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Editorial

Superbugged

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We thought that with the decline of the Covid-19 pandemic the worst had gone and that we could go back to normal life, maybe keeping one eye open on the evolution of the virus variants from time to time. Suddenly almost any news on TV about the pandemic has disappeared.

But we are not aware of the threatening risk of a super-pandemic for which we won’t have powerful weapons: antimicrobial resistance (AMR).

The phenomenon is well known in the scientific community but citizens are not informed that they can play a crucial role in avoiding this disaster.

Briefly, bacteria produce natural antibiotics to fight against other strains, and some develop resistance. When we use antibiotics without a real need, they kill good and bad bacteria, but those that develop resistance are free to proliferate. AMR can be transferred to deadly pathogens and we will not have any tool to control or limit infections. At the end, humans will not have efficient bullets against superbugs as they will have already mutated and become resistant to the most powerful antibiotics.

We (humans) are responsible for AMR. The wrong use of antibiotics is a common practice all over the world, in all countries. Often people take these drugs even in the case of diseases that are not related to bacteria, e.g. cold, flu and other infections like dengue and malaria. In other cases the patient stops assuming the antibiotic before the sickness and the infection are totally eradicated, with a potential relapse of the illness. We must not forget that expired antibiotics are often dispersed in the environment and not disposed of in the proper way.

Another terrific source of AMR comes from large livestock farms, where the animals are administered huge amounts of antibiotics to “improve” their health. While urban sites possess sewer ducts to collect waste waters and bring them to the treatment plants, the waste waters in animal farms are dispersed in the soil and can reach the groundwater streams without any control. In general, AMR in soils represents a serious risk to human health through the food chain and human–nature contact.[1]

Some data.

A recent World Health Organization (WHO) document reports high levels of AMR in 87 countries in 2020. The study concerns both bacteria that cause infections in the bloodstream, for example *Klebsiella pneumoniae* and *Acinetobacter spp* that become insensitive to carbapenems.[2] The same phenomenon occurs with more common bacteria, in fact more than 60% of *Neisseria gonorrhoea* isolates, a common sexually transmitted disease, have shown resistance to ciprofloxacin and more than 20% of *E.coli* isolates – the most common pathogen in urinary tract infections – became resistant to first-line drugs (ampicillin and co-trimoxazole) and to second-line treatments (fluoroquinolones).

In the past four years most AMR trends have remained stable, but bloodstream infections due to resistant *Escherichia coli* and *Salmonella spp.* and resistant gonorrhoea infections increased by at least 15% compared to 2017. More research is needed to identify the reasons behind the observed AMR increase and to what extent it is related to raised hospitalizations and increased antibiotic treatments during the Covid-19 pandemic.

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Antibiotics continue to be prescribed for diarrheal diseases and upper respiratory infections for which they have limited value.

During the chaotic treatment of Covid-19, patients were treated with antibiotics which resulted in more adverse effects.

A recent study carried out at the Indian Council of Medical Research showed that out of about 17,000 patients in Indian hospitals, more than half of them who acquired drug-resistant infections died.[3] The problem is extremely serious and is affecting Western countries as well.

In spite of all these warnings, broad-spectrum antibiotics – i.e. drugs that should be reserved for tackling the hard-to-treat bacterial infections – represent 75% of all prescriptions issued in India's hospitals.[4]

Of course, the environmental regulations that every single country adopt (or should do so) play another crucial role. Recently it was reported that several big pharmaceutical industries delocalized their plants in China and in India for the production of antibiotics, including the generic brands. Well, it was found that – astonishingly – the industrial waste waters carrying antibiotics and byproducts discarded their junk in the same stream where untreated raw sewage was released! Nobody could ever build a better bioreactor for the production of antibiotic resistance bacteria! In this case the responsibility of the companies to press and obtain from the governmental agencies the respect of the procedure to properly treat the industrial and urban wastes is clear.[5]

Even more recently scientists confirmed or realized that other chemicals can induce resistance in pathogens. This is the case of cationic surfactants,[6,7] often used as antimicrobial agents for example in household detergents, and antidepressants.[8]

The goal of this brief document is to recall how the problem is serious and to show that it must be treated efficiently and rapidly.[9]

The next (super)pandemic has already been announced, the perfect storm is approaching.

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Research Article

Equivalence of Electromagnetic Fluctuation and Nuclear (Yukawa) Forces: the π_0 Meson, its Mass and Lifetime

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Abstract. It is shown how Maxwell's equations for the electromagnetic field with Planck quantisation of allowed modes appears to provide a semiclassical account of nuclear interactions. The mesons emerge as plasmons, collective excitations in an electron positron pair sea. The lifetime and mass of mesons are predicted.

Keywords: Casimir-effect, Meson-theory, positron-electron-plasma, lifetime.

1. ELECTRODYNAMIC FLUCTUATION FORCES.

Feynman is reported to have believed that there had to be a connection between electromagnetic theory and nuclear forces. [1]. He never found such a link. It is shown how such a connection might come about.

1.1 Historical Background: Where Do Mesons Come From?

A hundred years ago Rutherford's team at Cambridge had shown that the atomic nucleus was comprised of protons and neutrons. The particles had a mass, 2000 times that of an electron ; protons were positively charged. A neutron could transform into a proton and a negatively charged electron. Electrostatic forces played a role in the interactions between nucleons. But whatever other forces held them together remained a mystery [2]. Quantum mechanics in its various manifestations, from Planck, Sommerfeld and Bohr, Schroedinger, Heisenberg, Dirac; and later quantum electrodynamics promised insights. In 1935 Yukawa had came up with a characterisation of this so called “weak nuclear interaction” that worked. The force was mediated by “particles” called mesons, mass 273 times that of an electron and variously charged. They were detected from cosmic ray decay by Powell in 1937. There were μ and π and later bigger K mesons. Particle physics developed subsequently culminating in the prediction of Higgs unifying boson. But the fundamental physics embodied in Maxwell’s equations for the electromagnetic field and quantum mechanics seemed to have nothing much to do with it. Somehow something was apparently missing. The electromagnetic forces seemed too small. But protons and electrons were charged. The mystery and disjunction remained.

1.2 Theory in Words Without Equations

The classic paper of Casimir in 1948 [3] on relativistic effects on the attractive forces between colloidal particles was motivated by, and applied to the newly developed Deryaguin-Overbeek theory of Colloid stability. Overbeek had posed the problem of these ”retardation” effects to his friend Casimir in Utrecht (BWN private communication with Overbeek). Casimir derived the forces due to quantisation of zero temperature electromagnetic fluctuations in the vacuum between two ideal metal plates. It stimulated a huge literature that still flourishes. It seemed to bear on our problem. But it could not due to its limitation to zero temperature. This and the term retardation are incorrect and unphysical [4-6].

Further insights into the nature of the electromagnetic vacuum had to wait on the development of Lifshitz theory for interactions between and across dielectric media [7] and included temperature. This theory at time appeared to be the culmination and triumph of quantum electrodynamics. It had been foreshadowed by P. N. Lebedev who discovered light radiation pressure. He was a friend of J. Clerk Maxwell and the stepfather of Deryaguin. Deryaguin had asked Lifshitz to work on the problem. In 1894 Lebedev wrote: ”If the solution of this problem ever becomes possible we shall be able, from the results of spectral analysis, to calculate in advance the values of the intermolecular forces due to molecular inter-radiation, deduce the laws of their temperature dependence, and, by comparing the values obtained with experimental results, solve the fundamental problem of molecular physics whether all the so-called ’molecular forces’ are confined to the already known mechanical action flight radiation mentioned above, to electromagnetic forces, or whether some forces of hitherto unknown origin are involved” as quoted by Deryaguin [8]. However the triumph was illusory. The generalisation of the Casimir effect involved some sleight of hand that approximated a non linear problem by a linear one [9].

This theory applied to Casimir’s two plate problem gives out automatically: the binding energy of two nucleons in nucleus in equilibrium and automatically replaces the problem by one with a virtual intervening electron positron pair sea with known density and therefore plasma frequency of excitations. The renormalisation is identical to the Klein Gordon equation for scalar mesons with mass identified from the plasma frequency. The implication is that positive and negatively charged π mesons are identifiable with bound electron-plasma and positron-plasma excitations. And what used to be called K mesons are higher order double plasma excitations known from solid state physics. What is quite new is that the identification of the scalar π_0 meson with a collective excitation in the electron positron sea allows us to calculate its lifetime, correctly. Taken together, binding energy, scalar meson mass , and lifetime all seem to add plausibility to our case. The simplified version of Lifshitz theory we have used is the same Lifshitz theory at the foundations of physical chemistry, molecular and colloidal particle interactions in the DLVO theory. There the limitations due to the linearisation approximation are very clear. If the equivalence we have drawn is correct so too must present theories of particle physics.

1.3 We First Outline What We Mean by Electromagnetic forces

A 1961 paper of Dzyaloshinski, Lifshitz and Pitaevski [7] applied quantum electrodynamics to the problem of molecular forces. It extended earlier work on electromagnetic fluctuation forces between molecules and colloidal particles of Casimir and Lifshitz to include effects of an intervening medium between the interacting particles. This impressive advance turned out later to be flawed. An approximation made in the derivation meant that the formidable mathematical formalism collapsed to a semi-classical theory. By this we mean Maxwell’s equations with boundary conditions and quantisation of allowed modes [6,9,10].

Technically the reason for this is that in the development of the theoretical formalism there occurs an integral equation for the polarisation operator that involves a non-linear coupling constant integration. An approximate solution can be found by linearising. The true polarization operator is then replaced by the macroscopic dielectric susceptibility. A detailed exposition can be found in Eq. 2.9 and Eq. 3.1 in Ref. [7].

2. THEORY

2.1 Model Assumptions and the Casmir Energy

We assume that the nucleons have a structure which involves electromagnetic forces somehow as protons have a positive charge and a magnetic moment. Then, how much of a role could electromagnetic forces play in nuclear interactions? Consider two nucleons. If the nucleons were perfectly reflecting spheres, calculation of the electromagnetic fluctuation forces would require an analytic solution of the Helmholtz equation. This is complicated [11,12]. So we simplify the model and approximate the nucleons by perfectly reflecting planes with the same cross sectional area as the (spherical) nucleons.

Then the attractive electromagnetic fluctuation energy of interaction (all energies in this work are given per unit area) across a vacuum at zero temperature is [3]

$$E = -\frac{\pi^2}{720}\frac{\hbar c}{d^3}. \tag{1}$$

Here d is the distance between the plates, $\hbar$ is Planck's constant and c the velocity of light. We take d to be the distance between surfaces of the protons. The effective surface area is $A=\pi r^2$, r=proton radius~0.8 fermi. A typical nucleon-nucleon surface to surface distance is of the order of one fermi. Then the available two nucleon-nucleon energy for binding in a nucleus from vacuum fluctuations is about 5 MeV. The implication is that there is enough electromagnetic energy available in the zero-point Casimir energy to account for nuclear interactions. The binding energy per nucleon varies in different atomic nuclei but is typically in the range from 1.1 MeV to 8.8 MeV.

2.2 Temperature Dependence of Electromagnetic Forces

The observation that the zero temperature Casimir vacuum fluctuation energy is enough to provide the binding energy of nucleons in a nucleus is suggestive. To take matters further we need to consider the effects of temperature. The Gibbs free energy extension of Casimir's result that does so is due to Lifshitz, it is [7,9,10,13],

$$G(d,T) = \frac{kT}{\pi}{\sum_{n=0}^{\infty}}' \int_0^\infty dq q ln\left[1 - e^{-2d\sqrt{q^2+\xi_n^2/c^2}}\right], \tag{2}$$

where k is Boltzmann's constant, T is temperature, q is the wavevector, and $\xi_n=2\pi nkT/\hbar$. The prime indicates that the zero frequency term carries a factor of one half. Explicitly, at small distances, or high temperatures, this has the expansion [14],

$$G(d,T) \approx \frac{-\pi^2\hbar c}{720 d^3} - \frac{\zeta(3)\,k^3\,T^3}{2\,\pi\hbar^2\,c^2} + \frac{\pi^2\,d\,k^4\,T^4}{45\hbar^3\,c^3} +.., \tag{3}$$

$\zeta(3)\approx 1.202$ is a zeta function. Here the first term is the attractive (zero temperature) Casimir result. The third term is the equilibrium black body radiation energy in the vacuum between the plates. It opposes the attractive Casimir term. Additional exponentially decaying terms are negligible in the regime of interest and have been omitted. Leaving aside the second term for the moment, we suppose that the first and third terms are equal at equilbrium. This then provides us with a temperature determined by the distance d between the two plates, $T=\frac{\hbar c}{2kd}$, at which the attractive and repulsive forces balance.

The Electron-Positron Sea

The second term, is a chemical potential term in the Gibbs free energy. We can recognise it explicitly as due to an electron positron pair sea formed from the photons in the gap by the reaction $e^{+}+e^{-}\leftrightarrow\gamma$ [15]. From the temperature at distance d we can calculate the density for this electron positron pair sea. As discussed by Landau and Lifshitz [15] the number of electrons and positrons are very nearly identical and both very large, even at temperatures of the order of mc^2. (An electron-positron plasma becomes more nearly perfect with increasing density so we can use perfect gas formulae and ignore correlations .)

The second term can then be re-written as

$$\frac{\zeta(3)\,k^3\,T^3}{2\,\pi\hbar^2\,c^2} = \frac{\pi(\rho_- + \rho_+)\hbar c}{6}, \tag{4}$$

where we use the expression for the density ($\rho=\rho_{-}+\rho_{+}=\frac{3\zeta(3)(kT)^3}{\pi^2\hbar^3\,c^3}$) of the electron-positron plasma [15]. The interpretation of the chemical potential term (the second term in Eq. (3)) is the key to the equivalence we seek.

2.3 Reformulation: the Klein Gordon Equation and Meson Mass

The imposition of a balance between the vacuum fluctuation and black body radiation forces has reformulated the problem to be that of an electromagnetic fluctuation force in which there are two metal plates separated by a medium. This medium, an electron-positron plasma, has the permittivity

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2}; \quad \omega_p^2 = \frac{4\pi(\rho_- + \rho_+)e^2}{m_e}, \tag{5}$$

where e is the unit electric charge and m_e is the mass of the electron. The electromagnetic fluctuation interaction energy between two perfectly conducting plates across a plasma can be derived from the equation for the scalar potential, in Maxwell's equations [9], which after a Fourier transform reduces to,

$$\nabla^2 \emptyset + \frac{\omega^2}{c^2}\left(1 - \frac{\omega_p^2}{\omega^2}\right)\emptyset = 0. \tag{6}$$

Yukawa [16] proposed that the nuclear interaction could be derived from the Klein-Gordon equation,

$$\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \nabla^2 + \mu^2\right)\emptyset_\pi = 0. \tag{7}$$

This equation has the solution $\emptyset_\pi \sim \pm \frac{g^2 e^{-\mu d}}{d}$ [16]. The range of the Yukawa potential is inversely proportional to the meson mass (m_π): $d_\pi = \frac{1}{\mu} = \hbar/(m_\pi c)$. One can proceed from this known relationship between d_π and m_π [2]. But, for later work on the lifetime it is useful to recall first the very basic physical assumptions used to relate the meson mass to the Yukawa decay length. As discussed by Wick [2], mesons act via emission and absorption processes of virtual excitations, and the time required for the excitation to travel between a pair of nucleons is of the order $\Delta t \sim \frac{d_\pi}{c}$. The relativistic energy, $\Delta E \geq m_\pi c^2$, obeys the Heisenberg uncertainty principle for energy [17]: $\Delta E \Delta t \geq \hbar$. These expressions for energy and time lead us to the required relationship: $d_\pi \cong \hbar/(m_\pi c)$.

The Klein-Gordon equation for Yukawa potential ($\emptyset$) after a Fourier transform may be cast into the form [16],

$$\nabla^2 \emptyset_\pi + \frac{\omega^2}{c^2}\left(1 - \frac{1}{\omega^2}\left(\frac{m_\pi c^2}{\hbar}\right)^2\right)\emptyset_\pi = 0. \tag{8}$$

We identify this equation with equation (6). Thus, we obtain after identification of Eq. (6) with Eq. (8)

$$\omega_p{}^2 = \frac{4\pi\rho e^2}{m_e} = \frac{c^2}{d_\pi^2} = \left(\frac{m_\pi c^2}{\hbar}\right)^2.$$

The meson mass follows as

$$m_\pi = \frac{2e\hbar}{c}\sqrt{\frac{\pi\rho}{m_e c^2}}. \tag{9}$$

This gives $m_\pi = 267 m_e$ in surprising agreement with the experimental result ($264 m_e$). We discuss this result further in section 3. In this scenario the charged π^- and π^+ mesons would emerge as electron-plasmon and positron-plasmon bound states.

2.4 Binding Energy of Nucleons Casimir-Lifshitz Theory

Returning to the model of Sec. 2.1, we have for the interaction of two perfectly conducting plates across an intervening plasma [14,18], the Gibbs free energy

$$G(d,T) = \frac{kT}{\pi}{\sum_{n=0}^{\infty}}' \int_0^\infty dq q ln\left[1 - e^{-2d\sqrt{q^2+\kappa^2+\xi_n^2/c^2}}\right], \tag{10}$$

where $\kappa = \omega_p/c$. For high temperatures at fixed separation, or large separation at fixed temperature, it follows [19,20] it has an expansion of the form:

$$G(d,T) = -\frac{kT\kappa}{4\pi}\frac{e^{-2\kappa d}}{d}\left[1 + \frac{1}{2d\kappa}\right] - \frac{(kT)^2 e^{-2\eta d}}{\hbar c}\frac{e^{-\rho^* \eta d}}{d} + O(e^{-4\eta d}), \tag{11}$$

where $\rho^* = \rho e^2 \hbar^2/(\pi m_e k^2 T^2)$, $\eta = \frac{2kT}{\hbar c}$ and κ is defined above.

Both the n=0 and n>0 terms behave similarly to the Yukawa potential [16]. Both provide a contribution to our model nuclear binding energy that agrees very well with the experimentally observed binding energy per nucleon. We will compare our theoretical results with the typical experimental results in Sec. 3.

2.5 Lifetime of Plasmons and Mesons

Our assumption is that at equilibrium the zero point fluctuation energies of the vacuum and the black body radiation energy cancel out. What is left are collective excitations, plasmons in the remaining electron -positron sea. These can be identified as pions. This allows us to estimate the lifetime of the meson. The lifetime is that for the decay of a plasmon into two electron-positron pairs [21]. These can decay to produce two photons. The theory of collective electron excitations plasmons is known. The broadening (ΔE) of the plasmon peak and its lifetime ($\tau \geq 1/\Delta E$) is known analytically and measured [22],

$$\Delta E \sim \frac{6\pi\varepsilon_F}{5\hbar}\left(\frac{q_\pi}{q_F}\right)^2\left(\frac{\hbar\omega_p}{2\varepsilon_F}\right)^3\left[10\ln(2) + 2 - 4.5\frac{\hbar\omega_p}{2\varepsilon_F} + O\left(\frac{\hbar\omega_p}{2\varepsilon_F}\right)^2 ..\right], \tag{12}$$

The entities involved are the Fermi energy ($\varepsilon_F \propto \rho^{2/3}$), plasma frequency ($\omega_p \propto \rho^{1/2}$), and Fermi wavevector ($q_F \propto \rho^{1/3}$). These depend on density and (in our case) on the distance between the nucleons. The lifetime dependence upon the electron-positron plasma density can be deduced once we have a model for the neutral pi meson (plasmon) wave vector. In order to calculate the lifetime of the plasmon we need an estimate for the q_π-vector. We use the relationship between q-vector and energy. The relativistic energy of the plasmon excitation (meson with mass m_π), $E{\sim}m_\pi c^2$, [2], is assumed spread into kinetic energy ($\frac{\hbar^2 q_\pi^2}{2m_e}$) for each particle of two electron-positron pairs (in general not all energy turns into the kinetic energy of these particles). This leads to an order of magnitude estimate for the wave vector of the plasmon: $q_\pi \le c\sqrt{\frac{m_\pi m_e}{2}}/\hbar$. As we have shown in Eq. (9) that $m_\pi \propto \rho^{1/2}$, the broadening and lifetime is apparently independent of electron-positron density (and independent of separation between nucleon pairs). A possibly better estimate subtracts off the relativistic energy for each of the particles created in the two electron-positron pairs from the relativistic energy of the plasmon. This leads to: $q_\pi \le c\sqrt{\frac{(m_\pi-4m_e)m_e}{2}}/\hbar$, with only a slight density dependence for the lifetime. The estimate will be seen to lead to the same numerical value (to the first decimal place) as the "naive" (Weinberg's word [23]), QFT (Quantum Field Theory) approximation for the uncharged pion lifetime. Both our result for lifetime and the "naive" one have the same order of magnitude (~0.2×10^{-16}s). This can be compared with the state-of-the-art QFT result (0.80-0.85×10^{-16}s) which agrees with the experimental value (0.834×10^{-16}s), cf. Sec. 3.

3. RESULTS

3.1 Numerical, Experimental and Selected QFT Results for Mesons

Meson Mass

The equivalent black box at a nucleon pair separation of 1 fermi or closer contains very nearly the maximum number of electron positron pairs. If we take d~1.5 fermi, the equivalent temperature is $kT{\sim}128m_ec^2$. This leads via Eq. (9) to a meson mass of $267m_e$ which compares remarkably favorably with the experimental results [24,25], $m_e\approx0.511$ *MeV* and $m_\pi\approx134.97$ *MeV*$\approx264m_e$. The dependence of the estimated meson mass on nucleon separation will be shown in Table 1.

Meson Lifetime

Using this distance for the lifetime in the equation given by Ninham [22], we obtain the π_0 lifetime $\ge0.16\times10^{-16}$s. Noteworthy, as we mentioned earlier the predicted lifetime is stable for different nucleon-nucleon separations unlike binding energy (which increases with decreasing separations). This is a curious consequence of the density dependence of the plasmon wavevector. This is applicable only at the very high temperatures we predict (corresponding to a plasmon with energy high enough to create particles). The experimental textbook result [24] is around 0.83×10^{-16}s. Our result is of the right order of magnitude. A "simple" QFT approximation [23] leads to an estimate for the lifetime around 0.22×10^{-16}s. (A theoretically plausible improvement of the "simple" QFT result discussed by Weinberg [23] leads to 0.52×10^{-13}s which is different by a factor 1000 from the experimental result). A better theoretical approximation, assuming among other things the number of colors for the quarks, leads to an estimated QFT lifetime for the neutral pion of ~0.9×10^{-16}s [23].

The decay of the neutral pion into two photons has its basis in the explicit breaking of the axial symmetry by quantum fluctuations of quark and gluon fields. The first four decay pathways [21] are: (1) $\pi_0\rightarrow\gamma\gamma$, (2) $\pi_0\rightarrow\gamma+e^++e^-$, (3) $\pi_0\rightarrow\gamma+$positronium; (4) $\pi_0\rightarrow e^++e^-+e^++e^-$. Our theory, taken with the reactions $e^++e^-\leftrightarrow\gamma$ and $e^++e^-\rightarrow$positronium$\rightarrow\gamma$, could account for the π_0 particle being able to produce these four decay pathways. Precise measurements of the decay width of the $\pi_0\rightarrow\gamma\gamma$ process give an average of 7.80 eV. This gives a lifetime of 0.834×10^{-16}s [26,27]. This is in good agreement with previous theoretical results and with its estimated 1.5% accuracy offers a benchmark test for the most sophisticated theoretical estimates including the prediction 0.804×10^{-16}s by Kampf and Moussallam [28]. High accuracy calculations of the lifetime also include those discussed by Larin et al. [26] and by Bernstein and Holstein [29]. These authors [26,29] discuss how the axial, chiral, anomaly originating from quantum fluctuations of quark and gluon field, and exploiting the number of QCD quark colors, drives the π_0 meson decay with a lifetime around 0.849×10^{-16}s.

Nuclear Binding Energy

Furthermore, the Lifshitz-Yukawa binding energy at this separation receives -0.9 MeV from the n=0 term and -3.6 MeV from the n>0 term leading to a total binding energy from electromagnetic fluctuation interaction of 4.5 MeV. The binding energy increases with decreasing nucleon-nucleon separation in line with the fact that binding energies of nucleons are different in different nuclei [30-32], and also in line with the fact that local surroundings influence the local structure of the nucle-

Table 1. The lifetime, meson mass and binding energy versus separation between a pair of neutrons (or protons). Recall the approximations in our model (Sec. 2.1), implying the nucleons to be replaced by conducting plates.

Separation	Lifetime	Meson Mass	Binding Energy	kT
1.0 fermi	1.61×10^{-17}s	$491m_e$	13.6 MeV	$193m_ec^2$
1.5 fermi	1.62×10^{-17}s	$267m_e$	4.5 MeV	$128m_ec^2$
2.0 fermi	1.64×10^{-17}s	$173m_e$	2.0 MeV	$97m_ec^2$

ons [30-32]. The binding energy per nucleon varies in different atomic nuclei from 1.1 MeV for deuterium to 8.8 MeV for Nickel-62. Also, the structure of neutrons and protons within different nuclei depends on the local environment (for references see the work by Feldman [31]). (Note also in passing the experimental data on nucleon binding energies in Ref. [33]. In that (controversial) paper the authors infer that neutron-neutron, just as proton-proton interactions are repulsive, whereas the neutron-proton interaction is attractive.)

Summary of Numerical Results

We summarize our numerical results in Table 1. The equivalent temperatures (note that: $m_ec^2/k\approx5.9\times10^9K$) are high enough to generate the electron-positron plasma. The effective surface area is taken to be $A=\pi r^2$ with r=proton radius~0.8 fermi. Improved estimates would, for example, require an expansion of our planar estimate to consider a pair of perfectly conducting spheres in a high-density electron-positron plasma.

4. SUMMARY AND CONCLUSION

We began this enquiry with the idea that if Feynman believed there ought to be a link between electromagnetic theory and nuclear forces, there might be something in it. It seems there is. From our semi-classical theory we have been able to predict better than order of magnitude estimates for the basic properties of the neutral pion, namely its decay length, mass, and lifetime. In the picture a high-density electron-positron plasma emerges quantitatively and naturally as a key player in nuclear interactions. A defect is the modelling of nucleon interactions by planar perfectly reflecting surfaces. There are two free length parameters, area and distance between the model ”nucleons”. But they are close to actual distance scales.

It would be more convincing if the theory also predicted the various decay modes for π_0, in terms of e^+e^- pairs and photons. Further, in such a theory the charged mesons, π^-/π^+, would emerge as an electron/positron bound to a plasmon.

One thing is clear. There is certainly enough energy available to account for nucleon interactions. And if the claim that our theory is not equivalent to the canonical theory, where has that energy gone? It is possible to push matters further by including magnetic suceptibilities in the formalism for interactions using a fully relativistic electron-positron plasma. There is a useful analytic framework available in the work of Daicic, Kowalenko, Frankel and co-workers [34-36]. In connection with this we observe that Larin et al. [26] performed some of the most precise measurements of the lifetime of the π_0 meson. Their weighted average final result for the $\pi_0\rightarrow\gamma\gamma$ decay width defines the new lifetime to be 8.337×10^{-17}s. Such surprisingly short lifetimes can in the QCD framework be obtained once axial anomaly is accounted for. The axial anomaly, which historically provided strong evidence in favor of the color-charge concept in QCD, seems to present us with state of the art knowledge about some of most fundamental aspects of nature—for example, by constraining the fundamental physics beyond the Standard Model and presenting opportunity to, e.g., measure the light quark mass ratio [26,27]. However, using a much simpler semi-classical theory we have found results that turn out to have exactly the right order of magnitude. This suggests an as yet unexplored link between our theory (expanded to magnetic anisotropic media) and one of the most profound theories in physical science.

There are wider implications: If the equivalence we seek can be firmed up, the consequences would be significant. The full QFT of interactions of DLP involves a nonlinear coupling constant integral equation for the polarisation operator. That awkward difficulty was resolved by replacing that by a linear integral, and the whole formalism collapsed to a semi classical theory.

The consequences of these mathematical simplifications have been a serious obstacle to progress in the biological and engineering sciences that depend on molecular forces in the disciplines of physical, colloid and surface chemistry [37-40]. The theories inconsistently treat electrostatic forces in a nonlinear theory and quantum fluctuation (dispersion) forces in a linear theory [37,41]. So central specific ion (Hofmeister) effects, and hydration effects are lost. The problem is being partially rectified [40]. But a proper fundamental theory requires the complete non linear theory to go further.

The same would be true for the theory of nuclear interactions. It should also be a non linear theory and not linear as it is now.

A partial version of this mss (BWN and Colin Pask, unpublished) was written in 1969. A brief version was published by two of us (BWN and MB) in 2003, but it omitted the meson lifetime. This version is more detailed and includes this important result. In the following 55 years what is new has been the application of Lifshitz theory to the foundations of physical chemistry. The literature is extensive. Classical theories ignore all important Hofmeister (specific ion effects). The problem can be traced to the same linearization approximation and rectified. The equivalence established between Lifshitz theory and pi zero mesons implies that particle physics suffers the same difficulties.

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Research Article

The Rate Constant – Reaction Free Energy Dependence for the Electron Transfer Reactions in Solutions. The Way to Interpret the Experimental Data Correctly

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Lev I. Krishtalik. Courtesy of Vasily Ptushenko.

Lev I. Krishtalik left a noticeable mark in electrochemistry and biophysics. His scientific career started in the mid-1940s, when the hardships of wartime were replaced first by hopes for the best, and then by persecution of the numerous segments of the population and many scientific schools in the USSR.

[†] 23.11.1927–26.02.2022

Fortunately, Lev Krishtalik survived these difficult years, although he had to work for 15 years in the industry, doing science only in his off-duty hours. Even in these hard conditions, he managed to perform an outstanding work on the experimental detection of barrierless electrode reactions (discharge of hydrogen ions). Later, he worked in the Alexander N. Frumkin Institute and contributed substantially to the theory of charge transfer reactions developed by Revaz R. Dogonadze and Alexander M. Kuznetsov and to its experimental confirmation. This was a cutting-edge field in chemistry and led to Rudolph A. Marcus' Nobel Prize in Chemistry in 1992. A little later, Lev Krishtalik developed his views on the catalytical abilities of enzymes.

The work of Krishtalik was well known at the time and his efforts were rewarded with the Frumkin Prize of the International Society of Electrochemistry in 2001. Note that he was a disciple and one of the closest colleagues of Alexander N. Frumkin, although he was never formally his student.

Along with his scientific interests, Lev Krishtalik also had interests and encyclopedic knowledge in different cultural fields, including poetry, music, painting, and architecture. One of his favorite cities was Florence, and the painting "La Catena" with the medieval/renaissance landscape of Florence was always on his bookshelf. His personal memoirs have been recently published (in Russian; https://7i.7iskusstv.com/avtory/krishtalik/).

Lev Krishtalik was a radiant personality. Even in the most difficult moments of his life, he remained friendly to people and grateful to fate.

This is the last manuscript which he worked on in his two or three last years of his life. Unfortunately, his illness did not allow him to publish the paper before his death.

Vasily Ptushenko

Abstract. The relative influences of the reorganization energies of the classical and quantum modes on the maximum position of the rate constant – reaction free energy curve have been studied. In the framework of the continuum electrostatics, the electron transfer reorganization energies in methyltetrahydrofurane solutions for the system biphenylyl – spacer – acceptor were calculated. For different acceptors, the solvent reorganization energy varies from 1.0 to 1.1 eV. When added with the rather small reorganization energies for classical intra-molecular modes we obtain 1.13–1.34 eV. With account of possible errors this coincides practically with the experimental estimate of the energy at the maximum of the rate–free energy curve $\Delta G_{max} \approx -1.2$ eV. Hence, we can conclude that the reorganization of quantum modes does not influence substantially the position of this maximum. To the contrary, in a non-polar solvent isooctane were the solvent reorganization does not play any role the reorganization of the quantum intra-reactants modes becomes determinant. These conclusions agree fully with the results of the general theoretical analysis and should be accounted for in the experimental data interpretation.

Keywords: Reorganization energy, Medium reorganization, Intra-molecular reorganization, Rate maximum.

List of Abbreviations: A – acceptor, BPH – biphenylyl, D – donor, MTHF – metyltetrahydrofurane, Py – pyrenyl, Sp – spacer, Q – benzoquinonyl.

1. INTRODUCTION

One of the fundamental problems of the chemical and electrochemical kinetics is the physical mechanism of the elementary act of the electron transfer, especially in condensed media. This question was intensively studied in many theoretical works (in particular [1-4]; a short review of them is given in Section 2. 1). Electron transfer is connected with some reorganization of the reactant's polar surroundings and reorganization of the molecules inner structure. These two processes are characterized by the corresponding parameters – the medium (solvent) reorganization energy λ_s and the intramolecular reorganization energy λ_v.

The relative contribution of these processes has been many times discussed. In liquid solutions the kinetics of the electron transfer proper can be distorted by kinetics of the mutual diffusion of the reactants. Therefore, most suitable for the comparison of the experimental results with the theory are the systems in which the donor and the acceptor are connected by a rigid linker ensuring a constant distance between the reactants. In the present paper, a typical example of such a system will be considered. In many papers dealing with the problem in chemical and biochemical systems [5-9], it has been a priori accepted that both the parameters – λ_s and λ_v – contribute substantially to the final result. Accordingly, both parameters were found by fitting the experimental data to the theoretical equation derived under the same assumption. The results of such a fitting are not quite unequivocal. Therefore, it is highly desirable to estimate the reorganization energies, both λ_s and λ_v by independent methods. As a vivid illustration of the possible problem the data of [7] can be mentioned. In this paper, the fitting for the system porphyrines – C_2H_4 – quinones in benzene and toluene has been performed with two sets of parameters – the first one λ_s = 0.18 eV, λ_V = 0.60 eV and the second λ_s = 0.60 eV, λ_V = 0.20 eV. The second set which is physically quite unrealistic gives the results almost so good as the first one. This shows again that one should use parameters obtained from the independent data. To emphasize this conclusion is the aim of the present paper.

Section 2 deals with the theory (2.1) and calculations (2.2); in Section 3, the results described and discussed; in Section 4, the conclusion are presented.

2. THEORY AND CALCULATIONS.

2.1 Theory

In this Subsection, a short description of the most important theoretical results used in this paper is presented.

Marcus [1] was the first who has given, in the framework of a semi-classical theory, the correct exponential dependence of the reaction rate on the reaction free energy ΔG and the reorganization energy λ. Levich and Dogonadze [2] have done a quantum–mechanical analysis of the problem. They have obtained the same exponent and a strict expression for the pre–exponential factor. The final result is

$$k = \frac{4\pi^2|V(r)|^2}{h\sqrt{4\pi\lambda k_B T}}exp\left[-\frac{(\Delta G+\lambda)^2}{4\lambda k_B T}\right] \tag{1}$$

Here k is the rate constant, $V(r)$ – the distance r dependent electronic coupling matrix element, h – Planck constant, k_B – Boltzmann constant, T - temperature. This equation is valid only at the high-temperature limit, e.g. under condition $\hbar w << k_B T$, where $\hbar w$ is the energy of vibration coupled to the electron transfer.

