improvement of its attrition resistance produced by operating cycles in fluidized regime were clearly identified. Also, modifying the silica/alumina ratio, usually at 65/35, allowed better product yields. In 1952, the silica/magnesium catalysts were introduced with increases in gasoline yield but a worsening of octane, their bad behavior in regeneration prevented their commercial success. An important revolution in the technology of catalytic cracking was the synthesis and catalytic use of zeolites. This constitutes one of the innovations with the highest impact on refining technology.[35]

Crystalline silica-alumina zeolite compounds have been known for more than 150 years and are present in nature. They had been used in ion exchange applications, but their catalytic properties were discovered in the late 1950s. The zeolites can be synthesized by modulating their acid character and pore size. It can be said that the synthesis of zeolites allows to design an appropriate catalyst for each reaction. The first attempts to use the zeolites in catalytic cracking failed, and for a long time it was thought that their regular and uniform pore structure was inferior to the pore distribution of amorphous materials and given that the reactions occur inside the pores of the catalyst, zeolites were not useful for this purpose. In the mid-1950s, the Union Carbide Corporation commercialized the first synthetic zeolite of the Faujasite X and Y type. Initially, they were used as adsorbents although soon later were used as catalysts.[36]

In 1960, Rabo's work, once again, drew attention to the use of zeolites as catalysts for the isomerization reaction, but it was Plank and Rosinsky at the Socony-Mobil Corporation who stabilized the X and Y zeolites so that they could withstand the temperature and the presence of steam in the reaction-regeneration cycles of catalytic cracking, without losing their crystalline character. This catalyst had greater activity and selectivity than the amorphous silica-alumina catalysts of the time. Although they were initially used in the Thermofor (TCC) process at the end of 1961, zeolites were quickly applied to the FCC. The high selectivity of these catalysts reduced the amount of feed oil required to produce gasoline. In fact, between 1964 and 1970, the rate of installation of FCC units was reduced by one million barrels per day, thanks to the good yields of the new catalyst that allowed to supply the gasoline market without the need of adding more FCC capacity. Extrapolated to savings in crude oil to be distilled in the refinery, this meant about $ 200 M per year with oil prices prior to the 1973 crisis. As in the Dubbs process, there was a lawsuit over the priority in the patents of the catalyst that lasted ten years and ended giving Plank and Rosinsky the rights of his patent over several oil companies.[37]

Following the introduction of the zeolite-based FCC catalyst, a number of improvements increased its stability and selectivity. In 1977, Mobil Oil launched a new generation of catalysts that included a combustion promoter that contained less than 50 ppm of platinum on alumina. This allowed the regeneration of the catalyst to very low levels of coke at lower regeneration temperatures and also the conversion of carbon monoxide generated in the regeneration to carbon dioxide, reducing emissions and improving the heat balance.

In 1974, Mobil Oil introduced a new zeolite, Figure 5, called ZSM-5 (Zeolite Socony Mobil), with applications in many processes such as the FCC (where it increased the production of propylene and butenes) catalytic reforming, catalytic removal of waxes in lubricating oils, isomerization of xylenes and disproportionation of toluene, etc. The description of the huge development of zeolites since the ZSM-5 discovery onwards, exceeds the scope of this manuscript, but we can say that zeolites are present in virtually all refining processes and have con-

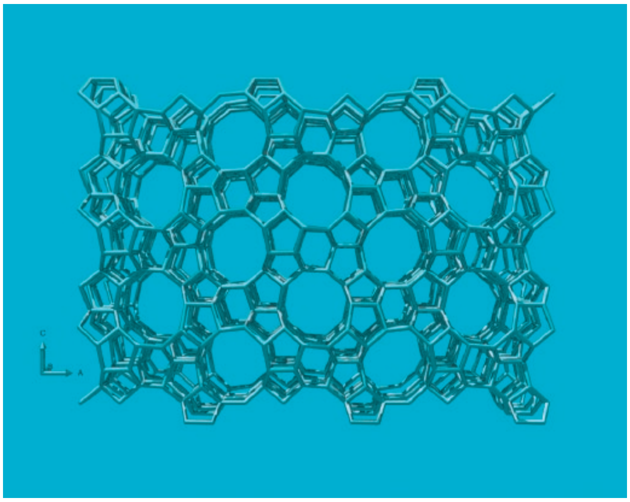


Figure 5. ZSM-5 Zeolite. Adapted from *Chemical Society Review* **2015**, 44, 7342-7370 - Published by The Royal Society of Chemistry.

tributed to the present and future development of the refineries. [38, 39]

CATALYTIC REFORMING AND HYDROTREATMENT

After World War II, the availability of FCC and alkylate gasoline meant that low octane naphtha produced by distillation had no place in the formulation of high octane gasoline. In the late forties, the development of a new process that constitutes an important technological innovation in the oil refining industry took place. This process known as catalytic reforming had a precedent in the thermal reforming of naphtha developed in the thirties, but as in thermal cracking, the reaction mechanism was not very productive towards high octane gasoline and gave low yields. Catalytic reforming converts low octane naphtha into high octane gasoline, also known as reformate or reformed gasoline. The catalytic reforming of naphtha improves the octane number by catalyzing reactions like isomerization of paraffins to branched paraffins, dehydrocyclization of paraffins to aromatics, dehydrogenation of naphthenes to aromatics and hydrocracking of some paraffins. The reformate product is rich in aromatic hydrocarbons such as benzene, toluene and xylenes. Over time, this formed the foundation for the aromatic-based petrochemicals associated with oil refineries.

During World War II, the catalytic reforming was used to produce toluene from methylcyclohexane, as a raw material for explosives and aviation gasoline. In 1947, Standard Oil of Indiana, launched a fluid bed catalytic reforming unit. Unfortunately, an explosion destroyed the unit and delayed this development by thirty years highlighting the difficulty of operating with hydrogen at high pressures. In 1950, there was a sharp advance in reforming technology when UOP introduced Platforming, based on a bifunctional catalyst of platinum on acid alumina developed by Vladimir Haensel, a disciple of Ipatieff. Other similar developments such as Catforming of the Atlantic Reforming Company or Houdryforming from the Houdry Process Corporation were marketed, but the success of the Platforming process was overwhelming, as the platinum content needed was as low as 0.3% by weight. The catalyst employed gamma-alumina whose acidity was maintained by adding small amounts of hydrochloric acid to the unit charge. The operating conditions were between 25-40 k/cm^2 pressure and 430-510°C temperature. The operating cycles lasted between six and twelve months and the activity was maintained by gradually increasing the reaction temperature. After the operating cycle, the unit was stopped and the catalyst was replaced by a fresh one. The discarded catalyst was sent to disposal after being subjected to a platinum recovery process. Very soon it was learned how to regenerate the catalyst in the unit itself through oxidation and activation of the catalyst loaded into the reactors. [40, 41, 42]

A fundamental advantage of the reformer unit for the refinery was that during the reforming of naphtha, hydrogen was produced and could be used for hydrotreatments or hydrocracking reactions. In fact, the catalytic reforming process provided a high percentage of the hydrogen demand of the refinery. The bifunctional character of the reforming catalysts, where the reforming reactions occur in the active centers of platinum and alumina, was described in 1953 by Mills, Heinemann, Milliken and Oblad. In 1953, it was discovered that eta-alumina was more stable and active than the catalyst based on alumina. In 1954, Standard Oil of Indiana introduced the Ultraforming process, and in 1956 ESSO introduced the Powerforming process. These processes operated at lower pressures and favored aromatization reactions producing reformate with more aromatics and better octane numbers.

The reforming reactions are mainly endothermic and therefore the best design is to alternate unit reactors and furnaces to get conditions as close as possible to an isothermal profile. Generally, three reactors are installed, in the first two the endothermic dehydrogenation reactions occur, while in the third reactor the slightly exothermic hydrocracking and hydrogenation reactions take place. To favor a low pressure drop in the reaction system, the reforming reactors have a radial flow with a specific design that is part of the technology.

In 1967, there was a great technological advance with the introduction of bimetallic catalysts. Chevron developed the Rheniforming process whose catalyst was platinum-rhenium on alumina, and this combination gave great stability to the catalyst by prolonging the cycle length and increasing the resistance to poisons such as sulfur. In 1975, Exxon developed a catalyst from iridium and platinum allowing a stable operation at low pressures. In 1970, Larry Stines from UOP developed another important milestone in this technology, the continuous catalytic reforming process, licensed as "Continous Catalytic Regeneration" (CCR), which eliminated the need to stop the operation of the unit to regenerate the catalyst.[43, 44, 45]

The catalytic reforming platinum catalyst is rapidly deactivated in the presence of poisons such as sulfur, which may be present in the unit feedstock. Sulfur is part of all crude oils in greater or lesser proportions and, as the use of catalytic reforming was expanded by industry, it became necessary to develop a technology to remove sulfur and other contaminants from the unit's feed.

The hydrotreatment process dates back to 1869 when Berthelot studied the hydrogenation of coal to liquid hydrocarbons. Following the research work of Sabatier (1897), Ipatieff in 1900, and Bergius in 1910, the first coal hydrogenation plant was installed in Leuna in 1927. In 1940, the I.G. Faberindustrie successfully employed tungsten and molybdenum sulphide catalysts on alumina. In the first half of the twentieth century and during the war, Germany was the leader of the hydrogenation technology. Due to the shortage of oil, Germany was forced to produce hydrocarbons from coal in this way, and in 1944, 3.5 million tons where produced through this process. In the US, the first plant was installed in 1928 in Baton Rouge belonging to the Standard Oil Company of Louisiana, other companies such as Humble Oil and Shell installed plants in the forties, but their use was limited by the lack of hydrogen availability in the refineries. In the fifties the introduction of catalytic reforming provided abundant and cheap hydrogen and hydrotreatment units were installed for treating naphtha and other oil cuts. The hydrotreatment process used the hydrogen generated by the catalytic reforming unit and a cobalt and molybdenum sulfide catalyst was used to remove sulfur, nitrogen and other poisons from the reforming catalyst. The hydrotreatment process was also used to remove these contaminants from the distillates produced in the refinery. The hydrotreatment acquired more and more relevance in the configuration of the refineries from 1970s onwards.[46]

As a complement to the hydrotreatment of refinery cuts and to improve the quality of LPG and light gasoline and kerosene, the chemical treatment processes of these streams or sweetening were improved, based on the oxidation reactions of mercaptans with chemical substances such as sodium plumbite or the use of liquid phase catalysts based on iron chelates, like in the Merox process of UOP.[47]

The manufacture of lubricating oils also experienced a great boom with the popularization of the automobile industry. The necessary technology is very specific and is not usual in refineries that produce fuels. The lubricant manufacturing process requires the use of crude oils from the Middle East whose vacuum distillates generate a highly paraffinic stream. The aromatic components are then removed by the furfural extraction process and heavy paraffins are also removed by solvent extraction, such as the methyl ethyl ketone (MEK) process, to improve their cold properties. After the development of appropriate catalysts, paraffins can also be removed catalytically in dewaxing reactors. Also, asphaltenes are removed from the heavy distillation cut by propane extraction. The lubricating oil is then subjected to a treatment to remove olefins and diolefins by passing through activated clay reactors or by severe hydrotreatment. Waxes obtained from solvent dewaxing undergo a residual oil removal before commercialization.