From Eq.1 follows that the rate constant – reaction free energy dependence presents a symmetric parabola with maximum at

$$-\Delta G_{max}=\lambda \tag{1a}$$

For the purpose of qualitative treatment of results it is instructive to recall the Marcus formula for the medium reorganization energy (2).

$$\lambda_S = e^2\left(\frac{1}{\varepsilon_0}-\frac{1}{\varepsilon_S}\right)\left(\frac{1}{2a_1}+\frac{1}{2a_2}-\frac{1}{R}\right) \tag{2}$$

Here e is the charge to be transferred, ε_o and ε_s are optical and static dielectric permittivities of the medium, a_1 and a_2 are the radii of the spherical reactants, and R is the inter-center distance. This simple analytical solution is obtained for the case of two spherical reactants in an infinite homogenous medium. At a more complex geometry and an inhomogeneous medium one employs the numerical methods of calculation (section 2.2) with the same physical rationale as for derivation of the Marcus Eq.2; hence the latter is suitable for the qualitative discussion.

Dogonadze et al. [3] have considered a more general case when different oscillators are present with a wide range of the frequencies. They have shown the principal difference in the behavior of the intramolecular vibrations that have a high frequency $\hbar\omega >> kT$, i.e. much more than own vibrations of liquid solvent ($\hbar\omega << kT$). Consequently, they are much faster, and hence cannot influence the reorganization energy. It should be noted that the condition of low frequency (condition of the classical behavior) can be fulfilled not only for the solvent but also for some intramolecular movements.

Jortner [4] has presented in an explicit form the expression for the rate constant in the case of the presence of different oscillators.

$$k = \frac{2\pi}{\hbar^2\omega}|V(r)|^2 e^{-S(2\bar{n}+1)}\left(\frac{2\bar{n}+1}{\bar{n}}\right)^{P/2} I_P\left[2S\sqrt{\bar{n}(\bar{n}+1)}\right] \tag{3}$$

where $V(\boldsymbol{r})$is the electron tunneling matrix element, $\hbar w$ is the energy of the nuclear vibration coupled to electron transfer, S is λ/hw. Here λ is the total reorganization energy equal to the sum of intramolecular (vibrational) component λ_v and the medium (solvent) reorganization λ_s; n is $[\exp(hw/k_B\ T) - l]^{-1}$ where T is the absolute temperature, k_B is Boltzmann constant (it is the thermal population of a mode with vibrational frequency w), $I_P(z)$ is the modified Bessel function, and P is $-\Delta G/\hbar\omega$. This expression calculates the thermally weighted contribution of the Franck-Condon overlap integral from each vibrational quantum level to the rate.

Jortner's Eq.3 also predicts a parabolic k – ΔG dependence but the asymmetric one: at larger ΔG the rate is enhanced due to involvement of exited vibrational levels. The maximum of the rate is determined by the condition

$$-\Delta G_{max}=\lambda_v+\lambda_S \tag{3a}$$

Let us consider the high-temperature limit, e.g. under condition $\hbar w << k_B T$, where $\hbar w$ is the energy of vibration coupled to the electron transfer. This situation usually exists when the reorganization takes place due to the change of the polarization of the surrounding dielectric medium. The latter can be described as a set of the low-frequency phonons. Hence, for this case the Jortner's Eq.3 simplifies to Eq.1

2.2 Calculations

Calculations of the medium reorganization energies are performed in the framework of continuum electrostatics – the approach successfully used for the several intra-protein charge transfers [10]. For the numerical solution of the Poisson–Boltzmann equation the finite difference method was employed [11], the program DelPhi v.4 release 1.0. This program permits to account for the presence of several dielectrics with the different permittivities. To find the reorganization energy one should calculate the dielectric response energy (reaction field energy) upon the simultaneous charging of reactants by +1e and –1e in optical and static dielectric media. Response in the optical medium (dielectric permittivity ε_o) corresponds to the inertialess polarization, and response in the static medium (permittivity ε_s) corresponds to sum of the inertialess and the inertial polarizations. The difference of these responses gives the effect of the inertial polarization, i.e. the reorganization energy.

Parameters

The ±1e charge is supposed to be distributed equally among all of the aromatic hydrocarbons heavy atoms. For quinone molecules, the additional charge appearing upon their reduction were obtained from quantum–chemical calculation by density functional method at the B3LYP/6-311++G(d,p) level. The results are: -0.202e at each of carbonyl oxygen, -0.194e at carbon atoms connected with O, and -0.052e on other C atoms. It should be noted that variation of the charge distribution in reasonable limits result in changes of the reorganization energy by few millielectronvolts.

Electrostatic reorganization energy is often estimated using Eq.2 which accepts the spherical shape of the reactants. In many cases, in particular for large flat molecules this leads to a drastic underestimation of the reorganization energy. For a more realistic description of the reactants' size and shape, the Pauling van der Waals radii of atoms were employed (their more detailed list is given in the PARSE parameterization [12]). Using these radii and partial charges the Poison–Boltzmann equation can be solved numerically.

The probe radius implies the spherical shape (or somewhat similar to that) of solvent molecule. However, the MTHF molecule is a flat one. Therefore, one must use some approximations. As the minimal value the radii of O atom or CH_2 group contacting immediately the reactants, i.e. 2Å. As the approximate maximum effective radius, the radius of a sphere circumscribing the flat figure of tetrahydrofurane was accepted. It equals to 3.2 Å. Calculation of λ_s with these radii gives values differing by 10–12 meV. As the final result for each pair the average figure rounded up to one hundredth of electronvolt was chosen. Its error due to uncertainty of radii hardly exceeds 5–6 meV.

The calculations were performed with the grid size 0.15 Å, box filling 80 %. The salt concentration was accepted formally as 10^{-4} M what allowed to neglect the reorganization of the ionic atmosphere.

The experimental values of the dielectric permittivities, static and optical, for the solvent methyltetrahydrofurane (MTHF) are ε_s=7.0 and ε_o = 1.98 [13]. The permittivities inside the reactants are $\varepsilon_{in} = \varepsilon_s = \varepsilon_o = n^2$ (n is the refractive index). because there is no orientational polarization (dipoles reorientation) inside the molecules, The corresponding values for the reactants under study are absent in the literature. They were estimated by comparison with the data on ε_o for the following molecules: benzene 2.25, naphthalene 2.53, phenantrene 2.55. acetone 1.85, vinylmethylketone 1.98, acetylacetone 2.14. Pyren is the next in the series of aromatic hydrocarbons, hence its ε_o can be estimated as ~2.6. For BPH one should expect ε_o higher than for benzene due to the interaction of phenyl groups but this interaction should be substantially weaker than in naphthalene; the estimated ε_o is 2.35. Q is not an aromatic compound but an unsaturated diketone. With the account of additional conjugation the estimate is $\varepsilon_o \approx 2.45$. Further, by computations reason it is more convenient to use a unique value of ε_o for each pair of reactants. These figures are 2.4 for BPH–Q pair, and 2.5 for BPH–Py pair.

Given the approximate nature of these values the calculations with various ε's were performed. The variation in ε_o by 0.1 leads to change of λ_s not exceeding 6–7 meV. Therefore, this approximation seems to be quite acceptable.

3. RESULTS AND DISCUSSION

Among the entire systems donor (D) – spacer (Sp) – acceptor (A), the most suitable for theoretical analysis is the system biphenyl – a spacer of steroidal type– different acceptors that is studied in detail by Miller, Closs, and their coauthors [5, 14–19]. The most data relates to spacer 5-a–androstane. They were used in our analysis.

The advantages of using this and similar spacers are, first, that it provides a constant inter-reactant distance and their orientation. The second advantage is that the long chain of s–bonds excludes any marked electron transfer between the reactants before the reaction starts. Therefore, one can sure use in electrostatic calculations the full integer charges of reactants.

The last remark. In the experiments of Miller et al., reaction was initiated by the pulse of the high-energy electrons. The solutions were without the supporting electrolyte. Hence, in these systems cannot be operative the effect discussed by Kuznetsov [20] for weakly polar media, namely reorganization of ionic pairs formed between the reacting ions and the ions of the background electrolyte.

Below, two typical systems will be considered.

3.1. BPH – Sp – A in MTHF.

For calculations two acceptors were chosen – Py, having the largest size, and Q, having the smallest one; correspondingly, they have the smallest and the largest electrostatic energy of interaction with the dielectric medium. For all the other acceptors the medium reorganization energy has the intermediate value. As described in Section 2.2 the calculations account for the real size and shape of reactants.

The calculated λ_s are for BPH–Sp–Py 1.00 eV, and for BPH–Sp–Q 1.11 eV. Besides medium reorganization there are some other practically classical degrees of freedom.

The first of them is the torsional movement around s – bond connecting two phenyl fragments of BPH; their frequency is estimated theoretically as 55-125 cm^{-1} (reviewed in [21]). Hence, they are classical ones. The corresponding reorganization energy has been estimated experimentally by comparison of the reaction rates with BPH and with 2-(9,9'dimethyl)fluorene having a similar energetics and electronic structures, but for the fluorene derivative the torsional component of λ is absent due to sterical hindrance. Therefore, the difference in rates can be ascribed to $\lambda_t = 0.13 \pm 0.03$ eV [18]. Similar value has been obtained by quantum chemical calculation of two rotamers energy [18].

The second component is the intramolecular low-frequency vibrations. Borrelli and Dormcke [23] have performed *ab initio* calculation of the full benzoquinone vibration spectrum. The main contribution to its reorganization energy is due to five modes with the frequencies near ~440, ~780, ~1140, ~1500, and ~1600 cm^{-1}. The same frequencies were obtained by Fischer and Van Duyne [24] from the data on Raman spectroscopy. It is important that all they are connected with some shift of the polar CO group. The total λ_v due to all vibrational modes is 0,45 eV. The mode with the frequency 440 cm^{-1} behaves practically classically and gives the reorganization energy λ_v= 0.10 eV. The behavior of the mode 780 cm^{-1} is intermediate between classical and quantum ones, nearer to quantum. Fortunately, its full reorganization energy is only 0.01 eV, and hence its contribution to the total classical reorganization energy can be neglected.

In [23], the full analysis of the Mg-porphyrin spectrum was also given. The total vibrational reorganization is about 0.1 eV. Classical vibrations give only 0.0003 eV. In this molecule, all the polar groups are incorporated in a rigid ring structure. Therefore, it is reasonable to accept that in cyclic aromatic hydrocarbons containing no polar groups $\lambda_v \approx 0$.

In total, all the classical components give the $\lambda = \lambda_s + \lambda_t + \lambda_v$. For BPH-Sp-Py λ = 1.13 eV, for BPH-Sp-Q it equals to 1.34 eV. This is rather close to -ΔG_{max} = ~1.2 eV found experimentally from the *k* – ΔG curve. With account of the possible errors of two estimates one should conclude that the closeness of the calculated and experimental values is quite acceptable.

Thus, Eq.3a does not describe the experiment satisfactorily while Eq.1a does. This is especially clear for the system including Q where the quantum contribution to the total λ_v equals to 0.35 eV, and the classical one only 0.1 eV. In other words, the reorganization of the solvent (plus other classical components) determines the total reorganization energy. This is fully consistent with the theoretical conclusion by Dogonadze et al. [3]. Jortner [22] also notes that in liquid solvents where exist low-frequency phonons they exert the predominant effect on the reorganization energy.

From this point of view it is interesting that the rates of electron transfer between anion – radical and the neutral reactant and from the neutral reactant and the cation – radical coincide [16] what shows that determining is an electrostatic effect.

The fact that reorganization energy is determined by the solvent and other classical modes does not mean that intra-molecular vibration modes do not influence kinetics, and in particular the shape of the rate – free energy dependence. At $|\Delta G| > |\Delta G_{max}|$, e.g. in the inverted region, the excited vibration levels come into play making *k* – DG curve asymmetric.

3.2. BPH–Sp–A in isooctane.

The data on this system are presented according to [14] at Fig. 1. The dashed curve is tacked from [14]. It is calculated with the following parameters: λ_s = 0.15 eV and λ_v= 0.45eV. Strictly speaking, in the nonpolar solvent isooctane $\lambda_s = 0$. However, with account of the torsional component the accepted value is reasonable for the classical reorganization energy. For the vibrational component the authors quite logical accepted the same value as was obtained previously by fitting the data for the same system in MTHF. However, as it is clear from Fig.1 the agreement of this calculation with the experiment can be hardly considered as satisfactory one. The deviation of the experimental points from the theoretical curve in some cases can be as large as ~ 4 orders of magnitude while for MTHF there is only for one experimental point with the maximal deviation not exciding 0.3 orders. Moreover, the experimental data cannot be described as a bell-shaped dependence. Therefore, it is hardly possible to establish definitely the value of ΔG_{max}.

The reason for that lies, most probably, just in the mechanism of the elementary act of the electron transfer. In absence or at quite small classical reorganization energy the initial and final electronic energy levels can be equalized only at the expense of the excitation of intra-molecular vibrations. Just this idea is accounted for in Jortner equation. However, this equation in fact does not imply the same λ_s and also the same total λ_v for all acceptors. However, as it is shown in Section 3.2 for the different reactants λ_s and, especially, λ_v can be substantially different. This is very likely the reason of the discrepancies between experiment and calculations represented on Fig. 1.

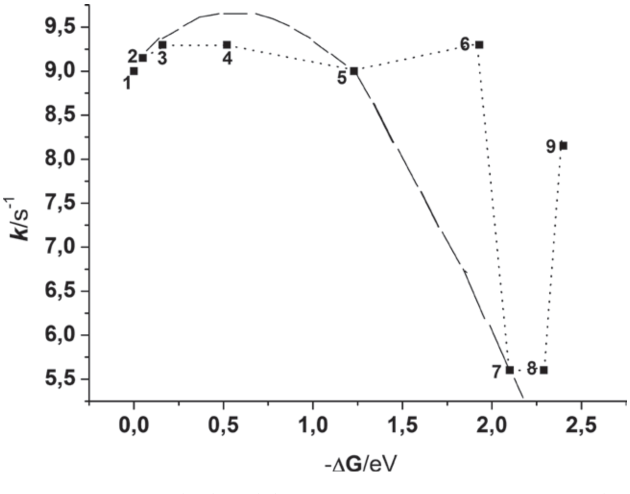

Figure 1. System biphenylyl–spacer–acceptor in isooctane solutions. Dashed line correspond to calculations [14] with the following parameters: λ_s = 0.15 eV, λ_v = 0.45 eV, ω = 1500 cm^{-1}, V = 6.2 cm^{-1}. Dotted line is just a guide for eye that is drawn according to the sequence of the reaction free energies. The symbols indicate experimental data: *1*— 4-biphenylyl, *2*— 2-naphthyl, *3*— 9-phenanthryl, *4*— 1-pyrenyl, *5*— 2-(5,8,9,IO-tetahydronaphthoquinonyl), *6*— 2-naphthoquinonyl, *7*— 2-benzoquinonyl, *8*— 2- (5-chlorobenzoquinonyI), *9*— 2-(5,6-dichlorobenzoquinonyl).

Two additional remarks seem to be proper. First, in the presence of several modes the total λ_v equals to the sum of the corresponding parameters for each mode (the model calculations of Ulstrup and Jortner [25]). Second, there exists a wide set of less effective modes, forming a quasi- continual spectrum important at gradual excitation.

Note also that the difference in the intra-molecular quantum frequencies does not influence the data for MTHF because in polar liquid solvent the location of the rate maximum is determined by the classical reorganization only.

4. CONCLUSION

Nowadays, experimental data processing often uses Jortner formula which implies a substantial contribution of both reorganization energies (of the intra-molecular quantum modes and the classical medium modes) into the total reorganization energy. The latter determines the reaction free energy corresponding to the maximum reaction rate. However, the values of the two reorganization energies are usually taken not from some independent sources but obtained by fitting the kinetic data to Jortner equation. Correspondingly, there is not any attempt to prove the basic condition of a comparable effect of the two reorganization energies.

The specific feature of the approach advanced in this paper is determination of all the parameters not by fitting the kinetic data but basing on the independent experimental data. The medium reorganization energy has been calculated electrostatically. For this purpose, not the simplified Marcus formula implying spherical shape of the reactants but the more general method of the numerical solution of the Poisson–Boltzmann equation was employed. This method allows accounting for the real shape and size of the reactants. The calculations performed for solutions in a polar solvent MTHF show that the medium reorganization gives the predominant contribution to the total reorganization energy. To the contrary, in a non–polar isooctane, the medium reorganization does not play any substantial role, and the intra-molecular reorganization becomes predominant. In the latter case, the shape of the rate – free energy curve is rather complex due to differences in vibration spectra of various molecules. All these results are in agreement with the general theoretical conclusions.

From the above, the algorithm for processing experimental data follows. In the case of reaction in polar solvent one should perform a strict electrostatic calculation of the medium reorganization energy and try to analyze the other possible classical modes. For the reaction in a non-polar medium one should analyze the vibration spectra of the reactants and calculate the corresponding reorganization energies.

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Research Article

Training of Future Chemistry Teachers by a Historical / STEAM Approach Starting from the Visit to an Historical Science Museum

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Abstract. The visit to a scientific historical museum represents a great opportunity for future science teachers to develop educational activities and effective laboratories for high school and first year undergraduate students. In this paper, a pilot educational project experimented in the frame of the course of '*Fundaments and methods of chemistry education*' held at the University of Pisa (Italy) during the academic year 2019-2020, aimed to train future chemistry teachers, is described. The main steps of the project, from the visit to the Museum 'Galileo' in Florence (Italy) to the design of educational hands-on activities by the undergraduate students, are discussed. Emphasis will be given to the role of historical scientific collections, such as the Galilean thermoscopes and other historical thermometers' collection, in stimulating the creativity and higher order thinking skills.

Keywords: High Order Thinking Skills, Education, History of Chemistry, STEM, STEAM, Historical teaching approach, Inquiry-based Learning, hands-on activities.

1. INTRODUCTION

Non-formal learning and teaching are considered important aspects in science education as well as in chemistry education.[1-4] Since the European Community has recognized the role of life-long learning and its impact on the education of aware citizens,[1,2] non-formal contexts started deserving the attention of scientists dealing with education and in particular science education. Among non-formal contexts, science museums[5-8] and scientific festivals, as typical example of contexts hosting open-science and outreach activities,[9-11] were the object of several research studies focusing on their role in increasing the scientific literacy and the engagement of students toward science.[5-13] Several papers, published in the recent years, show that out-of-school programs and outreach activities designed for children, families and/or for school students are effective in terms of acquired knowledges and skills in specific topics about science and technology.[14-18]

Traditional science museums, historical collections linked to high schools or universities and interactive science centres are nowadays strongly connected with schools of any levels, from primary to high schools, and they have developed numerous activities, mainly laboratorial and interactive ones, where science is presented in its relationship with Society and with other disciplines.[5,7,8,18] This approach is an effective alternative to the more traditional and scholastic ways of teaching science through its concepts, laws and more formal aspects. On the other hand, science teachers' training is now focused on a more multidisciplinary and interdisciplinary approach,[18] which is also referred to as the so-called STEM (*Science, Technology, Engineering, and Mathematics*) teaching and learning philosophy.[19] According to this idea, students are encouraged to 'think as a scientist', developing high order thinking skills, such as the ability to solve complex problems by using knowledges and competences typical of different disciplines. In the recent years, this teaching method evolved towards the STEAM approach, which includes 'Arts' to the STEM.[20-23] However, the letter 'A' in the STEAM acronym has a more general meaning: it can be extended to all human disciplines, such as music, history and languages. The basic idea of this teaching and learning method is that a multidisciplinary approach, combining scientific and logical thinking with creativity and multiple intelligences,[21-23] can help students to understand the complexity of the real World and possibly find new solutions to everyday life problems.

This teaching approach has influenced chemistry education, too. The role of human disciplines, such as history and philosophy, as well as the multidisciplinary approach and the use of contextual or situated educational methods[24] to teach chemistry at high school and undergraduate levels can be related to well-known chemistry education models, such the tetrahedral model proposed first by Peter Mahaffy[25] and then structured and reinterpreted by Talanquer[26] and Sjostrom,[27,28] who added relevance dimensions and explained different levels of chemistry understanding and implications in chemistry education.

Within the tetrahedral chemistry education model and its variants,[25-28] teachers are invited to analyse different facets of chemistry education, such as the pedagogical, sociological, ethical, historical and philosophical ones,[29] when working with their students. In line with this model,[25-28] the use of historical approaches to teach chemistry at different school and university levels[30,31] and the introduction of specific courses of 'history of chemistry' and 'chemistry, ethics and society'[32-35] in the curriculum of future chemists represent additional elements of novelty in chemistry education.

Based on these premises, historical science museums and collections of historical objects, such as glassware, scientific instruments, historical books and reactants, as well as ancient artifacts,[6-8,18,30-39] acquire novel roles and values for chemistry teachers who can take advantage of such contexts to teach specific chemical topics and try to engage them with more interactive teaching methods.

In this paper, a pilot educational project[40] experimented upon in the frame of the course of '*Fundaments and methods of chemistry education*' held at the University of Pisa (Italy) during the academic year 2019-2020, and aimed to train future chemistry teachers, is reported.[41,42] The details of the methodology optimized and experimented within this course of chemistry education are reported and discussed in a previous paper.[18] Here, the main steps of the teaching method and the pilot educational project, from the visit to the Museum 'Galileo' in Florence (Italy)[43] to the design of educational laboratorial activities by the undergraduate students, are described and commented on. Emphasis will be given to the role of historical scientific collections, such as the Galilean thermoscopes and other historical thermometers,[44-47] in stimulating the creativity[48] and higher order thinking skills in future chemistry teachers.

2. THE TEACHING METHOD

2.1 The course of Chemistry Education to train future chemistry teachers

The course of '*Fundaments and methods of chemistry education*' of the degree in Chemistry at the University of Pisa[41,42] has been active since 2013 and it is included in the national training program and 'public national competitions' for chemistry teachers to be employed in the secondary schools. As reported in ref. 18, the course is an optional one (3 CFU; total of 24 hours of lessons in the first semester of the third year of the degree course in Chemistry) and it is structured with initial 10-12 hours of lessons aimed to introduce students to the main pedagogical theories and the fundaments of the most used active teaching strategies applied to chemistry education. Emphasis is given on the inquiry-based education and problem-solving methods, different kinds of laboratorial strategies, the basis of the cooperative learning and peer education, and, among the structured knowledge approaches, the 'conceptual maps' method. During these first introductory lessons, students are asked to master these interactive teaching strategies, to read the materials provided during the lessons, through the e-learning platform,[42] to answer some on-going (*in itinere*) interactive quiz and to prepare short presentations. The second part of the course (about 12-14 hours of lessons plus additional extra-hours of activities) is focused on examples of interactive activities aiming to show the best practices in teaching chemistry at intermediate and high schools (from K6 to K12 levels, corresponding to students of the age from 11 to 18 years old). In this second part of the course, a teaching methodology, developed in the last ten years to train future chemistry teachers, called '*STEAM project-based learning*',[18] is applied, as will be discussed in the following paragraph. At the end of the course, students are required to present and discuss a didactic sequence or an educational project, designed and discussed during the second part of the course, in extra-time hours. To prepare the educational activities, students are encouraged to work in group of three-four units according to the cooperative learning method. Moreover, students are invited to follow an instruction scheme, which refers to a hierarchic instructional model,[2,18] which is usually discussed during the progress of the course. Finally, the educational projects designed by students can be put into practice with real school students or with children or families in non-formal contexts, such as science museums, or during open days organized at the *Dipartimento di Chimica e Chimica Industriale*, or they can be presented at Festivals of sciences, such as the one organized in Genova.[9,18,49-52]

2.2 Scheme of the 'STEAM project-based learning' teaching methodology

The scheme of the '*STEAM project-based learning*' methodology[18] adopted within the course to train future chemistry teachers is structured in nine steps:

1) *Visit at the Science Museum*. A visit at a natural or historical science museum, is organized at the beginning of the course in order to get inspiration and to know all key-aspects of a typical non-formal context.

2) *Brain storming and collective discussion*. During the visit, students are stimulated to observe the collections and activities carried out at the museum. Some guided questions are given in order to stimulate students' thinking. Thereafter, a brain storming followed by a collective discussion is performed with the aim of allowing discussion on specific topics related to chemistry to emerge.

3) *Selection of the main topics of the project*. Students usually select few key topics from the previous collective discussion, such as 'mixture among chemical substances', 'the history of the separation techniques', 'colorimetric chemical reactions', 'the chemistry of pigments', and so on. The selected topics are usually strongly related to the museum and to the scientific collections.

4) *Design of the educational activities*. Once the topics have been selected, students start designing the educational activities, which are normally structured following a general hierarchical scheme provided and discussed during the lessons. It is important that the students decide first what the target is (children, families, high school students, …), the context (formal, like a school class, or non-formal, like a laboratory at the science museum) and the main objectives of their educational project. This is the core of the 'STEAM project-based method', where students' knowledges and creativity combine giving rise to the development of higher-order thinking skills.

5) *Preparation of the materials*. The design of the educational activities encourages the students to ask themselves how to put the project into practice, estimate the timing of activities, search for the best materials, such as reagents, bearing in mind safety and environmental issues.

6) *Simulation in class*. When the educational activities are ready, an important step of the methodology is the 'simulation'. This means that students can test their activities during the extra-curricular hours, with their mates, and eventually propose some changes or discuss critical aspects.

7) *Activities with students (at school or at the Museum)*. The most exciting part of the project is the carrying out of the projects with students in a real class or with the more heterogenous attendants of activities in the frame of open days, science festivals of laboratories organized at the science museum.

8) *Analysis of the students' feedback and discussion*. At the end of the educational pathway, students should be able to evaluate their activities, the efficacy of the project and the achievement of the educational objectives. This part of the methodology concerns the meta-cognition level, namely, the developed ability to make self-evaluation and to critically analyse their works. The use of initial and final surveys, as well as the design of specific evaluation tests related to the topics of the project are encouraged.

9) *Conclusion and final report*. At the end, students usually present their work during the final exam or at an event, and discuss all aspects of the project, underlining positive and negative aspects and possible developments. Within this last step of the project, communication skills are also evaluated.

3. THE CONTEXT OF THE SCIENCE MUSEUM AND THE PARTICIPANTS TO THE PROJECT

3.1 Museum of Science 'Galileo'

The non-formal context chosen to put into practice the '*STEAM project-based learning*' method in the academic year 2019-2020, was the Historical Museum of Science 'Galileo' in Florence (Italy).[43]

The Museum 'Galileo' has a long tradition: some of the scientific collections, such as the *Medicean collection* of scientific instruments, were first collected in 1562 by Cosimo I de' Medici (1519-1574), who was the 'Duke' of Florence from the 1537, and then the 'Grand Duke of Tuscany' until his death in 1574. The first location of the historical geographic maps, celestial and terrestrial globes and other scientific objects was Palazzo Vecchio; then they were transferred in Uffizi Gallery, together with other historical scientific instruments. Among them, after the foundation of the '*Accademia del Cimento*' in 1657, inaugurated by Ferdinand II (1610-1670) and Leopoldo de' Medici (1617-1675), the collection was enriched with thermometric, barometric and pneumatic instruments used mainly for research. Additional instruments of mathematics, physics, meteorology and electricity, were added to the scientific collection in the XIX century. Some microscopes, telescopes, micrometers and spectroscopes were specifically built to be hosted in the museum, which became managed by the Institute of the History of Science during the first part of the XX century and finally moved to the actual location, the Palazzo Castellani in the centre of Florence. After 1930, the historic and scientific collections were opened to the public. In the recent decades the Museum 'Galileo' has been largely renovated with the inclusion of didactic interactive expositions and the addition of an increasing number of temporary activities specifically devoted to school students and families.

As it will be discussed in section 4, the Museum 'Galileo' offers several occasions to be in close contact with historically relevant objects and instruments related to chemistry. The famous Table of Affinities (*Tabula Affinitatum*) realized by Franz Huber Hoefer, around the year 1766, is one of the examples of very inspiring historical scientific object conserved at the museum 'Galileo'.[53] This table, in fact, is a first tentative to organize in a systematic way the known elements on the basis of their 'affinities', which are actually connected with elements' chemical reactivity, as reported in ref. 54, and for the analogy with the systematic work done almost one century later by several scientists, as Dimitri Mendeleev, it can be considered a sort of precursor of the Table of Elements. Another example is represented by the historical glassware, containing artifacts such as retorts, alembics, chemical apparatus, eudiometers, precision balances, thermoscopes and thermometers.

3.2 The participants to the project

The education activities here described refer to the academic year 2019-2020, with 23 students attending lessons during the first semester. Among them, 15 students participated in the integrated activities and in almost all steps of the '*STEAM project-based learning*' project, including the visit to the Museum 'Galileo' in Florence, and the design of educational activities for high school students. At the end of the course, 22 of 23 students passed the final exam, with an average grade 28.23 / 30 and their feedback about the project was eccellent.[18] As will be described in the main part of the paper, students attending the 2019-2020 academic year designed their educational activities, stimulated by the visit to the Science Museum, and in particular their focus was the history of thermoscopes and thermometers. This activity was integrated with the usual lessons of the course of '*Fundaments and methods of chemistry education*' and the project was supported by the University of Pisa with a specific didactic project.[40] Unfortunately, due to the covid-19 pandemic, the final part of the project, namely the carrying out of the activities designed by the undergraduate students with real school students, was not carried out in-person.

4. PUTTING THE EDUCATIONAL PROJECT INTO PRACTICE WITH FUTURE CHEMISTRY TEACHERS

4.1 From the visit at the Science Museum…

The first step of the educational project was the visit to the Science Museum 'Galileo' in Florence the 26th of October 2019. The visit was planned in advance with the collaboration of dr. Andrea Gori who is the responsible of the education activities carried out at the science museum. A special guided tour was organized to let students know and enjoy the scientific and historic collections starting from the Medici's and Lorenese collections of historical instruments and maps, and the large collection of instruments of mathematics, physics and astronomy (see Figure 1).[43] The visit to the scientific museum was enriched by an interactive lesson, of about one hour, held in the historical library of the museum (see Figure 1). Here, dr. Andrea Gori talked with undergraduate students about the educational projects and activities typically organized in the science museum, involving children and school students.

Figure 1. Pictures taken during the visit at the Museum 'Galileo' under the guide of the curator of the educational activities at the science museum, dr. Andrea Gori. (photo credit: Valentina Domenici).

Figure 2. Pictures of historical objects present in the Museum 'Galileo' related to Chemistry. On the left: collection of thermoscopes and thermometers designed by Ferdinando II de' Medici in the middle of the XVII century in Florence. On the right: original of the '*Tabula affinitatum*' made by Franz Huber Hoefer in 1766.[56-59] (photo credit: Valentina Domenici).

Students had the opportunity to receive a detailed explanation of the history and scientific relevance of the objects and instruments hosted in the room dedicated to '*Chemistry and the Public Usefulness of Science*' and of the glassware collection in '*The Accademia del Cimento: Art and Experimental Science*' room (see Figure 2).[53,55-57]

Before visiting the museum, students received an 'observation guided template' with some guided questions aimed at giving them some non-formal instructions on how to better observe the collections and to visit the museum with a critical attitude (see Table 1). Moreover, students were invited to prepare some questions concerning the laboratorial activities designed for students and for children by the museum 'Galileo'. Thanks to the competence and availability of the curator, dr. Andrea Gori, students could have a concrete idea how laboratorial activities for school students are designed and performed in a science museum.

After the visit to the museum, a lesson was dedicated to a collective discussion (step 2 of the project) concerning the experience at the science museum and an interactive activity was organized to put together students' impressions and observations during the guided tour. Some posters were prepared hosting their answers to the questions reported in Table 1 and other comments made by students (see some details of the posters in Figure 3).

Step 3 of the '*STEAM project-based learning*' methodology, namely the selection of chemistry-related top-

Table 1. 'Guided questions' given to the students before visiting the Museum.

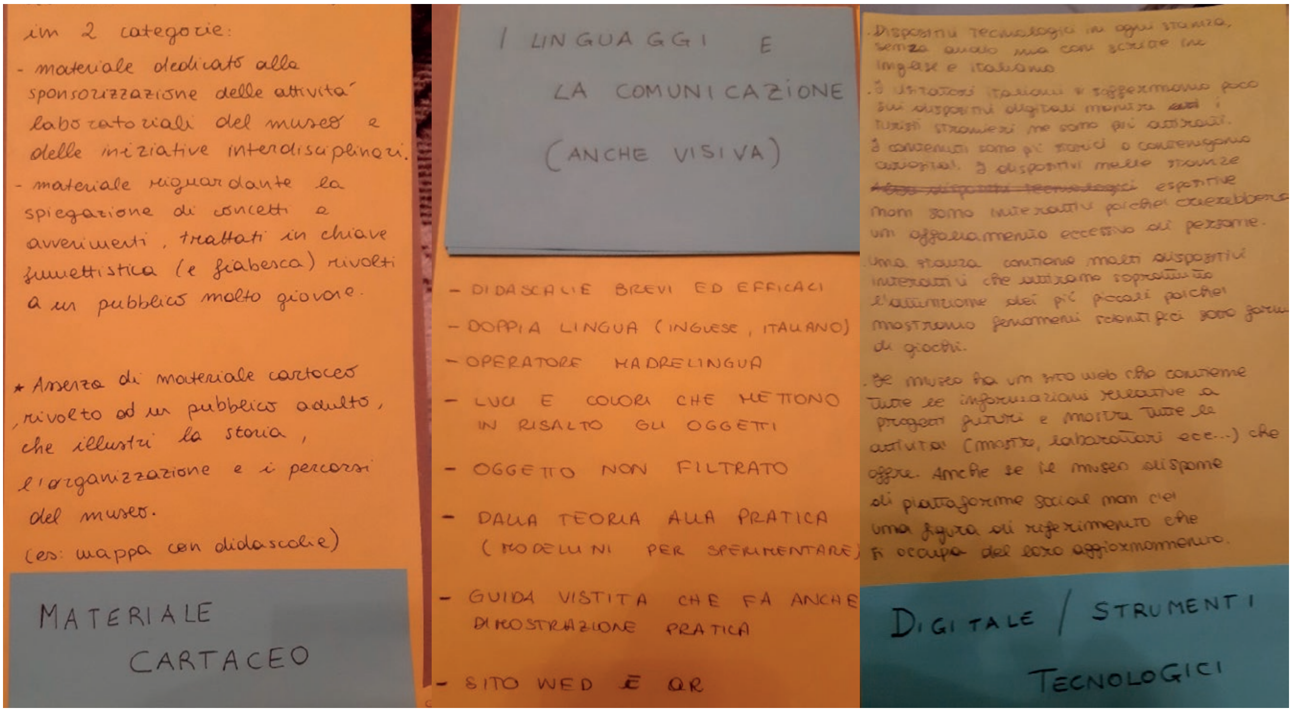
Observe the 'texts'	Are there written captions close to the scientific objects? Are there texts in different languages? How long are the captions? Do you think they contain all important information? How big and readable are the texts? Other comments…
Observe the 'collections'	What is the criterion of exposition? How are the expositions and the collections organized? Describe how the museum is structured and choose a room as an example. How are the scientific instruments and historical objects exhibited?
Observe the 'digital and media tools'	Are there digital tools in the museum? What are they like? Are there video projections? Are they used by the visitors? Describe one of these tools.
Observe the 'didactic laboratory' and 'educational activity' room	Is there a room or a space dedicated to the laboratorial activities with school students? How are the permanent exhibits specific for school students and children organized? Find all details about the planning and design of activities and ask to the guide relevant information, such as: how many students visit the museum every year? What is the main target? Are the laboratorial activities related to some specific objects or instruments present in the collection? What are the typical approaches used during the laboratorial activities? …
Observe the 'catalogues'	Examine the catalogues. Are there in print and / or digital ones? Are there informative materials for children? What is the language used? Are there photographs or pictures in the catalogue? Are the catalogues complete/ non complete / …? Are there brochures, posters and so on?
Observe the 'accessibility' of the Museum	Comment on the accessibility of the Museum to people with different disabilities. Do you think that all people can easily access to the museum? What are the limitations, if any?

ics inspired by the visit to the science museum, was an interesting part of the students' work. Students were very impressed by some historical objects, such as the Antonio Santucci's Armillary Sphere[60] and other mathematical instruments, and as a first activity, they tried to make some analogies between these historical models of the Universe and the models of the Atom developed at the end of the XIX and beginning of the XX centuries. Despite of the stimulating discussions, students moved their focus on 'more-chemical' objects, such as the '*Tabula affinitatum*' and the glassware collections of the museum 'Galileo'. At the end of this collective work, students decided to choose the historical thermoscopes and thermometers[59] for their further activities. Among them, it is worth noticing some particular thermoscopes, such as the *cluster thermometer*, consisting of six phials clustered on a column and resting on a round pedestal. Each phial contains a small glass sphere having a different density: density is the physical property at the basis of the motion of these spheres in the six phials when temperature changes. A series of *fifty-degree thermometers* with coloured liquids and a set of *thermometers with snail stems* also attracted the undergraduate students. As most of the thermometers collected at the Museum 'Galileo', the invention of these thermometers is attributed to Grand Duke Ferdinand II de' Medici and they were used by the members of the *Accademia del Cimento* mainly for meteorological applications. In addition, the historic collection at the museum 'Galileo' contains several thermoscopes, as the so-called 'Galilei's thermoscope, which was invented by Galileo during his stay in Padua in 1597.[61] These thermoscopes and thermometers were the object of educational activities devised by students, as will be described in the following paragraphs.

4.2 … to the design of the educational activities

The step 4 of the project is the design of educational activities to be carried out at school (formal context) or at the science museum or during open days at the University (non-formal context). Undergraduate students who participated to the visit to the museum 'Galileo' in Florence were divided in three groups of five students; then each group started working on some sub-topics related to the more general theme of '*Thermoscopes and the thermometers*'. Students decided to focus on the history of the thermoscopes and thermometers present in the science museum 'Galileo', such as the history of the discovery of the thermoscope by Galileo Galilei. One group decided to design a laboratorial activity concerning the construction of a thermoscope and the calibration of a thermometer. All activities were planned for high school students following a general hierarchic scheme of educational instruction (see Table 3 in ref. 18). Some educational aspects of the activities are reported in Scheme 1 for the three projects designed and proposed by the undergraduate students and in Figure 4 some photographs and drafts of the thermometers and thermoscopes object of investigation by the students during their educational project are reported.

During this activity (step 4 of the project), undergraduate students were very much interested in the sto-



in 2 categorie:
- materiale dedicato alla sponsorizzazione delle attività laboratoriali del museo e delle iniziative interdisciplinari.
- materiale riguardante la spiegazione di concetti e avvenimenti, trattati in chiave fumettistica (e fiabesca) rivolti a un pubblico molto giovane.

* Assenza di materiale cartaceo, rivolto ad un pubblico adulto, che illustri la storia, l'organizzazione e i percorsi del museo.
(es: mappa con didascalie)

MATERIALE CARTACEO

I LINGUAGGI E LA COMUNICAZIONE (ANCHE VISIVA)

- DIDASCALIE BREVI ED EFFICACI
- DOPPIA LINGUA (INGLESE, ITALIANO)
- OPERATORE MADRELINGUA
- LUCI E COLORI CHE METTONO IN RISALTO GLI OGGETTI
- OGGETTO NON FILTRATO
- DALLA TEORIA ALLA PRATICA (MODELLINI PER SPERIMENTARE)
- GUIDA VISTITA CHE FA ANCHE DIMOSTRAZIONE PRATICA
- SITO WED E QR

. Dispositivi tecnologici in ogni stanza, senza audio ma con scritte in inglese e italiano.
. I visitatori italiani si soffermano poco sui dispositivi digitali mentre ~~[illegible]~~ i turisti stranieri ne sono più attratti.
I contenuti sono più storici o contengono curiosità. I dispositivi nelle stanze ~~[illegible] dispositivi tecnologici~~ espositive non sono interattivi poiché creerebbero un affollamento eccessivo di persone.
. Una stanza contiene molti dispositivi interattivi che attirano soprattutto l'attenzione dei più piccoli poiché mostrano fenomeni scientifici sotto forma di giochi.
. Il museo ha un sito web che contiene tutte le informazioni relative a progetti futuri e mostra tutte le attività (mostre, laboratori ecc...) che offre. Anche se il museo dispone di piattaforme social non c'è una figura di riferimento che si occupa del loro aggiornamento.

DIGITALE / STRUMENTI TECNOLOGICI

(a) (b) (c)

Figure 3. Observations and comments made by the students during the visit at the Science Museum concerning several aspects as indicated in Table 1: comments about (a) the presence of catalogue, captions and brochures; (b) the language used, the type of communication, the presence of a web-site, eventual videos and animations; (c) the presence of interactive and digital tools, educational exhibits.

ries around the attribution to Galileo Galilei of the discovery of thermoscopes and thermometers. In fact, they knew about the Galileo's thermometer, which was not actually discovered by him, and they didn't know about the Galilei's thermoscope. This last one, as that reported in Figure 4a, was invented by Galileo Galilei to measure temperature when he was professor in Padua in 1597.[61]

This thermoscope consists of a small ampule with a long neck. The ampule is heated by the hands and then it is reversed and partially immersed in a container filled with water. When the hands are removed, the air in the ampule becomes colder and contracts, so that the water rises in the neck. The changes in air density due to the change of temperature are easily visualized by the increase or decrease of the level of water in the neck. It seems that the first liquid used by Galileo was the spirit of wine and later still the Grand Duke Ferdinand II of Florence, a former pupil of Galileo, used coloured spirit of wine and reduced the dimension of the tube to get a more precise instrument.

The so-called Galilei thermometer, as that shown in Figure 4b, was actually invented by members of the '*Accademia del Cimento*' in Florence, between 1657 and 1667, and for this reason is also called 'Florentine thermometer'.[46,47] It consists of a sealed glass cylinder containing a transparent liquid with suspended small glass spheres, called floaters, containing a coloured liquid. Each floater contains a liquid with a slightly different density, associated to a temperature tag. The principle of working is based on the temperature-dependence of the density of liquids. The liquid in the cylinder is in contact with the external air through the glass and it is supposed to be in thermal equilibrium. When the temperature increases the liquid in the cylinder decreases its density due to volume expansion, and floaters containing a liquid with lower density start moving up, while floaters with higher density go down. The temperature of the liquid of the cylinder is something in between the two floaters closer to the centre of the cylinder (such as the green and yellow floaters in Figure 4b).

During steps 5 and 6 of the project, which are focused on the preparation of materials and the simulation of the designed activities, undergraduate students were very much interested in the historical part. For instance, they realized that the motivation at the basis of the invention of the thermoscopes and thermometers, mainly related to meteorology (i.e. knowing the air temperature, and the changes during the day or during a

Scheme 1. Main aspects of the three educational projects designed by the undergraduate students who visited the science museum ‘Galileo’ in Florence.

Relevant aspects	**Description**
Activity n. 1 (first group of students)	
Scientific topics	The thermoscopes. History of the thermoscopes of the scientific collection at the museum ‘Galileo’
Target	High school students (first year)
Main chemical-related topics	Glassware, liquid and gas states of matter, expansion of gases and liquids and temperature effect, density of liquids, temperature.
Guided questions / inspiring questions to start the activity	What is a thermoscope and what is its use? Who invented the first thermoscopes? Look at these objects (real ones or photographs, as the ones reported in **Figure 4a**) and search for information about their history, inventors, functioning (guided activities on the web).
Methodology	Inquiry-based activities; historical approach.
Timing	2 hours
Notes	This activity is particularly useful to introduce the topic of ‘temperature’ and how different chemical substances behave by changing the temperature, and how liquids and gases behave at different temperatures.
Main educational objectives	Search for information about the history of an instrument by using materials provided by the teacher and on the web. Understand the principles of functioning of a ‘thermoscope’. Understand the phenomenon of gas expansion by changing the temperature. Understand the role of the shape of glass components of a thermoscope. Know the role of the first thermoscopes and their first applications.
Activity n. 2 (second group of students)	
Scientific topics	The ‘Galilei’s thermometer: the real history and inventors. How does it work?
Target	High school students (second year)
Main chemical-related topics	Glassware, liquid and gas states of matters, expansion of gas and liquid, density of liquids, miscibility / immiscibility among liquids, solutions, concentrations, temperature-dependence of some chemical-physical properties.
Guided questions / inspiring questions to start the activity	How does the so called ‘Galilei’s thermometer’ work? What are the principles of functioning? Do you know the history of this thermometer? Who were the real inventors of this thermometer? What are the uses of this thermometer? What is the sensitivity and what are the applications of this thermometer?
Methodology	Inquiry-based learning; cooperative learning; historical approach.
Timing	3 hours
Notes	This activity consists in three parts. First, students are divided in groups according to the cooperative learning method, some groups are invited to search for information about the so-called modern ‘Galilei’s thermometer’ (see **Figure 4b**) and the principles of functioning. Other groups have a different task: search for the historical origin of this thermometer: why it is referred to Galileo Galilei and who are the real inventors? The second part of the activity is a collective discussion aimed at sharing the relevant information obtained by the groups. The third part is the preparation of a poster and some educational materials (i.e. brochures) about the history, scientific principles and main applications of this thermometer.
Main educational objectives	Understand the differences between thermoscopes and thermometers; understand the working principles of the Galilei’s thermometer; understand the temperature-dependence of the density in liquids; search for scientific and historic information on resources on-line and read a scientific paper provided by the teacher concerning thermoscopes and thermometers.
Activity n. 3 (third group of students)	
Scientific topics	From the thermoscopes to the thermometers. Let’s build our own instruments.
Target	High school students (second year)
Main chemical-related topics	Glassware, liquid and gas states of matter, expansion of gas and liquid, density of liquids, miscibility / immiscibility among liquids, solutions, concentrations, temperature-dependence of some chemical-physical properties.
Guided questions / inspiring questions to start the activity	What is the difference between a thermoscope and a thermometer? What are the basic principles of an alcohol thermometer? How is the graduate scale on a thermometer determined? What are the main uses of a thermoscope? And of a thermometer?
Methodology	Inquiry based and laboratorial activity

Relevant aspects	Description
Timing	3 hours
Notes	This is a laboratorial activity made of two steps. The first step is the building of a thermoscope and the second step is the calibration of a thermoscope to be used as a thermometer. These activities are relatively simple and the materials to be used are usually available (see for instance refs. 55 and 63).
Main educational objectives	Understand the differences between thermoscopes and thermometers; put into practice the scientific knowledge and design of a simple thermoscope; use common materials to build a thermoscope and a thermometer; acquire some practical skills related to the building of an instrument; estimate the sensitivity of the instrument; apply the instruments to measure the temperature of different systems.


(a) (b) (c)

Figure 4. Some of the thermoscopes and thermometers as object of the investigation and educational activities planned by the students. (a) An historical thermoscope similar to the ones contained in the collection of the science museum 'Galileo' (photo credit: Wikipedia: https://commons.wikimedia.org/);[55-57,62] (b) An example of a modern and commercial version of the so-called 'Galilei's thermometer' (photo credit: Wikipedia: https://commons.wikimedia.org/);[46,47] (c) draw of a thermoscope made by a student during the educational activities.

period of time) are very important from the educational point of view. Another aspect which merits some attention by the teachers is the counterintuitive functioning of the Galilei's thermoscopes with respect to modern bulb thermometers. In fact, the increase of temperature of the air contained in the ampule corresponds to a decrease of the level of the water (or alcohol or other coloured liquids) in the thick neck.

It's worth noticing that during the preparation of the educational materials of the three projects students used their creativity and skills related to their ability to draw, organize the materials and use interactive tools and resources. In this respect, several steps of the project allowed me to note the potentialities of a STEAM approach, combined with the effectiveness of the cooperative learning methodology.

As previously stated, undergraduate students could not put their projects into practice (step 7), which were planned during the second semester when the covid-19 pandemic started. The project concluded with the presentation of their cooperative works during the final exam of the course and the efficacy of the methodology was verified by analysing their feedbacks and final evaluation tests.[18]

5. CONCLUSIONS AND FUTURE PERSPECTIVES

The pilot study here reported concerns a structured method for training future chemistry teachers, called '*STEAM project-based learning*', which is centred on the role of science museums and historical scientific collections on learning science and, in particular, chemistry. As reported in this paper, the visit to a science museum represents a great stimulus for students and teachers, since a simple object in a collection can instil original ideas of how to approach a specific scientific topic or to build a non-formal activity related to a chemical concept. This methodology has been optimized within a course of 'chemistry education', as reported in refs. 2 and 18, and the feasibility of this approach at undergraduate level has been discussed. In the literature, other examples of activities about chemistry with educational approaches typical of science museums have been also reported at high school level.[2,5,7,64,65] All these experiences and research works demonstrated that non-formal hands-on activities centred on scientific museum or historical collections are very be effective in engaging students, improving their interest toward scientific topics and developing communication skills. As in the case reported here, where students decided to focus their attention on historical thermoscopes and thermometers held by the science museum 'Galileo' in Florence (Italy), the educational activities can be designed to include history of science in an interactive and constructive way,[30] with the aim to develop skills, which are usually indicated as higher order thinking skills, typically reached at the high school educational level. The STEAM philosophical approach is particularly suited for non-formal contexts, such as the science museum, and in this work, it is one of the key aspects of the methodology adopted during the course of '*Fundaments and methods of chemistry education*'. In the educational activities designed by the undergraduate students, the interdisciplinarity aspect is related to the main scientific disciplines, chemistry and physics, and to history of science, among humanistic disciplines. A key part of the project is the hands-on activity, since laboratorial activities need to have a high level of active participation in all steps, from the planning to the putting into practice, as also reported in other cases.[7,18,66] The only limitation of this project and in general of this educational approach is that it needs much more time than normal lessons, and it require a very good preparation by the teachers, who need to visit the museum in advance, prepare the materials and dedicate extra-curricular hours to let students work to their project. In the case study reported in this paper, it is important to underline that the undergraduate students who participated were able to explore some scientific concepts, such as the temperature, the temperature-dependence of density, the miscibility among liquids, the density as chemical-physical property of a chemical substance, by using non-formal educational methodologies starting from the investigation of the history of some objects collected in the science museum. Among the active methodologies at the basis of the activities designed by future chemistry teachers, the inquiry-based, cooperative and laboratorial learning methods were used in combination with the historical approach, which underlines the role of the 'humanistic' level in chemistry education teaching and learning models. From the evaluation of the project done by the students at the end of the course and from their final exam, I can conclude that this pilot project merits to be continued and implemented with the hope to be able in the next years to put into practice the activities planned by the students at the end of the project.

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Feature Article

A New Response to Wray and an Attempt to Widen the Conversation

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Abstract. This article begins by examining a recent claim by Brad Wray that the discovery of atomic number and isotopy constitutes a scientific revolution in the sense of the later writings of Thomas Kuhn. I argue that although Kuhn's criteria may apply to the change from the Ptolemaic to the Copernican model of the universe, they do not apply in the above chemical or atomic case. I also examine the wider issue of Kuhn's turning away from internal scientific issues to a consideration of lexical issues. I conclude, as others have done before me, that this may have been a wrong turn in view of the emphasis being placed on questions of sense rather than reference.

Kewords: Kuhn, scientific revolution, periodic table, atomic number, natural kinds, sense and reference, isotopes

1. INTRODUCTION

In teaching introductory philosophy of science, one makes a distinction between Popper and Kuhn and the fact that for Popper a decisive refutation such as the discovery of black swans is supposed to lead to the abandonment of the 'law', that all swans are white, provided there are no non ad-hoc moves that can rescue the theory.

By contrast Kuhn's account is said to be more permissive because it allows for the occurrence of anomalies, although these events do not cause the sudden downfall of the paradigm. One needs to wait for more anomalies, which eventually lead to a crisis, a revolution, and eventually the establishment of a new paradigm. An important aspect of this scenario is that there need to be several anomalies.[1]

In the case of the periodic table there were just two anomalies in which ordering the elements according to their atomic weights failed to classify a total of four elements in their correct groups, as revealed through their chemical properties. These so-called pair reversals consisted of the more significant case of the elements tellurium and iodine with an atomic weight weight difference of 0.7 atomic weight units and the nickel cobalt anomaly

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[1] I am referring to the original account by Thomas Kuhn as stated in his classic book, *The Structure of Scientific Revolutions.*

(0.2 units). This situation clearly did not constitute a scientific crisis, on its way to becoming a scientific revolution in the sense of Kuhn's early account.[2]

The modification made by Mendeleev and other discoverers of the periodic table of reversing the positions of tellurium and iodine as well as of cobalt and nickel was not ad-hoc, since it accommodated the known properties of these elements. The paradigm of the periodic table was rescued successfully, in that all the other elements could still be ordered according to increasing values of atomic weight.

The anomalies that Mendeleev and his contemporaries experienced eventually led others to discover isotopes, rather than refuting or revolutionizing the periodic table. Similarly, the discovery of numerous radioisotopes in the early 20th century did not lead to the downfall of chemistry's central paradigm of the periodic table.

In the Copernican revolution however, it was not just a matter of one or two planets not orbiting as they should, but a major turning inside-out of the prevailing geocentric paradigm. Later on, one or two planets were found to have anomalous orbits. This fact did not lead to an overthrow of the Copernican paradigm but indeed to the successful prediction of the planet Uranus. So much, for the time being, for the way that Kuhn originally envisages scientific revolutions.

The philosopher of science Brad Wray has proposed that the discovery of atomic number and change in the manner that elements were defined represented a scientific revolution (Wray, 2018).[3] However, as I previously responded, once the focus had been narrowed from protons and neutrons to just protons (from atomic weight to atomic number) everything fell into place and there was no revolution to speak of (Scerri, 2021).[4] As I see it, science develops via a process of greater focus, greater specialization[5] and looking at increasingly more microscopic components. For example, the major changes in modern biology and chemistry have come about due to a focus on DNA and the electron, in biology and chemistry respectively. Science does not progress by merely changing the manner in which scientific entities like planets and elements are defined. Science is more about ontology than about the manner in which human beings classify the world. Of course, our concepts can prejudice what we observe, experiments are theory-laden and so on. But one need not go overboard in thinking that scientific discoveries cannot occur until the appropriate terminology is available.

I suggest that Kuhn may have been wrong to place such a big emphasis on scientific lexicon in his later work.[6] Such a step may have been motivated by needing to respond to his many critics, but he may have thereby taken a step away from what matters most in scientific practice.[7]

Regardless of whether it may be a revolution in the later Kuhnian sense, what is more important, or perhaps more interesting, is the question of whether the change from atomic weight to atomic numbering ordering and the related change in the definition of an element is a revolution in a broad sense that other philosophers of science or even scientists themselves might accept. The answer to this latter question must be a resounding no, in my view. Neither the change from the use of atomic weight to using atomic number for ordering the elements, nor the way that the term "element" should be understood, represented a scientific revolution in this broader sense.[8]

2. ARE THERE *ANY* REVOLUTIONS IN CHEMISTRY?

In the field of physics there have clearly been some developments which one might want to identify as being of a revolutionary nature. One need only think of Einstein's special and the later general theory of relativity. In addition, the development of quantum mechanics can rightly be considered to have been a major scientific revolution in many respects. In biology one may speak of the Darwinian revolution whereby all living creatures, and indeed also plants, became regarded as having descended from a common origin.

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[2] At later stages in the history of the periodic table two further atomic weight anomalies of this kind also emerged. One of them followed the discovery of the noble gas argon, which has an atomic weight that is lower than the element potassium although their ordering is such that argon is placed before potassium. The fourth atomic weight anomaly concerns thorium and protactinium, the latter of which was only discovered in 1917. Although protactinium is a whole atomic unit lighter than that of thorium, its place in the periodic table follows that of thorium. This fourth example represents the largest atomic weight anomaly of the four known cases. Neither of these further examples were known to exist at the time of the discovery of the periodic system.

[3] One of the reviewers of this article reminds me that Wray's suggested revolution concerning the discovery of atmomic number and isotopes is not especially original, since it had previously been discussed by Jensen in 1998.

[4] This statement is somewhat ahistorical in that neutrons were not identified until the year 1930.

[5] Kuhn makes precisely this point about increasing specialization as science develops in his later writing (Kuhn, 1990).

[6] At the same time, I do not wish to neglect the relevance of lexicon and linguistic aspects in general in the development of scientific ideas. I am only suggesting that Kuhn may be placing too much emphasis on these factors.

[7] Others have even suggested that this was Kuhn's biggest mistake (Garber, 2016).

[8] My view is supported in a recent article by Pieter Thyssen who points out that Paneth emphasized the continuity with the older definition of elements while providing a new definition in terms of atomic number which was adopted by IUPAC (Thyssen, in press).

Has the field of chemistry experienced anything as remotely momentous as these revolutions? I believe not, apart from what is generally called the Chemical Revolution, which is mainly attributed to the work of Lavoisier, although even in this case there are many who doubt whether it may have been a genuine revolution (Blumenthal, 2013).

Indeed, the lack of the existence of a philosophy of chemistry, which persisted until relatively recently, can perhaps be attributed to the lack of any major revolution that could compare with the above-named examples from physics and biology.[9] The periodic table, which is undoubtedly one of the paradigms of modern chemistry, has stood for over 150 years since its discovery in the 1860s. There has yet to be, I claim, anything resembling a revolution in post-Lavoisier modern chemistry.

I believe this general background is important when weighing Brad Wray's proposal that the discovery of atomic number, isotopy and the new way of identifying elements, that took place in the 1910s and 1920s should be regarded as any kind of scientific revolution.

3. WRAY'S ATTEMPT TO DRAW AN ANALOGY BETWEEN THE COPERNICAN REVOLUTION AND THE EVENTS THAT TOOK PLACE IN CHEMISTRY IN THE 1910S AND 1920S

Wray begins by explaining that before Copernicus, all bodies observed in the night sky were regarded as stars, except those that wandered, which were said to be planets. Following the Copernican revolution, the Earth, Sun and Moon ceased being identified as planets. Of course, they still continued to 'wander' but they became deprived of their planetary status.

In Mendeleev's time there were about 60 elements which shared the characteristic of each possessing a unique atomic weight. Notice that there is no analogous contrast between stars and planets in the chemical case in question. All the observed microscopic entities were classified as belonging to one kind, namely elements. This is the first of what I take to be dis-analogies to the astronomical case that was just discussed.

Following the discovery of atomic number by Moseley, and of isotopes by Soddy, some observed chemical entities with particular atomic weights were no longer classed as elements. This episode is taken by Wray as being a significant analogy to the change accompanying the Ptolemaic and Copernican view of planets. However, this attempt fails in the chemical case because one could equally well say that all isotopes were now regarded as having unique atomic weights, while some of these weights also corresponded to the weights of elements. I am referring to the not insignificant number of elements which are mono-isotopic.[10] For example, the element iodine only has one isotope. The atomic weight of this isotope thus succeeds in identifying this element and in distinguishing it from all other elements.

Returning to the astronomical case, some of the observed objects, namely the Sun, Moon and Earth changed their status and ceased being planets. In the chemical case some of the detected microscopic entities characterized through their atomic weights ceased being identified as elements. However, in the astronomical case the status of planethood and non-planethood are mutually exclusive. In the chemical case, some of the thousans of microscopic entities whose weights have been determined ceased being regarded as distinct elements, but by no means all of them. Being an isotope and being a distinct element are not mutually exclusive. The isotopes of monoisotopic elements are both members of the general class of isotopes but also members of the class of isotopes which happen to also count as elements in their own right.

This is precisely the kind of overlap that Wray does not seem to be aware of when he claims that this chemical case represents a violaion of Kuhn's no-overlap principle. As I have just explained, it is simply not the case that atomic weight per se fails to identify all elements. A single isotope of iodine, to return to the same example, can be identified with the only microscopic particles of the element iodine that exist.

Yet a third dis-analogy has to do with the fact that the term planet is not a natural kind but more of a conventional label assigned by popular consent. One only needs to consider the notorious 'Pluto affair' that took place in the year 2016, when the International Astronomical Union ruled that Pluto was no longer a planet because of some of the characteristics of its orbital motion (Bokulich, 2014).

No similar ambiguity exists regarding what is, or is not, an isotope of any element. If a microscopic atomic entity has a unique mass, it counts as an isotope. Similarly, each element has a unique atomic number. If an

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[9] The philosophy of chemistry as an academic discipline came into being in the mid 1990s and has continued to develop since them. For example, the International Society for the Philosophy of Chemistry has held an international meeting during each of the previous 26 years, while the official journal for this society, *Foundations of Chemistry*, began publication in 1999.

[10] Perhaps Wray is not aware of the existence of many mono-isotopic elements which include, beryllium, fluorine, sodium, aluminum, phosphorus, scandium, manganese, cobalt, arsenic, yttrium, niobium, rhodium, iodine, caesium, praseodymium, terbium, holmium, thulium and gold.

atom is found to have a particular atomic number this identifies it as one of the currently 118 known elements. Conversely, the identification of any given element, such as gold for example, is uniquely associated with having an atomic number of 79. Said otherwise, the possession of a particular atomic number is both necessary and sufficient for identifying any particular element. None of this kind of precision applies to the conventionally stipulated term of planet. Simply put, elements are natural kinds whereas planets are not.[11]

4. THE ORIGINAL KUHN AND THE LATER KUHN

The refinement in the meaning of a paradigm that took place in Kuhn's later work is not supposed to dismiss the original view, a feature that Wray seems to agree with. The two Kuhnian senses of what constitutes a scientific revolution are not radically different. Kuhn's later understanding of a revolution, as Brad Wray concedes, is only meant to be a refinement of his earlier one.

> In reconceptualizing the notion of a scientific revolution, Kuhn was not intending to change his view fundamentally. Rather, he regarded his later reconceptualization as a refinement of the view presented in Structure. Thus, he thought of the new definition as picking out the same sorts of changes that he identified as "paradigm changes" in Structure (Wray, 2022).

However, the way that Wray portrays matters suggests that there is a little by way of intersection between the earlier and later Kuhn views, except perhaps for the case of the Copernican revolution. And even in this case, on Wray's reading we are invited to believe that the real revolution is not the simple fact that the earth and other planets circle the Sun, but rather the far less important point that the Earth, Sun and Moon and no longer classified as planets.

As some Kuhn scholars have written, the more important difference between the Ptolemaic and the Copernican paradigms had more to do with comets than with the reassessement of whether any particular celestial body was a planet or not (Andersen, Barker, Chen, 2009).

There is presumably no sense in which scientific revolutions according to the early and the later Kuhn can be considered as incommensurable or said to be populating different worlds. I take it for granted that Kuhn did not wish to claim that his youthful and later selves inhabited radically different worlds.

More importantly perhaps, it appears that for the later Kuhn, the paradigm no longer concerns the ontological question of what objects moves around which other object, but a terminological question of whether to call the sun, for example, a planet or not. But the question of terminology belongs in the realm of human construction, regardless of whether we are speaking of planets or elements. What matters more is the behavior of these entities. In the case of atomic weight and atomic number what matters is whether one concentrates on the proton (atomic number) or on the whole atom (atomic weight). It is more a matter of reference than of sense, or a matter of extension rather than of intension.

5. SPECIFIC RESPONSES TO WRAY'S RECENT ARTICLE

In an article published in 2022 Brad Wray returns to our debate concerning whether the discovery of atomic number and isotopes constitutes a scientific revolution in the sense of Thomas Kuhn's later views. In his opening remarks Wray writes,

> …one reason Scerri and I have different views about this particular case in the history of chemistry is that we are not attending to the same Kuhnian account of scientific revolutions (wray, 2022).

I find this statement rather odd, given that I went to great lengths to examine Wray's claim in the light of Kuhn's later, as well as his earlier accounts of scientific revolutions and concluded that he was referring to the later view (Scerri, 2021)

Wray returns to this point a little later and says,

> I have said that the revolution in twentieth Century chemistry is a "classic" Kuhnian revolution, and Scerri is critical of this claim (see Scerri 2021, 7.3). This, I think, is simply a verbal dispute. Kuhn's later account of scientific revolutions (see Kuhn 2000), the one I draw on, is somewhat different from the account he presents in his 1962 classic, *The Structure of Scientific Revolutions* (see Kuhn 1962/2012). There, as noted above, Kuhn characterized scientific revolutions as paradigm changes. Perhaps Scerri is correct to insist that the "classic" Kuhnian view is the view expressed in The Structure of Scientific Revolutions, not the view Kuhn later developed, which is the one I draw on. By "classic" I merely meant typical (Wray, 2022)

In any case I am glad that Wray and I appear to be focusing our debate a little more closely on Kuhn's later view and that Wray seems to regret his use of the term "classic" in this context. Before moving on I would just

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[11] Indeed, elements are perhaps the epitome of natural kinds and have served as the prime example of such in innumerable philosophical articles on the subject (Kendig, 2016; Scerri, 2020).

like to remark that this new qualification by Wray, to mean typical cases, raises some new problems, since I am not aware that Kuhn or any other authors have re-examined many of his earlier revolutions such that one may speak of typical cases in the later sense. As far as I am aware Kuhn speaks of the Copernican revolution and the Chemical Revolutions but no other specific examples after his lexical turn.[12]

Returning to Wray, he also writes,

> Kuhn classified the change from the Ptolemaic Theory to the Copernican Theory as a scientific revolution, and most philosophers of science would agree with Kuhn's assessment.

Here, after assuring us that he only wishes to consider Kuhn's later view, Wray appears to be returning to the more general claim concerning revolutions or the earlier Kuhnian view. Yes, it may indeed be the case that most philosophers of science would agree that this astronomical example constitutes a revolution, but especially not for the reasons that the later Kuhn claims it to be so.

Most philosophers and indeed scientists too, would consider this case to be a revolution because it involved an almost literal 'turn-around' or inversion of the previously held view. Whereas the Ptolemaic universe holds that the earth is the focal point around which everything revolves, the Copernican view involves an inversion such that everything revolves around the sun. Philosophers and scientists do not regard this case as a revolution because of the lexical changes that may have taken place and because a few astronomical bodies were no longer considered as planets as a result.

But Wray's regression to speaking of revolutions in the more general sense is rather inevitable, given that the later Kuhnian view is supposed to generalize his earlier one, and not intended to provide an altogether different sense. In the final analysis, it may not be possible to divorce the early from the later Kuhnian view of revolutions, since the later view was meant only as a refinement of the earlier one.

In his recent response, Wray also claims that my use of a Venn diagram in which I aimed to show the relationship between atomic weight and atomic number is misleading,

> Scerri's diagram for the chemical revolution has circles representing the parts of an atom—proton, neutron, and electron. This diagram masks over the revolutionary nature of the change that occurred in chemistry. Indeed, this diagram is focusing on the wrong concepts, specifically, atomic weight and atomic number. In order to understand the revolutionary nature of the change, we need to focus on the change in the extension of the term "chemical element." The extension of the term is significantly different before and after the discovery of atomic number.

While I accept that part of the alleged revolution in the sense of the later Kuhn is supposed to be concerned with the term element, I must insist that the question of the relationship between atomic weight and atomic number is crucial to the discussion. The way in which certain isotopes ceased to be regarded as elements was precisely due to their having a distinct atomic weight, while sharing the atomic number of an element that was already recorgnized as such. Moreover, I am claiming that these two concepts show a great deal of ovelap rather than standing side by side as distinct ontological categories in the manner that Wray appears to conceive of them, in his own Venn diagram that he proposes in his most recent contribution.

Wray dismissal of my Venn diagram which seeks to clarify the relationship between atomic number and atomic weight is puzzling, given that his initial article on this subjected treated two issues, (1) change from atomic weight ordering to the use of atomic number and (2) the discovery of isotopes of elements on a par. For example, the opening words of his original article were,

> The aim of this paper is to provide an analysis of the discovery of atomic number and its effects on chemistry. The paper aims to show that this is a classic textbook case of a Kuhnian scientific revolution (Wray 2018, 209).

In the same article he also writes,

> Perhaps most significant in this process was the discovery of atomic number.

as well as,

> Contemporaneous with this research on atomic number was another research program examining the various anomalous chemical elements that shared the same chemical properties but differed with respect to atomic weight (Wray, 2018).
>
> These two discoveries complimented each other. Once chemical elements were thought of as essentially defined by their atomic number, the notion of an isotope was no longer a conceptual impossibility.

Another problem with Wray's account is his constantly referring to the discoveries of atomic number

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[12] Indeed, it would be rather useful is somebody were to undertake the task of re-examining Kuhns earlier revolutions to see whether they stand up in the light of his new criteria having to do with lexical changes, diversification of disciplines and the no-overlap principle.

and isotopes as bringing about a change of theory in chemistry. However, these specific anomalies did not contribute to bringing about a radical change of theory in chemistry. As I already pointed out in my earlier response, the discoveries of atomic number and of the phenomenon of isotopy did not bring about any change whatsoever to the prevailing chemical theory. The discovery of a better means of ordering the elements does not constitute a theory by any stretch of the imagination and nor does the realization that atoms of the same element may differ in their weights. Theories are generally understood as being explanatory frameworks such as quantum theory or the theory of relativity in physics, and not as specific discoveries that resolve equally particular anomalies in any particular discipline.[13]

6. KUHN AND THE VIOLATION OF THE NO-OVERLAP PRINCIPLE

Kuhn's later discussions of scientific revolutions is centered around his principle of the violation of no-overlap. Kuhn wrote very little on this principle which he first introduced in an article of 1987 titled, 'What are scientific revolutions? (Kuhn, 2000). He revisited this theme in 1990 while giving a presidential address to the Philosophy of Science Association (Kuhn, 1990).