THE HYDROCRACKING

In the late fifties and early sixties, the emergence of turbojet engines in commercial aviation led to an increase in the consumption of kerosene as aviation fuel. The demand for kerosene had declined since the days of the kerosene lamp, when it was the star product of the refinery, but jet fuel demand turned kerosene again into a key product of the refinery. The turbine manufacturers demanded from the industry that, for security reasons, aviation kerosene came exclusively from the crude distillation. With the development of the hydrocracking process in 1960, the industry had a technology that produced excellent aviation fuel. The hydrocracking, like hydrotreatment, was developed mainly in Germany from 1910 until the end of the war. Between 1925 and 1930, the I.G. Faberindustrie in collaboration with the Standard Oil of New Jersey developed the high pressure hydrocracking of heavy to light cuts. In 1960, Chevron Research Co., Unocal in collaboration with Esso and UOP launched several processes that popularized the technology.[48]

Hydrocracking is a very versatile process that can use heavy vacuum distillates as feedstock to obtain LPGs, light naphtha, naphtha, aviation kerosene, diesel and an unconverted residue with excellent properties for manufacturing lubricants. The process also removes all contaminants such as sulfur, nitrogen and oxygenated compounds, thus, the quality of the products meet in many cases the specification of the commercial product. Hydrocracking reactions occur in the presence of hydrogen with a silica-alumina catalyst or zeolites at very high pressures. A disadvantage is the high cost of the process due to the need to use equipment with a high pressure and temperature design; on the other hand, hydrogen consumption raises the operating costs over other conversion processes such as FCC.

The oil refining technology experienced dramatic technological improvements from 1940 to 1970, mainly due to WWII and the post-war economic boom, many of them are shown in Figure 6.

The continuous incorporation of new technologies to the configuration of a refinery improved the availability and quality of petroleum cuts, but increased their blending complexity in order to meet the quality specifications and the economic optimum. Linear programming had been introduced during the war to optimize many problems of manufacturing military supplies. In 1948, George B. Dantzig discovered the Simplex method that facilitates the resolution of large systems of linear equations subject to restraints and from there, linear programming spread throughout in the industry as a way to optimize refinery operations. Linear programming requires a large number of equations to find how to supply the refinery markets with the crude available, taking into account the yields and qualities produced by the refinery. Whereas its initial use required great simplifications, the increasing power of computers gradually provided the basis for the economic management of any refinery.[49]

THE PETROCHEMISTRY

In 1907, a Belgian chemist, Leo Hendrik Baekeland, synthesized the first plastic from phenol and formaldehyde, Bakelite. Years later, a pioneer in polymer research, Wallace H. Carothers confirmed the work of Hermann Staudinger, and took the company E.I. du Pont de Nemours to market the first synthetic rubber, neoprene, in 1932 and the first synthetic textile fiber, Nylon, in 1939. [50, 51]

But it was not until there was a high availability of raw materials that petrochemicals developed fully. Once again, thermal cracking was the origin of a basic technology for petrochemicals. The Steam Cracker or Cracker originated when C.P. Dubbs introduced steam into its cracking process and verified that there was a decrease in coke formation because the steam decreased the partial pressure of the hydrocarbon molecules and therefore, the coke formation reactions; in addition, the production of olefins increased dramatically. In the 1920s, Union Carbide and Standard Oil of New Jersey were the

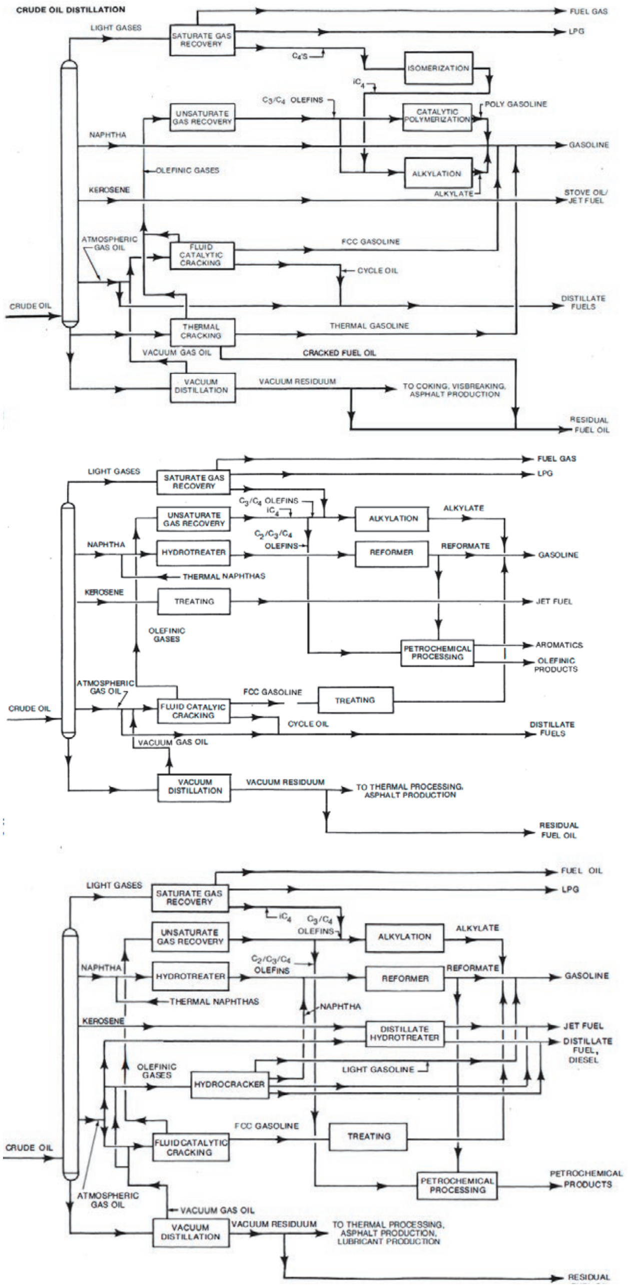


Figure 6. Refinery Configuration Evolution in 1940, 1950 and 1970. Reproduced from *U.S. Petroleum Refining: Meeting Requirements for Cleaner fuels and Refineries. Appendix C. History and Fundamentals of Refining Operations,* National Petroleum Council, **1993**.

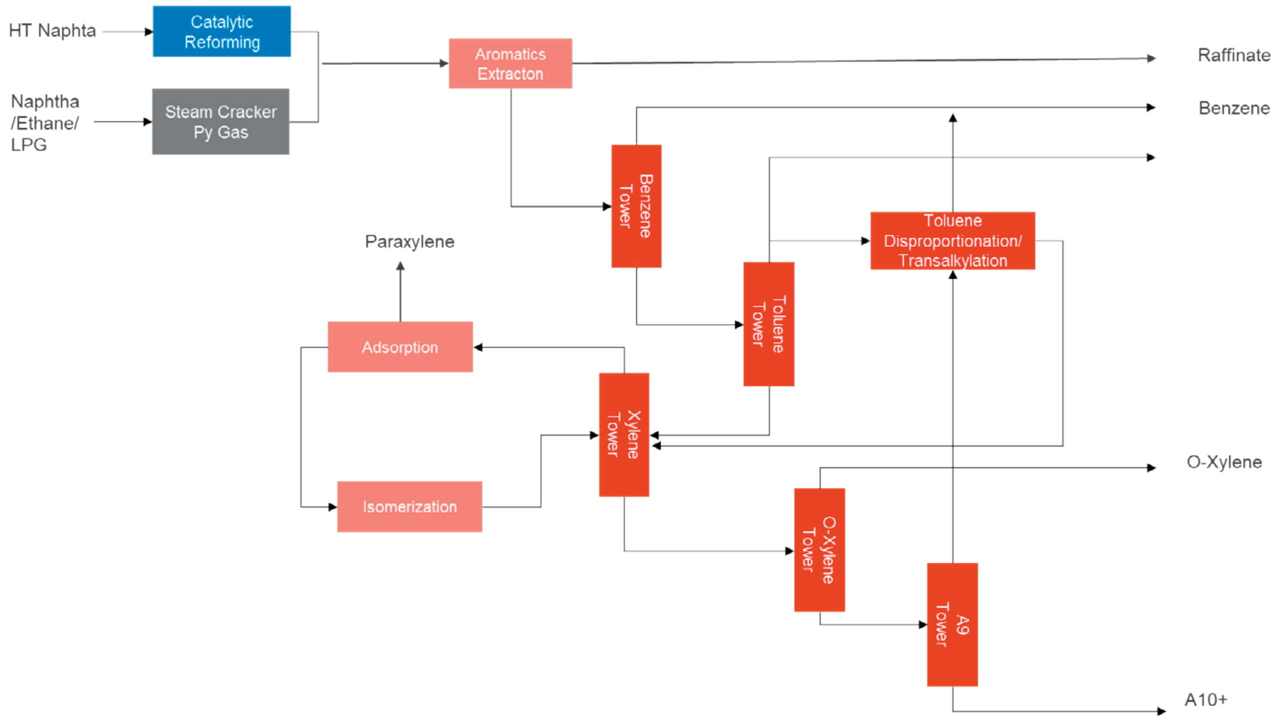


Figure 7. Aromatic Extraction Plant.

first companies to develop crackers for the production of ethylene and propylene.

The Cracker is currently the foundation of the chemical industry and produces three of the most demanded molecules such as: ethylene, propylene and butadiene. The cracker is versatile as several different feedstocks, i.e. LPGs, naphtha, natural gas or diesel can be used to produce other light olefins and aromatics such as benzene and toluene employed in the petrochemical industry.

The lack of some raw materials during World War II, such as rubber, whose production areas were occupied by Imperial Japan, promoted governmental efforts to obtain rubber substitutes from petroleum, such as butadiene[53]. The post-war economic development raised the demand for petrochemicals such as polyethylene, polypropylene, PET, phenol and synthetic detergents. In the refinery, and in order to separate the aromatic compounds in the reformed naphtha, aromatic extraction units with solvents such as sulfur dioxide or glycols followed by separation processes of benzene, toluene and xylenes began to be installed. The pioneer of the aromatic extraction technology was the Romanian Lazar Edeleanu who in 1907, developed a sulfur dioxide extraction process to improve the quality of kerosene, eliminating the aromatics that produced lamp fumes from burning. In 1912, the Royal Dutch Shell began studying the process and in 1916 it was marketed in Europe. The American company evaluated its installation at the Martinez refinery in California in 1915, but different problems were found and the process was not in service until 1927. The technology was extended to other companies such as California Standard Oil, Associated Oil and the Union Oil in those years. In 1928, Shell and Tidewater began using the Edeleanu process to extract aromatics from the lubricant bases, improving their quality. [52, 53]

At the end of the 1950s, improvements in the design and reliability of the alkylation units with sulfuric or hydrofluoric acid led to the progressive abandonment of the catalytic polymerization units as a way to convert light olefins into high octane gasoline. The polymerization found its place in the petrochemical industry where the development of catalysts by Ziegler and Natta, founded the polymer industry from ethylene and propylene. In 1951, while trying to convert propylene into gasoline, J. Paul Hogan and Robert L. Banks of Philips Petroleum obtained polypropylene and a short time later polyethylene was also obtained. [54]

Since 1960, the petrochemical industry developed in the fifties, experienced great success; especially the production of light olefins for plastics. The demand for

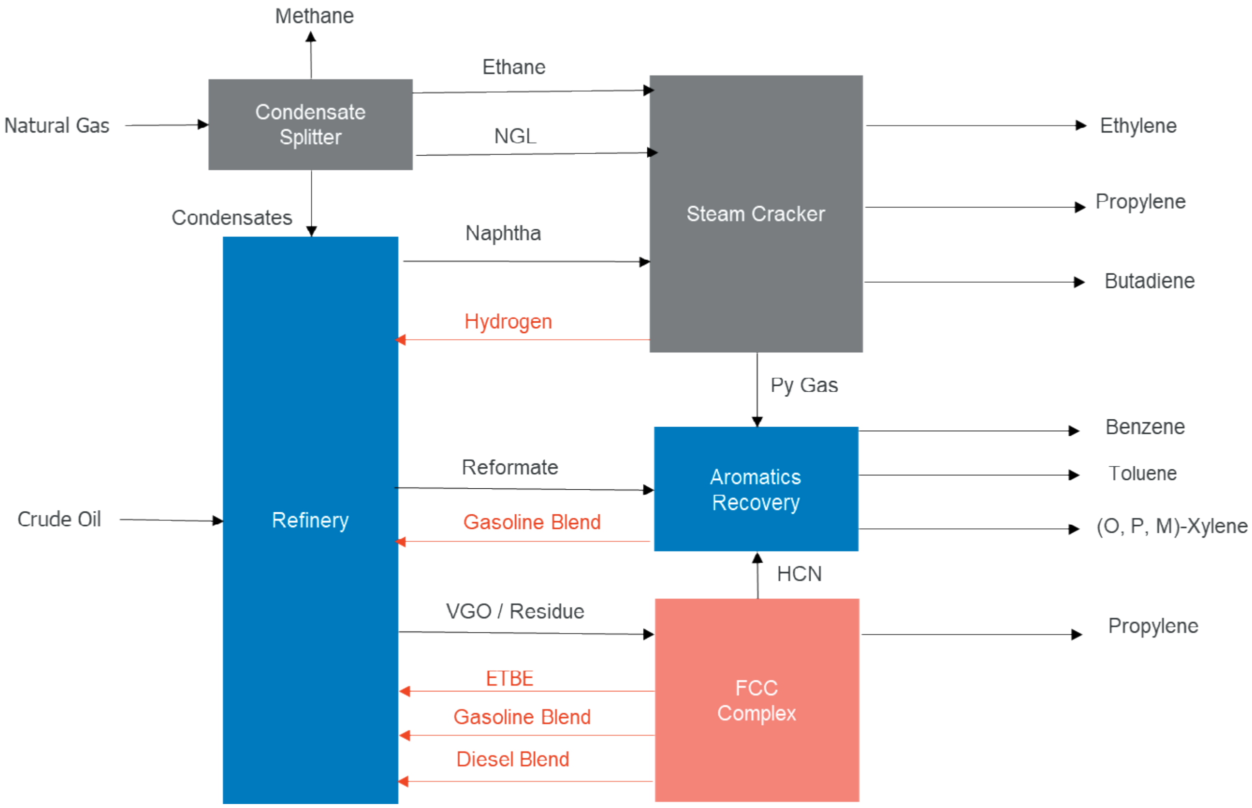


Figure 8. Refinery-Petrochemical Integration.

ethylene tripled in those years. In the refineries, the aromatic extraction from reformed naphtha benefited from the synthesis of new solvents such as Sulfolane synthesized by Shell or Morfilane by Uhde, these new solvents increased the stability and safety of the process. The aromatic production plants became more complex thanks to the development of zeolitic catalysts and molecular sieves that increased the selectivity to produce preferably the para-xylene isomer, a raw material in the production of plastics; as well as the conversion of toluene, with lower commercial demand, into xylene and benzene through disproportionation or dealkylation reactions, Figure 7.

The integration of the refinery and one or several petrochemical plants is an incentive for the growth of large industrial complexes, with both, operational and process synergies between the refinery and the petrochemical plant, Figure 8. Typical examples of integration are the production of phenol, cumene and acetone by the Hock process, using benzene from catalytic reforming and propylene from FCC and the manufacture of linear alkyl benzene (LAB) as a detergent base material, again by the alkylation of benzene with paraffins extracted from the kerosene cut, UOP-CEPSA process. Another example is the production of purified terephthalic acid (PTA) from para-xylene from the aromatic complex of the refinery, a process developed by the Scientific Design Company; the reaction of PTA with ethylene glycol produces polyethylene terephthalate (PET), a raw material for plastic or fiber bottle manufacturing. [55]

The large increase in propylene demand in the 21st century has changed the role of FCC and in some parts of the world such as Asia and the Middle East, propylene has replaced gasoline as the main product. The technology involved alters the catalyst to include a larger proportion of ZSM-5 and also changes the design of the reactor internals to modify the contact time. In some cases, the designs add a second riser reactor where cracked naphtha is processed obtaining propylene yields of 30-40 % compared to yields less than 10% in a conventional FCC. The petrochemical complex based on FCC complements the aromatic plant in the production of petrochemical products in the modern refinery.

THE OIL CRISIS

During the oil crisis caused by the Yom Kippur war in 1973 and the fall of the Shah in Iran in 1979 due to the Ayatollah's revolution, the price of crude oil rose from 2 to 12 dollars per barrel. Thereafter, OPEC maintained the price of crude oil at high values with the consequent impact on the profit margin of the oil refineries. The response of the refining industry to this important change affected two aspects of the technology.

Oil refining is a technology that requires high energy consumption, the processes described so far require high temperatures and pressures, as well as the transfer of large volumes of liquids, and those are high energy demanding processes. On average, and depending on its configuration, a refinery consumes 5% of the processed crude oil to supply the necessary energy for the process. The oil crisis led the technology to focus on efficiency and energy recovery in the refinery, affecting both, existing processes and new projects with very demanding energy consumption objectives. The main modifications to the technology involved the installation of heat exchangers, heat recovery from waste streams like the heat from the furnace stacks, or the generation of steam with process streams and the cogeneration of electricity from waste gases. All steam and electricity utility systems were also analyzed to optimize energy use. Finally, new tools were developed to design energy recovery systems such as the "pinch" analysis developed by Linnhoff and Vredeveld at the end of the seventies, looking for the optimal way to exchange process streams from the point of view of energy recovery. [56]

The rise in crude oil price revived the technologies for conversion of heavy oil cuts to light cuts, and many refineries incorporated FCC units and to a lesser extent hydrocracking so that less oil was necessary to achieve the same amount of high value-added products. This trend also revived the technologies for the conversion of the so-called Bottom of the Barrel or vacuum residue; among them we have cited the Delayed Coker as the heir of thermal cracking, which allowed 70% conversions to light products and a coke that was used as fuel in cement plants or to manufacture electrolysis anodes. Also, a modality of soft thermal cracking known as viscorreduction or Visbreaker was developed with conversions that dropped to 20%, but a fuel oil with commercial viscosity was obtained. This unit was oriented to the production of marine fuels with viscosities of 180 or 360 cSt and its advantage was that it eliminated the need to mix the vacuum fuel oil with light products to decrease its viscosity and density, with the consequent savings in distillates that could be directed to formulate other more valuable products. The energy crisis also triggered the emergence of the vacuum residue hydrocracking technology, in this case the conversion of the residue occurred in the presence of hydrogen on a catalyst at high pressures and temperatures. The reactor type ranged from fixed bed to ebullated or fluidized bed, giving rise to different processes. Units were installed in the eighties and nineties but the high cost and the need for hydrogen favored the Delayed Coker technology.

THE ENVIRONMENT

In the 1970s, concerns about the impact of hydrocarbons on human health and the environment increased greatly. This trend continues today, largely leading the evolution of refining technology. In summary, regulations with an impact on refining technology began with the elimination of tetraethyl lead (TEL) as an improver of the octane number of gasoline. The main regulations with an impact on refining technology can be summarized as follows:

- the changes in fuel quality specifications eliminating the contaminant content,
- the regulations related to emissions from refinery effluents,
- the introduction of biofuels
- and finally the decarbonization of oil refining, which will surely have a strong impact in the future of the industry.

In 1974, a period began that lasted until the 1990s in which the TEL was eliminated from the gasoline formulation as an octane improver. There was a great concern about the composition of vehicle effluents. The installation of a combustor with a platinum catalyst, which converts both nitrogen compounds and the remaining hydrocarbons into inert molecules solved this problem; for that purpose no poisons were allowed in the car effluents that could damage the platinum catalyst. Lead is a permanent poison for platinum catalysts, therefore, its removal was necessary, apart from the harmful nature of lead compounds for humans. This fact increased the importance of catalytic reforming in refineries, making reformate the main contribution of octane to gasoline formulations. The gasoline components produced in other process units such as FCC, alkylation, hydrocracking and polymerization have a relatively constant octane number. The product of catalytic reforming has octane numbers from 80 to more than 100. Unfortunately, as the severity of the operation increases to raise the octane number, the gasoline yield decreases. The normal performance in reforming can vary from 70 to 90% in feed volume, depending on whether the octane is high or low.

In the eighties, the process of etherification of four or five carbon olefins from the FCC unit with methanol was developed as an alternative to TEL to produce methyl tert-butyl ether (MTBE) or tert-amyl ether (TAME). These ethers have a high octane number and good properties as a gasoline component and their use extended from 1980 onwards. In the 1990s, the regulations regarding oxygenated compounds in gasoline were updated. Subsequently, MTBE was replaced by ethyl-tert-butyl ether (ETBE) due to various aquifer contamination episodes with MTBE caused by its high water solubility. In those years, the direct injection of ethanol into gasoline also began, although there are limitations in several quality specifications that advise against exceeding 10% in ethanol content. [57]

The next environmental impulse came from the 1990s and continues today, fuel specifications hardened the limit values of pollutants in the benefit of human health and the environment. In a very general way, this affected especially the sulfur content in fuels and limited the content of aromatic and unsaturated compounds. Additionally, the density of fuels was limited in order to obtain lighter products with less complex and harmful combustion products. In Europe, the AUTO OIL program was the framework for the development of these new specifications in which the automobile industry, the refining industry and the European Commission were represented. The evolution of the EURO specifications resulting from this analysis, strongly increased the regulatory pressure that oil refining technology had to solve. The impact of the new specifications on the manufacturing technology of automotive fuels covered several complex aspects.[58]

The limitation of sulfur forced the industry to rethink the use of FCC naphtha in gasoline, the FCC naphtha sulfur content depends directly on the FCC feedstock. The first option is to hydrotreat the FCC feedstock. Since the sulfur specification virtually eliminates this compound, hydrotreatment is often not sufficient. The injection of additives based on magnesium oxides that react with sulfur and remove it from reaction products has also become popular. The most widespread solution has been the hydrotreatment of FCC naphtha, this process was a technological advance after an in-depth study of the distribution of sulfur compounds and olefins in FCC products.