In the course of these writings Kuhn gave very few examples, and of the few that he did provide, only one was a scientific case, namely the turn from the Ptolemaic to the Copernican universe. I am not aware of whether he ever returned to elaborate fully on this 'principle'. In the course of his speech to the PSA Kuhn alludes to a book that he is in the process of writing to finally answer his critics but, as is well known, such a book has never materialized.[14]

Given the rudimentary and underdeveloped nature of this principle, I suggest that it may be a little risky for commentators like Wray to connect their claims for new revolutions quite so firmly with it.

It should also be noted that Kuhn's use of the double negative in the concept of violation of no overlap is rather confusing. Such a double negation could amount to saying that there is in fact overlap. And if this state of affairs does exist between two paradigms, or two competing scientific lexicons, there seems to be no reason whatsoever for claiming any form of incommensurability.

If the manner in which the Earth, Sun and Moon was classified did show overlap between the Ptolemaic and Copernican paradigms, there would be no lack of agreement as to whether they were planets or not.

Clearly such a reading of the violation of no-overlap is not what Kuhn had in mind. What then did Kuhn mean to say regarding which heavenly bodies were considered to be planets before and after the Copernican revolution in connection with his principle? For a more correct, although I still claim rather convoluted use of his principle, I am grateful to Vincenzo Politi for providing the following passage.

> Ptolemy's and Copernicus's cosmologies are taxonomically incommensurable, because there cannot exist a conceptual taxonomy in which the moon is both a planet (as in the Ptolemaic classification) and a satellite (as in Copernicus's): such a taxonomy would clearly violate the no-overlap principle (Politi, 2022).

In other words, if the principle was not violated, there would be overlap between the two paradigms since the Moon *would* be a member of both natural kinds. If that were so there would be no incommensurability. But of course, Kuhn wants to claim that such a lack of overlap implies incommensurability and consequently the occurrence of a scientific revolution.

Or as James Marcum writes,

> Another important property of kind terms is conceptual, regarding the relations between kind terms and referents. These relations are governed by a non-overlap principle. Kuhn notes that "no two kind terms, no two terms with the same kind label may overlap in their referents unless they are related as species to genus" (Ibid.). For example, there are no gold rings that are also silver rings, but there are red things that are also beautiful. If two kind terms do have overlapping referents in a speech community, communication failures are inevitable: people simply do nt know how to name those referents in the overlapping region (Marcum, 2018).

In the case of atomic particles, the objects in question can be characterized by their masses, with each object having a unique mass. In former times such massive particles were all classified as elements. However, since Moseley's work they can be classified as isotopes of a particular element, but some such particles can be classified as both. An isotope of iodine, to return to my earlier example, is an example of a unique isotope but also a case of an atomic particle of a unique element.

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[13] Needless to say, I do not deny the epistemic significance of the discovery of isotopes in the development of our knowledge of the structure of atoms and its relevance to understanding the periodic table in a more profound manner than was previously available. I thank a reviewer for suggesting this qualification.

[14] It appears that Kuhn gave the text of the book to James Conant so that he might complete it, something that has not yet occurred.

Such isotopes provide examples of where there is overlap and therefore no violation of Kuhn's no-overlap principle. The paradigm which dealt only with elements and the later paradigm which deals in isotopes as well as elements, are not taxonomically incommensurable in the case of monoisotopic elements. Kuhn would therefore have to conclude that there is no scientific revolution involved in the change of taxonomy that was brought about by the discovery of atomic number and of isotopes. There are approximately 15 elements that only have one isotope in the same way that iodine has.

Isotope and element are not at the same taxonomic level, in the same way that cat and dog, two of Kuhn's favorite examples are. An isotope is a subclass of the concept of element in the majority of cases, namely all the elements that are not monoisotopic. It would appear that Wray is not aware of these points, otherwise he would not be suggesting that the astronomical case is analogous to the atomic case. The discovery of isotopes does not represent a revolution in the sense of the later Kuhn in the same way that the change from the Ptolemaic to the Copernican model may do.

If one places more attention on the reference of the terms planet, or isotope, I believe that the alleged incommensurabiity dissolves. The fact that the moon circles the earth leads to the moon being classified as a satellite in the Copernican model rather than as a planet. But this change only concerns how this astronomical body is being classified. The referent is still that unique astronomical body which waxes and wanes in the course of each month and that we are all familiar with.

Of course, the situation is a little more complicated than I have just implied since the manner in which natural kinds are identified appears to have undergone an almost cyclic change in the history of philosophy (McCulloch, 1989). Very briefly, according to Frege, natural kinds were identified by means of sense or through a description of their attributes. In the 1970's Kripke and Putnam famously posited their causal theory of reference in which natural kinds were to be picked out according to their intrinsic properties such as the fact that the element gold was and substance whose atoms have atomic number of 79. It is significant that the causal theory of reference was also used to counter Kuhn's talk of incommensurability and to restore the commonsense view that descriptions may change as science develops but the entities in question do not.

More recently the Kripke-Putnam view has been subjected to a good deal of criticism since it seems to completely exclude any form of interest dependence on the part pf scientists. In response, Richard Boyd has introduced his homeostatic property cluster theory (HPC). Boyd postulates the existence of a homeostatic mechanism capable of explaining why those properties are statistically associated with each other and shared by the members of a given kind (Boyd, 1991). But none of these recent developments in the study of natural kinds represent a rejection of the attention that contemporary philosophy of science places upon matters of scientific ontology.

7. THE WIDER QUESTION

One can only hope that Thomas Kuhn might have approved of Wray's desire to find further examples of scientific revolutions in the later sense of Kuhn. Moreover, Wray's defence of Kuhn in this way appears to be a form of 'normal Kuhnian philosophy of science', to coin an analogous term to Kuhn's talk of normal science, within which scientists do not challenge the prevailing paradigm. Brad Wray, who has carried out much work on the views of Kuhn, appears to be working only within the limitations of Kuhn's views, albeit the later and supposedly more refined view. Wray does not seem to want to pose the question of whether the discovery of atomic number and of isotopes constitute a revolution in the way that other philosophers of science might view the concept.

I propose to now take an alternative view of the situation, and one that I believe many of Kuhn's critics might also share. It is well known that Kuhn's original position received a great deal of criticism from historians as well as philosophers of science especially on the question of incommensurability (Shapere, 1964; Hacking, 1981; Scheffler, 1967; Putnam, 1981; Davidson, 2001; Kitcher, 1978).

As a more recent critic writes,

> He [Kuhn] argued that these criticisms depended on the "literally correct but regularly overinterpreted assumption that, if two theories are incommensurable, they must be stated in mutually untranslatable languages." Now, if the two theories could not be stated in a single language, they could not be compared. Furthermore, these critics claimed that if Kuhn were right, then archaic scientific theories could not be translated into modern language. But in *Structure* and elsewhere, that is exactly what Kuhn did: he both compared supposedly incommensurable theories with one another and he translated them into modern language. In both cases, his practice would seem to be inconsistent with his conception of incommensurability. (Garber, 2012, 505)

and in another article,

> Kuhn's extended attempt to answer the philosophers has always struck me as one of the great tragedies in the his-

> tory and philosophy of science. It didn't have to be this way. There is much that was right in Kuhn's idea of the incommensurability of paradigms at the very beginning, in *Structure*. The history of his later struggles with incommensurability is a sad story of a great thinker who allowed himself to be led down a dead end (Garber, 2012, 506)

Indeed, Kuhn spent the remainder of his working life in attempting to explain what he had really meant, as well as in modifying what he had originally stated.

Here is how Kuhn expressed himself on this process,

> My own encounter with incommensurability was the first step on the road to *Structure*, and the notion still seems to me the central innovation introduced by the book. Even before *Structure* appeared, however, I knew that my attempts to describe its central conception were extremely crude. Efforts to understand and refine it have been my primary and increasingly obsessive concern for thirty years (Kuhn, 2000, 228).

One of the main qualifications, if not an outright departure from Kuhn's original position, was his turn to an analysis of scientific lexicon and the nature of language more generally. Would it be so preposterous to suggest that Kuhn's program began to degenerate from the moment when he started to alter his original bold and startling claims, which so caught the professional and public attention when they were first published?

As several authors have written, the main reason why Kuhn was mistaken in devoting so much attention to the language of science was that it diverted attention from ontological aspects to terminological ones. Said differently, Kuhn appears to be taking sides with those philosophers who place greater importance on sense rather than on reference in the long-standing philosophical debate that dates back to Frege and even earlier (McCulloch, 1989).

Kuhn's move from a concern from matters of scientific ontology to an emphasis on sense has of course been eloquently criticized by Alex Bird,

> Whereas The Structure of Scientific Revolutions is naturalistic in approach, drawing upon empirical, scientific discoveries where appropriate, his later work is much more philosophical in style and a priori in method. For example, in The Structure of Scientific Revolutions Kuhn's explanation of the relationship between observation, theory and reality was informed by gestalt psychology and by the results of research carried out by his Harvard colleagues, the experimental psychologists Bruner and Postman. Later, by contrast, Kuhn supported his view with quasi-Wittgensteinian considerations from the philosophy of language, while he characterized that view in terms of Kantianism (Bird, 2002).

Bird continues by claiming that Kuhn's earlier views would have benefited from a continued naturalistic development and suggests that his later, philosophical approach was not only a failure, but what Bird calls a "wrong turning" which contributes to a lack of significance in contemporary mainstream philosophy and even philosophy of science. Some of this wrong turning is also attributed to Kuhn's lack of philosophical training.

Whereas the early Kuhn drew many examples from the history of science, he abandoned his use of empirical science for a more a priori approach that was initially motivated by the writings of Quine. While the early Kuhn focused on the development of science while drawing from many historical episodes, his later output turned almost exclusively to the nature of the language that is used in science. Moreover, Kuhn later denied that an evolutionary epistemology need be a form of naturalised epistemology, and even regretted an overemphasis on the empirical aspect of his earlier writings.

Kuhn's attempt to cast incommensurability within the philosophy of language had begun in the 1960s, when he drew inspiration from Quine's indeterminacy of translation thesis (Quine, 1960). Furthermore, Kuhn seems to have also drawn from Quine the notion that what differs between incommensurable languages is the way they divide the world into kinds of thing, or in other words the notion of natural kinds.

But a result of Kripke and Putnam's work in the 1970s, philosophers have tended to downplay the fact that natural kind terms are picked out by their sense but have focused on a reference that is fixed by a causal connection between the use of the term and the reference itself. The claim is that water refers to that familiar transparent liquid because it has a causal connection to the substance that was baptized as water in the remote past and not because of any description of the liquid. In this respect the later Kuhn is very much out of step with contemporary philosophical thinking. Stated otherwise, wheras Kuhn's earlier work was very much focused on actual scientific matters or one might say ontological aspects, his later work is seen by many to consist of a retreat to an analysis of language, a shift from reference to the world itself to an analysis of how one describes and categorizes the world. It is for these further reasons that I too believe that Kuhn's reformulation of scientific revolutions may have been misguided.

Meanwhile Brad Wray is attempting to have things both ways, since he does plunge into a considerable amount of scientific detail concerning atomic weight, atomic number and isotopy while using Kuhn's later approach to the analysis of scientific change with its emphasis on the language of science and all that this entails.[15] I have to conclude that Kuhn might not after all have approved of Wray's attempt to support his later writings.

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[15] As a reviewer of the present article also points out, Wray is incorrect in claiming that Cannizzaro proposed using the atomic weights of the elements as a means of classifying them. The use of Cannizzaro's atomic weights to classify the elements was rather carried out by at least six discoverers of the periodic system, of whom Mendeleev is the best known.

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Feature Article

Boxing Partula: 25 Years After

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Abstract. The comprehension of form generally assumes a euclidean three-dimensional perspective. I argue here that non-euclidean geometry has much to offer in understanding structures of atomic crystals, molecular liquid crystals and related mesoporous inorganic materials and biominerals.

Keywords: Curvature, Crystallisation, Mesostructure, Liquid Crystals, Non-Euclidean Geometry.

I have been pleasantly surprised by the continuing interest of colleagues in the note, which offers an alternative perspective of topologically complex structures from the conventional the-dimensional euclidian view. Hence this slightly updated version. Naturally, my choice of examples to illustrate the thesis that many structure can be fruitfully described as two-dimensional hyperbolic patterns has dated somewhat. For example, the theoretical crystalline schwarzites discussed here remain undiscovered, despite their likely theoretical stability. The focus on such materials has shifted, with more recent report of amorphous schwarzites.

Stephen T. Hyde

1. INTRODUCTION

This essay is a story about "ways of seeing", and how those ways run beneath the more visible tracks that mark the course of the hard sciences. I am interested in exploring the applications of geometry, particularly non-euclidean geometries, to our comprehension of form, shape and dimension. The story is focused on the world of atoms and molecules, and their condensed forms.

The title of this article is adapted from the movies. *"Boxing Helena" is* a provocative film by Jennifer Lynch, that appeared in 1993. Its notoriety centres on the story: an obsessed surgeon keeps a beautiful young Helena – limbless – in a box, in an attempt to capture her heart. Of course, he fails. To this geometer, the movie is an attractive metaphor for the ultimate sterility of conventional euclidean geometric descriptions, that imprison all forms into the box-like grid of euclidean space. Many forms are perhaps better described within curvilinear grids, which lie at the heart of non-euclidean geometries.

Form is too sterile an issue for most physicists, who opt to explain the energetics of form. Biologists, following Goethe' s example, explore the *morphology* of living things, and classify according to phenotype. I stand betwixt these extremes, asking what are the possibilities of form? and how much are they constrained by the shape of space itself? This is a surprisingly vexed subject, and I can only offer some preliminary insights, which were inspired by the recognition of unusual forms in solid and liquid crystals (explored at length in HYDE *et al.*, 1997; see also VON SCHNERING and NESPER, 1987). However, these insights alone lead to some interesting reflections on the nature of science, and the fragility of some of its unquestioned assumptions about seeing, and perception of shape.

2. MORPHOLOGY IN THE LARGE: SNAIL SHELLS

The writings of the Harvard biologist, Stephen Jay Gould, unfailingly elicit a sense of wonder at the palaeontologists' careful unravelling of the multi-stranded skein of life's evolutionary processes. Gould' s own field is the evolution of land snails. In a recent story, "*Unenchanted Evening*", Gould recounts a poignant tale of the demise of an indigenous Tahitian snail, genus *Partula*, due to the introduction of the voracious *Euglandina* snail by over-zealous and ignorant French scientific bureaucrats (GOULD, 1993). *Euglandina* were introduced in 1977; by 1988, *Partula* was gone forever from most of the islands, and over seventy years of continuous research on *Partula* by a number of eminent snail biologists was abruptly terminated.

This work began in 1917, when Henry Edward Crampton undertook the first of twelve expeditions to the Tahitian islands. Crampton was to spend the next 50 years of his life trekking though the lush, inaccessible terrain of the islands, collecting specimens of *Partula*, followed by painstaking analysis. Crampton compared different populations and the effect of local environment and genetic isolation on the evolution of *Partula*. He elected to index specimens by the shape of their shell. Over 200,000 specimens were subjected to Crampton' s vernier calipers.

The morphology of these shells is pretty much like that of the common garden snail: a twisted and curved cone like the final flourish atop a meringue. To reduce this form to numbers, Crampton made four measurements on each shell, illustrated in the beautiful engraving reproduced in Fig. 1, taken from his own work. Notice the rectangular grid imposed on the shell. Crampton measured the lengths AB, FB, CD and ED for each shell, and then calculated averages and standard deviations for each population (to eight significant figures – by hand!).

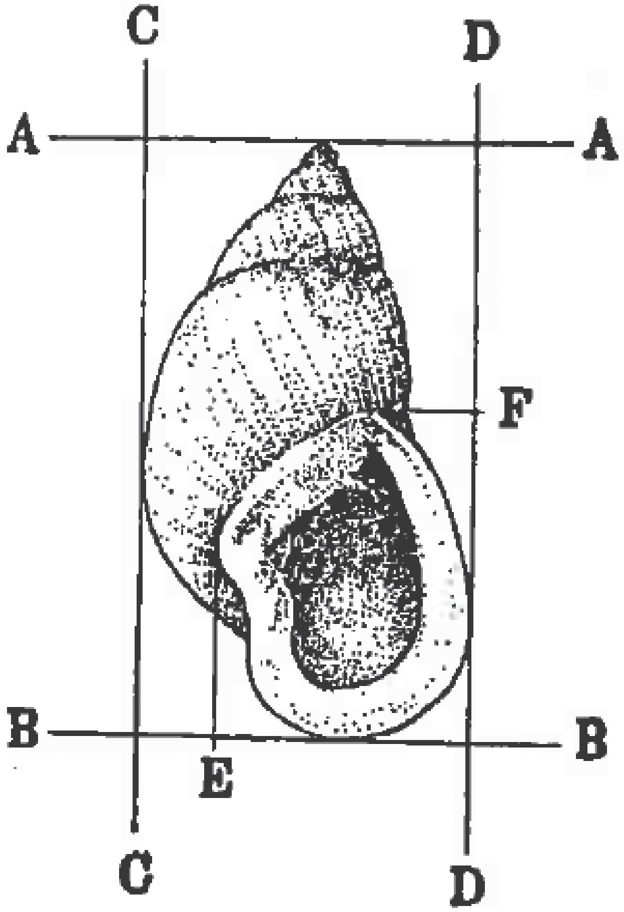

Figure 1. Crampton's engraving of the *Partula* shell, overlayed with his measuring grid.

According to Crampton, "*These figures, together with a single line of text, may be all that represents two to eight weeks of mathematical drudgery … Yet the employment of such methods is justified in the final results.*" (quoted in GOULD, 1993).

How "justified" was the persistent Crampton in his final upbeat assessment of half a century of work? According to Gould, the work ranks with the best evolutionary studies. Yet I can't help feeling that Crampton could have profited better from a more careful choice of metrology of the form of these shells. His rectilinear dimensions seem to me to be a classic case of shoehorning (to borrow a favourite word of Gould), forcing the swirling, twisted shells into flat rectangular boxes: one around the outer form and a second around the opening of the shell. To recall the analogy with Hollywood: as Helena is constrained by a box, so Crampton' s beloved *Partula* is unnaturally confined between a pair of boxes!

Geometry is a far more versatile tool than the rectilinear lengths Euclid's codification suggest. It underwent a revolution last century, following utter failure to justify Euclid's parallel postulate. After more than two thousand years, the *ad hoc* nature of that postulate was realised, and its removal was shown to yield no collapse of the edifice that is Geometry – rather, a multitude of new "Non-Euclidean" Geometries were immediately erected. Gauss, Lobachevsky, Bolyai, (1820's) and Riemann (1850's) are credited with these advances (although Gauss refused to publicise his findings in the area, terrified of "the clamour of the Boeotians"). The work did not filter through to mathematicians until the end of the last century, largely due to the efforts of Helmholtz in Germany and Clifford in England.

Despite the sea-change in geometry, Euclid's program remains largely unchallenged as the definitive geometry for all but the most curious students of space and form. Rectilinear grids, like Crampton' s, and the euclidean vocabulary of form – polyhedra, spheres and cylinders – are still routinely assumed to span the variety of possible forms in the sciences.

3. MORPHOLOGY OF ATOMS AND MOLECULES

In my own area of research – condensed matter – similar spatial assumptions to that unknowingly invoked by Crampton abound [1]. Consider, for example, the complex atomic arrangements in zeolites. These materials are central to modern society, used as catalysts to "crack" crude oil, forming petrol. Millions of tonnes of a single zeolite catalyst, faujasite, are used annually to make petrol. Zeolites are made up of complex (predominantly) silica frameworks – over one hundred distinct frameworks have been reported to date (MEIER and OLSON, 1992). Although they are solids, the interior of a zeolite crystal is accessible to sufficiently small molecules, which can diffuse along the channels in the framework. From the perspective of non-euclidean geometry (detailed later), they are all surface, and no volume! It is not surprising then that zeolites are excellent catalysts, for catalysts generally work by enhanced reactivity due to surface adsorption (Blum *et al.,* 1993).

Understanding of the chemical functionality of these materials relies on comprehension of their atomic structures: i.e. the relative arrangements of atoms, and bonds, in space. Ball-and-stick models emphasise the topology of the bond network, that links the silica units into an infinite polymer. Alternatively, they are described in terms of packings of convex polyhedra. Examples of both representations are shown in Fig. 2.

Both descriptions are implicitly euclidean and three-dimensional, involving linear links between atoms and plane-faced convex polyhedra. The polyhedral language is a rich one – see for example (O'KEEFFE and HYDE, 1996) – though we shall see it is not necessarily optimal for all purposes.

Our second example of atomic structures concerns allotropes of carbon. The simplest structure of (sp^2 hybridised) carbon is that of graphite, which contains stacked flat hexagonal sheets of carbon atoms. But we now know that this is not the only possible form that sp^2 hybridised carbon polymers can adopt. Warped forms of graphitic carbon result in cage-like fullerenes (Fig. 3).

Fullerenes can be described as faceted balls or rounded polyhedra, in contrast to the extended flat sheets of graphite. The "shapes" of these allotropes can be quantitatively related to their atomic structure by Euler' s equation, which asserts that the numbers of faces (***F***)**,** edges (***E***) and vertices (***V***) in a closed (convex) polyhedron fulfil the condition:

$$\boldsymbol{V}-\boldsymbol{E}+\boldsymbol{F}=2 \qquad (1)$$

We can rewrite this equation in a more useful form for closed polyhedral networks, such as those of the fullerenes. Each ring (a shortest circuit) in the net is a face, and each link between vertices an edge. Denote the number of edges meeting at each vertex by z, and the (average) size of the rings in the network by *n.* For a polyhedral net, containing ***R*** rings, (1) becomes:

$$\left(\frac{n}{z}-\frac{n}{2}+1\right)R=2 \qquad (2)$$

Graphite, whose ring size is equal to 6 and connectivity is equal to 3, can only just be described as a convex polyhedron – an infinitely large one (of infinite radius – flat). Indeed, if $n = 6$ is inserted into (2), the sum

$$\left(\frac{n}{z}-\frac{n}{2}+1\right)=\left(\frac{6}{3}-\frac{6}{2}+1\right)=0 \qquad (3)$$

so that an unlimited number of rings are required, forming a (flat) infinite polyhedron. On the other hand,

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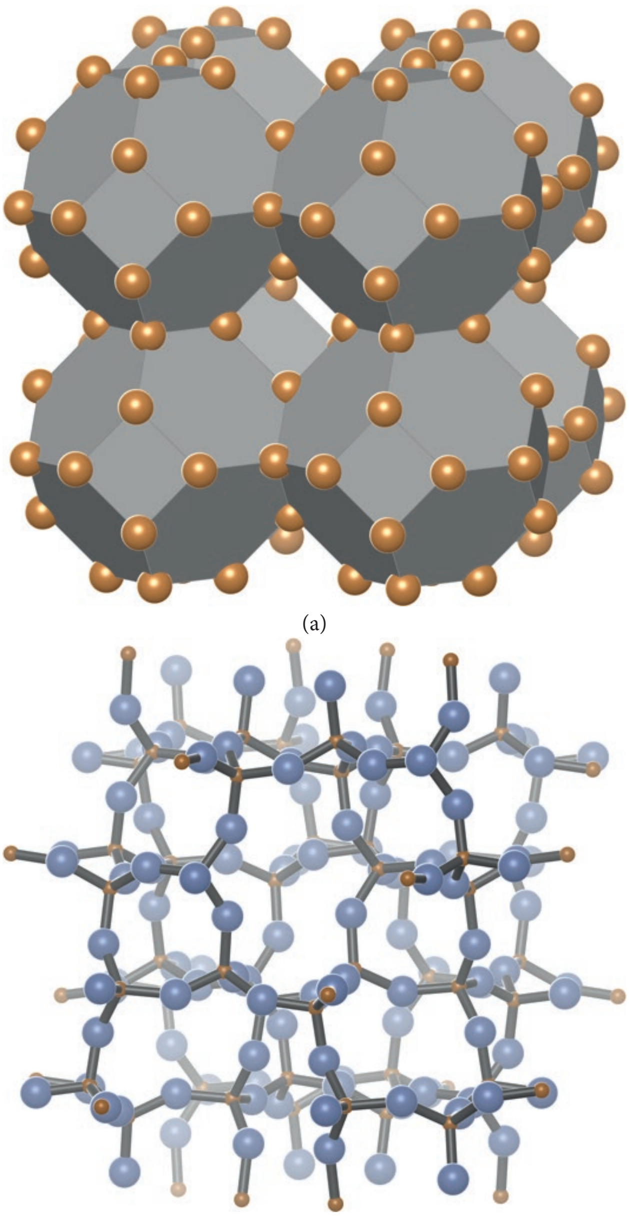
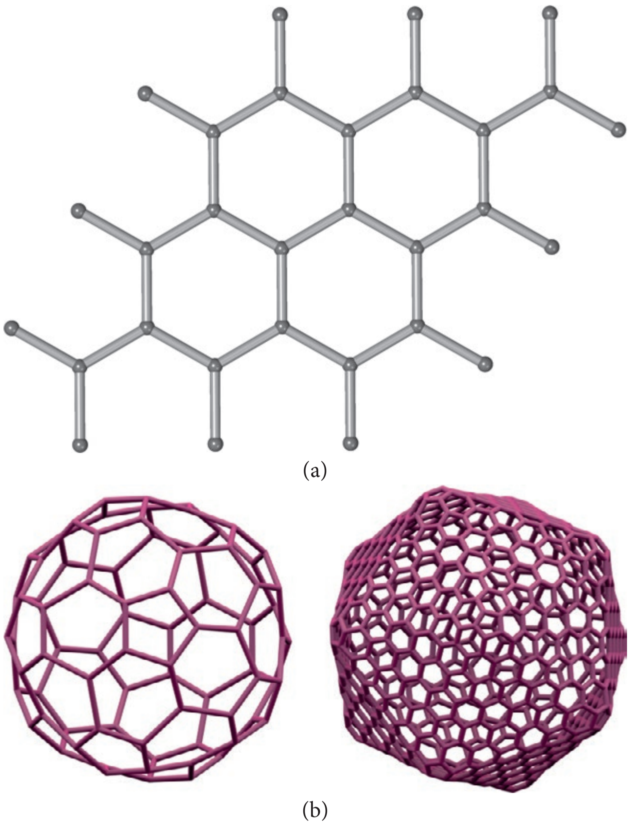
[1] With the notable exception of physicists including Maurice Kléman, Jean-Franccois Sadoc, Nicolas Rivier, Remy Mosseri and colleagues, see "Geometry in Condensed Matter Physics", World Scientific, Singapore, 1991.



(a)

(b)

Figure 2. Pictures of zeolites: (a) Ball and stick model of the analcime framework. Links represent Si-O-Si bonds in the idealised silicate, balls the Si positions. (b) Polyhedral model of the structure of sodalite (face-sharing truncated octahedra), with Si at the vertices.



(a)

(b)

Figure 3. (a) The planar network of (three-connected) carbon atoms in graphite, (b) some (three-connected) fullerene networks (carbon atoms lie at each vertex): (L to R) C_{60} and C_{740} (courtesy of Myfanwy Evans).

if the ring sizes in graphite were exclusively equal to 5, the number of rings, ***R,*** in a polyhedron fulfils Eq. (2):

$$\left(\frac{5}{3}-\frac{5}{2}+1\right)R=2, \quad R=12 \tag{4}$$

Indeed, the simplest hypothetical closed fullerene contains just twelve 5-rings and twenty carbon atoms (C_{20}), lying at the vertices of the Platonic polyhedron, the dodecahedron (Fig. 4).

A curious property emerges from Eq. (2). The addition of an arbitrary number of 6-rings does not change the number of 5-rings in the closed shell polyhedron, since (from (3)), 6-rings do not contribute to the equation. Thus, regardless of the number of 6-rings, twelve pentagons – and only twelve – are to be found in all closed-shell fullerenes (built of 5- and 6-rings). If more than 12 pentagons are inserted, Eq. (1) no longer holds, and the network instead continues to spiral inwards around itself, producing a network which shares many of the characteristics of the *Partula* shell. The network no longer closes on itself seamlessly, but contains spiral edges, shown in Fig. 5. Such exposed edges – along which the carbon atoms have only two bonds – are not going to remain so for long. These structures are unlikely to form under normal conditions.

What happens if 7- or 8-rings are introduced to these three-connected networks? From Eq. (2), it is clear that the presence of these rings precludes the formation of convex or flat polyhedra, since

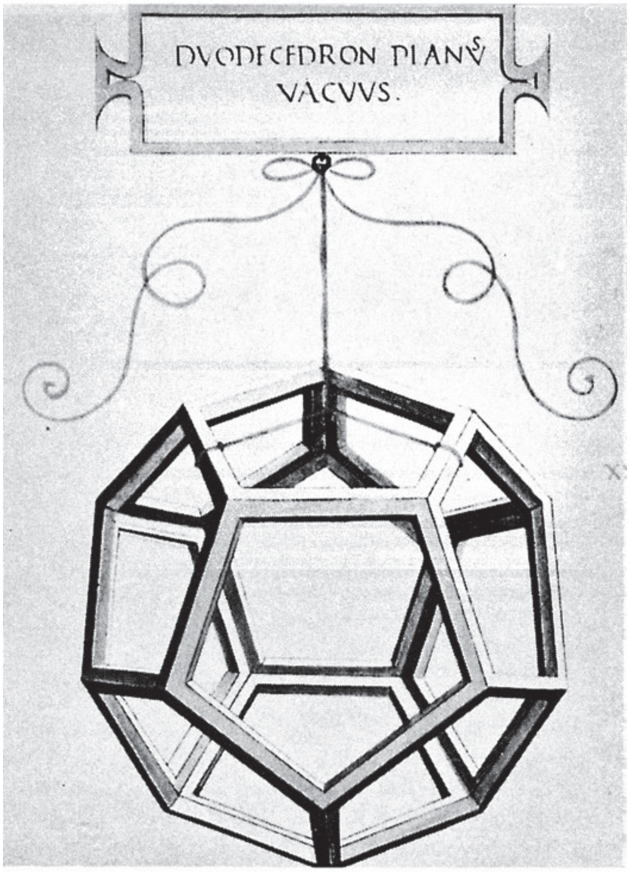


Fig. 4. Da Vinci' s engraving of a regular dodecahedron, whose vertices locate the relative positions of carbon atoms in the fullerene, C20.

$$\left(\frac{n}{z}-\frac{n}{2}+1\right)=\frac{2z+(2-z)n}{2z}=1-\frac{n}{6} \tag{5}$$

is negative (so that formally, a negative number of rings must be found in the convex polyhedron, cf. Eq. (2)). To cope with the shapes formed by three-connected networks containing larger rings than 6-rings, we need to generalise Euler's equation (1), introducing a new parameter, χ, known as the Euler-Poincare characteristic.

$$\left(\frac{n}{z}-\frac{n}{2}+1\right)=\chi \tag{6}$$

The contribution to the Euler-Poincare characteristic of 7- and larger rings is, from Eq. (5) above, negative. What does this mean in space?

Three-connected nets containing >6-rings are forced to warp, so that they lie on saddle-shaped surfaces, in contrast to the convex polyhedral surfaces formed by 5-rings. It is useful to think of the curving of graphite layers as a disclination process: 5- and 7-rings resulting in positive and negative disclinations respectively (Fig. 6).

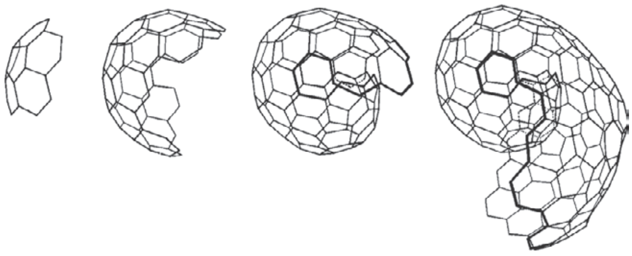


Figure 5. Kroto and Mackay's hypothetical spiral graphitic carbon structures, adapted from KROTO (1988).

The saddle-shape that results by insertion of negative disclinations in graphite is most evident when the average ring-size is close to 6, but slightly larger. (This situation can be realised simply by inserting a large number of hexagons into a cluster of 7-, 8-, … rings, since the hexagons do not affect the value of the characteristic, χ) Depending on the number and arrangement of heptagons or octagons, seamless crystalline porous frameworks or disordered sponge-like sheets can result, analogous to the boundary-free fullerenes shown in Fig. 3.

The Euler-Poincare characteristic, (Eq. (6)), is "quantised" for boundary-free surfaces, and related to the number of channels within surface. If the underlying surface is periodic, the characteristic per unit cell is likewise quantised, and so discrete families of frameworks containing 7-, 8-, … rings are possible, analogous to the twelve 5-rings present in a closed shell fullerenes containing only 5- and 6-rings. Such structures have been proposed as possible modifications of graphitic carbon. They have been christened "Schwarzites", in honour of the celebrated nineteenth-century German mathematician, Hermann Amandus Schwarz (MACKAY and TERRONES, 1991). Examples of hypothetical schwarzite frameworks are illustrated in Fig. 7.

What happens as the density of negative disclinations (and the average ring-size) increases? For example, insertion of 8-rings, rather than 7-rings results in frameworks that are no longer clearly sheet-like, rather they appear three-dimensional, and morphologically similar to zeolite frameworks (Fig. 8).

Geometrically, no quantitative transition accompanies this apparent shift of form of three-connected schwarzite frameworks with increasing disclination density; rather our perception of the structural form is changing. When the ring-size barely exceeds six, the larger rings surrounding tunnels of the network are perceived to be open, while we mentally "fill in" the

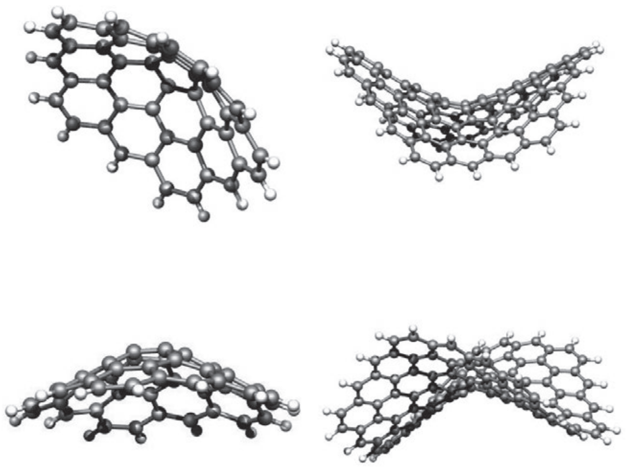


Figure 6. (Left/Right) The formation of rings less than/greater than 6-rings in a flat graphite sheet (tiled by hexagons) leads to positive/negative disclinations. Copyright Chris Ewels (www.ewels.info).