Compounds that give a high octane number to FCC naphtha are olefins and aromatics and hydrotreatment reactions in the presence of hydrogen tend to saturate those compounds, thus removing their aromatic and unsaturated character and reducing the desired octane number. Refining technology elegantly solved this problem by discovering that the light fraction of the FCC unit contained the highest proportion of the compounds that contribute to the octane number and the heavy part contained the sulfur compounds. Various technologies were developed by separating both parts of the naphtha and selectively hydrotreating the heaviest part with catalysts that desulfurized keeping the high octane compounds intact to a large extent. The technologies designed by ExxonMobil, UOP and especially Axens solved this challenge and nowadays FCC gasoline is still the main component of gasoline. [59]

The next major challenge for gasoline was the limitation of aromatic content and especially of benzene in its formulation. Aromatic compounds have a high octane number and high density, which favors compliance with the vapor pressure of gasoline. The greatest contribution of aromatics to gasoline is made through reformed gasoline, refiners had to limit this component in the formulation and increase the contribution of FCC naphtha, oxygenated ethers and gasoline from alkylation. An added problem was to eliminate benzene from reformed naphtha, also in this case there was a technological analysis of how benzene was formed during catalytic reforming and two strategies were designed for its elimination. One strategy was the elimination of the so-called proto-benzenes or compounds that give rise to benzene during the reforming reactions and which were removed by distillation of the light part of the charge to the catalytic reforming. The other option was to eliminate the benzene present in the reformate by distillation. The limitation in aromatics and benzene was not a major problem in complex refineries, but in those without an FCC unit, it was a serious problem since its formulation was based on reformed naphtha, and they were forced to buy FCC naphtha to make their gasoline formulations, seriously compromising their future.

The other major automotive fuel, diesel, was also deeply affected by the new specifications. In this case, the technology focused on the removal of sulfur by hydrotreatment. Although diesel was desulfurized since the seventies, the almost total elimination of sulfur was an important technological challenge. Firstly, the different sulfur compounds present in the diesel were identified and it was determined that depending on the position of the sulfur atom in the hydrocarbon molecule, its elimination could be more or less difficult. This implied that it was relatively easy to remove compounds with accessible sulfur atoms, but it was very difficult when sulfur atoms were in a position that hindered their access to the catalyst. Dimethyl dibenzothiophenes are an example of molecules resistant to hydrotreatment for this reason. This fact induced two important technological advances, a great development of cobalt-molybdenum and nickel-molybdenum catalysts supported on alumina, improved with advances on the understanding of the desulfurization reaction mechanisms, and the design of suitable reactors to carry out this process. Catalyst manufacturers like Abermarle, UOP, Haldor Topsoe, Axens, etc., made an important effort to put these catalysts on the market in a few years. [60]

It is worth discussing in more detail the design of the hydrotreatment reactors for sulfur removal. During the diesel hydrodesulfurization reaction, liquid diesel, partially vaporized and hydrogen in the gas phase are present in the reactor, therefore, the flow in the reactor is mixed in the so-called "trickle-bed" reactor system. This is a problem since one requirement for efficient reaction on the catalyst is that the reactants are well mixed facilitating their access to the catalyst surface. Since 2000, there was a technological change in the design of the hydrodesulphurization reactor internals. Using tools such as Computerized Flow Design (CFD), the designs of the gas-liquid distributors were improved to obtain reactors of increasing diameter and, therefore, units of greater capacity. Today we can find mixed flow reactors of six meters in diameter when in the nineties three meters was an insurmountable limit. [61]

As we have seen, the refineries have been forced to hydrotreat most of their products prior to their marketing. The question then became what to do with all the sulfur compounds that are removed from gasoline and distillates, and indeed, this is another technological and environmental challenge that the industry has had to solve. Hydrodesulfurization reactions remove sulfur from the oil cuts in the form of hydrogen sulfide, this compound is incorporated into the refinery gas system that channels all the gaseous streams produced in the different refining processes and that are used as fuel in the furnaces of the process units. Prior to environmental regulations, these sulfur compounds were oxidized to sulfur dioxide during combustion, and were emitted from refinery furnace stacks. European and American emission regulations began to regulate refinery emissions in the 1980s. The technology solved this new challenge by installing sulfur absorption units with ethanolamine-based compounds, which react quickly with hydrogen sulfide. Ethanolamine captures hydrogen sulfide and in an absorption-regeneration cycle produces a stream of light sulfur-free hydrocarbons that are sent as fuel to the furnaces of the refinery and a so-called acid gas with a 95% content of hydrogen sulfide that is sent to the sulfur recovery units for conversion into solid or liquid sulfur that is marketed. This transformation is carried out in Claus units, based on the reaction discovered by Friedrich Claus in 1883 and modified by IG Farbenindustrie AG in 1937. The Claus process partially oxidizes hydrogen sulfide to sulfur dioxide that reacts with the remaining hydrogen sulfide to produce elemental sulfur. Sulfur recovery in a refinery exceeds 99.5% in this way, and can reach 99.9% through the waste or tail gas treatment unit, prior to its emission. [62]

The next fuel subjected to quality specifications, Marine fuel oil, is still an issue for refiners. Marine fuel oil or bunker moves the engines of ships and is formulated with heavy distillates and vacuum residue. The International Maritime Organization (IMO) regulated a maximum sulfur content in marine fuels of 0.5% after 2020. Marine fuel is typically formulated with heavy cuts, which cannot undergo further valorization in the refinery process units. There are many refineries that use delayed coking units to convert all their heavy residue into naphtha and distillates. The less complex refineries or those serving the bunker markets employ their production of vacuum residue and heavy distillates for this purpose. An advantage of bunkering production used to be that marine fuel, whose sulfur specification was 3.5% by weight prior 2020, was a sink for much of the sulfur entering the refinery, this is not possible after 2020.

Alternatives to meet the sulfur content of marine fuels, include the installation of scrubbers with seawater that remove sulfur dioxide from the effluent of ship's engines. Another option is to change the fuel for products with lower sulfur content, such as natural gas, since it is possible to adapt the engines to these other fuels. A final option for the refineries is to produce marine fuels similar to the current ones but with a sulfur content less than 0.5%. The price of marine fuel has historically been below the price of crude oil and this raised doubts about the price of this new low sulfur fuel, and whether the necessary investments in hydrotreatment processes of vacuum residue and distillates involved in its formulation were justified, considering a solution similar to that of gasoline and diesel.

Many refineries rely on distilling low sulfur crude, whose residue allows a marine fuel to be obtained that meets the sulfur specification. From the technological point of view, there are processes for the conversion of the residue into more profitable products such as delayed coker or solvent deasphalting, but they do not produce fuel oil and would force the refinery to leave the bunker market. Other technologies such as residue hydrocracking obtain conversions to gasoline and distillates in the vicinity of 70% and allow the refinery to formulate low sulfur fuels by desulfurization of the vacuum residue. Residue hydrocracking technology (RHC) has undergone a breakthrough in recent years since its inception in the 1980s, and recently ENI, CLG and UOP have introduced the "Slurry" technology with a very small particle size catalyst that allows conversions of up to

90%, practically eliminating the residue from the refinery. The evolution of the markets after the new specification of sulfur for marine fuels, will consolidate the best option for refineries in terms of conversion of the Bottom of the Barrel.[63]

THE BIOFUELS

The third area where environmental requirements have had an impact on the configuration of the refineries is biofuels. These constitute renewable energy and are defined as fuels suitable for use in internal combustion engines that have been produced from biomass obtained through biological processes, and in general they consist on a mixture of organic compounds with a high oxygen content. Their use is justified by the hypothesis that the carbon content of biomass comes from the photosynthesis process and eventually turns back into the atmosphere as a result of burning and carbon dioxide emissions, making the net carbon balance neutral. This last statement is subject to debate, and there is extensive bibliography discussing the net result of the carbon balance.

The biofuels consumed in the world are primarily ethanol, an alcohol produced by the fermentation of agricultural crops or lignocellulosic materials; biodiesel, a methyl ester resulting from the esterification of vegetable oils, such as palm oil, and methanol; and finally hydrotreated vegetable oil (HVO), which is manufactured by removing the oxygen present in vegetable oils by reactions in the presence of hydrogen. Biofuels are under great debate due to the effects that their production in large quantities has had on the food price, with which they share raw materials such as corn, wheat, palm oil, etc.; and also to due to changes in land use, either by varying the original yield of agricultural lands for cultivation or by dedicating areas of high biodiversity to the cultivation of biofuels. The last two phenomena are known as Indirect Land Use Change (ILUC) and have significantly conditioned European legislation. Nowadays, those biofuels coming from edible raw materials are known as conventional biofuels, and those whose raw materials are residues, animal fats, non-edible vegetable oils and cellulosic materials, and have no effect on the change of agricultural land use, are termed advanced biofuels. The regulations have increased the content of biofuels and the specification will lead refineries to introduce 10% biofuel (measured as equivalent energy) in the formulations of automotive fuels.

The refineries have been pioneers in the production of biofuels since the 90s, Figure 9; they included Bio-ETBE (EthylTercButil Eter) into the gasoline blending. ETBE is an oxygenated derivative of ethanol and butenes produced in the refinery. It is a good oxygenated component in the formulation of gasoline, thanks to its

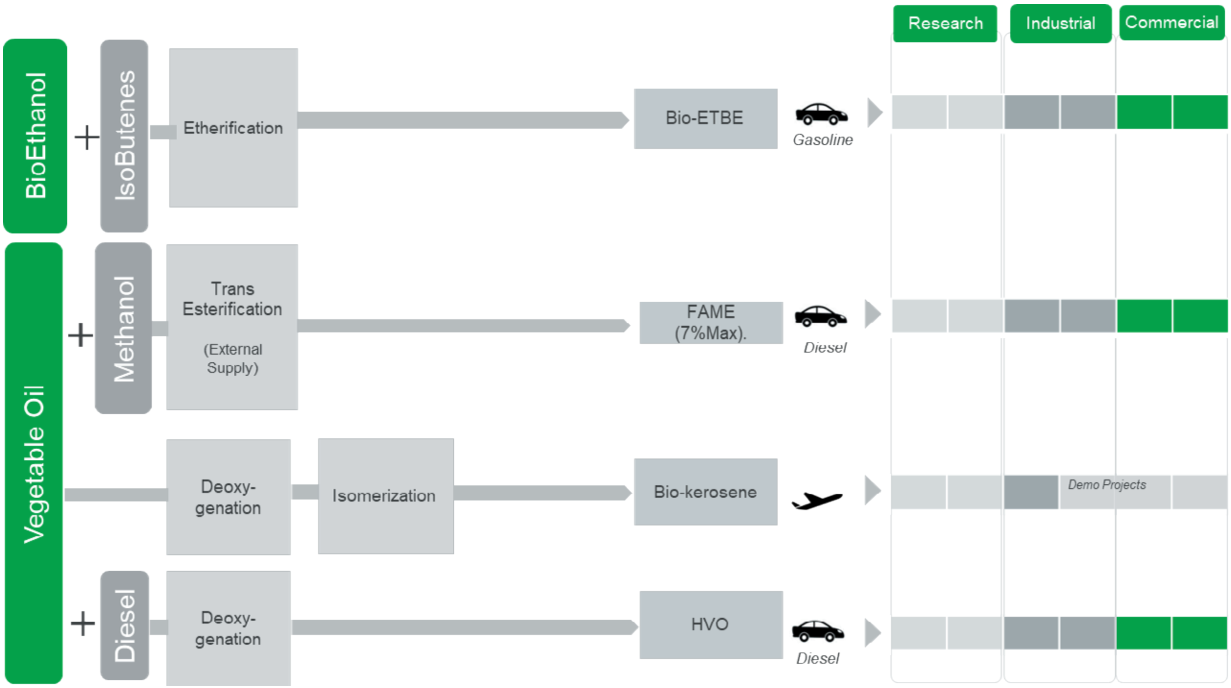


Figure 9. Biofuels production in refineries.