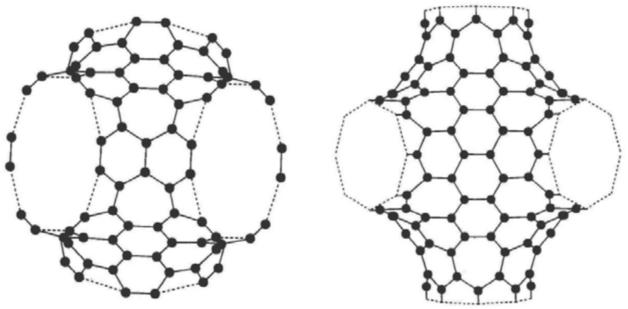
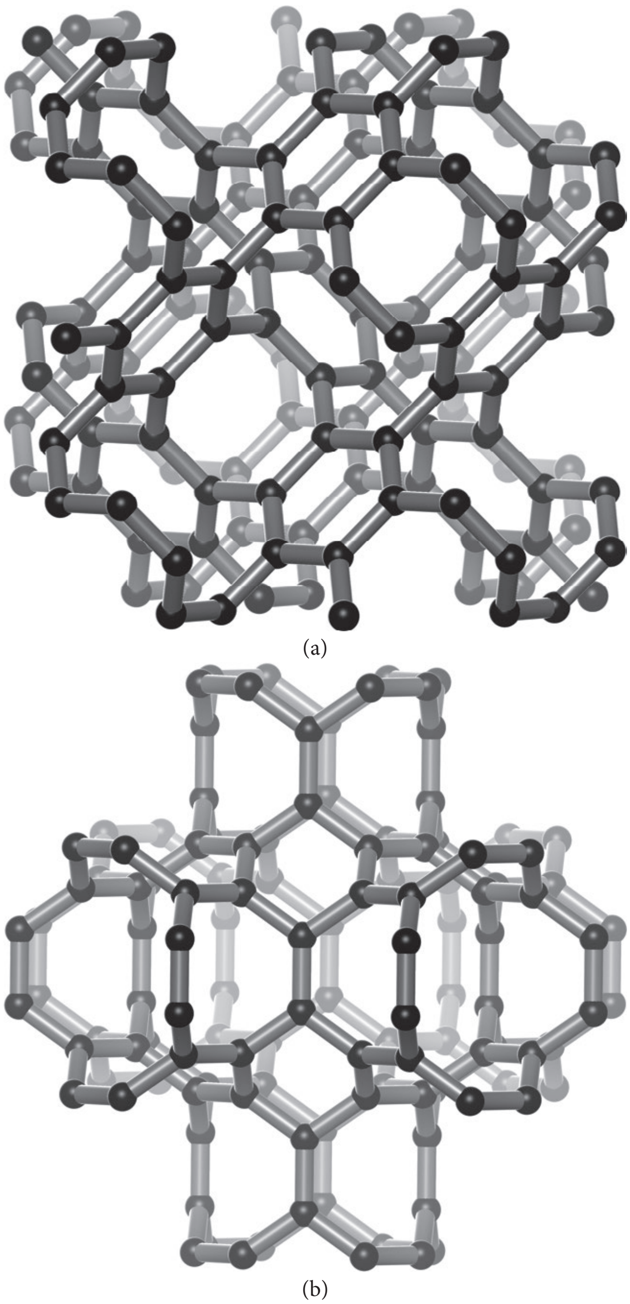


Figure 7. Bonding networks in some hypothetical crystalline “schwarzites”, due to LENOSKY *et al.* (1992) (confined within a unit cell). The average ring-sizes here are equal to 6.2, including 6- and 7-rings only.


(a)

(b)

Figure 8. Cubic schwarzites containing only 6- and 8-rings: polybenzene (a) *D* and (b) P (O’KEEFFE *et al.,* 1992).

smaller rings, to form a continuous (and open) saddle-shaped sheet. By contrast, when the ring-size in the surface becomes significantly larger than six, the rings surrounding pores approach the same size as the rings in the saddle-shaped sheet, and we mentally fill in tunnels (closing them off) and sheet-rings, leading to the (closed cell) infinite-polyhedral description, such as the sodalite description shown in Fig. 2. An apparently uniform network twists through space, and the structures are perceived as conventional three-dimensional frameworks.

Complex zeolite-like morphologies can also be found in molecular materials. It now appear that porous arrays are common in macromolecular assemblies, including biological systems (GUNNING, 1965; LANDH, 1995; HYDE *et al.,* 1997). These shapes too lie beyond the usual vocabulary of (euclidean) form, and descriptions have inevitably been deficient. For example, biologists studying the shapes of organelles within cells have resorted to exotic terms such as “undulating tubular bodies” or “tubulo-reticular structures” to account for the complex forms deduced from stained optical-microscopic sections of membranes in cells (Fig. 9).

Whereas the channels in zeolites are typically a few Angstroms in diameter, those in cell organelles are

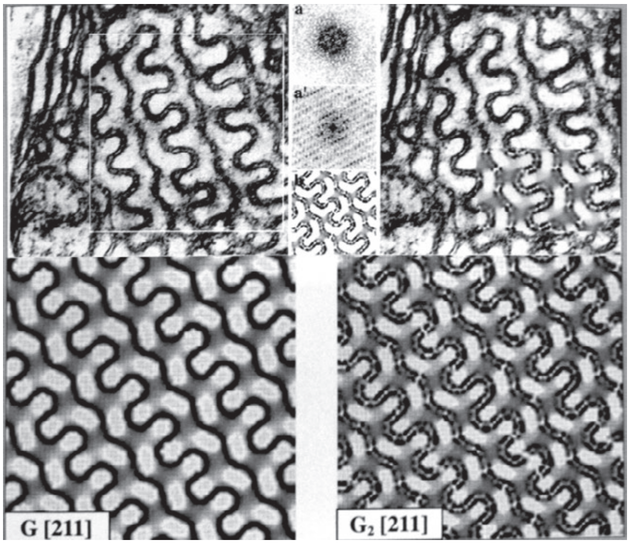


Figure 9. Stained sections through the pro-lamellar body (the light-harvesting photosynthetic centre) of a dark-adapted plant. (Insets: Fits due to Landh, described later in the text.) Adapted from HYDE *et al.* (1997).

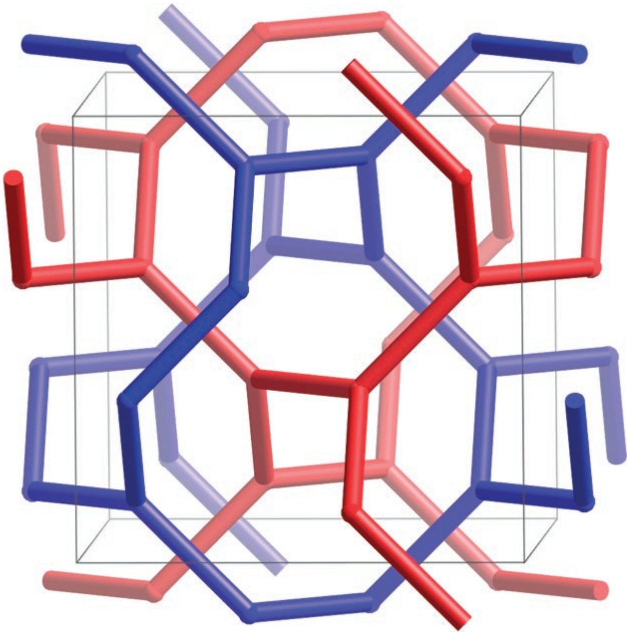


Figure 10. LUZZATI and SPEGT'S model (1967) of the mesostructure of a cubic phase, consisting of two intertwined rod networks, enclosing water (reversed phases) or the lipid/surfactant chains (normal phases).

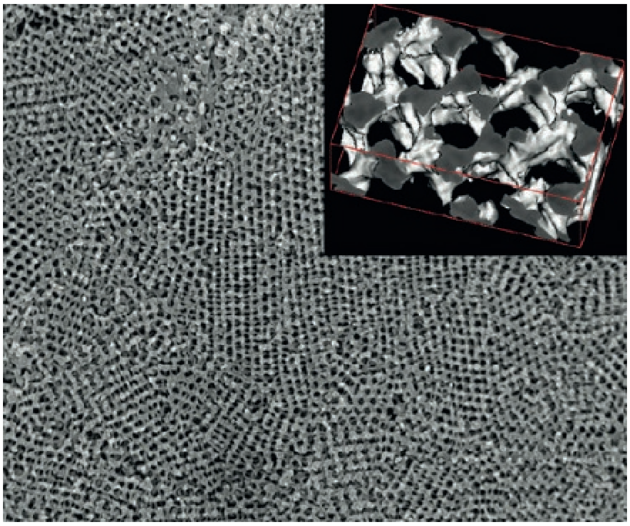


Figure 11. Electron micrograph of silica templated from a copolymer material, whose nanostructure (inset) corresponds to a single rod network in Fig. 10. Image courtesy of Hirokazu Hasegawa.

microns. The very large dimensions of cell membranes are not yet understood.

The major component of cells is the lipid bilayer. Synthetic bilayer membranes can be reconstituted *in vitro* using only lipids (and water). Lipids, or related synthetic surfactant molecules (collectively called surfactants), spontaneously assemble in water to separate the oily chains – which abhor water – from the polar and water-soluble head groups. In some cases, namely "bicontinuous cubic phases" of surfactant- or lipid-water mixtures, the membranes display identical morphologies to those of the organelle membranes. These structures were originally described in terms of intertwined arrays of channels (Fig. 10), similar to the tunnel arrangements in zeolites (LUZZATI and SPEGT, 1967). In contrast to the membranes *in vivo,* the channels of these *in vitro* membranes are typically 20-50 Å across.

Identical structures are also found in inorganic materials "templated" with surfactants, with pore sizes ranging between 20-150 A (BECK *et al.,* 1992; ALFREDSSON and ANDERSON, 1996), and copolymer mixtures (typically 1000 A diameter) (HASEGAWA *et al.,* 1987, 1993; HAJDUK *et al.,* 1994) (Fig. 11).

It turns out that there are deep structural similarities between zeolites, schwarzites, surfactants and polymer molecular aggregates. In fact, all of these materials can be described by a generic structural *motif,* the hyperbolic surface. These materials can be related to periodic hyperbolic surfaces. The most prevalent examples found to date are cubic surfaces: the D-surface (or "diamond" surface), the *P* surface and the gyroid, shown in Fig. 12.

The possibility of describing "three-dimensional" atomic frameworks, such as those of zeolites and schwarzites, in terms of two-dimensional hyperbolic spaces is

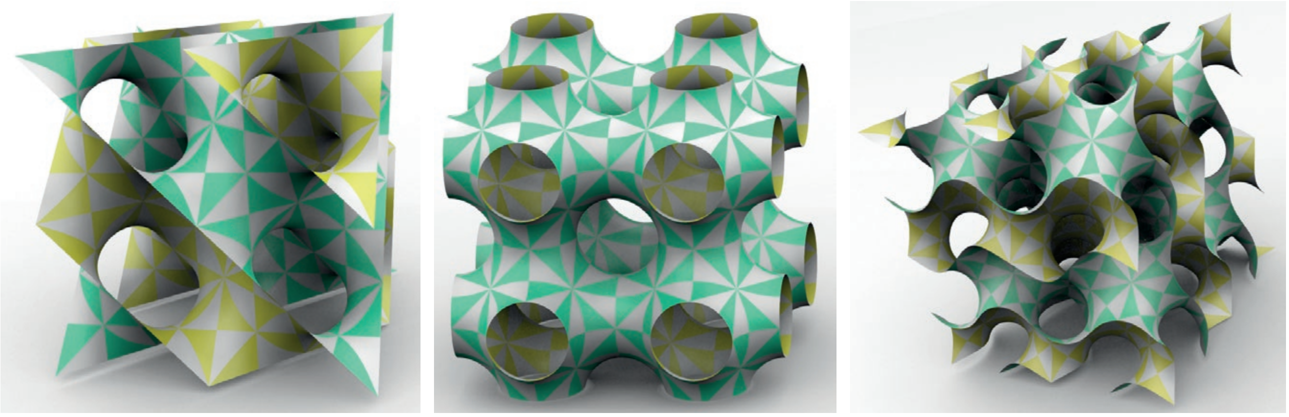


Figure 12. (Left to right) Portions of the D-surface, the ***P*** surface and the gyroid. Figure courtesy Myfanwy Evans.

evident in the examples shown in Fig. 13. Some molecular assemblies too are perfectly described in terms of these surfaces. For example, the membrane sections agree exactly with calculated sections through the *D* surface (insets, Fig. 9). In order to map these frameworks onto two-dimensional hyperbolic space, the edges of the frameworks must be curved, to form geodesics in that space.

Description is the first stage of science. I hope that the examples shown above reveal the complexity of this step alone, and the dangers inherent in too limited a catalogue of form. The next step requires some explanation of why that description is a useful one. Some progress has been made towards that second goal, outlined below.

4. DIFFERENTIAL GEOMETRY, NON-EUCLIDEAN GEOMETRY AND TOPOLOGY

In order to appreciate the nature of non-euclidean structures, the concept of dimensionality and the importance of periodic hyperbolic surfaces in these materials, we need first to digress a little into geometry.

No-one is able to offer a complete catalogue of form. Geometric studies following the program outlined by Riemann in 1853, and still in progress, suggest that the variety of forms relevant to physical systems in n-dimensions (n-manifolds) is rich. The problem of enumerating all four- (and higher dimensional) manifolds is unsolvable; the jury is still deliberating in the case of three-manifold (THURSTON, 1997). Two-dimensional surfaces can however be catalogued to a limited degree using concepts from differential *geometry* and *topology*. Differential geometry is concerned with the local shape of a surface – the shape of a small patch on the surface. By contrast, topology deals with the global structure, the connectivity, of the surface.

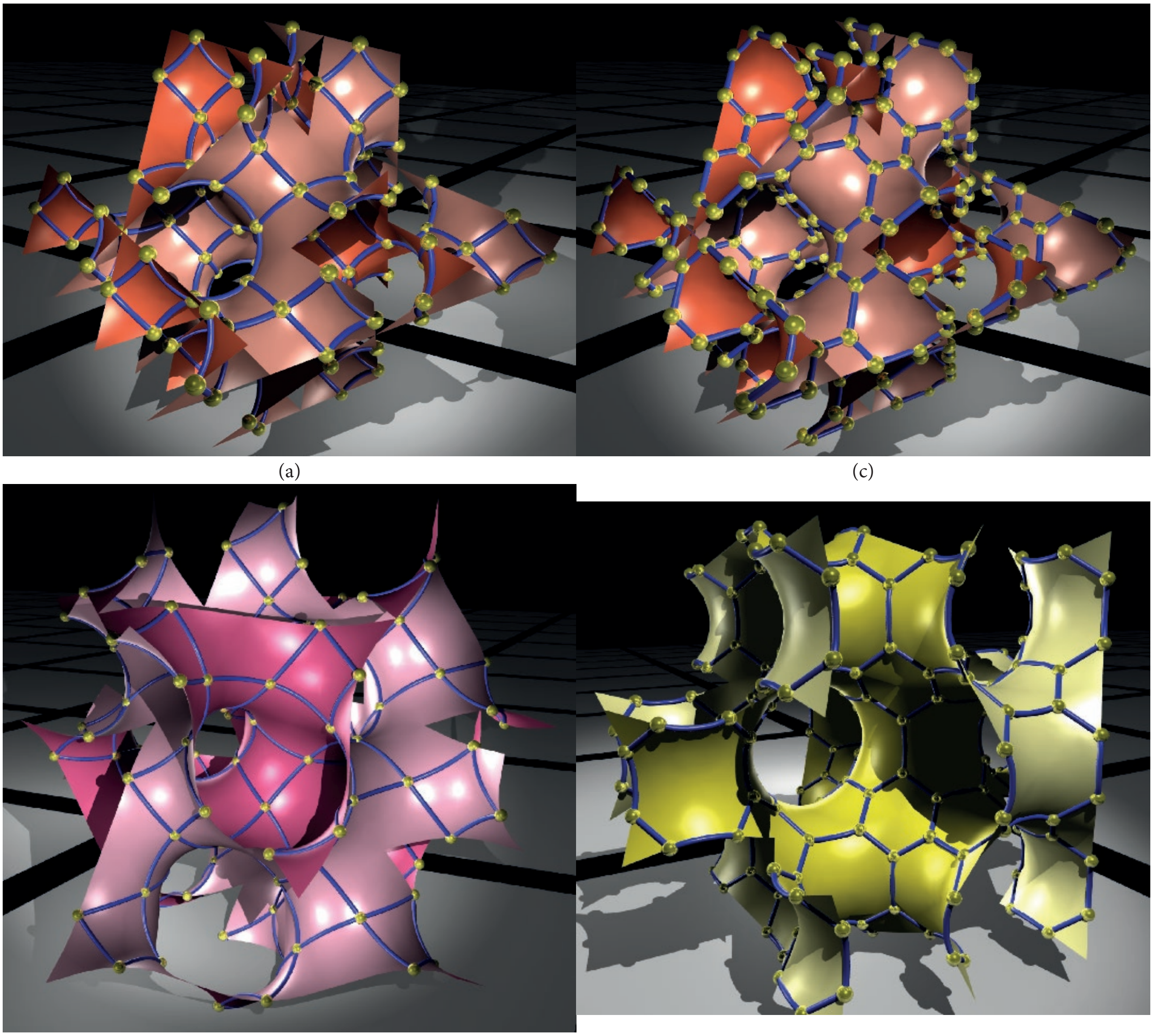
The shape of a surface patch can be succinctly described by its Gaussian curvature, which can be positive, negative, or zero (Fig. 14).

Surfaces of zero Gaussian curvature are called flat, despite the fact that they can be planar, cylindrical or conical. Why? Because it turns out that a rectangular flat grid, such as that adopted by Crampton, can be wrapped onto any surface of zero Gaussian curvature, without distortions of the distances between vertices or the right-angles between edges (measured along the surface patch rather than through space). This fact is known to us all: a flat sheet of paper can be wrapped onto a cylinder without any stretching or crinkling.

The case of zero Gaussian curvature is that examined in detail in euclidean geometry. The other cases correspond to (two-dimensional) non-euclidean geometries: saddle shapes belong to *hyperbolic* geometry and spherical (or ellipsoidal) caps to *elliptic* geometry.

In fact, Euclid also analysed other shapes, such as polyhedra, and spheres. But he saw these shapes exclusively within the context of three-dimensional (flat) space – in his view the convex polyhedra and sphere marked the boundaries of a filled inner volume. Within the curved two-dimensions lying on the surface of these forms, many geometrical features would have surprised Euclid. For example, a triangle – all of whose sides are "lines" in the sense that they are the shortest trajectories between the vertices (great circles) – can be traced on the sphere whose vertex angles sum to $3\pi/2$, rather than the customary π (Fig. 15).

A sheet of paper *cannot* be wrapped onto a sphere without folding the paper so that some doubling up occurs. In the process, the euclidean rectangular grid drawn on the sheet becomes distorted, and lengths and/or angles within the grid on the sphere are no longer the same as those in the original flat grid. Indeed, the



(a) (c)

(b) (d)

Figure 13. (a): The sodalite zeolite framework lying in the D-surface. Vertices of the framework occupy identical cartesian locations to those in Fig. 2, the edges have been curved to lie in the surface. (b): Fragment of the analcime framework in the *D* surface, marked in black on the surface. (c), (d): Two schwarzite frameworks: polybenzene *D* and *P*. (Pictures courtesy of Stuart Ramsden.)

elliptic cap – of positive Gaussian curvature – results from excision of a sector from the plane and regluing. Similarly, if a wedge is inserted into the flat sheet, a hyperbolic saddle-shape results, of negative Gaussian curvature.

This local classification scheme based on Gaussian curvature may appear at first sight trivial, but it is the simplest universal geometric classification. Look, for example, at the shapes of potato crisps (Fig. 16): you'll find blistered chips, of positive Gaussian curvature, flat portions (zero Gaussian curvature) and saddles (negative Gaussian curvature)!

Another happy hunting ground for local shape can be found in leaves. (This was first pointed out to us by William Thurston.) Cabbage leaves, for example, are elliptic, many eucalyptus leaves are euclidean, and mignonette (or "coral") lettuce leaves are decidedly hyperbolic. Some examples are shown in Fig. 17.

The rich structural variety within the hyperbolic domain – readily apparent from the variety of shapes

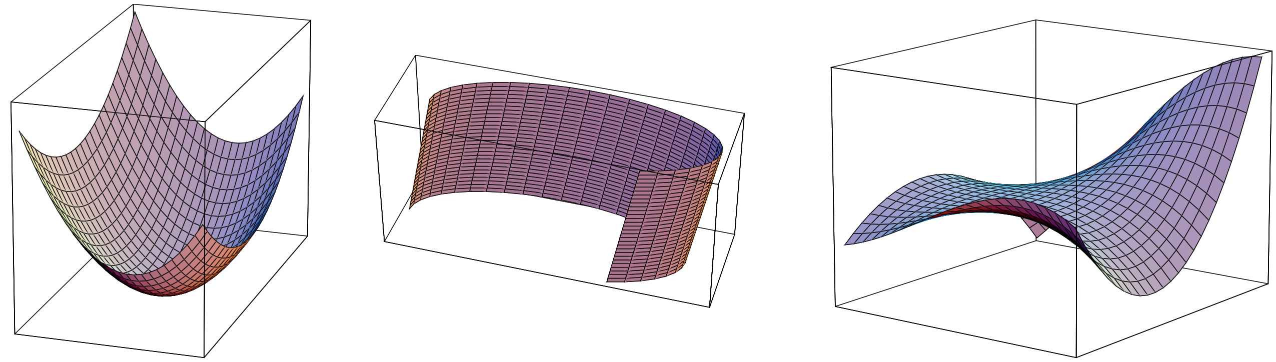


Figure 14. Caps, sheets and saddles with positive, zero, and negative Gaussian curvature.

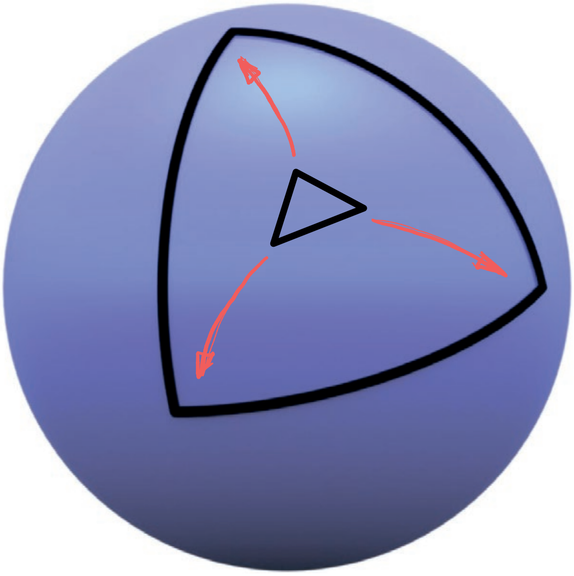


Figure 15. A flat euclidean triangle placed on the sphere builds a spherical triangle, whose vertex angles add up to an angle exceeding to 180°: the example shown has an angle sum of 270°. Figure courtesy Myfanwy Evans.

in mignonette leaves – is difficult to appreciate without some familiarity with the concepts of global structure, described in part by the topology of the surface. Topology is often called "rubber sheet geometry", since surfaces which can be bent into each other (without tearing or gluing) are topologically equivalent.

For example, all convex polyhedra are topologically equivalent (called "homeomorphic") to the sphere. Imagine a rubber balloon stretched over an inner skeleton shaped to form the edges of a polyhedron. Blow the balloon up more, until the skeleton rattles within it – a sphere results. Topologically speaking, convex polyhedra and spheres are indistinguishable – all have an Euler-Poincare characteristic of two (Eq. (6)). The difference between spheres and faceted convex polyhedra lies in their distribution of Gaussian curvature over the surfaces; for the sphere it is everywhere homogeneous, while it is concentrated at the isolated vertices of polyhedra.

Figure 16. The variety of surface form in potato crisps.

For two-dimensional surfaces in three-dimensional euclidean space, geometry and topology are inextricably linked by the Gauss-Bonnet theorem. This theorem reveals the importance of Gaussian curvature in a topological sense. To understand the theorem, we need to introduce a dimensionless curvature measure: the "integral curvature", which is defined to be the integral of the Gaussian curvature ($\iint_{surface} K da$) over the area of the surface.

This integral curvature is proportional to the Euler-Poincare index, provided the surface is closed, and thus free of boundary arcs:

$$\iint_{surface} K da = 2\pi\chi \tag{7}$$

This result is strikingly succinct. It asserts that no matter how a surface is stretched or squashed, its integral curvature remains fixed, since these distortions do not affect the Euler-Poincare index. In other words, its

Figure 17. (L to R): Cabbage (elliptic), eucalyptus (parabolic) and lettuce (hyperbolic) leaves with positive, zero and negative curvature.

Gaussian curvature distribution and area are coupled to give constant integral curvature. The Euler-Poincare index is simply related to another topological measure, known as the "genus" of the surface. For the usual "two-sided" surfaces the surface genus, g, is related to the Euler-Poincare characteristic by the equation:

$$\chi=2-2g \tag{8}$$

(The formula does not hold for "one-sided" or "non-orientable" surfaces, such as the Mobius strip, or for surfaces with boundary arcs.)

The shape – give or take the bending or stretching allowed within topology – of *any* orientable surface is always homeomorphic to a single sphere, decorated with some number of distinct handles. An orientable surface of genus g is topologically equivalent to a sphere with g handles, so that the genus is equal to the number of handles. That is the origin of the quantisation of topology mentioned above. Thus the *average* value of the Gaussian curvature, $<K>$, defined by the ratio of the integral curvature to the surface area,

$$\langle \mathrm{K}\rangle\equiv\iint_{surface} K da/\iint_{surface} da$$

is positive for genus zero surfaces, zero for genus one, and negative for genus two, three, … surfaces. This topological characterisation offers a useful classification of surface forms.

Convex polyhedra, which are homeomorphic to the sphere, are genus zero forms. The next case, genus one, includes all donut-shaped surfaces, cups, … all are homeomorphic to a sphere with one handle (illustrated in Fig. 18).

Since the donut has a genus equal to one, its average value of the Gaussian curvature vanishes, and its average geometry is flat! How is this so? Well, the integral curvatures of the hyperbolic and elliptic regions cancel exactly, no matter how asymmetric the torus: from a coffee cup, or a ball with a single tiny handle spanning its surface (Fig. 19). We say that the donut is *inhomogeneous,* in that its Gaussian curvature changes from point to point along the surface.

The "flat torus" is a donut-shaped surface – unrealisable in euclidean three-space, but realisable in three-dimensional spherical space – which is *homogeneous* in its Gaussian curvature. Thus, its Gaussian curvature is everywhere zero, in contrast to the inhomogeneous donut in three-dimensional euclidean space, whose Gaussian curvature oscillates about zero. The flat torus can be reticulated with a distortion-free square (two-dimensional Cartesian) grid of arbitrary mesh size.

A particularly interesting way to represent the torus, which reveals its average euclidean geometry follows from gluing of opposite edges of a rhombus. If the horizontal edges of the rhombus are glued together, a cylinder results. Gluing the other pair of edges (now loops), closes the cylinder on itself, forming a torus (Fig. 20).

Given our interest in spatially periodic structures, which underlie the arrangement of atoms in crystals, this is a very suggestive construction, reminiscent of the repeated zone scheme in quantum mechanics, and Born-von Karmann boundary conditions. Indeed, this construction allows a single unit cell of the two-dimensional

Figure 18. Homeomorphism between a donut, a sphere with one handle and a cup. Image from Roy and Kesselman, ArXiV 2201.06923.

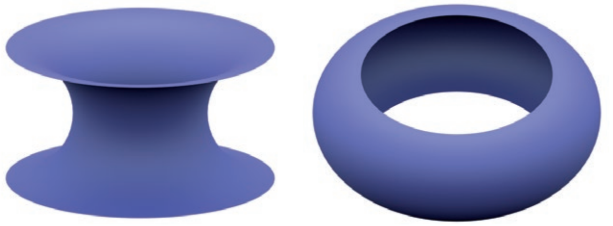


Figure 19. Decomposition of a torus into (left) a hyperbolic surface ($K<0$) and (right) an elliptic surface ($K>0$). On average, the torus is flat, as the hyperbolic and elliptic fractions have equal and opposite integral curvatures, for any torus, regardless of its particular geometry.

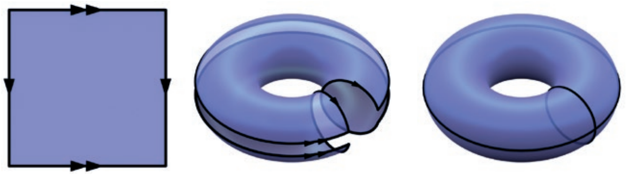


Figure 20. Gluing protocol for a torus from a rhombus. Figure courtesy Myfanwy Evans.

lattice, or periodic array (the rhombus), to be mapped into the torus.

An infinite two-dimensional lattice can be wrapped an infinite number of times around the torus, covering the torus once for each unit cell. (In mathematical jargon, the plane, tiled by a two-periodic lattice, is the *universal cover* of the torus.)

The construction begs to be extended to the domain of true crystals which exhibit three-dimensional lattices. In this case, the unit cell is a rhombohedron. Just as (opposed) *edges* separated by a lattice vector of the two-dimensional lattice are glued to form the torus, opposite *faces* of the unit cell can be glued to form a three-dimensional (solid) version of the torus, called naturally enough, the 3-torus.

Alternatively, we have seen that three-periodic hyperbolic surfaces can be used to describe three-periodic structures, by mapping these three-dimensional structures onto the two-dimensional crystalline hyperbolic surfaces. These infinite surfaces have unbounded genus. However, they have a finite number of handles within a single unit cell, and they can be catalogued according to their symmetries, and genera per unit cell. The unit cell topology is that of the boundary-free surface, formed by imposition of Born-van Karman boundary conditions, "gluing" boundary elements in pairs. Since they contain three independent lattice vectors, they must have genus (at least) three per unit cell, in contrast to the (genus-one) torus characterising a two-dimensional planar lattice. If the "unfolding" procedure of Fig. 20 is generalised to a higher genus g-torus, the resulting "flattened" surface is a polygon containing (at least) 4g sides (just as the torus of genus one gives a four-sided rhombus), shown in Fig. 21 for a two-torus.

It was noted above that the flat torus – a homogeneous parabolic structure (i.e. of constant Gaussian curvature) – is unrealisable in euclidean three-space. Are there homogeneous hyperbolic surfaces in this space? This question is a deep one, which was answered partially in a famous paper on non-euclidean hyperbolic geometry by the Italian geometer Beltrami in 1856 (STILLWELL, 1982). Just as euclidean (two-dimensional) geometry lies in the flat plane, hyperbolic geometry lies in the so-called "hyperbolic plane". Beltrami showed that some essential features of the hyperbolic plane were to be found in a homogeneous hyperbolic surface, called the "pseudosphere", shown in Fig. 22. In fact, the hyperbolic plane can be considered as the universal cover of the pseudosphere, since it wraps an unlimited number of times about the pseudosphere (STILLWELL, 1982).

Notice that this surface contains a cusp at its waist. Early this century, David Hilbert proved that any homogeneous hyperbolic surface in euclidean three-space necessarily contains such singularities. In the terminology of contemporary condensed matter physics, hyperbolic geometry is necessarily "frustrated"[2] in our space, unlike (two-dimensional) euclidean or elliptic geometries.

"Pseudosphere" refers nowadays to any surface of constant negative Gaussian curvature. All such surfaces

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[2] An uncharacteristically emotive term for physicists, perhaps misplaced. After all, the frustration lies with us rather than condensed matter!

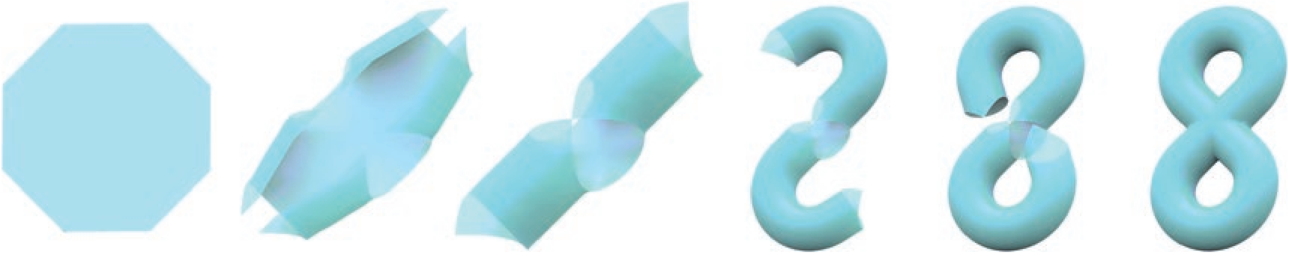

Figure 21. An octagon can be glued to form a genus two surface. Figure courtesy Myfanwy Evans.

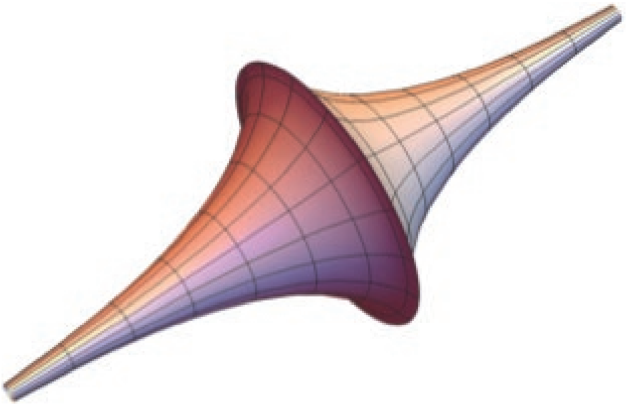

Figure 22. The pseudosphere, a surface of constant negative Gaussian curvature.

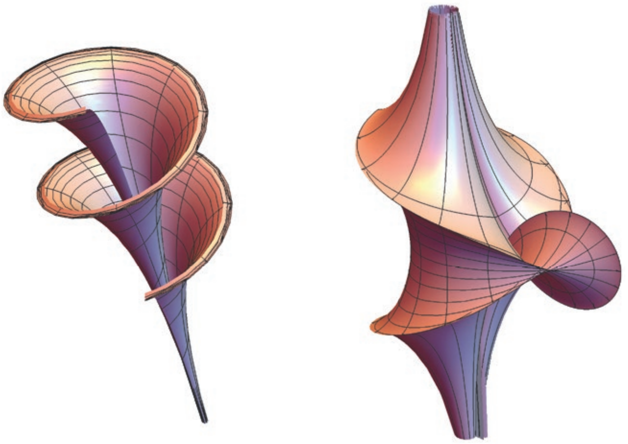

Figure 23. Some pseudospheres: (Left) A cusp-free section of one member of Dini' s surfaces. (Right) Kuen's surface, including cusps.

are equivalent in a two-dimensional sense, despite the fact that their global shapes – their embedding in euclidean three-space – can vary. Other examples are shown in Fig. 23.

A simple model of the pseudosphere can be constructed from the euclidean plane as follows. Build a plane from equilateral triangles – six around each vertex, in order to tile the plane without overlap or gaps. Now insert a seventh triangle at each vertex (a negative disclination), and stitch the "plane" back together. As the size of the plane grows, the structure becomes less and less rigid, and a number of different global shapes can be formed. The presence of tunnels – common to the more complex hyperbolic surfaces – can be seen in the natural tendency of the sheet to wrap onto itself, surrounding open "pores". Indeed, as the warped plane grows outwards, the surface is forced to either self-intersect or spiral around itself (Fig. 24). This feature of hyperbolic geometry can be ascribed to the limited "space" available to contain surfaces in three-dimensional euclidean space: there is not enough room to contain the hyperbolic plane.

Many leaves, particularly ivies, display locally homogeneous two-dimensional hyperbolic geometry. Adjacent portions of growing leaves necessarily crowd onto each other, and further growth cannot continue without deforming their homogeneous form, and flattening the growth fronts (Fig. 25). The inhomogeneous geometry of these leaves is due to the structure of three-dimensional euclidean space itself!

This frustration – inherent to homogeneous hyperbolic geometry – means that we need to look beyond pseudospheres and consider nearly-homogeneous hyperbolic surfaces, free of cusps. The best candidates found to date are the three-periodic hyperbolic surfaces. (The simplest examples of these surfaces are called Infinite Periodic Minimal Surfaces, or IPMS, named by Alan Schoen, the NASA physicist who discovered many examples in the 1960's (SCHOEN, 1970).)

While these surfaces are free of cusps, their Gaussian curvature varies from point to point, and they are inhomogeneous. Further classifications of IPMS can be made. We consider here only those (orientable) surfaces which are free of self-inter sections (also called embedded triply periodic minimal surfaces, of ETPMS). Examples of IPMS (which are all embedded) are shown in Figs. 12 and 26.

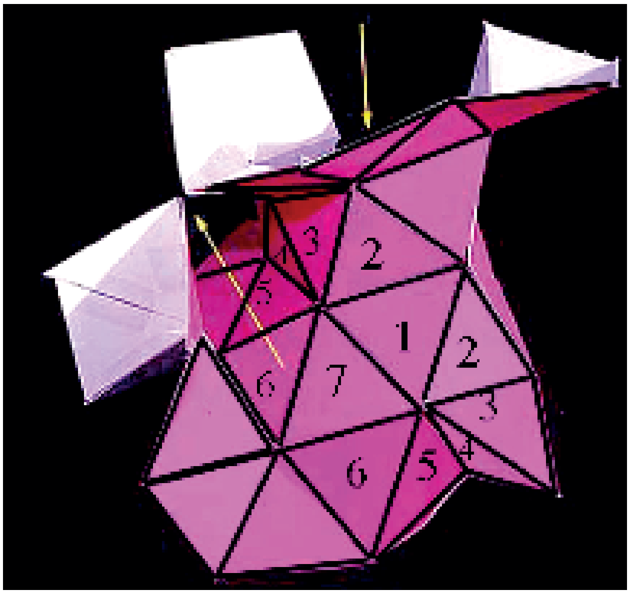

Figure 24. A faceted model of the hyperbolic plane, containing seven equilateral triangles at every vertex. The arrows mark pores.

The importance of IPMS lies principally in their topological structure, rather than their local geometric form characteristic of minimal surfaces (zero average curvature). They provide us with a much fuller catalogue of surface form than had been available until very recently. In many physical systems, the structures formed need not be precisely minimal surfaces (i.e. equally concave and convex at all points on the surface).

It appears that the most nearly homogeneous hyperbolic three-periodic minimal surfaces are those of genus three per (geometric) unit cell and cubic crystallographic symmetry: the *D*, *P* and gyroid surfaces illustrated in Fig. 12. These crystalline surfaces are topologically the most complex hyperbolic forms possible (of unbounded genus), and it may seem surprising that they are nearly homogeneous structures in our space. But lower genus hyperbolic forms necessarily contain elliptic regions, or boundary "ends" that are asymptotically flat; both cases lead to larger curvature inhomogeneities than those of IPMS and related surfaces. It is more difficult to compare the homogeneity of crystalline hyperbolic surface with related "molten" surfaces. But limited data reveal that the homogeneity of minimal surfaces increases with genus per unit cell, so that crystalline surfaces are naturally favoured. Some examples of genus three and four surfaces are illustrated in Fig. 26.

If that hypothesis is confirmed, it offers a novel view of crystallinity in the physical world. The conventional three-dimensional euclidean perspectives ascribes crystallinity to long-range interaction across space (and minimisation of the resulting energies). Within a hyperbolic perspective however, the induction of three-dimensional periodicity may be driven by the local (and two-dimensional) requirement of minimisation of curvature variations. The occurrence of triply-periodic hyperbolic forms is the natural consequence of a striving for a single preferred curvature. The physical meaning of curvature – a hitherto "hidden variable" – can be recast into more conventional terms, described below.

5. QUASI-HOMOGENEOUS HYPERBOLIC FORMS IN CONDENSED MATTER

Euler' s equation, and its generalisations, imply that the generic form of a network depends only on the average ring size and network connectivity. From Eq. (7), a

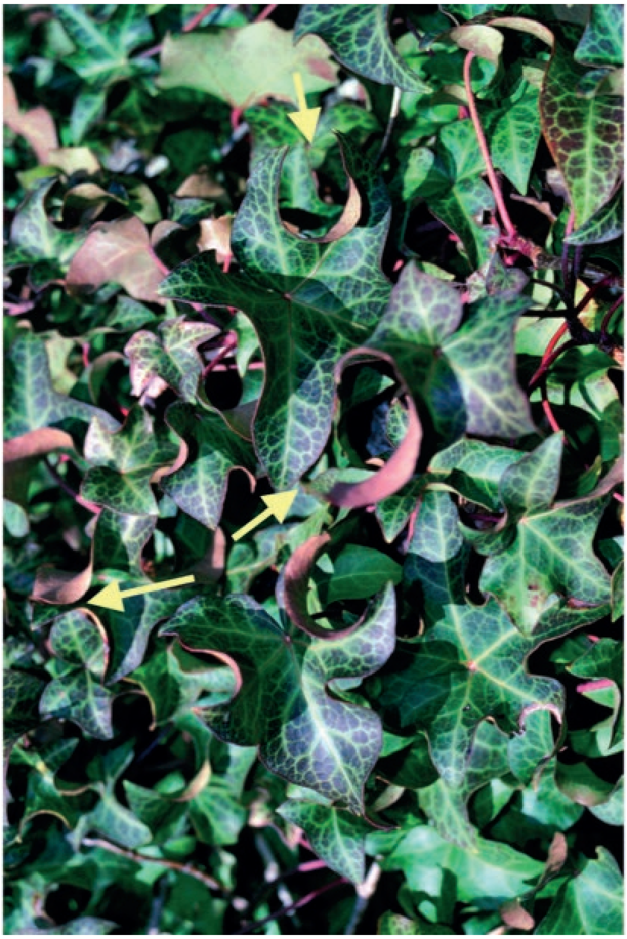

Figure 25. Some nearly-homogeneous hyperbolic leaves (arrowed) in an ivy. Notice the crowding of growing leaves, particularly evident in the arrowed leaves.

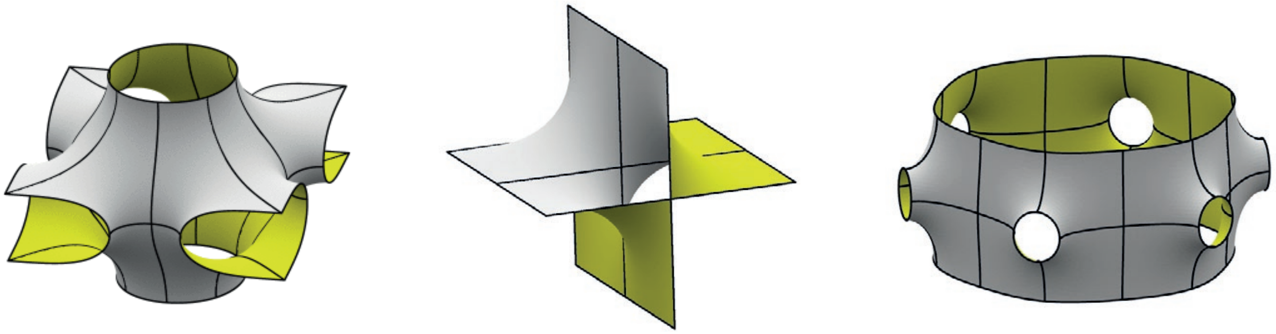

Figure 26. Unit cells of some IPMS (left to right): S'-S" surface (genus 4), CLP surface, H'-T surface (both genus 3). Images courtesy of Ken Brakke.

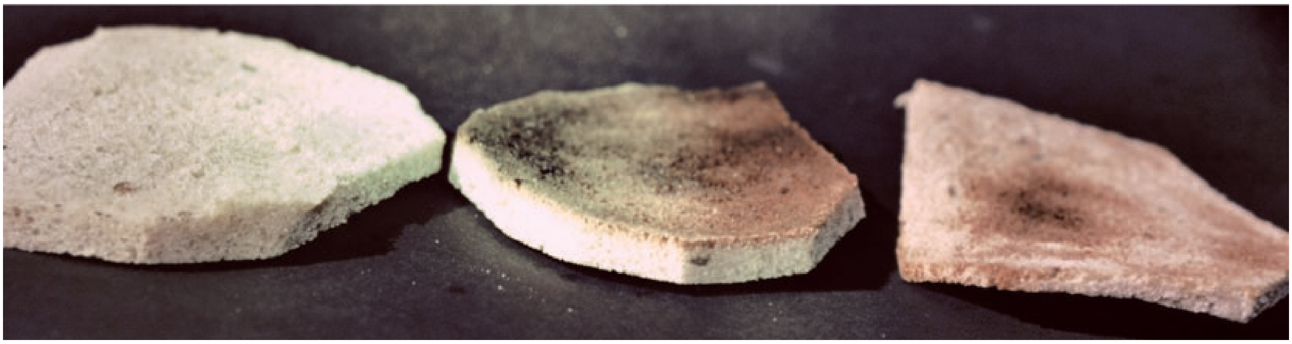

Figure 27. The shape of a bread-slice can be changed by selective grilling. If the flat slice (left) is grilled on one side only, it becomes elliptic (middle); further grilling of the other side as well gives a hyperbolic slice (right).

hyperbolic layer structure results whenever the Euler-Poincare characteristic is negative, once the average ring size in the network, n, and the connectivity of the network, z, fulfills the inequality (cf. Eq. (6)):

$$\left(\frac{n}{z}+\frac{n}{2}+1\right)<0\ i.e.\,(n-2)(z-2)>4 \qquad (9)$$

The connectivity of covalent chemical frameworks is set by the bonding arrangement of the atoms. For example, in all but the densest silicates each silicon is bonded to four oxygen atoms. Further, this situation favours tetrahedral coordination around each silicon (or framework aluminium) atom, favouring ring sizes of at least five. Thus, most silicates are hyperbolic (cf. Eq. (8)). The conventional geometric parameters of covalent frameworks – preferred bond lengths, bond angles and torsion – can be translated to give a preferred Gaussian curvature for the framework, which, by the argument above, is necessarily negative (HYDE, 1993a; HYDE *et al.,* 1993). The standard concepts of solid-state chemistry then imply a preferred Gaussian curvature for silicate networks – i.e. a homogeneous hyperbolic surface on which the silica lies. The formation of networks lying on crystalline hyperbolic surfaces is, in the light of this argument, quite natural.

This thesis is a controversial one and further work is required to determine its general applicability. However, it does lead to useful insights regarding the silicate density and the link between density and ring sizes in the framework, noted elsewhere (HYDE, 1993a; HYDE *et al.,* 1993). Further, it allows for clear definition of the pore geometry in low-density silicates, such as zeolites. Many other silicates form nets on crystalline hyperbolic surfaces that self-intersect (and are not embedded), leading to three, two-, one- and zero-dimensional channel systems (FISCHER and KOCH, 1996).

The non-euclidean approach also affords particularly simple estimates of relative energies of schwarzites, graphitic tubes and fullerenes, derived from plate elasticity theory (applied to graphitic monolayers!) (HYDE and O'KEEFFE, 1996) and suggests common stability criteria for both molecular assemblies, such as liquid crystals, and atomic crystals. At a more philosophical level, this description challenges conventional notions of dimensionality in these systems.

A two-dimensional hyperbolic perspective also offers novel insights into structures and genesis of so-called "bicontinuous phases" (such as cubic phases) in surfactant-water systems. Here too, the complex convoluted forms adopted by these systems can be traced to the requirement of a homogeneous hyperbolic structure, a frustration best relieved by the formation of IPMS or similar structures.

These structures are not bonded by the strongly directional covalent linkages present in the atomic frameworks considered above. Rather they are held together by hydrophobic and other weak interactions. A topological analysis based on ring sizes is thus not useful in these molecular systems. Another feature of hyperbolic geometry is at work in these systems. The lipid layers are themselves made up of chemically distinct components: their head-groups are exposed to water on both external surfaces, and their interior contains the oil-like chains. So in contrast to the surface model for atomic frameworks, lipid layers are modelled by films, of finite thickness, wrapped onto surfaces. The film shape is governed by the variation of cross-sectional areas through the molecular film.

This feature can be simply demonstrated with the aid of a slice of bread and a griller. The uncooked slice can be considered a flat film. If the bread is grilled from one side only, it will emerge from the grill curved exclusively towards the cooked face – the once-flat slice is now elliptic. This curvature is due to the fact that the heated bread surface has shrunk in area compared with the other, cooler, surface. Now grill the bread on the other side. The resulting toast is no longer elliptic, but hyperbolic, resembling a saddle. In this case, *both* external faces have shrunk compared to interior – a situation that can only be resolved by the formation of a saddle (Fig. 27).

If a potato slice is substituted for the bread, deep-frying the potato forms a potato crisp. Here too, surface shrinkage results in the characteristic saddle-shaped potato crisp, shown in Fig. 16. (The blistered, elliptic crisps in Fig. 17 are presumably due to local moisture gradients that result in some stretching of the surface.)

A lovely example of our poor intuition of hyperbolic forms is displayed in Fig. 28, which reveals a most unlikely form for a potato crisp: the crisp is elliptic, its boundary hyperbolic! The image is reminiscent of Cramptons' euclidean boxes; here the hyperbolic form is recognisably curved, yet its form has been "shoehorned" into a more familiar elliptic geometry.

A similar explanation accounts for the shape of tenside assemblies in water. The form of these assemblies depends on many factors; the most important being molecular shape and water content. The molecular shape can be characterised by a generalised shape parameter, related to the difference in cross-sectional area at both ends of the molecule. If these areas are equal, aggregation of the molecules into a sheet can be accommodated without any curving of the sheet. If the head-group cross-sectional area is less than that at the chain ends, the sheet must curve towards the head-groups to accommodate the cone-shaped molecules, just as the slice of bread toasted on one side only curves elliptically (Fig. 29). The form of the molecular monolayer is thus dictated by the area difference across the monolayer (ISRAELACHVILI *et al.*, 1976; HYDE, 1990). If the molecules assemble to form a bilayer, three surface areas must now be accommodated – the two head-group areas on both external faces of the bilayer, and the area of the mid-surface through the bilayer, set by the chain-ends (Fig. 30).

Figure 28. Roman signwriter's view of an unlikely elliptic potato crisp, whose boundary is hyperbolic (cf. Fig. 16).

Again, if all of these areas are equal, the bilayer is flat. If the head-group area exceeds the that of the chain ends, the configuration is frustrated in euclidean three-space, and a "blistered" bilayer results (cf. the bubbles in crisps). If the cross-sectional area of the mid-surface set by the chain-ends is larger than that of the outer faces (set by the head-group area), the bilayer must warp – just as the toast cooked on both sides – and adopt a hyperbolic geometry. These average molecular dimensions determine a preferred Gaussian curvature of the bilayer. If the bilayer contains a single chemical species, that preferred curvature has a single value, and the resulting membrane morphology is one that satisfies that value as nearly as possible within the constraints of

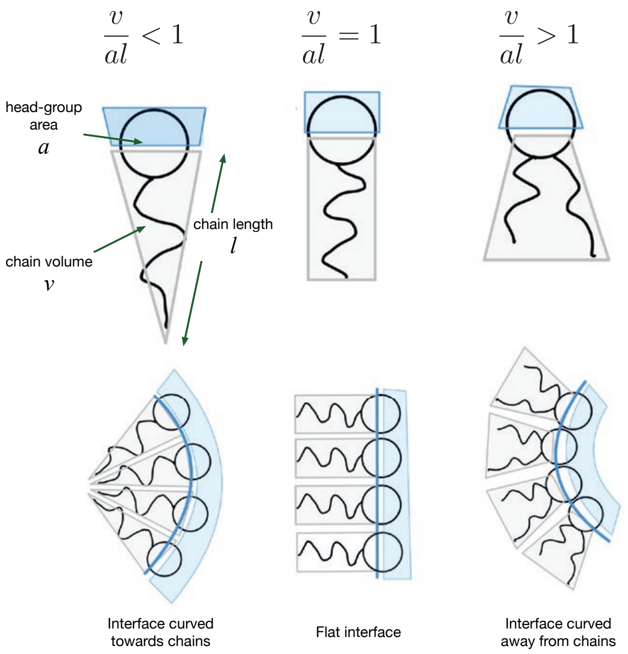

Figure 29. Schematic view of the relation between the average "wedge-shape" of a lipid or surfactant molecule (top) and the curvature of a monolayer of such molecules immersed in water (bottom).

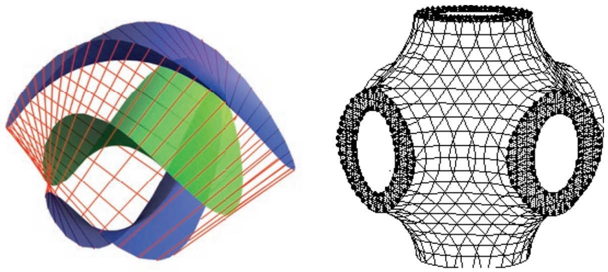

Figure 30. Left: View of a hyperbolic molecular bilayer, showing the (green) interface, which traces the surface running through the centre of the bilayer between the chain ends and parallel interfaces (blue) traced out by the head-groups in both monolayers. Right: Global view of one possible hyperbolic bilayer geometry – the P-surface.

three-dimensional euclidean space. Clearly then homogeneous geometries are preferred, and the formation of (meso)crystalline hyperbolic membranes – as in cubic phases – is not surprising (Fig. 30).

The formation of curved films due to area mismatch between parallel layers is also common in atomic systems. A beautiful example of this is the mineral imogolite, found around the base of tropical volcanoes. Imogolite consists of two bonded layers: silica and gibbsite (CRADWICK *et al.*, 1972) (Fig. 31). The slight differences in bonding dimensions between these two structures lead to a mismatch of areas, which is accommodated by regular curving of the alumino-silicate sheets, into long 20 Å cylinders (HYDE, 1993b). The formation of cylinders, of zero Gaussian curvature, is possible without changing the local atomic arrangement (i.e. ring sizes, connectivity) in either (originally) layer, viz. regular hexagonal nets. That follows from Eqs. (6) and (7), since the integral curvature remains zero, and so the effective Euler characteristic also remains zero. Hyperbolic and elliptic forms – structured at larger distances than are usually associated with atomic structures – are also likely in other silica composites, such as allophane, asbestos, and many serpentines.

Solids can also be structured at the ultrastructural level – typically microns. The biological world is replete with examples of such materials, particularly in animal skeletons. A striking example can be found in the hard calcite plates in many sea-urchins. Scanning EM images reveal complex "fenestrated" crystals, whose morphology bears remarkable resemblance to the P-surface (NISSEN, 1969; DONNAY and PAWSON, 1969). There is some distortion of the cubic symmetry of the *P* morphology, perhaps enough to reflect the underlying rhombohedral symmetry of calcite (Fig. 32). Here the calcite gives the sea-urchin a lightweight suit of armour: it is riddled with tunnels, and its strength-to-weight ratio exceeds that of concrete!

One side of the surface contains the hard inorganic calcite crystal, the other the life-giving proteins. How does this extraordinary ultrastructure form? Clearly, it is influenced by the presence of proteins, both water-insoluble structural ones and soluble material. Could it be that the proteins assemble to form an ultrastructured aqueous container – in the shape of one labyrinth system of the P-surface – in which the calcite is precipitated? It is likely to be more complex than pure templating. For example, smoothly curved magnesian calcites can be crystallised *in vitro* from solutions containing small amounts of organic additives, such as citric acid (F. C. Meldrum, private communication) suggesting that occluded proteins within the crystal assist in the formation of the curved surfaces.

Perhaps the most enigmatic feature of these shells is their glassy properties, conchoidal fracture and smoothly curved faces – coupled with apparently perfect crystallinity (as evidenced by X-ray diffraction) (LOWENSTAM and WEINER, 1989). Note, however, that the fractures along individual traberculae are often flat, and typical of cleavage planes of calcite.

It may be more than coincidental that smoothly curved inorganic crystal aggregates (alkiline earth car-

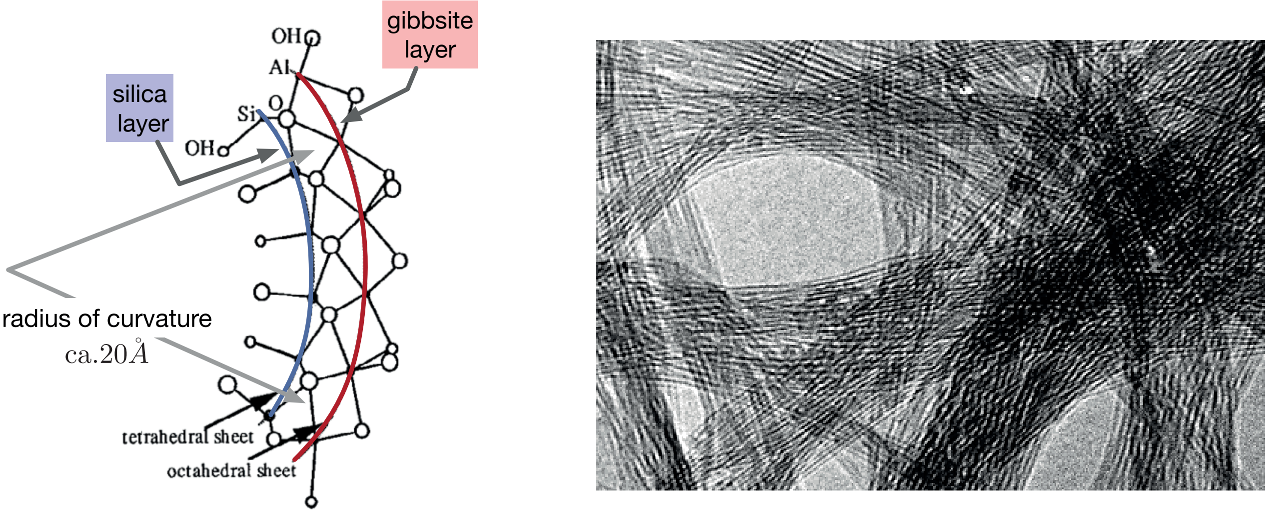

Figure 31. (Left) Cross-section through a sector of cylindrical imogolite sheet (image adapted from CRADWICK *et al.,* 1972) (Right) Electron microscopic image of imogolite cylinders (scale bar 200 Å, image adapted from WADA, 1987).

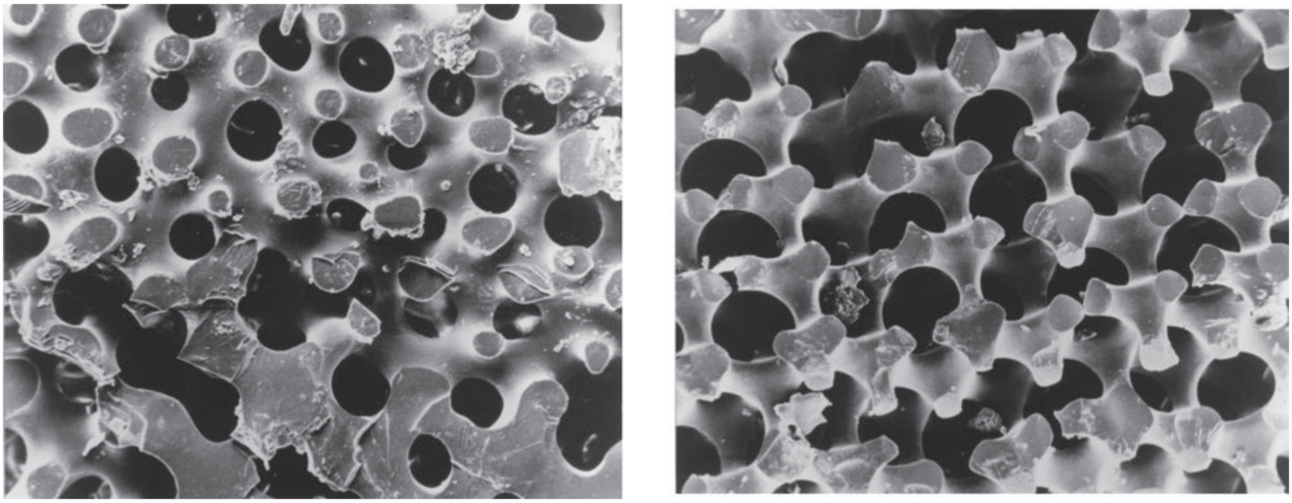

Figure 32. Scanning EM images of a skeletal plate of the sea-urchin Cidaris rugosa, after chemical treatment of the plate to remove proteinaceous tissue which lines the open channels in the living creature. The channels are microns wide (images courtesy Hans-Udde Nissen).

bonates, including calcite) can be "crystallised" in silica gels to form smoothly curved shapes, that act optically as single crystals, but whose diffractions patterns are powder-like (GARCIA-RUIZ, 1985; GARCIA-RUIZ and MORENO, 1997). The formation of curved morphologies is conventionally ascribed to the biological realm, yet these aggregates are purely inorganic (Fig. 33).

A final example is the mineral, saddle dolomite, which exhibits well-defined crystallinity, yet grows to form smoothly curved faces, with radii of curvature of the order of centimetres. The origins of curvature in this mineral (and related minerals such as ankerite) are unclear: its very occurrence severely strains conventional three-dimensional euclidean pictures of crystals and crystal growth.

6. FINAL THOUGHTS

This exploration of the world of condensed matter has been designed to highlight the often forgotten active role of space and geometry in our perceptions of form and shape. Indeed, it has been argued by a number of respectable scientists that much of physics is no

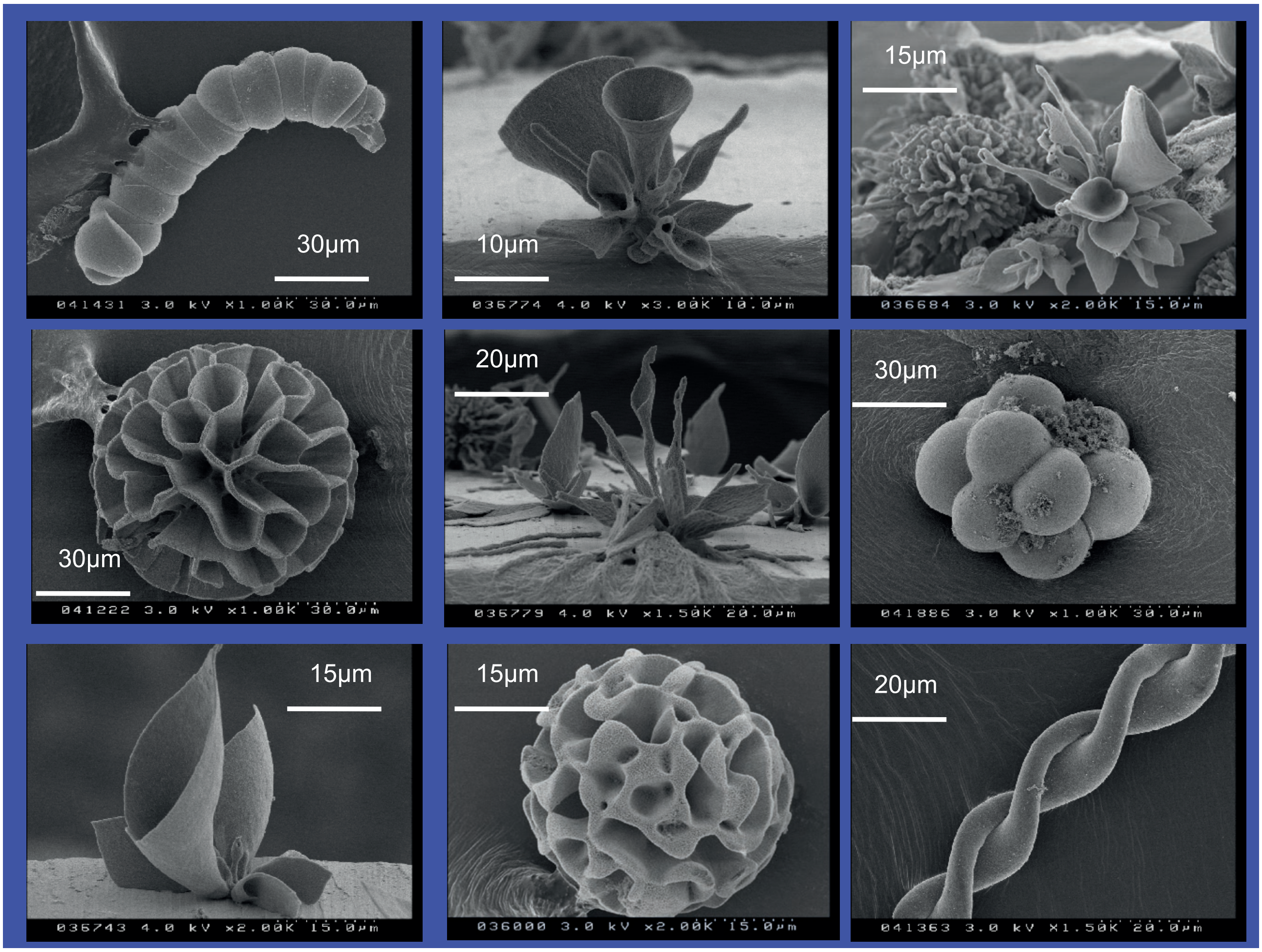

Figure 33. Field emission scanning EM images of barite crystals grown in silica gels (pH ca. 12, photo courtesy Anna Carnerup).

more than geometry; witness the remarkable statement of Arthur Stanley Eddington, the noted British cosmologist, earlier this century: "A *field of force represents the discrepancy between the natural geometry of a coordinate system and the abstract geometry arbitrarily assigned to it*". This idea, only possible post Riemann, bears some reflection. At the smallest length scale, in the sub-atomic world and at huge length scales, in the cosmological Universe, the assumed geometry of a reference frame is laid bare, and scientists regularly confront issues of dimensionality and curvature. Yet those of us probing matter between these extremes of length persist with the familiar euclidean assumptions. In 1959, Lancelot Whyte wrote, *"Exact science is mainly built on the sense of sight, and if no one has ever seen a straight line 'looking straight', or rather if no one knows exactly what that means, and if continuous straight objects are really open patterns of discrete particles, why does physical theory still prefer to assume that the fundamental laws are engraved on continuous rectangular frames as fields extending to infinity?"*

How much does Whyte's complaint hold true for biology and chemistry? Let's go back to the Tahitian islands, and the humble *Partula* of Crampton. Recall his nearly one million measurements of the form of the *Partula* shell, and detailed statistical analyses? Following our exploration of elliptic and hyperbolic forms, it seems desperately crude to engrave the exquisite swirls and twists of these shells on Crampton' s rectangular frame! Rather, curvature and torsion seem to be the outstanding morphological features of these shells. How that curvature and torsion is encoded during growth of the shells is unknown, but – given the extraordinary ability of organic "soft matter" such as lipids and proteins to fashion the morphology of "hard" inorganic matter – the general features of the form itself should not surprise us. That form is far removed from Crampton' s carefully drawn rectangles, boxing *Partula* forever in a euclidean grid.

ACKNOWLEDGMENTS

Many thanks are due to Gehan Wijeyewardene for lending me *"Eight Little Piggies"*, to Vince Craig for showing me the ivy, to Barry Ninham and Bruce Hyde for useful comments on the manuscript.

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Feature Article

Surface Inactivation of Bacterial Viruses and of Proteins

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Due to the Covid-19 pandemic an enourmous number of papers have appeared in the literature. Here we republish, with permission, the paper written by M.H. Adams in 1948 for the remarkable contribution in Physiology and in other fields. A short introduction by Barry W. Ninham precedes the paper.

MISSED OPPORTUNITIES AND FASHIONABLE PURSUITS

by Barry W. Ninham
Department of Materials Physics, Australian National University, Canberra, Australia

The extraordinary paper of Mark H. Adams: *Surface Inactivation of Bacterial Viruses and of Proteins* appeared in a mainstream Journal of Physiology, in 1948.[1]

It was neglected and has been ever since.

In retrospect this was and is a tragedy for science of the very first order.[2]

Adams was recognised in his time as a brilliant bacteriologist who, sadly, died young (1912-1956). His peers completed a partially finished book on his work in 1959.[3]

It was forgotten in the rush to join the DNA biological revolution. In that revolution the physical sciences, the physical chemistry of solutions, colloid and surface science have played almost no serious *conceptual* role at all.

The biological/medical and the physico-chemical sciences have diverged almost completely, to a point where their languages are mutually incomprehensible.[2] Of course, characterisation and diagnostics of disease by myriad new techniques has been essential to progress in medicine and biology. But the gap remains. We are missing something.

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Adams paper circumscribes that something.

To see why we remark that 1948 was the same year that Overbeek's landmark thesis on colloid stability marked the basis for the DLVO theory of colloid stability.[4,5] It introduced long ranged quantum mechanical, dispersion forces of interaction between particles and dominated thinking about forces until now. Its limitations were spelt out by Derjaguin and Overbeek. Many of these limitations appeared to be resolved by sophisticated further extensions that embraced many body forces via Lifshitz theory, on charge regulation, on effects due to solvent structure and molecular size. Direct force measurements between surfaces that confirmed theory, a challenge dating back before Newton, appeared to represent a triumph.[6]

But there was and remained an uneasy juxtaposition with the classical theories of the physical chemistry of electrolytes and electrochemistry, and colloid science. These theories, of pH, of activities, of pKas, of conductivity, the electrical double layer, of zeta potentials that were developed before quantum mechanics, and ignored it. Dispersion forces between ions and ions and surfaces are the key to specific ion (Hofmeister) effects essential to biology. And hydration was unquantified. Add to that the fact that undefined anthropomorphic words like hydrophilic and hydrophobic figured prominently in the conversation and we have an unquantifiable mess. That is explicit in that standard measurements like pH and zeta potentials were based on inadequate theory.