stability and high octane number. Refiners also incorporate biodiesel frequently produced in facilities near the refinery into diesel formulation. Biodiesel has some stability problems and its content is limited by the specification. Refining technology has developed processes for the production of hydrotreated vegetable oil (HVO) by selective deoxygenation of the fatty acids in the vegetable oil that are converted into paraffins. This process has a high hydrogen consumption and requires expensive construction alloys given the corrosive nature of vegetable oils. ENI, UOP, Haldor Topsoe, NESTE and AXENS have commercialized units and the production of HVO is today a common process in the refinery. In countries like Spain, where it is permitted by current legislation, it is common to co-process vegetable oil up to 5-7% by volume in existing hydrotreatment units. HVO has excellent properties as a diesel component. [64, 65]

The manufacture of HVO has resulted in a specific refinery configuration that today has two examples at the ENI refinery in Porto Marghera and La Mede refinery owned by TOTAL. Both are based on obsolete refineries without conversion capacity and whose economic viability was compromised. The refinery feedstocks are vegetable oils, animal fats, used cooking oils or recycled plastics; the hydrogen for the reactions involved can be provided by the existing catalytic reforming unit or by a hydrogen plant and the products obtained are separated and stored in the refinery facilities for distribution. The refinery produces renewable diesel or green diesel, renewable naphtha or green naphtha, LPGs and potentially aviation fuel. ENI is considering converting the Gela refinery in Italy to this scheme. There are technologies to produce bio-kerosene for jet fuel, however, despite its use in test flights, the implicit safety concerns in air transport means that the introduction of aviation biofuels is not expected soon. [66]

THE FUTURE

The refineries have been implementing advances and technological innovations such as those we have described to satisfy their markets and the specifications applicable to their products, Figure 10. The choice of a refining technology is based on the specific circumstances of its operation and depends on the type of crude oil, the demand and quality of the products and economic factors such as the cost of crude oil and products, availability of services such as steam, water, electricity, etc., type and cost of catalysts and the cost of the necessary equipment for its operation.

Considering our current knowledge on the past and present of oil refining technology, it is worth asking whether the refinery will remain as a supplier of essential products for society or there are risks of the industry being overcome by new technological advances or even disappearing. If we look in the past and the successive energy transitions, we see, for example, that the oil industry began in 1859, but it took more than a century

Figure 10. Complex Refinery (CEPSA Gibraltar San Roque) in 2021. Reproduced with permission from Cepsa.

for coal to cease to be the main source of energy. Oil, in turn, represented 5% of energy consumption in 1840 and its growth was slow until 1900 when it represented 50% of the energy supply, sharing the leadership with fuels as exotic as whale oil. In general, history tells us that energy transitions are slow phenomena and also that usually the preceding energy sources do not disappear and remain in niches of consumption in considerable quantities, for example, around 1960, oil was the main source of energy surpassing coal, but since then, coal consumption has tripled despite being a secondary source of energy. [67]

Historically, the transitions from one energy source to another have been due to the emergence of new technologies, better prices and lower energy costs and often to policies looking for more secured supplies. Nowadays, it is the climate change who is causing the transition from low-cost energy sources to energies whose costs are currently higher but seek to reduce the emission of greenhouse gases (GHG). The difference in costs is covered by different types of subsidies, incentives and regulations, until investments in research and development make those energies competitive. However, it should not be forgotten that the wealth growth in the world has always been associated with an efficient and cheap source of energy.

Petroleum refining technologies, as we have seen, have been responding to the environmental challenges that have been presented, but the last one we have mentioned, decarbonization, affects the very nature of its products that are made of carbon atoms. Next we will make a brief analysis of where it is more feasible to replace petroleum products and which of them will be maintained over time.

Vehicles with an internal combustion engine can be replaced by electric vehicles, hydrogen, hybrids, natural gas, etc., car manufacturers have understood this trend and regardless of the legislation they are making large investments in developing electric vehicles. As in the past, the automobile industry can dictate the demand for fuels and contribute to a significant decrease in diesel and gasoline consumption. At the moment, advances that allow the commercialization of electric heavy transport vehicles or the replacement of aviation fuel seem less viable. Therefore, the demand for diesel and especially aviation kerosene should be maintained for the next decade. Marine fuels, as we have already described, have the alternative of natural gas that would have a significant bunker market share in the coming years. Hydrogen also appears as a long term option for decarbonizated bunker fuels. The future of transport fuels is therefore a challenge, perhaps the most complicated one that the refining industry has to face.

Road paving is another market where the use of asphalt mixtures seems to be the most economically and technically viable alternative, and therefore, the demand for asphalt can be maintained over time. The future of lubricants, already threatened by synthetic lubricants, is associated with that of the internal combustion engine. If this disappears, a large part of the manufacture of lubricants will also disappear, although some demand will still exist for other lubrication applications such as oils for machines, greases, waxes, etc.

An area where oil seems irreplaceable is petrochemicals, this market demands 12% of the crude oil production and maintains sustained annual growth, especially in areas such as Asia where the standard of living is growing rapidly. The refineries have increased their integration with petrochemical plants starting with 5-10% of their products being petrochemicals to more than 20-30%.

In recent years, chemical products based on renewable raw materials have been developed. Although technically possible a disadvantage is the low production yield that makes large quantities of raw material necessary, and often leads to irrational demands on land availability and logistics. The recycling of plastics is also a booming trend.

The high demand for petrochemical products is giving rise to a new refinery configuration known as “Crude to Chemicals”, which is a good example of what the future could be. In these refineries, existing technologies and new developments are combined to directly convert crude into petrochemical products with conversions that exceed 50%. We have examples of these refineries in Saudi Arabia and China where the direct conversion of crude oil is the technological challenge; in that vein, Exxon at its Jurong refinery, launched in 2014, a process of direct crude cracking. The number of refineries that might follow this production strategy is a concern due to the small size of the petrochemical market in comparison to the fuel market. [68, 69]

CONCLUSIONS

Presently, 85% of the world’s energy consumption is generated by fossil fuels. The task of reducing the energy contribution of oil, requires time and substantial investments. It will be the society who will determine where and when this energy transition will materialize. Renewable energies should have the role of feasible energy alternatives without prejudice for the standard of living.

Finally, the refining industry is facing its most important challenge that must be solved thanks to new feedstocks and products, new technologies and to innovative mentality and adaptation to demand, which has always characterized oil refining.

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Historical Articles

Albert Ladenburg (1842-1911) – The Distinguished German Chemist and Historian of Chemistry of the Second Half of the XIX Century (To the 110th Anniversary of His Death)

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Abstract. Albert Ladenburg (1842-1911) was an outstanding German chemist and historian of chemistry of the second half of the 19th century. He ascertained the formula of ozone as O_3 and proposed a triangular prism structure for the molecule of benzene. He studied the structure of aromatic hydrocarbons and organic compounds of silicon and tin, and devoted his work to explaining the structure of alkaloids and their synthesis. The purpose of this paper is to familiarize readers with the important events in the life of Ladenburg and his writing and research activities, in particular some of his experimental results, as well as his selected publications.

Keywords: A. Ladenburg, Organic chemistry, Ladenburg's prism formula for benzene, Coniine, Germany – XIX century.

> *In the minds of all chemists now living, and of all those who, in the future, trace the development of the science of our time, the name of Ladenburg is, and always will be, closely associated with the chemistry of those interesting and wonderful products of nature's laboratory, the vegetable alkaloids.*
> Frederic Stanley Kipping (1863-1949).[1]

1. THE IMPORTANT EVENTS IN THE LADENBURG'S LIFE

Albert Ladenburg was called a great man with highets achievements, "who his life worthily devoted to the advancement of knowledge",[2] and "an indefatigable worker and investigator".[3] One hundred and ten years have passed since his death, but in that time little has appeared in the literature about this eminent man. He went down in the history of chemistry as a researcher of the structure of aromatic hydrocarbons and organic compounds of silicon and tin. One of his achievements as an experimenter was the synthesis of alkaloids and the elucidation of their structure.[4]

Albert Ladenburg was born into a renowned Jewish family in Mannheim on July 2, 1842, as the second son of Dr. Leopold Ladenburg (1809-1889), a lawyer, and his wife Delphine, née Picard (1814-1882).[5-6] His grandfather Wolf Haium Ladenburg (1766-1851) founded the private *Banking House Ladenburg* in Mannheim in 1785.[7-8]

At the age of 15, after study at a *Realgymnasium* at Mannheim, he continued his education (1857-1860) at the *Polytechnische Schule* in Karlsruhe. In 1860, at eighteen years of age, he went to Heidelberg, where his interest in chemistry was inspired and directed by Robert Bunsen (1811-1899). In the Bunsen's laboratory he met, among others, Carl Graebe (1841-1927), and Hermann Wichelhaus (1842-1927), who remained his close friends. Here he also met the British chemist Henry Roscoe (1833-1915), who often visited Bunsen. He also attended lectures on mathematics at the University and studied physics under Gustav Kirchhoff (1824-1887).[9]

On June 2, 1863, he "took the Ph.D. degree at Heidelberg University, *summa cum laude* in chemistry, physics, and mathematics."[10] During this time, he met Emil Erlenmeyer (1825-1909), which led to a lifelong friendship between them. Then he worked in a small private laboratory of Georg Ludwig Carius (1829-1875), *außerordentlicher professor* at the University.

In the spring of 1865 he went to Ghent, where he spent a semester to work in the University Laboratory of August Kekulé (1829-1896).[11] Figure 1 is a photograph taken in Ghent.[12-15] From left to right, standing: August Mayer (1844-?), Wilhelm Körner (1839-1925), Kekulé's private assistant and secretary, Esch, Semmel, Behrend, and Ladenburg. Seated, from left to right: Théodore Swarts (1839-1911), Kekulé, and Carl Glaser (1841-1935), Kekulé's private assistant.[16]

Figure 1. Ladenburg with August Kekulé and the group of his assistants and students at the Ghent University (Public domain, from reference 12).

In 1866, after his stay in Ghent, he went briefly to London, where he visited the British chemist Edward Frankland (1825-1899), after which he moved to Paris.[17] Following the advice of Kékulé,[18] he asked Marcellin Berthelot (1827-1907) for permission to become one of his students. His "request was granted forthwith, but when he proceeded to inquire where he should work, he was shown a large, empty room, devoid of all fittings, of which he would be the sole occupant."[19]

However, he did not use Bertholet's offer and started work under Charles Adolphe Wurtz (1817-1884) in his laboratory at the *Faculté de médecine de Paris*. He met there, among other, Charles Friedel (1832-1899), Joseph Caventou (1795-1877), Alfred Joseph Naquet (1834-1916), and Armand Gautier (1837-1920). In the years 1866-1867, he worked for 18 months with Friedel. He carried out with him series of researches in the laboratory in the *École nationale supérieure des mines de Paris*.

After obtaining his habilitation, on January 8, 1868, he became *Privatdozent* at the University of Heidelberg. The British chemist and historian of chemistry Thomas Edward Thorpe (1845-1925) wrote about his stay in Heidelberg at that time as follows: "At Heidelberg, as in many other centres of chemical instruction, there was a small Chemical Society, composed of the Extraordinary Professors, the Privat-docenten, and assistants, together with the senior or more active students in the various laboratories who were elected into it by favour of the teachers. In my time it numbered amongst its members Erlenmeyer, Ladenburg, [August Friedrich] Horstmann [(1842-1929)], [Ernst] Ludwig [(1842-1915)], [Emil] Cohen [(1842-1905)] (the mineralogist), Rose, and [Adolph] Emmerling [(1842-1906)]. Its president was Bunsen, and the occasions on which he took the chair were the red-letter days of the session."[20]

In the fall of 1868, Ladenburg attended the *Naturforscherversammlung* (Meeting of Naturalists) in Frankfurt am Main. There, he met Kekulé and the Russian chemist Aleksandr Mikhaylovich Butlerov (1828-1886), whom he "knew already from Heidelberg" and with whom he "had entered into closer relations at a dinner given by Erlenmeyer."[21-22]

On March 30, 1870, he was appointed extraordinary professor at the University of Heidelberg, and on October 25, 1872 he went to Kiel [23] as full professor of chemistry and director of the new chemistry laboratory at the University. He became the successor of Karl Himly (1811-1885),[24] and he worked there for seventeen years. He "was presumably the first nonbaptized chemist who received a full professorship in chemistry at a German university."[25-26] In the academic year 1884/1885 he was the Rector of this University.[27]

On September 19, 1875, he married Margarethe Pringsheim (1855-1909),[28] the daughter of the Nathanael Pringsheim (1823-1894), professor of botany at the University of Berlin.[29-31] The spouses had three sons: Erich (1878-1908), Rudolf (1882-1952) and Kurt (1884-1901).[32]

On October 1, 1889 he went to Breslau in Silesia in the Kingdom of Prussia (now, Wrocław, Poland), where he started working as a professor of chemistry at the *Königliche Universität zu Breslau* (Royal University of Breslau). He, as the successor of Carl Jacob Löwig (1803-1890), became the director of the *Chemische Institut* (Institute of Chemistry).[33]

In 1901, the Ladenburg's youngest son, Kurt, died prematurely at the age of 17. Seven years later, his eldest son Erich, a physicist[34] who made a scientific career at the Royal University of Breslau, died tragically. He drowned in a sailboat accident on Lake Müggel.[35-36] His third son, Rudolf, became a German-American atomic physicist.[37]

In 1905, he has had to undergo amputation of the right leg.[38] The German chemist Walter Herz (1875-1930), professor of physical chemistry at the University of Breslau, wrote about it as follow: "Ladenburg not only lost his right foot as a result, but also the whole right leg up to the middle of the thigh. His friends fearfully wondered whether this new, large wound would now heal and whether the now 63-year-old man would still be able to learn to walk with an artificial leg. The healing progressed slowly, but in the autumn of 1905 Ladenburg was ready to return to his office thanks to the loving care of his wife. Everyone who saw him was surprised at how well he had recovered from this severe blow."[39]

Nevertheless, he continued the duties of his Chair until October 1, 1909, when he resigned from teaching due to illness. Towards the end of his life, he wrote a autobiography, which his son Rudolf published under the title *Lebenserinnerungen* in Breslau in 1912.[40] It is worth emphasizing that this book does not contain "a single mention of antisemitism or even prejudice".[41] Ladenburg was not "*practicing*" Jew and was "fully assimilated" German. He "was in fact an atheist; for reasons that he does not explain, he finally underwent baptism in 1891."[42] According to a document written by him two years earlier, dated November 16, 1889, and stored in the Archives of the University of Wrocław, he called his confession *Evangelisch reformierte* (Evangelical Reformed).[43]

Ladenburg died on August 15, 1911 in Breslau. Herz in his obituary wrote: "When I went to the laboratory early on August 15, I first sent a telegram congratulations on the [Rudolf] Ladenburg wedding at a post office. When I arrived at the laboratory, I had barely started my work when the telephone notification arrived that Ladenburg had gone to sleep on the night of August 14th to 15th (at 1:00 am). He did not live to see his son's wedding."[44]

He was buried on August 18th. At his funeral, *der Geistliche der reformierten Hofgemeinde* (the Clergyman of the Reformed Court Community) Pastor Renner, the mineralogist Carl Hintze (1851-1916), and the Lord Mayor Dr. Georg Bender (1848-1924) spoke at his grave alternately.[45]

Two of his obituaries were published in 1911 by anonymous authors in *the Chemical News*,[46] and *American Chemical Journal*.[47] Two year later, on October 23, 1913, the English chemist Frederic Stanley Kipping (1863-1949) delivered a lecture in memory of Ladenburg at a meeting of the Royal Society.[48]

2. LADENBURG'S PARTICIPATION IN THE SCIENTIFIC CELEBRATIONS

In August 1877, he attended celebrations of the 400th Anniversary of the University in Uppsala (Sweden) as a representative of the University of Kiel.[49] Twenty-three years later in 1900, he visited Berlin to participate in the conference devoted to the 200th Anniversary of the *Königlich Preußischen Akademie der Wissenschaften* (Royal Prussian Academy of Sciences). Figure 2 is a photography made during this celebration.[50] The American biochemists Benjamin Harrow (1888-1970) inserted this photo on the one of first pages of his book entitled *Eminent Chemists of Our Time.* He also wrote that it "showing several eminent chemists was taken at one of the international scientific gatherings."[51]

Figure 2. Ladenburg with the group of the prominent chemists (Public domain, from reference 50).

Photograph was published by Harrow thanks to the kindness of the Dutch chemist Ernst Julius Cohen (1869-1944).[52] Ladenburg is first from the left in the second row; to his left are the Danish chemist Sophus Mads Jørgensen (1837-1914), the Finnish chemist and historian of chemistry Edvard Hjelt (1855-1921), the German chemist Hans Heinrich Landolt (1831-1910), the German chemist Clemens Alexander Winkler (1838-1904), who discovered germanium in 1886, and T. E. Thorpe. Seated from the left to right in the front row are the Dutch chemist Jacobus Henricus van't Hoff (1852-1911), who won the Nobel Prize in Chemistry in 1901, the Russian – German chemist Friedrich Konrad Beilstein (1838-1906),[53] the Scottish chemist William Ramsay (1852-1916), who found neon, argon, krypton, and xenon in air and was awarded the Nobel Prize in Chemistry in 1904, the Russian chemist D. I. Mendeleev, who discovered the Periodic Law in 1871, the German chemist Adolf von Baeyer (1835-1917), who received the Nobel Prize in Chemistry in 1905, and the Italian chemist Alfonso Cossa (1833-1902).

Harrow in the further part of his book described certain incident, which happened during banquet given by the organizers in this occasion and involving Ladenburg. "In 1900 the Prussian Academy celebrated its two hundredth anniversary, and the University of Petrograd sent Mendeléeff as its delegate. At the banquet van't Hoff presided over one of the side tables, with Ladenburg (the Breslau representative) to the right, and Mendeléeff to the left over him. Mendeleéff was an inveterate smoker, and simply chafed because he could not smoke alternately. Ladenburg tells us that immediately after the soup Mendeléeff began to pump those around him as to whether he could be allowed to smoke. They answered him that was out of the question. But he repeated his question after the first, and after the second courses. Then dear old van't Hoff, who hated to see anyone suffer so, stepped in with the risky suggestion that he also would join in a smoke. And the two went to it, to the great relief of Mendeléeff, who from then on proved an enjoyable companion. But the sad side of the incident was that van't Hoff, who had begun to show incipient signs of tuberculosis, had been expressly forbidden smoking."[54]

3. LADENBURG'S WORKS

The list of works published by Ladenburg includes 276 papers and books published over forty-seven years from 1865 to 1912.[55] The majority of these are the articles presenting the results of his experimental works, published in *Berichte der deutschen chemischen Gesellschaft* as well as in other German, French and British journals. Among them are his original articles devoted to the problems of the isomerism of benzene derivatives,[56] the researches on organic compounds of tin,[57-59] the studies of ozone,[60-66] as well as accurately determination of the atomic weight of iodine.[67-68]

A large number of the results of the experimental research carried out by him were published in *Justus Liebigs Annalen der Chemie, Zeitschrift für angewandte Chemie* and *Journal für praktische Chemie*. A few his articles were published in French in *Comptes Rendus Hebdomadaires Des Séances De L'Académie Des Sciences* and *Annales de Chimie et de Physique*. One of his articles entitled *Contribution to the characterisation of racemic compound*s was published in the *Journal of the Chemical Society, Transactions* in 1899.[69]

His first paper in the field of organic chemistry entitled *Eine neue Methode der Elementaranalyse* (A New Method of Elemental Analysis) was published in 1865. There he described the results of several experiments, for instance, with naphthalene and with diethyl ether.[70] At the end of an article (p. 24), written in February 1865 in Heidelberg, he wrote thanks to Carius for making it possible to carry out experiments in his laboratory: "Finally, I would like to express my thanks to Professor Carius, in whose laboratory the experiments described have been carried out, for his assistance, which he has given me very generously."[71]

In the Kekulé's laboratory, he carried out two studies on benzene derivatives, the results of which were published in 1866, one on *Synthèse de l'acide anisique et de l'un de ses homologues* (Synthesis of Anisic Acid and One of its Homologues) and the other in collaboration with Fitz called *Sur quelques dérivés de l'acide paroxybenzoïque* (On Some Derivatives of Paroxybenzoic Acid).[72-73] In the same year, from the Wurtz's Laboratory, he published with Carl Leverkus (1804-1889) a paper entitled *Sur la constitution de l'anethol* (On the Constitution of Anethol).[74]

In the years 1866-1867, he and Friedel published several papers with the results of studies of the structure of aromatic hydrocarbons,[75-76] and organic silicon compounds such as mixed silico-acetic anhydride,[77] silicochloroform,[78] and silicon chloroitydrosulphide.[79] One of the studies was devoted to revealing the analogy between carbon and silicon.[80]

The experimental work of Ladenburg and Friedl was continued also in the years 1868-1870. The fruits of this collaboration were a three papers *Ueber das intermediäre Anhydrid von Kieselsäure und Essigsäure* (About the Intermediate Anhydride of Silicic Acid and Acetic Acid),[81] *Einige Derivate des Radicals Silicoallyl* (Some

Silicoallyl Radical Derivatives),[82] and *Sur l'acide silicopropionique* (On Silicopropionic Acid).[83]

Ladenburg's research interests also focused around synthesis of alkaloids. In 1879, he carried out the artificial production of atropine ($C_{17}H_{23}NO_3$),[84] and in 1894, he and M. Scholtz synthesized piperic acid ($C_{12}H_{10}O_4$) and piperine ($C_{17}H_{19}NO_3$), which was the main alkaloid of black pepper.[85] In 1880, he also isolated hyoscyamine ($C_{17}H_{23}NO_3$),[86] and hyoscine ($C_{17}H_{21}NO_4$) also called scopolamine.[87]

In 1886, he for the first time synthesized in the laboratory an optically active compound identical with the alkaloid *coniine* ($C_8H_{17}N$) found in the hemlock plant.[88] Kipping wrote about this achievement of Ladenburg as follows: "The synthesis of *dl*-coniine, followed by the resolution of the synthetic alkaloid into its optically active components, the culminating point of these researches, was perhaps the greatest of Ladenburg's successes."[89]

At a time when the Kekulé formula for benzene was the subject of much controversy,[90-91] Ladenburg 152 years ago, in 1869, proposed a triangular prism structure for the molecule of this compound,[92-93] that was symmetrical, but didn't contain double bonds, and turned out to be erroneous.[94] In 1876, he summarized his views on the structure of the benzene molecule in his book entitled *Die Theorie der aromatischen Verbindungen* (The Theory of Aromatic Compounds).[95] Thirty-five years later, an anonymous author wrote: "His prism formula for benzene, although now practically universally rejected, has been of great use in the development of chemistry in that, as early as 1868, it showed the necessity of taking into account steric considerations in the formulation of the constitution of chemical compounds."[96]