It got worse when it was realised that even the apparently impressive addition of Electromagnetic Quantum Field theory embodied in Lifshitz theory was flawed too, and that the ansatz of additivity of electrostatic and electrodynamic fluctuation (dispersion) forces, the one treated in nonlinear theory, the other linear, violates the laws of physics.[7,8]

Since hardly anyone understood mathematics or physics, it did not matter.

Matters reached a nadir in the 1980s when the leading speaker at a Nobel symposium, from a Swiss drug company began his lecture with slide: NMR. No, not nuclear magnetic resonance he said. It means NO MORE RESEARCH!

By which, he explained, the game was over. Modern computer simulation with 70,000 effective molecular interaction parameters without water, could design any required drug or protein or enzyme with ease.

A laconic biochemist asked; What happens if you raise the temperature above body temperature of 37 degrees. Ha! Easy. We change the parameters!

Such mind-blowing idiocy continues and marks the end of an era.

Faraday would be turning in his grave.

We can forgive the medical and biology people for ignoring what ought to be the enabling discipline of physical chemistry on the reasonable grounds that they have more than enough to do than be confused by the subtleties of the physical sciences; especially if even the quantum electrodynamicists produce a flawed theory.

But there is much more, and here we come to Adams.

The physical theories (and simulation) ignore any effects due to dissolved atmospheric gases. The ancient Greeks tell us that there were 4 elements. These are: fire (temperature), water, earth, and air. Take away air and hydrophobic interactions go away; emulsions become stable, chemical interactions cease, enzymes working. The simplest of experiments is bubble-bubble interactions in salt water. Bubbles do not fuse above a concentration of 0.17 molar for 1:1 salts like NaCl.[9,10] Not coincidently, that corresponds exactly to the ionic strength of

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Derjaguin and Landau publications in Russian were not easily accessible in the west during the 2nd world war. Landau was appallingly scathing of Sam Levine who nearly had the theory first. He did so because Sam replaced a nonlinear coupling constant integration in calculating the double layer free energy by a linear one. It is therefore ironic that Landau's students Dzyaloshinski, Lifshitz and Pitaevski made the same mistake in their *tour de force* of Quantum Electrodynamic forces. See also: Ninham, B. W.; Brevik, I.; Boström, M. Equivalence of Electromagnetic Fluctuation and Nuclear (Yukawa) Forces: The Π_0 Meson, Its Mass and Lifetime. *Substantia* **2022**. Just Accepted https://doi.org/10.36253/Substantia-1807.

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salts in the blood. The phenomenon occurs for a whole range of salts. But for other ion pairs, no such effect occurs. There are strict rules that govern which ion pairs "work" and which do not. The effects occur at higher concentrations for sugars. They occur at much lower concentrations for amino acids.[11]

Classical physical and colloid chemistry are impotent in the face of such a challenge.

The answer seems to lie in the fact that in any solid or liquid impurities aggregate, in much the same way that surfactants aggregate to form micelles.

There is a natural critical salt concentration for stable nanobubble formation. This shows up in conductivity measurements in salt solutions with and without dissolved gas.[12]

Such nanobubbles inhibit bubble-bubble fusion by known depletion forces.

Nanobubbles that form spontaneously in enzyme-substrate interactions produce free radicals that drive catalysis.

Cavitation produced by ship propellers, a very major economic transport problem, disappears if a jet of air deficient water is projected onto the propeller.[13]

The tensile strength of water is two orders of magnitude higher when gas is removed, a fact known for more than a century, and explained immediately by Griffith's theory of. the strength of solids if gas aggregates of nanobubbles impurities occur.

Much more to the point stable nanobubbles of CO_2 produced by metabolism produce a foam that forms the endothelial surface layer lining all cells and tissues. It is extremely effective in killing viruses like covid and other pathogens.[13,14,15]

Nanobubbles of oxygen/nitrogen are delivered by the lungs to capillaries, not molecularly and catalyse many reactions.[16]

The present state of affairs as it exists in Colloid Science can be seen in Ref. 17.[17]

It is seems clear that dissolved gas is a hidden variable that is essential to understanding the properties of condensed matter. The effects are dramatic. The Greeks told us so. Our theories have ignored dissolved gas. They compare gas-free models with real world soft matter that does contain gas. A simple example is the deviation from theory of the measured Debye length in a 1:1 electrolyte above the critical concentration for nanobubble formation.

It is impossible to simulate these effects.

Adams paper on effects on proteins of shaking test tubes containing physiological saline, or not, containing gas or not covered all this 75 years ago. A pity we missed it. There is nothing we can do about it except wonder at what might have been had he lived.

There are appearing now a number of good papers that are following Adams lead.[18]

And finally we can note that the extinction of species after various ice ages makes sense if we allow dissolved gas to do its job. During an ice age salt is precipitated out. After the ice age the melt water is salt depleted below the critical concentration for bubble-bubble (and nanobubble) fusion. All single celled creatures would die of the bends.

Some few souls are beginning to shake things up and surprised at what they see.

Barry W. Ninham

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It has been noticed previously that certain viruses can be rapidly inactivated by shaking or by bubbling gases through the virus suspensions. Campbell-Renton (1) studied the effect of violent mechanical shaking on bacteriophages and found them to be fairly rapidly inactivated, at rates which were characteristic for each phage. Grubb, Miesse, and Puetzer (2), while studying the effect of various vapors on influenza A virus, noted that bubbling air at the rate of 1 liter a minute through the virus suspension resulted in detectable reduction in infectivity in 10 minutes. In a somewhat more extensive study McLimans (3) found that both Eastern and Western strains of equine encephalitis virus were rapidly inactivated by shaking in buffered saline suspensions. The inactivation also occurred when gases were bubbled through suspensions of the virus. The rate of inactivation was the same whether oxygen or helium was the gas used, indicating that the inactivation was probably a physical process, rather than the result of chemical interaction between virus and gas. He also noted that the rate of inactivation increased markedly as the pH was reduced from 7 to 5, though control suspensions at rest suffered no inactivation.

The inactivation of certain physiologically active proteins such as enzymes (4) and toxins (5) on shaking is a familiar phenomenon. Perhaps not quite so well-known is the fact that this kind of inactivation can be specifically prevented by the presence in the diluent of very small amounts of proteins. It has been demonstrated that the spreading of a protein at a gas-liquid interface results in the denaturation of the protein, since the spread protein becomes completely insoluble in water (6) Presumably the role of the shaking or bubbling in the inactivation of viruses and physiologically active proteins is simply that of enormously increasing the area of the gas-liquid interface, and hence increasing the chances of the susceptible protein being spread on that surface. This paper is devoted to the kinetics of the inactivation of bacteriophage by shaking and to the effect of environmental influences on the rate of inactivation.

MATERIALS AND METHODS

The group of seven coli-dysentery phages studied by Demerec and Fano (7) was used. The properties of this group of bacterial viruses have been summarized by

De1bl-tick (8). These phages were grown on *Escherichia coli,* strain)3, in a chemically defined medium of the following composition:

NH_4C1	1.0 gm.
$MgSO_4$	0.1 gm.
KH_2PO_4	3.5 gm.
Lactic acid	9.0 gm.
NaOH	about 4.0 gm. or to a final pH of about 6.5
H_2O	1,000 ml.

Since T_5 is not produced in the absence of calcium ion, calcium choride to a concentration of 0.001 M was added when preparing stocks of this phage. All phage stocks used contained about 10^{10} plaque forming particles per ml. All phage assays were made on strain B of *E. coli* using the agar layer technique of Gratia as modified by Hershey (9).

The saline buffer diluent used in the inactivation experiments contained 0.15 M NaCI, 0.001 M MgSO4, 0.01 M buffer, and other additions as noted. Most experiments were performed using phosphate buffer at pH 6.5. Inorganic chemicals were reagent grade; the gelatin was Eastman ash-free calfskin gelatin; the bovine serum albumin was Armour's fraction V; yeast nucleic acid was a purified specimen from Eimer and Amend; the thymus nucleic acid was a highly viscous Hammarsten type preparation.

In the bubbling experiments nitrogen was passed through a coarse grade Corning sintered glass filter at the rate of 1 liter per minute producing a vigorous effervescence in the virus suspension held in the filter. The gas was saturated with water vapor and the gas stream as well as the filter and its contents was in a constant temperature bath.

The shaking experiments were carried out in test tubes 15 mm. × 100 mm. with a capacity of 16 cc. These tubes as well as dilution tubes were cleaned with hot acid dichromate, well rinsed, and twice boiled with distilled water. Pipettes were similarly acid-cleaned and rinsed with hot distilled water The test tubes were closed with rubber stoppers which were boiled with sodium hydroxide, well rinsed, then twice boiled with distilled water before each use. The most meticulous cleanliness was essential in obtaining consistent results. The shaking machine had a horizontal reciprocating motion of 320 cycles per minute and the carriage traversed a distance of 7 cm. The test tubes were shaken with the long axis parallel with the direction of motion of the carriage.

EXPERIMENTAL

Kinetics of the Inactivation Reaction. — Bacteriophage T_7 at an initial concentration of 6×10^9 plaque-forming particles per ml. was diluted in the saline-buffer diluent to a concentration of about 10^4/cc. The conditions of the experiment were: phosphate buffer of pH 6.5, temperature 26°C., volume of phage suspension 5

Table I. The Inactivation of TT Bacteriophage by Shaking in Saline-Buffer Diluent at 26°C. and pH 6.5

Time	Sample	Count	Survivors per 0.1 ml.	*Pe/Pt*	In *Po/Pg*	K
	ml.					
0	0.02	136	*Av.* 753			
0	0.02	165				
2	0.05	225	450	1.67	0.51	0.26
4	0.05	104	208	3.6	1.28	0.32
6	0.05	68	136	5.5	1.7	0.28
8	0.05	45	90	8.3	2.1	0.27
10	0.1	52	52	14.4	2.7	0.27
15	0.1	13	13	58	4.1	0.27
35	0.1	1	1	753	6.6	(0.19)
						Av. 0.28

cc., shaker stopped every 2 minutes for sampling. The log per cent survivors proved to be a linear function of time indicating that the rate of phage destruction was proportional to the concentration of surviving phage;

$$-\frac{dP}{dt} = KP$$

or $K=1/t \ln P_0/P_t$

The data of this sample experiment are given in Table I. The first order velocity constant for the inactivation of T_7 under the stated conditions was 0.28 min^{-1}. There was no recovery of activity on standing in buffer diluent or broth, and inactivation occurred at a significant rate only during the periods of shaking (Table I).

The velocity constants for the inactivation of each of the seven *coil* phages and of two of their mutants at pH 6.5 and 26°C. are given in Table II.

From the data in Table II it may be noted that the small phages T_1, T_2, and T_7 are inactivated more rapidly than the larger phages. Phage T_{4r+} and its rapid lysing mutant (10) T_{4r} are much more stable than the other phages. With both T_2 and T_4 phages there was no significant difference between the stabilities of wild type and rapid lysing mutant. Also in mixtures of wild type and mutant forms, the proportion of the two types remained constant during the inactivation.

The volume of phage suspension was varied from 4 cc. to 7 cc. per 16 cc. tube without affecting the velocity of the inactivation. However, if the tube is filled with virus suspension so that no air space is left, there is no perceptible inactivation of the phage during 40 minutes' shaking, even when half a dozen glass beads are added to the tube. Because of the possibility of inactivation of phage through adsorption to the glass walls of the tube or to the rubber stopper, both of these surfaces were coated with melted paraffin. In the paraffin-coated tube the rate of inactivation of phage was the same as in uncoated tubes even though the paraffin surfaces were not wetted by the suspension of phage. If loss of activity were due to adsorption, the virus must adsorb equally well to glass and to paraffin. From these experiments it would appear that the shaking or agitation of the fluid suspension in contact with glass surfaces is not the cause of the inactivation of virus, but rather that the inactivation occurs at the gas-liquid interface which is present in enormous area when tubes half filled with liquid are violently shaken.

Table II . The Average Velocity Constants for the Shaking Inactivation of coli Phages at 26°C. and pH 6.5.

Phage	Velocity constant
T_1	0.59 min.$^{-1}$
T_{2r+}	0.24
T_{2r}	0.23
T_3	1.2
T_{4r+}	0.05
T_{4r}	0.07
T_5	0.24
T_6	0.20
T_7	0.48

The variation of velocity constant of inactivation as a function of pH is shown in the curves of Fig. 1. From these curves it is evident that the rate of inactivation by shaking is minimal between pH 5 and 8 but increases rapidly outside this range.

The small phage T_7 is much more rapidly inactivated at all pH values than are the larger phages, and repeated assays at a given pH are less reproducible with the small phages, resulting in a more erratic looking curve. All phages were markedly unstable in the absence of shaking at pH 3 except T_4. At pH 4 the phages were more stable than at pH 3 but in a few cases there was a 10 to 50 per cent loss in activity on standing at room temperature for 1 hour. At the higher pH values studied there was no detectable loss in activity in unshaken controls during the course of the experiments. Phage T_7 which is very rapidly inactivated by shaking at pH values above 7 is not detectably inactivated in unshaken control tubes after 1 hour at pH 8.7.

The effect of temperature on the velocity constants of inactivation was determined for phages T_1 and T_7. The averages for a number of determinations at 0°, 25°, and 38°C. are given in Table III.

From these values, using the Arrhenius equation, the Arrhenius constant

for the shaking inactivation of phages T_1 and T_7 appears to be about 10,000 cal./mol. This value is higher than the reported values for the heat of activation of denaturation of proteins by urea and by shaking (11) and far less than the values for heat denaturation of proteins.

In the presence of 1 mg./ml. of gelatin all phages were stable on shaking for 1 hour at room temperature at pH 6.5. Therefore, the protective effect of various concentrations of gelatin on phage T_5 was determined. The results are summarized in Fig. 2.

It will be seen from Fig. 2 that as little as 0.01 γ per ml. of added gelatin has a definite protective effect on phage **T5** while 1 γ/ml. gave complete protection for 14 minutes. However, after 20 minutes of shaking with 1 γ/ml. of gelatin the phage activity began to decrease. It would appear that the duration of the protective effect of gelatin is a function of the concentration of gelatin, and that the gelatin also appears to be inactivated by shaking. If the survival time of the gelatin is taken as the time when the inactivation curve becomes parallel to the inactivation curve in the absence of gelatin, then it becomes possible to estimate the rate of disappearance of the gelatin. The disappearance of the gelatin under these conditions appears to follow the kinetics of a first order reaction with a half-life of about 2 minutes. This relationship does not hold for concentrations of gelatin

Table III. The Average Velocity Constants for Inactivation of T_1 and T_7 at 0°, 25°, and 38°C.

Temperature	Velocity constants for	
	T_1	T_7
cc.		
0	**0.31**	**0.09**
25	**0.59**	**0.48**
38	**0.97**	**0.70**

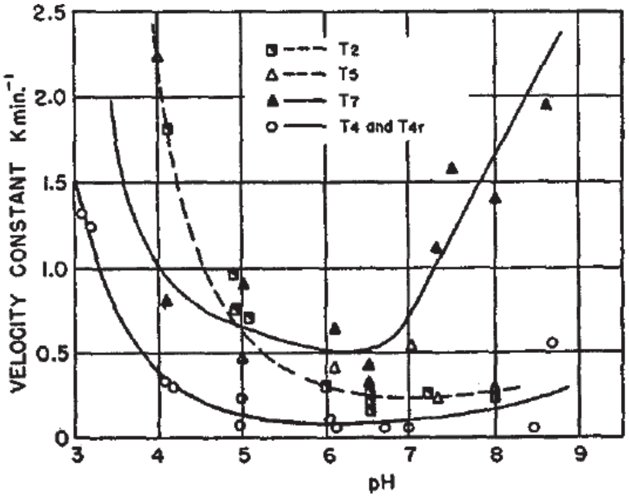

Figure 1. Velocity constants, K minute^{-1}, as a function of pH for the phages T_2, T_4, T_5, and T_7 at about 26°C.

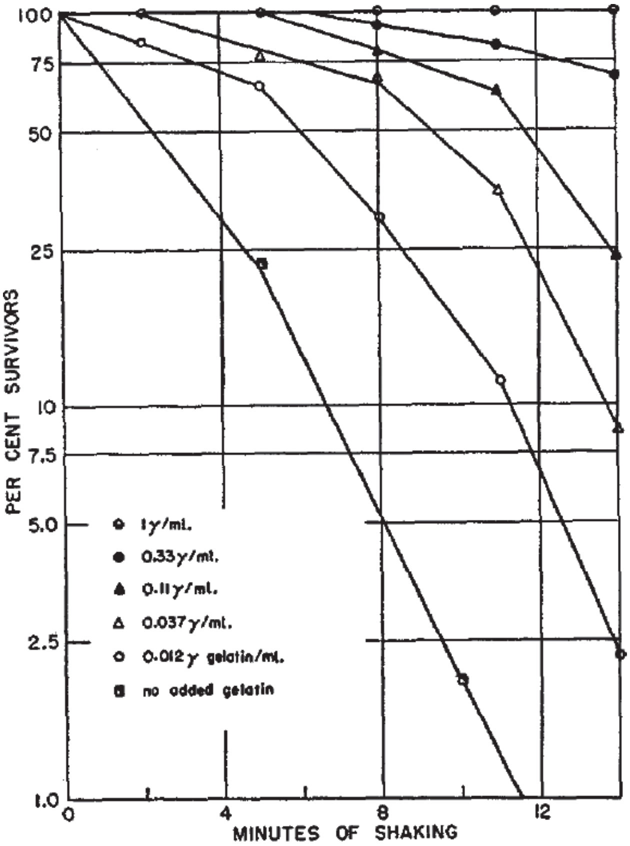

Figure 2. The inactivation of phage T_6, shaken in the presence of various amounts of gelatin.

above about 0.5 γ/ml. since as the protein concentration becomes higher the kinetics change from those of a first order reaction to those of a zero-order reaction in which the rate of inactivation is determined by the available surface rather than by the concentration of protein in solution (11).

If this supposition is correct, preshaking of the gelatin solutions before adding the phage should destroy the protective effects of the gelatin. The experiment illustrated in Fig. 3 is identical with the previous experiment except that the dilutions of gelatin in saline-buffer diluent were preshaken for 15 minutes before addition of phage. Then after phage addition the tubes were shaken and samples withdrawn at intervals for assay. It may be seen from Fig. 3 that the protective effects of all quantities of gelatin through 0.33 γ/ml. are destroyed by shaking for 15 minutes so that the resultant inactivation curves are identical with the curve with no added protein. There is little appreciable diminution in the protective effect of 1 γ/ml. of gelatin after 15 minutes of shaking.

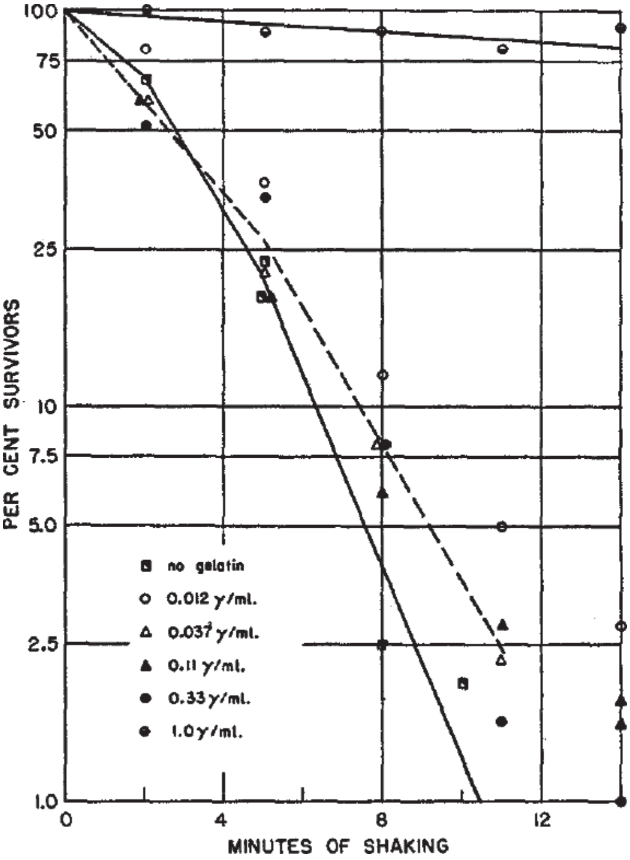

Figure 3. The inactivation of phage T_5, shaken in the presence of various amounts of gelatin which had already been shaken for 15 minutes before addition of phage. The symbols correspond to the same gelatin concentrations as in Fig. 2. The solid line is the curve for no added gelatin and the dotted line is an average curve for the tubes containing added gelatin.

Similar experiments have been carried out using various concentrations of gelatin with T_7 and T_{2r}, with very similar results.

Since gum arabic is a colloidal substance with reputed protective effect against inactivation of tuberculin (12) it was tested for its effect on the shaking inactivation of phage T_5. As may be seen from Fig. 4 gum arabic gives a family of curves similar to those given with gelatin, except that about 100 times as much gum arabic is required to equal the effect of gelatin. It is probable that the protecting effect of the gum arabic is due to contamination with about 1 per cent of protein. This agrees with previously made quantitative estimates of the protective effect of gum arabic against the surface inactivation of tyrosinase (13).

In a similar manner yeast nucleic acid and thymus nucleic acid prepared according to Hammarsten were tested for possible protective effect. Both of these substances had a protective effect equivalent to about 1 per cent of their weight of gelatin. Since no amino acid anal-

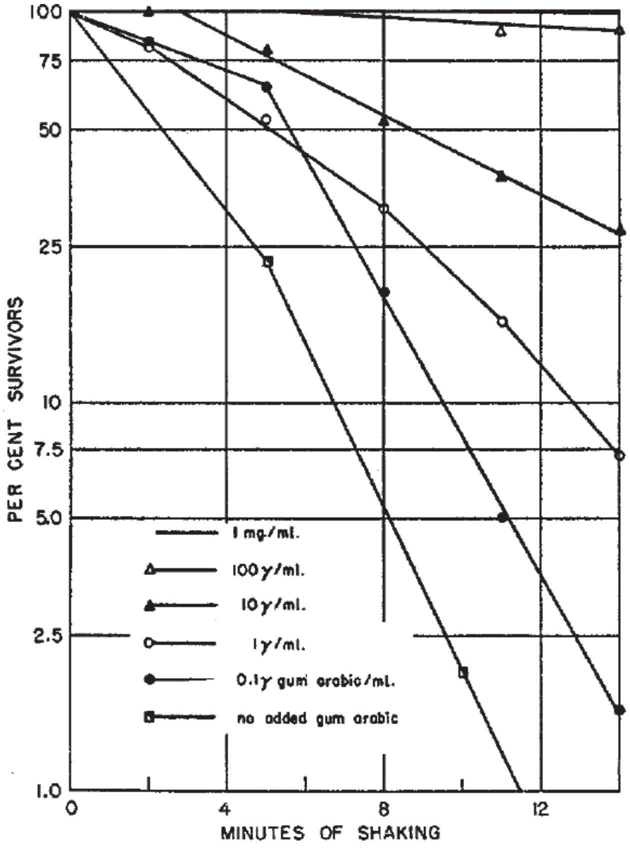

Figure. 4. The inactivation of phage T_5, shaken in the presence of various amounts of gum arabic.

yses were available for these samples of nucleic acid we cannot say whether the protective effect is due to contamination with protein or is an inherent property of nucleic acids.

A commercial sample of bovine serum albumin (Armour fraction V) prepared by alcohol fractionation was tested for its protective effect with the results shown in Fig. 5.

By a comparison of the curves of Fig. 5 with the curves with gelatin in Fig. 2 it may be seen that serum albumin is about one-tenth as active in protecting the virus from inactivation as is gelatin. This observation is in accord with experiments of Berger, Slein, Colowick, and Cori (14) on the inactivation of hexokinase in which the protective effect of serum albumin was about one-tenth that of insulin or rabbit muscle protein. It also agrees qualitatively with reported effects on the stability of diphtheria toxin diluted for the Schick test. Edsall and Wyman (15) reported that 500 γ/ml. of human serum albumin gave incomplete protection while 1 mg./ml. gave excellent protection. Moloney and Taylor (16) using similar test conditions reported that 12.5 γ/ml. of gelatin gave considerable protection while 25 γ/ml, of gelatin gave complete protection for 6 months.

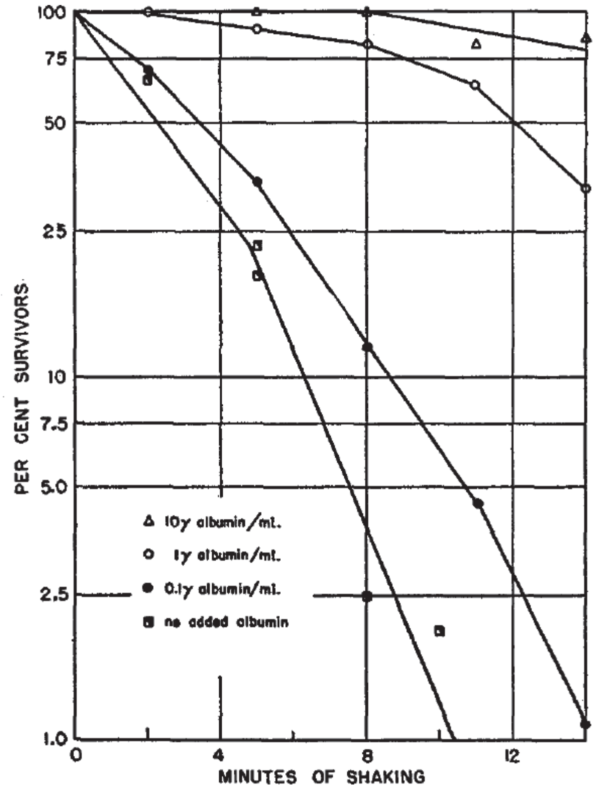

Figure 5. The inactivation of phage T_5, shaken in the presence of various amounts of bovine serum albumin.

If the inactivation of bacteriophages is due to some change occurring at the surface of gas bubbles produced in the fluid by shaking, this same kind of inactivation should occur when an inert gas is bubbled through a suspension of the virus. Accordingly 25 ml. of buffer-diluent at pH 6.5 containing phage T_{2r} at a concentration of 2.5×10^4 infectious particles per ml. were placed in a Corning sintered glass filter of coarse grade. This was held in a water bath at 30°C. and nitrogen gas was bubbled through the filter at the rate of 1 liter per minute. Samples were withdrawn at 5 minute intervals for an hour without interrupting the gas flow. The inactivation followed the kinetics of a first order reaction throughout this time with a velocity constant of 0.047 minute^{-1}, as compared with 0.23 minute^{-1} for shaking with air at 26°C. Similar results were obtained with T_7 although the rate was somewhat faster with this phage.

DISCUSSION

The denaturation of proteins probably involves the unfolding of a highly specific globular structure into a relatively unspecific polypeptide chain. This change exposes hitherto hidden -SH and phenolic groups to the action of chemical reagents, and results in the loss of solubility and of the specific physiological activity of the protein. Denaturation may be brought about by the action of heat, of chemicals such as urea, of detergents, of excessive concentrations of H^+ or OH’ ions, and by shaking. All of these denaturing agents will also bring about a destruction of the infectious properties of viruses.

That vigorous shaking will cause the precipitation of proteins from solution has been known for a long time. The precipitation of egg albumin from 1 per cent solutions on vigorous shaking follows the course of a zero-order reaction since the high concentration of protein maintains the gas-liquid interface in a saturated condition. The rate-limiting factors are the amount of surface available, and the rate at which the surface is renewed by agitation (11) With highly diluted proteins however, one might expect the kinetics of the reaction to be first order since the number of protein molecules arriving at the surface in unit time will be proportional to the protein concentration. There is very little data on this point in the literature. Shaklee and Meltzer (4) in 1909 studied the effect of shaking on the stability of pepsin in HCl. From their data it can be calculated that the inactivation of pepsin follows the course of a first order reaction with a velocity constant of 0.029 minute^{-1}- at 33°C. Since no characterization of the pepsin was made it is impossible to say how much pepsin was present or even how much total protein was present in the shaking experiments. However, it is significant that the addition of peptone stabilized the pepsin, there being a loss of only 25 per cent of the pepsin activity on shaking for 24 hours at 33°C. in the presence of peptone. Shaklee and Meltzer made certain observations that agree closely with our own observations on the inactivation of bacteriophage by shaking, namely:

1. Presence of glass beads did not accelerate shaking inactivation.
2. No inactivation of shaking full bottles, with or without glass beads.
3. Results in paraffined bottles were same as in nonparaffined glass bottles.
4. Results in sealed glass tubes were same as in rubber-stoppered bottles.
5. Inactivation rate increased with increasing acidity.
6. Results were the same with air, CO_2, or H_2 as the gas phase.

MacFarlane and Knight (17) in 1941 studied the α toxin of *Cl. welchii* which they demonstrated to be an enzyme, lecithinase. This enzyme when highly diluted was rapidly inactivated by bubbling air or nitrogen through the enzyme solution. They did not follow the course of the inactivation over a sufficient range of activities to make it possible to decide whether the kinetics are those of a zero order or a first order reaction.

It has been observed repeatedly that physiologically active proteins on high dilution often show a spontaneous loss of activity which may be prevented by carrying out the dilution procedure in the presence of other proteins. In Table IV is listed a number of examples of this phenomenon culled from the literature. Included are the concentration at which the activity of the protein in question is measured and at which the inactivation is observed, together with the concentration of added protein which has been found to prevent this inactivation. It should be noted that in many cases the concentration given is the lowest concentration of protein tested for protective effect since no titration of the protecting protein was made. It may also perhaps be significant that many of the enzyme activities are assayed in a Warburg or similar manometric apparatus in which a vigorous shaking of a highly diluted enzyme preparation is part of the assay procedure.

From Table IV it may be noted that the physiologically active proteins with which this type of instability has been observed are all proteins in which the specific activity is measured at a final protein concentration of 4 γ/ml. or less. Presumably proteins which must be assayed at higher concentrations do not show this phenomenon. Also it may be noted that where the protecting protein has been assayed, the amount required has varied from 1 γ/ml. of gelatin in the case of short duration experiments with bacteriophage to 25 γ/ml. of

Table IV. A summary of data from the literature concerning physiologically active proteins which are unstable when highly diluted, including the concentration at which the protein is usually assayed and at which its lack of stability is noted, and the concentration of protective protein employed to stabilize it.

Physiologically active protein	Concentration at which protein is markedly unstable	Concentration of protective protein employed	Reference
Diptheria toxin in Schick test	0.02 to 0.2 γ/mi.	1 mg./ml. serum albumin	15
		25 γ/ml. gelatin	16
Tetanus toxin	M. L. D. is 3×10^{-4} γ protein	10 mg./ml. peptone*	18
α toxin of *Cl. welchii* or lecithinase	M.L.D. is 0.2 to 0.5 γ γ protein	5 mg./ml. gelatin*	19
		10 mg. /ml. serum albumin*	20
Botulinus toxin	M.L.D. is 10^{-4} γ protein	2 mg./ml. gelatin*	21
Invertase		2 to 4 γ/m1. gelatin	22
Tyrosinase	1 γ/ml.	10 γ/m1. gelatin	13
Ascorbic acid oxidase	1 γ/ml.	6 γ/m1. gelatin	23
Carbonic anhydrase	1.6 γ/mi.	33 γ /ml. peptone	24
Catalase	<3 γ/ml.		25
Desoxyribonuclease	3 γ/ml.	100 γ/ml. gelatin*	26
Hexokinase	4 γ/ml.	6 γ/m1. insulin or 60 γ/nil. serum albumin	14
α glycerophosphate dehydrogenase	2.5 γ/ml.	1 mg./ml. gelatin*	27
Bacteriophage	10^4 particles/ml.	1 to 10 γ/m1. gelatin	

* Protective effect not titrated, concentration given is lowest one tested or only one given in reference cited.

gelatin needed to stabilize Schick toxin for 6 months at room temperature. Serum albumin when it has been compared with other proteins such as insulin or gelatin has been much less effective as a protecting agent. It is highly significant that proteins present in solutions of less than a few γ/ml. concentration are highly unstable, and that they are protected from inactivation by the presence in solution of other proteins at a concentration higher than a few γ/ml. It has been shown that proteins will unfold at a gas-liquid interface to form a monomolecular film about 10Å thick and covering an area of about 10 cm.^{2}/γ of protein (28). This protein film is insoluble in water, and once formed on a quiet surface will effectively prevent more protein molecules of the same or different type from reaching the surface. On stirring or agitation of the surface however, the protein film will be folded upon itself to form an insoluble coagulum of denatured protein, leaving a fresh interface for the unfolding of additional protein. A physiologically active protein present at a concentration of 1 γ/ml. could then be completely spread and inactivated at a total interface corresponding to 10 cm.^{2}/ml., an area readily obtainable with very little shaking. In the presence of a second protein, the rate of inactivation of the physiologically active protein would be a function of the relative concentrations of the two proteins, of their respective diffusion constants, and of the relative ease with which they unfold once they reach the surface. A protective protein present at a concentration of 10 γ/ml. should effectively exclude from the surface a protein of similar properties present at a concentration of 1 γ/ml. Also if a physiologically active protein is present at a concentration of 10 γ/ml. or higher, the available surface will be saturated with an undetectably small fraction of this protein and hence no loss in activity will be noticed unless the shaking is more violent and prolonged than in the usual assay procedures in the Warburg apparatus for instance.

Langmuir and Schaefer (29) derived an equation for the diffusion of solute molecules to the surface, assuming only that every molecule which reached the surface stayed at the surface. This is a reasonable assumption for protein molecules if every molecule which reaches the surface unfolds into a film. The equation is

$$n = 2n_0 \left(\frac{Dt}{\pi}\right)^{1/2}$$

where *n* is the amount of protein reaching 1 cm.^{2} of surface in time *t*, n_o is the concentration of protein per cm.' and *D* is the diffusion constant of the protein. For egg albumin at 20°C. and a concentration of 100 γ/m1., the surface should be saturated in 1 second, whereas at a concentration of 5 γ/ml. it would take 26 minutes to saturate the surface. Bull (30) measured the rate of fall of surface tension with time in solutions containing various concentrations of egg albumin. At albumin concentrations higher than 50 γ/m1., the major portion of the surface tension drop occurred in less than a minute, while at a concentration of 5 γ/ml. there was no noticeable drop for several minutes, then the major fall in surface tension occurred between 5 and 15 minutes, the surface tension approaching the equilibrium value in 30 minutes.

At a concentration of egg albumin of 1 γ/m1., the albumin will reach the surface in the quantity of 10^{-2} γ per cm.^{2} of surface in 100 seconds. If the surface to volume ratio is increased by shaking or bubbling it is obvious that a large proportion of the total protein would reach the surface in a fairly short time especially since Langmuir and Schaefer (29) point out that in stirred solutions the amount of solute reaching the surface is proportional to time rather than to the square root of time as it is in solutions at rest.