Experimental studies carried out in the 1970s confirmed that Ladenburg prism can be obtained in the laboratory. In 1973, a pure sample of "the simple molecule C_6H_6, known as prismane [tetracyclo[2.2.0.0^{2,6}.0^{3,5}] hexane], in which six carbon-hydrogen units are disposed at the corners of a triangular prism", was synthetized by the American organic chemists Thomas J. Katz, and Nancy Acton from the Department of Chemistry at Columbia University.[97]

The chemical literature review results indicate an interest in Ladenburg's works, for instance, information about some of his articles appeared in the *Gazzetta Chimica Italiana* in 1872.[98] His experimental studies and their results were introduced to readers, among others by Ed. Willm and Maurice Hanriot (1854-1933) in 1889,[99] H. E. Roscoe and Carl Schorlemmer (1834-1892) in the years 1888-1890,[100-102] Julius Wilhelm Brühl (1850-1911), E. Hjelt, and Ossian Aschan (1860-1939) in 1900,[103] Amé Picket (1857-1937) in 1904,[104] as well as Hans Meyer (1871-1942) in 1916,[105] and 1922.[106] In the 1960s, the results of selected Ladenburg studies in the field of organosilicon chemistry were discussed by Richard Müller from Institute for Silicone and Fluorocarbon Chemistry in Radebeul/Dresden (Germany).[107] At the beginning of the 21st century, these results were presented by Dietmar Seyferth from Department of Chemistry at Massachutets Institute of Technology (U.S.A.).[108]

4. OTHER WORKS OF LADENBURG IN CHEMISTRY

Ladenburg, at the age of 27, became famous for his book on the history of chemistry. It was published first in German and later in three other languages. In 1869, the first edition of his *Vorträge über die Entwicklungsgeschichte der Chemie in den letztem hundert Jahren* (Lectures on the History of the Development of Chemistry Over the Last Hundred Years) was published in Braunschweig.[109] One year later, the German chemist Hermann Kolbe (1818-1884) praised this book in his article published in the *Journal für Praktische Chemie*.[110-111] He wrote as follow: "Far from wanting to give a truthful, strictly scientific development of the chemical theories (which task young Ladenburg ... has recently undertaken with seriousness and diligence...)."[112]

The fourth German edition of this book appeared thirty-eight years later under the title *Vorträge über die Entwicklungsgeschichte der Chemie von Lavoisier bis zur Gegenwart* (Lectures on the History of Chemistry from Lavoisier to the Present Day). He dedicated the book from this edition to his wife.[113]

In 1900, the first English edition of Ladenburg's book was published with the title *Lectures on the History of the Development of Chemistry since the Time of Lavoisier*.[114] The revised editions of this book appeared in 1911.[115] The translator was the chemist Leonard Dobbin (1858-1952), lecturer on Chemical Theory and assistant in Chemistry at the University of Edinburgh.

In the preface to the English Edition of this book written in September 1899 in Grassendale, Southbourne-on-Sea, Ladenburg wrote: "Thirty years after the appearance of the first edition of this book, an English translation of it is now being prepared. I regard this as a favourable indication of the permanent value of the book, since it is evident that the standpoint then adopted is intelligible at the present day and is still unsuperseded. Moreover, it may be concluded that the exposition of the subject is not marred by national prejudices. … The English edition is a faithful translation, and, so far as I am able to judge, it is written in a good style. For these features my best thanks are due to the translator."[116]

The first French edition of Ladenburg's *Histoire Du Développement De La Chimie Depuis Lavoisier Jusqu'à Nos Jours* (Lectures of the Development of Chemistry from Lavoisier to the Present Day) was published in 1909,[117] and the second, in 1911.[118] The translator was Arthur Corvisy (1855-1930), associate professor of physical sciences at the *Lycée Gay-Lussac* and *Professeur Suppléant* at the School of Medicine and Pharmacy.

In 1917, the first Russian edition of his *Lektsii po Istorii Razvitiya Khimii ot Lavuaz'ye do nashego vremeni* (Lectures on the History of the Development of Chemistry from Lavoisier to our Time) was published in Odessa. The translator of the fourth German edition of this book was Evgeny Semonovich Elchaninov (1879-1922), privat-docent of the Novorossiysk University.[119]

In the years 1882-1895, Ladenburg worked intensively on his *Handwörterbuch Der Chemie* (Concise Dictionary of Chemistry), which was published in thirteen volumes in Breslau.[120-121] The general register created on the basis of the registers of individual 13 volumes of this book was published in 1896. Among the co-authors are the names of 50 chemists who participated in the creation of this great work in different years during of thirteen years.[122]

One of Kekulé's works was published by Ladenburg in 1904 in the *Ostwalds Klassiker der Exakten Wissenschaften* series.[123] In the years 1907-1910, three papers written by French chemists Louis Pasteur (1822-1895),[124] Wurtz,[125] and Berthelot and Léon Péan de Saint-Gilles (1832-1863)[126] were translated from French into German by Ladenburg and his wife and published in the same series.

5. CONCLUSION

Albert Ladenburg was one of the prominent chemist of the second half of the XIX century. In the years 1880-1910, he was elected a member of three academies of sciences. He became a member of the *Nationale Akademie der Wissenschaften Leopoldina* in 1880.[127] He was elected a corresponding member of *the British Association for the Advancement of Science* in 1887,[128] and the *Académie des sciences de Paris* on December 13, 1909.[129] On January 6, 1910, he became a corresponding member of the *Königlich Preußischen Akademie der Wissenschaften*.[130] He was a corresponding member of *the Philadelphia College of Pharmacy*.[131] On April 26, 1892, he became an honorary member of *the Manchester Literary and Philosophical Society*,[132] and on August 4, 1884, he was appointed Doctor *honoris causa* of Medicine at the University of Bern. On February 2, 1888 he became an honorary and foreign member of *the Chemical Society of London*.[133] In the years 1901-1911, he was a foreign corresponding member of the *Académie Nationale De Médecine* in Paris.[134]

In 1899, *the Pharmaceutical Society of Great Britain* awarded him the Hanbury Gold Medal for his work on alkaloids and their derivatives.[135] It is awarded every five years, in memory of the British botanist and pharmacologist Daniel Hanbury (1825-1875). "The medal was formally received by Baron [Wilhelm] von Mirbach [(1871-1918)], representing the German Embassy, and a letter was read from Dr. Ladenburg expressing his thanks for the honour done him, and regretting that he had been unable to be present to receive the medal personally."[136]

In 1905, he was awarded the Davy Medal "for his researches in organic chemistry, especially in connexion with the synthesis of natural alkaloids."[137-138] It is named after the English chemist Humphry Davy (1788-1829) and is awared annually since 1877 to an outstanding researcher in the field of chemistry by *the Royal Society of London*.[139] Two years later, in 1907, he nominated Berthelot and Mendeleev for the Nobel Prize in Chemistry.[140] However, the award went to the German biochemist Eduard Buchner (1860-1917) "for his biochemical researches and his discovery of cell-free fermentation."[141] Later, in 1909-1911, he worked at the University of Breslau.[142]

After Ladenburg, not only his papers and books survived. In addition, several of his portraits were produced. One of them was included by the German chemist Richard Anschütz (1852-1937), professor of chemistry at the University of Bonn, in his biographical book on Kekulé.[143] Three other photo appeared in the articles written by Herz,[144] Kipping,[145] and Colin Archibald Russell (1928-2013).[146] The photographer Adèle Perlmutter (1845-1941) from Vienna photographed him in 1869,[147] and in the years 1870-1880 his portrait was taken by a photographer Emil Bühler in Mannheim.[148] Another two of his portraits can be found in the *Österreichische Nationalbibliotek* collection,[149] and in a book written by the American chemist Henry Monmouth Smith (1868-1950).[150]

In 1911, the 100th Anniversary of the Royal University of Breslau was celebrated. On this occasion, a book entitled *Festschrift zur Feier des hundertjährigen Bestehens der Universität Breslau, Zweiter Teil, Geschichte der Fächer, Institute und Ämter der Universität Breslau 1811 – 1911* was published, in which one of the chapters written by Ladenburg and Buchner was devoted to the history of the Institute of Chemistry at the University. The authors also presented short biographical notes of chemists who obtained their habilitation there.[151]

The great achievements of Ladenburg in the field of alkaloids synthesis were noticed by English pharmacists. On October, 1899, William Martindale (1840-1902), President of the Pharmaceutical Society of Great Britain said about it: “Dr. Ladenburg was best known to English pharmacists by his synthetic work in the production of homatropine.[152] By splitting up atropine he obtained tropic acid and tropine as derivatives; the latter he combined with amygdalic acid to form a compound which is easily converted into oxy-toluyl-tropeine or homatropine, an artificial alkaloid which, with its salts, has proved of the greatest service to ophthalmic surgery.”[153]

Walter Herz wrote about Ladenburg’s great achievements in chemistry as follow: “Like only a few, Ladenburg has been granted forty years of great success in developing his science. His contributions to the constitution of benzene, his investigations into the heterocyclic compounds, his successes in the synthesis of alkaloids will always be regarded as classic examples of great chemical achievements. His uncommon scientific versatility was evident in his work on racemy, his excellent treatises on ozone and iodine, and his critical-historical perspective in his valuable history of chemistry.”[154]

It is worth emphasizing that Ladenburg was put “in the first rank of chemists as a theorist.”[155] Moreover, he was not only an experienced experimental chemist, but also an excellent pianist. His acquaintance with the great German pianists and composers such as Clara Schumann (1819-1896) and Johannes Brahms (1833-1897) began at his young age.[156] In a letter written to Schumann in Ischl, a city in Austria in June 1895, Brahms informed her about the meeting with Ladenburg: “... Professor Ladenburg from Breslau spent the Whitsun holidays here with his wife, we were very cozy together and talked a lot about you.”[157]

This outstanding German chemist and historian of chemistry took forever a firm place in the history of chemistry. His name is associated with the beginning of intensive research in the field of organic synthesis. The results of his original experimental studies have been published in scientific journals in Germany, France and Great Britain. His *Vorträge über die Entwicklungsgeschichte der Chemie* has been published many times, not only in Germany but also in Great Britain, France and Russia. His multi-volume dictionary *Handwörterbuch der Chemie* has served many generations of chemists around the world. His name is given to “a distilling flask with bulbed neck”, the so-called *Ladenburg flask*.[158] For example, one of its varieties is a flask with three-bulb.[159]

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Book Review

Review of "Ethics of Chemistry: From Poison Gas to Climate Engineering" by Joachim Schummer & Tom Børsen, eds. World Scientific Publishing, Singapore, 2021

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BRINGING THE ETHICS OF CHEMISTRY TO THE CLASSROOM AND THE EXISTENCE OF A DOMAIN OF KNOWLEDGE

Whoever has attempted to bring ethical discussions on chemistry to a student audience of chemistry and related fields knows of the problem: in contrast to the relatively robust bioethical literature, the literature of chemical ethics is poor, disconnected, and scattered all around the place even in rare cases that it exists. This is an interesting fact, especially if one considers the extended moral (and moralist) discussions over chemistry and its products, and that a great part of the bioethical challenges of the last forty years or so have been generated not by biology (or medicine) per se, but from their marriage to chemistry and its practices. The lack of ethics of chemistry literature dictates to the lecturer unprecedented levels of creativity and demands extra workload to be effective –and this, in times where ethics courses, in general, have become a necessity. It is this gap that the editors of this book (Schummer and Børsen, Ethics of Chemistry: From Poison Gas to Climate Engineering, World Scientific, 2021) have detected, and they strove to create a collection of case studies to cover it. In the introduction of the volume, the editors state teaching as the first aim of its existence –and add the establishment of the ethics of chemistry as an autonomous discipline in its own right.

While the first aim of the book is quite effectively achieved, the second remains wanting at the end –not by fault of the editors or the contributors, but due to the current external conditions of the selected domain of knowledge. The problem introduced in the introduction as the quest for the ethics of chemistry remains unresolved in the whole volume because it is rather fundamental. Due to the chronic underdevelopment of the ethics of chemistry, substantial living space has been taken over by other "ethics" and their discourses. Even in cases where the basic underdetermination of new chemical substances is what is causing the moral issue, the reader cannot avoid

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thinking of these cases in terms of bioethics, ethics of technology, business and corporate ethics, or simply issues of public policy and law. Establishing the ethics of chemistry as a domain in its own right demands nowadays more than just offering cases where chemistry is the moral protagonist; calls also for a demonstration that chemistry is the primal and decisive protagonist, both on the level of problem and remedy –that the cases can and should be treated on this level.

In the intro of the volume, Schummer and Børsen do offer a brief introduction to ethics and ethics of chemistry (stressing the contrast with the ethics *in* chemistry), present their chosen classification of the subjects covered, and suggest how their volume should be used in the classroom. Their introduction to philosophical ethics is quite appropriate for the intended audience –undergraduate students of chemistry and related fields and, maybe, beginner teachers –and is well written and informative. Similarly, the categories in which the included studies are separated (Misuse and Misconduct, Unforeseen Local Consequences, Global and Long-Term Influences and Challenges, Challenging Human Culture, and Codes and Regulations) seem well thought and wisely chosen. What is however missing, is the crucial sub-chapter that would help the teacher justify the "ethics of chemistry" category of knowledge to the students –as opposed to bioethics, ethics of technology, business ethics, or just politics. The reply to the question "why ethics of chemistry, and not something else" could have been maybe articulated historically and philosophically. A short section of the introduction could explain to the reader that the wish-to-transform characteristic of our civilization, the wish-to-enhance and the means to do these, could be viewed as inheritances of alchemy and early chemistry, establishing thus the primacy of chemistry and its ethics vis-à-vis biology and industry (indeed almost as one of the editors does in later chapters). It´s not articulated in the introduction, however, and it is left somewhat hanging also in most of the 18 (otherwise superb) contributions. The editors opt instead for a short cultural history of chemistry (useful as an alternative organizing sub-chapter and principle for the essays), which does demonstrate why chemistry has a relatively bad name among the public –but not why it should have its own autonomous ethics discipline.

The ghost of this problem of living space for ethics of chemistry is haunting the greatest part of the book, more apparent in some cases and less in others. When presented with the emblematic case of thalidomide, for example, students tend to deal with it in terms of clinical trials and regulations, even though the issue had indeed been created by chemical underdetermination. The treatment of the subject by Ruthenberg in Chapter 6 is historically accurate and ethically solid, but, in the end, the reader is left with the impression that the average student is right to perceive the subject as one of medicinal ethics and public policy –and not primarily as a chemistry story. When presented with the Agent Orange story in the classroom, students tend to deal with it as a case involving primarily company and government. Jacob and Walters offer an excellent piece on Agent Orange in Chapter 7, discussing the responsibility of the chemist at the point of invention, and deploying Scummer´s older argument that, since the first synthesis is the causal step for the existence of a substance, the chemist is somehow responsible for it. And yet, it is clear (and visible to most students) that this attribution of responsibility – even without moral judgment – would be practically ineffective and even have adverse effects in the production of new chemical substances. Since a synthetic chemist wouldn´t know the adverse effects of a substance at the point of invention, and since these effects can be wholly investigated by a multitude of researchers of different fields (inside the company, or generally after publication, which, yes, means proliferation, but transparency too), the subject becomes once again an issue of company and government (the latter argument is appropriated from a student assignment of the year 2016, to make a point). Similarly, while a chemist might as well participate in the steering of a company (indeed historically, chemists were more often also businesspeople than any other scientific group), the decisions of a company are more often treated by business ethics and law than anything else. This is even admitted on the very title of Chapter 5, by Eckerman and Børsen on the lessons from Bhopal. Are such cases, cases in ethics of chemistry? If yes, it has to be demonstrated how, and why.

Thankfully, the case for an ethics of chemistry becomes clearer and more persuasive in other chapters of the book. The piece of Schummer on "chemists playing god" (Chapter 16) and the ambitions to create artificial life is significantly closer to mark in the quest for ethics of chemistry since it establishes the historical background linking current bio-scientific practices (and hopes) to chemical and alchemical views of centuries before, as well as the link of the current reactions to chemical products to religious views of the past. Such argumentation would have been of use in the introduction too –establishing chemistry as ethically and historically more fundamental than either biology or industry. Schummer´s piece again on the ethics of chemical weapons research (Chapter 3) does offer a case where the aforementioned responsibility at the point of the invention makes absolute sense: it is indeed involving a chemical decision and leads not only to the attribution of responsibility but also to heavy moral judgment. Contakes and Jashinsky follow a similar path in their contribution concerning the case of napalm and their criticism of the "just" war thinking (Chapter 4). That the two pieces are related to chemical warfare has of course something to do with their clarity of argument and effectiveness: weapons research is one of the few domains where the chemist knows beforehand (or, at least has good reasons to suspect, unless of course, he is too naïve) the aims, purposes, and potential uses of the substances that he or she is synthesizing –having thus clear responsibility for their existence and effects. However, the careful reader might become a bit uneasy reading exactly these cases –at least, if the subject of establishing an ethics of chemistry is dear to him or her. Do these stories mean that autonomous ethics of chemistry is possible only in a few special cases where the chemical underdetermination is canceled by the explicit a priori stating of the aims of the research?

On the level of creating a useful collection of case studies and essays for the classroom, the volume is absolutely and straightforwardly successful. The introduction offers all the basic knowledge that would be necessary to a student for an early engagement with the subject of ethics: basic philosophical terms are clarified, applied ethics is introduced, and the material of the book is logically and usefully organized. While the chapters form units, they can be read fully independently from one another –a characteristic that would make this volume extremely useful to every teacher. Furthermore, the cases are arranged in more than one way (a fact well thought to satisfy different categories of teachers or different types of courses): they can be viewed as cases according to topics, cases according to the cultural history of chemistry, and cases according to the fields of chemistry. It is imaginable that thus the volume might be of use also for students far removed from the study of chemistry –even for students of the humanities that might want to learn more about the moral challenges presented by the practice of one of the most transformative crafts of our (post-)modern world.

To this latter purpose, the part of the volume concerning the cases where chemistry is challenging human culture might be crucial. Admittedly, there could have been more chapters included here –both for interested chemists and non-chemists. After all, it is chemistry that it is about, and it is hardly impossible to think of another discipline that has been more challenging, improving and disrupting, to the human routines the last two centuries (to the point that, in most European languages, the word "chemical" is commonly deployed as the opposite of the word "natural"). As it is, the section contains three contributions: the "playing god" of Schummer (Chapter 16, mentioned already), Vishnubhakat´s "normative molecule" concerning patents and DNA (Chapter 17), and Birkholm´s Ethical Judgement on chemical psychotropics and nootropics (Chapter 15). Vishnubhakat does an elaborate job in presenting a case study of the Myriad Genetics lawsuit (a case that had caused noise concerning who can patent what and to what extent in the biotech and medical genetics world and is often discussed in bioethics courses and, presumably, in intellectual property courses). He demonstrates clearly how and why DNA is a special case, and why the application of patent legislation and norms of property might cause significant complications (the extended experience of the author in chemistry, law, and patents makes for an excellent read). At the end of the piece, however, the reader is left with the question of whether the special position of the DNA in the chemical ontology, makes it indeed a too special case.

Birkholm on the other hand presents an interesting case on chemical psychotropics applying his three-step model to raise the question of responsibility for their effect on population and culture. The broad, captivating, and well-informing piece is examining a serious issue with potentially disturbing social repercussions: psychotropics´ use has expanded through the years, leaving the domain of traditional treatments and colonizing everyday life, in dangerous and culture-altering ways. Indeed, it could be even claimed that psychotropics and nootropics cannot even be classified as pharmaceutical substances anymore. They are instead means of enhancement, intervention, and standardization (which is almost to be expected in a culture so focused on the "realization of one's potential" and "self-invention"). The return to Aristotle´s Epistēmē and Phronēsis, with Phronēsis being the most valuable of the intellectual virtues, had been an appropriate return to the Greek roots of ethics, and most welcome, and the proposed three-step model seemed useful. Still, however, the expansion of the pharmaceutical companies´ responsibility for the problem examined, to the individual employees of these companies left some argumentation to be desired (especially since it was built up by an analogy to the individual accomplices of the Third Reich).

The sections of the volume that would be of immediately visible value to students of chemistry were of course those involving misuse and misconduct (first thematic section, chapters 2-4) and codes and regulations (last thematic section, chapters 18-19). The first section contains the two pieces on chemical weaponry (discussed earlier) and a piece of Stemwedel on scientific misconduct. She chooses to present a fictional case ("the case of the Finicky Reactions", which has however tantalizing similarities to known real cases) to be able to control the setting, the conditions, and the known variables of her case. Her strategic choice proves correct (indeed, the narrative of real cases of misconduct can never be complete: the perpetrators have no motive to share their information with ethicists), and offers the reader an ethical chapter that reads as good prose. That at the end of each part of the drama, the reader is confronted with the appropriate ethical questions has an excellent teaching effect. The ethical analysis of the drama is complete and well written, ideal for students of science (and the fact that the protagonist of the story is called Anna Bijou can be taken to be a bonus to the reader). For teaching purposes, it would be helpful if this particular section of the volume had a bit more weight, and contained a couple of scientific misconduct cases more, similar to the one of Stemwedel. Similarly, the section of codes and regulations would have benefited from some case studies of relevant controversies and violations and their treatment.

Concluding this review, it should be stressed that this book constitutes a step forward on both fronts that its editors stated as aims. On the front of creating teaching material for classes on ethics of chemistry, it comes to fill an unquestionable gap, collecting high-quality pieces that would function pedagogically with a broad array of students. It is imaginable that chapters of this book will find their way into classes of ethics of chemistry, corporate ethics, history of science, cultural studies of science, science and society courses, climate science, law, and, of course, philosophy of science; and that is a major strength of this volume. On the other hand, this very strength on one front brings with it a weakness on the other. The very fact that the volume can be useful so broadly, and far away from chemistry and its students, demonstrates a problem of breathing space for the domain of ethics of chemistry. Historically, there is always a time lag between the naming of a new disciplinary domain –which constitutes a claim of existence –and the actual recognized existence of it, in academic circles and beyond. In the between, the discipline has to grow, achieve its means of communication and vocabulary of expression, and receive an organizational structure –and the ethics of chemistry is not there yet. It is of vital importance however that ethics of chemistry does indeed get there (even as a latecomer), and this volume is a step in the right direction. Meanwhile, and until the ethics of chemistry gets there, I know that I´ll be using this Ethics of Chemistry in my courses.

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