Failure to realize that the concentration of protein in solution was the critical factor in determining whether or not rapid spontaneous inactivation occurred on dilution, has resulted in the publication of probably erroneous conclusions. For instance Traub, Hollander, and Friedemann (31) concluded that broth and serum "potentiated" the lethal action of tetanus toxin. They considered the possibility that the added broth or serum prevented the inactivation of tetanus toxin but discarded this explanation, largely on the grounds that if the low titer of toxin in saline were due to inactivation it would have to occur with unreasonable rapidity, and because "potentiation" occurred in the case of titrations in small animals such as mice but not in large animals such as rabbits. Examination of their data reveals that with toxin lot 1556 the lethal dose in rabbits is 0.1 ml. of a 1/10 dilution in either broth or saline; whereas in the guinea pig the lethal dose is 0.1 ml. of a 1/2000 dilution in saline, and 0.1 ml. of a 1/128,000 dilution in serum. It seems not unreasonable to assume that culture filtrates containing tetanus toxin when diluted beyond 1/2000 in saline contain less than the critical 1 γ/ml. of protein; especially since in the titrations recorded in their paper, the *potentiating* effect of broth decreased to almost nothing when the broth was diluted 1/1000 in saline. The observations of Traub *et al.* on potentiation can be satisfactorily explained on the assumption that tetanus toxin is markedly unstable when it is diluted beyond a limiting value for total protein concentration, and that dilution in the presence of small amounts of protein prevents this loss of activity.

In the present paper we have discussed the inactivation of viruses by shaking as a process quite analogous to the surface denaturation of proteins. We do not

picture the inactivation of the virus as necessarily involving an unfolding of the entire virus particle into a protein layer 10Å thick. In fact Seastone has shown (32) that tobacco mosaic and vaccinia viruses do not readily unfold in the way that egg albumin does, but that never the less these viruses do form surface films. We merely suggest that once the virus reaches a gas-liquid interface it is subjected to such forces that it may very rapidly be deprived of the property of infectivity. This loss of infectivity may be prevented by saturating the gas-liquid interface with another protein, thereby denying the virus acess to the surface. In this respect the phenomenon is analogous to the surface denaturation of proteins.

The prevention of surface denaturation is not the only protective role which may be played by proteins. Sumner (33) has demonstrated that dilute solutions of crystalline urease are rapidly inactivated by traces by heavy metals. This type of inactivation can be prevented by the addition of proteins, as well as by gum arabic, hydrogen sulfide, amino acids, and many other substances. Urease can similarly be protected by proteins against inactivation by small amounts of oxidizing agents. Proteins should play a similar role in the protection of viruses against the inactivating effects of heavy metals and oxidizing agents. It is probably a summation of these various protective mechanisms which is responsible for the generally recognized fact that viruses are more stable when diluted in serum or broth than when diluted in salt solutions or distilled water.

SUMMARY

1. The seven bacterial viruses of the T group active against *E. coli,* are rapidly inactivated at gas-liquid interfaces.
2. The kinetics of this inactivation whether brought about by shaking or by bubbling with nitrogen are those of a first order reaction.
3. This inactivation may be prevented by the addition of enough protein to maintain the gas-liquid interface in a saturated condition.
4. The analogy between this phenomenon and the surface denaturation of proteins is pointed out and discussed.

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Addendum. — Since submitting this manuscript, we have found a paper by J. Steinhardt (34) on “The stability of crystalline pepsin” in which the inactivation of pepsin by shaking is noted. At a pH of 6, temperature of 25°C., and pepsin concentration of about 30 to 60 micrograms per ml., pepsin is inactivated by shaking in accordance with the kinetics of a first order reaction. The velocity constant was independent of pH over the range of 4 to 6 but was somewhat dependent on the rate of shaking. The inactivated pepsin separated from solution as an insoluble suspension.

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Historical Article

Johann Beckmann (1739-1811) and Modern Chemical Technology

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Abstract. Modern chemical technology, in the humanistic spirit of the Enlightenment, begins with Johann Beckmann (1739-1811). It followed pre-modern technologies associated with Cameralism and *Chemia Applicata*. Beckmann's holistic approach to technology, expressed in "Anleitung zur Technologie" (1777) and "Entwurf einer Allgemeinen Technologie" (1806), also engages with economic, social, cultural and ethical problems, giving the term 'technology' a new meaning. Viewed with skepticism in his time, there was a revival of Beckmann's ideas by Franz Exner (1840-1913) in 1878. Only in recent decades his contribution to technology was more extensively studied. Examples of Beckmann's ideas are presented.

Keywords: Johann Beckmann, history of chemical technology, practical chemistry before Beckmann, cameralism and *chemia applicata*, sugar industry, refutation of criticism of technology.

> *I believe I am only a fragment of humanity, but yet*
> *that I must try to look at things from the point of view*
> *of the whole, and not of the fragment.*
> (George Sarton)[1]

INTRODUCTION

Despite his overwhelming importance in the evolution of chemical technology, including its introduction as a university course, Johann Beckmann does not receive in many places the recognition he deserves. His name is frequently omitted from histories of chemistry. This omission is especially serious when we consider that his work began during the phlogiston era and continued under the aegis of Lavoisier's new oxygen theory. Beckmann's theoretical work, however, shows no break in continuity, no significant structural change, or no paradigm shift (in Kuhnian terminology). On the contrary, Beckmann's work on chemical technology is an example of a subject's linear evolution in terms of knowledge.

Beckmann's oblivion in many countries is not a consequence of opinions or attitudes against Beckmann himself, a typical representative of the Enlightenment, but a reaction against the very idea of technology being necessary. As an example, in contemporary Latin America there is a double origin for this pre-conceived idea against technology and innovation. The Iberian world is contrary to the concept of "technics", an idea succinctly expressed by Miguel de Unamuno (1864-1936), with his famous "… *que inventen ellos!*" ("let others invent!")[2] . Post-modern ideas, ever so popular in the Latin world, tend to minimize the role of scientific rationality and efficacy, often overemphasizing the importance of practical knowledge, and resisting "rationalization of work" – as Bruno Jacomy puts it[3].

The entry of Technology in History, in the History of Science – regardless of the semantic issue associated with the term – and, therefore, in Culture in general, occurred from mid-19th century. In general, in the pioneering countries of the Industrial Revolution, such as Great Britain and France, the revolution occurred with few concerns about technique and technology. In countries of more recent industrialization, such as Germany and the United States, there was a greater concern with a possible 'methodology of technological progress'. In these cases, it was part of the effort in favour of technology to awaken the interest of young people in the subject and to integrate the so-called 'technological' subjects in university curricula.

Obviously no theory, neither technological nor economic, caused the old method of "trial and error" to leave the scene – we are here in face of chance as cause of social and economic development. But real progress is rare. What is of importance is an efficient "methodology of technology", similar to an efficient methodology of scientific work. Also Johann Beckmann and his enlightened spirit are important. Science and Technology develop and advance by means of a pre-conceived, structured methodology, from time to time revised in accordance with its own principles, allowing a reliable application of the conditions underlying scientific knowledge, as defined by Sir Karl Popper (1902-1994) and by Imre Lakatos (1922-1974).

EVOLUTION OF SOME CONCEPTS

Some seemingly very modern concepts, like Technology and "Fine Chemistry" are in fact not so new. Such precursor periods in the 'arts' or 'techniques', of artisanal and pre-industrial production, were necessary for the emergence of a chemical technology and later of a chemical industry in a broader sense. The Alchemists by no means occupied themselves solely with transmutation or with the elixir of life, but they were possessors of a wide range of knowledge about mining, metallurgy, medications and chemical processes in general (production of saltpeter and gun powder, of several acids, dyes and pigments, dyeing and tanning, and many others). This explains the presence of alchemists in the courts of kings, princes and potentates in 16th and 17th centuries[4]. Leonhard Thurneysser (1531-1596), an alchemist of paracelsian tradition, was not only the physician of Prince-Elector John George of Brandenburg (1525-1598), but his consultant for mining and metallurgy. Thurneysser set up in 1574 in the Greyfriars Monastery, the former convent of the Franciscans in Berlin (now in ruins), a manufacturing plant for diverse chemicals, employing 300 workers and producing saltpeter, mineral acids, alum, colored glass, pharmaceuticals and several essences. These expensive products were sold, and had, as we would say today, 'high added value', so he earned considerable wealth. I see in Thurneysser the first representative of Fine Chemistry[5].

A first 'chemical technology' not yet methodologically or scientifically organized, but surpassing the purely practical aspects of the alchemists, arose in the 17th century, as an answer to immediate commercial necessities and availabilities, like the production of saltpeter and gun powder, or the economic reconstruction of Central Europe, devastated by the Thirty Years War (1618/1648). For the majority of historians, Johann Rudolf Glauber (1604-1670) was the most important representative of the period which Principe and Newman call 'chymistry', a term coined to avoid the parallel use of 'alchemy' and 'chemistry', to avoid speaking simultaneously about alchemical theories and practices and of chemical theories, concepts and activities[6]. However, due to his knowledge of chemicals it would not be wrong to consider him a precocious inorganic chemist, and also as the first chemical technologist[7]. I regard him as a precursor of chemical technology, a task for which his immense knowledge of inorganic chemicals was a deciding factor. In Schmauderer's opinion[8], this 'technology' begins in the spirit of the science of the baroque period, at first in obedience to a religious precept that states the researcher's responsibility in applying his knowledge as well as the natural resources presented to us by God for the welfare of his brothers. In the context of the mercantilism typical of the 18th century's economy, this ethical-religious precept changes, and allows a new 'technology' acting in the interest of the absolutist State, in which economic issues dictated the rules: protectionism, state monopolies, prohibition to export or import certain products. In his Amsterdam laboratories, Glauber began in 1650 his technological activities, surpassing the work of precedent 'technologists', which were specialized in metallurgy, or glass, or ceramics. Glauber's production was more widespread, ranging from fermentation to metal analyses, from preparation of acids to treatment of textiles. Glauber produced according to the capitalist concept: to obtain products with the best possible quality, with the least possible number of employees, and using the minimum of resources. He analysed the costs of each step of the proposed or necessary procedure, the yields, and even calculated the minimum quantity to be produced of each compound to warrant a cost-effective process. It must be said that these frankly capitalist system was preceded by 'pre-capitalistic' initiatives of predecessors, like those of Jakob Fugger the Rich (1459-1525) in Banska Bystrica (Neusohl), Slovakia, or in his mines in Tyrol or Carinthia in Austria.

The alchemist Johann Joachim Becher (1635-1682) is best remembered in connection with his creation of the phlogiston's theory and the chemical philosophy expressed in his *Physica Subterranea*.[9] His chemical technological achievements are undervalued by most historians of chemistry. As an entrepreneur, he was in disadvantage by his boundless imagination and lack of sense of practicality, visible for instance, in his dreams of colonisation in South America, in lands inherited from the Count of Hanau, between Suriname and the Amazon. This was already the opinion of John Stillman (1852-1923) a long time ago[10] . Today, Becher's activities are seen in a better light. His technological activities were mainly that of an organiser, in duty of the Duke of Bavaria (1664/1670) and the imperial Court in Vienna (1670/1672), where he founded the Chamber of Commerce, the *Kommerzienkolleg*, and several industries (chemicals, textile goods), frequently without the expected success. Sponsored by the imperial government, Becher founded in Vienna a chemical laboratory, where he produced saltpeter, salt-ammoniac, borax, vegetable dyes, pigments (cinnabar, minium), and constructed new equipments, like experimental ovens for the glass and ceramics industry. His plant in Tabor, near Vienna, founded in 1667, produced pigments (cinnabar, minium, verdigris, lead white), and incorporated plants for refining sugar, produce "Venetian" glass, as well as noble metals.

The third alchemist precursor of modern chemical technology is Johann Kunckel (1630-1703), famous for his vast experience with the technology of glass production ("*Ars Vitraria Experimentalis*", 1679) and the invention of the artificial ruby, a very valuable red glass (1679) [11]. Kunckel stood in the services of Prince-Electors John George II (1613-1680) in Dresden, and Frederick William the "Great Elector" (1620-1688) in Berlin. Frederick William presented him with the Peacock Island (*Pfaueninsel*), where he built not only his glass factory but also a "secret laboratory", which allowed him to work "without being disturbed or observed". His posthumous "*Laboratorium Chymicum*" (1716) describes a great number of chemical and metallurgical processes, showing that his importance surpasses by much the invention of the *Rubinglas*: he describes for instance how he obtained phosphorus in Dresden, and all the processes necessary to produce the artificial ruby, processes which he pretended to maintain secret.

Baroque science and technology had a religious origin, but gradually 18th century technology assumed a clear capitalist aspect, and almost all political economists of that time were alchemists: alchemists transform useless materials (our raw materials) in new and valuable materials (our commodities). The original intention of obtaining gold from less noble metals, turned into obtaining money and other financial resources, and in the opinion of Rudolf Soukup from the Vienna Polytechnic, it makes sense to call upon alchemists as economical consultants, and economical theory may be defined as the "alchemy of the future"[12] .

Glauber, Becher and Kunckel are forerunners from the same cultural context as Beckmann. There are of course many early contributions to a pre-technological activity from other contexts. The amalgamation process (*beneficio de patio*, *patio* process), developed in Mexico by Bartolomé de Medina (1503-1585) is a very important contribution to metallurgy and technology[13], ignored during centuries by European historians of science and technology. An important pioneer of technology was the Frenchman Jean Helot (1685-1766), particularly with respect to dyeing and porcelain making[14].

THE IMMEDIATE ORIGIN OF MODERN CHEMICAL TECHNOLOGY: CAMERALISM AND *CHEMIA APPLICATA*

Christoph Meinel suggests that the intertwined relation of cameralism and 18th century chemistry is similar only to the intertwined relation of chemistry and medicine observed a century earlier[15]. Cameralistics or cameralism (*Kameralistik*, *Kameralwissenschaften*), the science of public revenue, is typically a German university course, generally taught at Law Schools, addressed to future public servants; it may be viewed as a German version of mercantilism (whether cameralism is a form of mercantilism is still a matter of debate)

[16]. This course included the study of economical and administrative problems, arts and crafts, techniques and other topics of interest for the future public servant. It included general aspects about crafts, manufactures and industries, from which slowly emerged the "Chemical Technology". The first chairs of cameralism were created by the initiative of King Frederick William I (1688-1740) of Prussia in 1727 at the universities of Halle and Frankfurt-Oder; they were more practical than theoretical, and still directed to an agricultural economy. The new university disciplines were agriculture, forestry and veterinary (may be a surprise, however knowledge about dairy products, wool, leather, fats and oils were lectured).

For several reasons cameralism as a depositary of chemical knowledge was important for the evolution towards a Chemical Technology[17]:

- cameralism emphasizes the role of chemistry in modern Society.
- cameralism included chemistry in the wider economical and administrative objectives of the State.
- this substantiated chemistry as an independent academic activity.
- cameralism highlighted the importance of a scientifically based technological and industrial activity.
- Society learned about new perspectives of development, by means of the universities, through thoroughly trained graduate professionals.

During the first decades of the 19th century cameralism as a discipline began to break down. Matters related to finances and public administration were incorporated in Law or Economics, matters related to the arts, crafts and techniques were housed in the *Écoles Centrales* in France and in the *Gewerbeschulen* in Germany, and at university level in the Polytechnic Schools, the first and possibly most respected the *École Polytechnique* in Paris, founded in 1794 by the Commission for Public Works, under the leadership of Lazare Carnot and Gaspard Monge. In Germany, Austria, Switzerland, the Netherlands and the Scandinavian countries were created the *Technische Hochschulen*, viewed initially with certain contempt by the traditional universities.

In Sweden, long before cameralism was firmly established in Germany, chemistry was no more a subsidiary discipline for physicians and Medicine, but a subsidiary in economic activities, like mining, metallurgy, industry. The first chemistry chairs in Swedish universities were held by chemists involved with these practical activities. The dominant personality in formally organizing this "practical chemistry", the *chemia applicata*, was Johann Gottschalk Wallerius (1709-1785), professor at Uppsala University (1750/1767). In a publication from 1751, Wallerius distinguished between *chemia pura* and *chemia applicata*, defining them as follows:

> Chemia pura is a science on fundamental matter and its reactions (– mixtures). Chemia applicata is operative, is an art showing how by means of mixtures or decompositions of bodies we can prepare several new substances, possibly useful in daily life.

Wallerius separated theoretical from applied chemistry, but did not keep them as distinct entities, avoiding the artificial distance created by Pierre Joseph Macquer (1718-1784) when he published "Elements of Theoretical Chemistry" (1749) and "Elements of Practical Chemistry" (1751). Wallerius considered practical chemistry more important than theoretical chemistry, and classified *chemia applicata* in nine branches[18] : (1) medical chemistry; (2) mineralogical chemistry (*lithurgica*); (3) chemistry of salts (*halurgica*); (4) chemistry of combustion (*thejurgica*); (5), metallurgy; (6) glass chemistry; (7) agricultural chemistry (*chemia oeconomica*); (8) chemistry of colours (*chemia chromatica*); (9) chemistry of arts and crafts (*chemia technica, opificiaria*).

By advocating such posture, Wallerius contributed to promote and value practical chemistry, so we must not downplay his importance in the synthesis of several substances during the "chemical revolution", substances like sulphuric acid, ammonium salts and many others, as well in process improvements in the production of glass, porcelain and ceramics, sugar, beet sugar, bleaching, dyeing, among others. Wallerius was criticised by his colleagues, particularly by Torbern Bergman (1735-1784), his successor in Uppsala, for having done only a few experiments himself, using instead existing knowledge about these subjects. Wallerius was the first organiser and systematiser of a pre-technological chemistry, and in the opinion of B. Bensaude-Vincent, from the University of Paris, the correct proportion of theoretical and practical chemistry allowed a transition from Science into Art without great conflicts. Wallerius theoretical chemistry was phlogistonist, the same theory advocated by countrymen Bergman and Scheele and the one referred to in cameralism.

JOHANN BECKMANN AND CHEMICAL TECHNOLOGY

The first university professor to teach technological matters (metallurgy) was probably Johann Conrad Barchusen or Barkhausen (1666-1723), at the University of Utrecht, where he had been active since 1693[19] .

The philosopher Christian Wolff (1679-1745) tried in 1728, with little success, to introduce a modern concept of technology (*technologia*), in a short philosophical essay: “it is the science of the things which man produces by using the organs of the body, especially the hands”[20] .

But modern chemical technology begins with the publication in 1777 of “Anleitung zur Technologie” (Introduction to Technology) by Johann Beckmann (1739-1811). Beckmann coined the term “technology” (= *Historia Artium*), contrasting with Natural History, and in 1772 defined technology as: *“the science which teaches how to transform natural products, or the knowledge of the arts, industries and manufactures”* [21]. Before choosing the term “technology”, Beckmann considered using “*Handwerkswissenschaft*”, or the “science of tasks”[22]. Beckmann was also the first formal teacher of chemical technology, as professor of Philosophy (1766) and Economics (1770) at Göttingen University. “Chemical Technology” as a university discipline developed from cameralism. In 1878, centennial of the publication of Beckmann’s “Anleitung”, Wilhelm Franz Exner (1840-1913), professor of General Technology at the Vienna Polytechnic, published a biography and delivered lectures in Vienna, with the aim of preserving Beckmann’s memory. In Exner’s words[23] :

> The founder of Chemical Technology, Professor Johann Beckmann, has already fallen into oblivion among the public at large. Specialists from several fields still value his contribution and use his works, but even they probably know nothing about Beckmann’s life history.

In fact, outside the context of his profession, Beckmann is now unknown or undervalued. The decay of cameralism was also the decay of technology. The *Johann-Beckmann-Gesellschaft*, Hoya, founded 1987, tries to preserve his memory.

Johann Beckmann[24] was born on 4 June 1739 in Hoya, a small city at the Weser river, in Northwestern Germany, in the Principality (1806-1866 Kingdom) of Hannover, son of Nicolaus Beckmann (1700-1745), tax collector and administrator of the post office, and Dorothea Magdalena Beckmann (1718-1763). After his first school years in Hoya, he went to study in Stade, near Hamburg; in 1759 he enrolled at Göttingen University, studying theology, physics, mathematics and natural sciences; he undertook studies also in Leiden (where he entered a Masonic lodge), and with Carl von Linné (1707-1778) in Uppsala in 1765. Anton Friedrich Büsching (1724-1793), geographer and historian, professor and minister of the German community in Saint Petersburg, convinced Beckmann, then in need of money, to establish himself in the Russian capital (1763), where he stayed for only a short time. But even a short residence sufficed to turn Beckmann into an intermediary between Russian and German science. He travelled in Russia, Sweden, Denmark and the Netherlands, visiting mines and industries. In 1766 he was appointed extraordinary professor of *Weltweisheit* (literally “Wisdom of the World” = Philosophy) in Göttingen; very successful as a teacher, in 1770 he was appointed regular professor of Physics and Natural Sciences, and later of Economics.

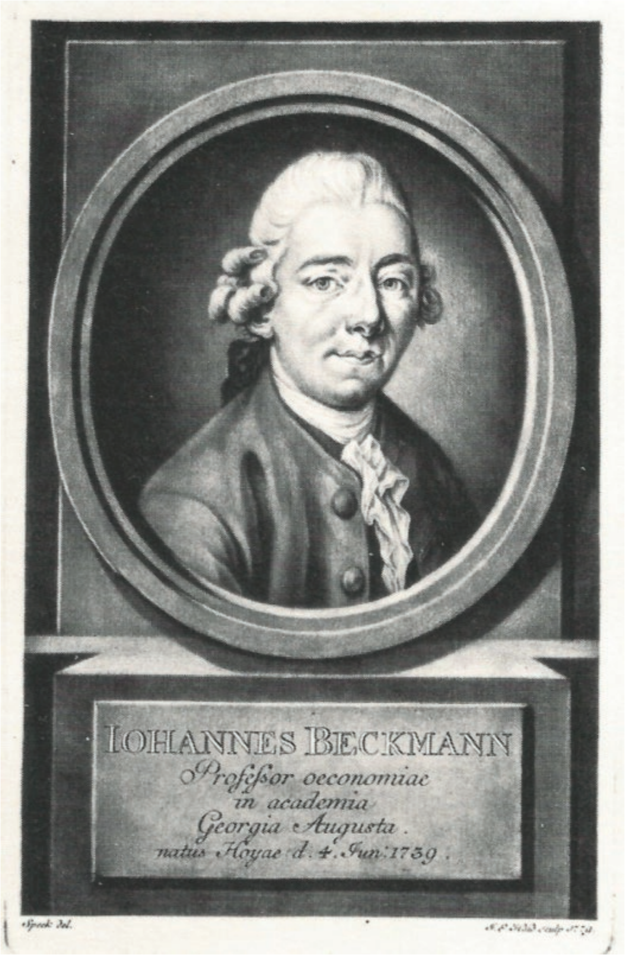


Figure 1. Johann Beckmann. Lithography by F. E. Haid. (Courtesy Johann-Beckmann-Gesellschaft, Hoya).

The University of Göttingen was founded in 1737, following planning by Adolf Baron von Münchhausen (1688-1770), innovative since its establishment, offering ‘modern’ disciplines, like geography and physics, and extracurricular disciplines like modern languages and design. Regular instruction in economics and technology belonged to the ‘modern’ disciplines. Beckmann approached the different industrial ‘arts’ and handcrafts, from both theoretical and practical viewpoints, in accordance with the principles of Enlightenment. In

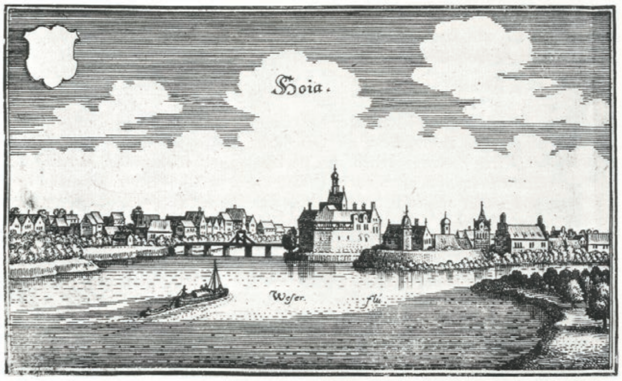


Figure 2. View of the city of Hoya, 17th century. Engraving by Matthäus Merian the Older (1593-1650). (Courtesy Johann-Beckmann-Gesellschaft).

each case, Beckmann was concerned about origin and evolution of the technique under study, including its history: in the opinion of Friedrich Klemm (1904-1983), from the *Deutsches Museum* in Munich, Beckmann is also the founder of the History of Technology[25]. Ruy Gama (1928-1996) concludes that Beckmann's main interest was to bring together scholars and manufacturers, taking to the Academy and to the University the production processes for different *commodities,* allowing the development of more rational and modern processes, a task performed also by other technologists[26]. The role of the University in the creation of technology and innovation can be found in this 'meetings of savants and craftsmen'. Technology entered Göttingen University even before its economic importance was properly appreciated. Johann Beckmann lectured at Göttingen for more than thirty years. He died in Göttingen on 3 February 1811, aged 71, likely from pneumonia. His lectures were famous, attracting students from other universities, like Alexander von Humboldt (1769-1859). His weekly classes on *Practicum camerale* were renowned, and constitute perhaps the first example of interdisciplinarity, or maybe of multidisciplinarity. His classes were theoretical and practical, including visits to mines and industries, and working in the '*Modellkammer*', a kind of simulation of the processes studied[27] .

Beckmann was a member of the *Academia Leopoldina* in Halle (1771), of the Göttingen (1772), Munich (1809), Saint Petersburg, Stockholm (1790), the Netherlands (1809) academies. Little is known about Beckmann's private life, and his biography is awaiting interested historians. In 1767, he married Sophie Karoline Schlosser, from Kassel. The couple had two children, the twins Samuel Johann Beckmann (1771-1841) and Johanna Petronella Sophie Beckmann (1771-1831). Today, Beckmann's descendants live in Germany, in the United States and in Brazil.

Figure 3. Stamp issued in honour of Beckmann in1989 by the former German Democratic Republic.

BECKMANN'S TECHNOLOGICAL WORK

Beckmann's fundamental contribution to Technology, the most important for the History of Technology, the most praised (and most criticized) is doubtless his "*Anleitung zur Technologie*" (1777, Göttingen, seven editions until 1823, "Guide to Technology"). It is not yet an exhaustive, systematic work including all branches of technology, but instead, an organized, formal, essentially qualifying and descriptive work on the diverse manufactures and handicrafts. The first edition (1777) still had as theoretical foundation the phlogiston theory; in the fourth edition (1796) Beckmann embraced "Lavoisier's anti-phlogistic theory". As mentioned by Otto Gekeler (1912-1999), Beckmann describes as follows the general concepts of his "*Anleitung*"[28]:

> – Handcrafts should be ordered not only following the used materials and the produced objects, but also following the common parts and analogies during their processing and the principles upon which these are based.
> – Knowledge of handcraft, fabrics and manufactures is indispensable: what has been made, ordered, qualified, handled, gained, used, and performed should at least be known and understood.
> – "when basic knowledge fails, the craftsman should be left upon his own or he will receive plans which cannot be performed".

In somewhat random fashion, Beckmann mentions 324 crafts, 58 of which relating to chemistry[29]. In the introductory section he emphasises the economic aspects of production (Beckmann was professor of economics), suggesting the use of by-products of a chemical process, or discussing costs related to labour, transportation of materials and final products, interest rates due to funding for the purchase of raw materials, which would be sold as products many months later.

He describes in detail, 32 manufactures, 23 of them chemical in nature, like production of soda, potash, sulphuric acid, nitric acid, vitriols and other salts, saltpeter, common salt, sugar, distillation of tar and coal, gun powder, porcelain and glass, dyeing of wool and silk, tanning, production of pigments (lead white, Prussian blue, ultramarine) and dyes (indigo, woad, litmus, India ink, carmine), fermentation processes for wine, beer, vinegar, liquors and other distillates, and many more.

The themes chosen and the approach to their discussion suggest two theses accepted by historians: Beckmann describes the manufactures still deficient in Germany, or he presents proposals intended to solve these deficiencies.

Many chairs of "technology" were created at several universities after publication of Beckmann's book, and "technological" literature appeared very quickly, and, as Gekeler, wrote:

> It is out of doubt that the actual presence of technology in the wide range of realisations depends directly upon the publication of this technological standard book, wherein, for the first time, several products such as paper, beer and porcelain are treated and classified in the way they can be produced[30] .

The first German universities in which technological matters were lectured were Giessen (1777), Stuttgart (1781, the *Karlsschule*), Vienna (1781), Ingolstadt (1782, today the University of Munich), Mainz (1784). Outside Germany, Beckmann's technology spread to a lesser extent: in France, Isaac Haffner (1751-1831) taught technology in Strasbourg and Jean Henri Hassenfratz (1755-1827) promoted the diffusion of technological contents in other institutions. In Italy, short lived lectures (1819/1823) at the University of Padua, and in Scotland there was a discipline of technology in Edinburgh, which did not survive the death of the lecturer, George Wilson (1818-1859)[31] .

The case of cane sugar production captured Beckmann's attention[32]. In the 1777 edition, still having the phlogiston theory as theoretical foundation, "*the components of sugar are water, earth, acid and a fine oily or combustible component*" (in this last component should be found the "sweetness" of sugar). The 4th edition (1796) follows Lavoisier's anti-phlogistic theory, and sugar is composed by carbon, oxygen and hydrogen, and the different qualities of different sugars, of tartaric acid and oxalic acid are due to different proportions of oxygen. Strangely, Beckmann does not mention the "*Sacharologia*" (1637) by Angelo Sala (1576-1637), probably the first monograph about sugar, published in German in Rostock[33] , and does not mention the discovery of beet sugar in 1747 in Berlin by Andreas Sigismund Marggraf (1709-1782) – most likely because the process was not yet exploited commercially, an exploitation which would occur in 1798 by Franz Karl Achard (1753-1821) in a small factory in Kunern, Silesia (now Konary, in Poland). Beckmann restricted his discussions and descriptions to processes used in his own time.

Anleitung
zur
Technologie,
oder
zur Kentniß
der
Handwerke, Fabriken und
Manufacturen,
vornehmlich derer, die mit der
Landwirthſchaft, Polizey und
Cameralwiſſenſchaft
in nächſter Verbindung ſtehn.

Nebſt
Beyträgen
zur
Kunſtgeſchichte.
Von
Johann Beckmann
ordentlichem Profeſſor der Oekonomie in Göttingen.

Mit einer Kupfertafel.

Göttingen,
im Verlag der Wittwe Vandenhoeck. 1777.

Figure 4. Front page of "Anleitung Zur Technologie", 1777 edition.

Still about sugar, Beckmann presents a historical introduction, classifications based on various criteria, geographical for instance (sugar from St. Thomas, Guadaloupe and Martinique, Madeira, Pernambuco, Bahia), or aspect, grades of purity, among others. He mentions other plants containing sugar (maples, *Aceraceae* like European *Acer campestre*, or Canadian *Acer saccharinum*), and briefly describes the production of cane sugar and sugar refining, an industrial activity still done mostly in Europe. Although interested in joining theory and practice, Beckmann describes in detail the sugar production process proper. From the many details presented, Ruy Gama (1928-1996), a Brazilian historian of technology and authority in the history of sugar production, says "we could think these authors [Beckmann and his contemporaries and successors, even Marx] knew the sugar factories", but this is obviously not the case[34] . Sugar refining is a perfect example of an activity in which chemical technology could offer great improvement: refining at the places of production would reduce costs and increase productivity. Beckmann suggests that refining in the same place where sugar cane is produced would improve profitability. Charles Edward Howard (1774-1816), a self-educated English scientist, designed a new vacuum evaporator and other accessories for the sugar industry (first patented in 1812), which were used in West Indian factories and elsewhere[35] .

Gun powder is another product discussed by Beckmann[36]: its origin, he says, is unknown, but it certainly is not an invention of Bertholdus Niger[37]. Beckmann discusses the properties of powder and the desired qualities of its ingredients, he distinguishes "strong" from "weak" powder, which resulted from the different proportions of saltpeter, sulphur, and carbon. In his time, the best powder was produced in Essone, France (we know about Lavoisier's efforts in improvement of powder), and its typical composition would be: 75 pounds of saltpeter, 9,5 pounds of sulphur and 15 pounds of carbon. Beckmann's observation that powder was used in mining, in Rammelsberg by the year 1200, before its military use, is indeed surprising. The mines of Rammelsberg are located near Göttingen, and he may have heard this from local miners, so that the information may be not devoid of truth.

The "*Anleitun*g" knew six more editions, in 1780, 1787, 1796, 1802, 1809 and 1823. This text from 1777 is greatly responsible for Beckmann's reputation and importance, but the first of his books to draw attention was the "*Grundsätze der Deutschen Landwirtschaft*" ("Basics of German Agriculture", 1896), from 1769, one of the most read 'technological' texts of its time, responsible for introducing agriculture as a university discipline, the first economic activity to gain university status.

"*Vorbereitung zur Waarenkunde*" (Göttingen, 1793/1800), or "Introduction to the Commodity Sciences", is probably the first general treatise on what we call today the commodities (*Waren* = marketable products). Beckmann describes in detail 42 products or groups of products, qualifying them as natural products or products of "the arts". These *Waren* included the so called *Kolonialwaren*, products which the Europeans brought from their colonies: cotton, rubber, soy, coconuts, ivory, musk, indigo and other dyes. Beckmann endeavoured to turn these raw materials into useful products, but also showed concern with the possible extinction of some of them[38]. Alexander Kraft relates that in 1772 king Frederick II the Great (1712-1786) ordered Andreas Sigismund Marggraf (1709-1782), from the Berlin Academy, to try to obtain artificial chocolate and vanilla aromas from small-leaved linden tree (*Tilia cordata*) barks and fruits. Cocoa and vanilla were too expensive, and Frederick forbade their import[39] .

Among many other publications by Beckmann, the five volumes of "*Beiträge zur Geschichte der Erfindungen*" (Leipzig, 1782/1805), published in English as "History of Inventions, Discoveries and Origins" (1798, 4th edition 1846), deserves some commentaries. It is a collection of easy-to-read texts aiming at diffusing science and technology. But it also contained detailed descriptions of the evolution of some chemical processes, like the process for obtaining alum. The collection shows the breadth of the historical knowledge of the author, dealing with a wide range of themes: Italian Renaissance accounting, gold refining, the origin of the names of the elements, plants, animals and minerals, street lighting, glass engraving... Friedrich Klemm (1904-1983) considers this collection the very beginning of the historiography of technology[40]. History of Technology was restricted to the evolution of practical and productive activities in a European context, and activities or even innovations originated in peripheral countries were of no interest in face of the innovations of the Industrial Revolution[41] .

A very important book, in Exner's opinion, is Beckmann's "*Entwurf einer Allgemeinen Technologie*" (1806, Göttingen, "Draft on General Technology"). A new edition in 2006, organised by Bernd Meier and Helmut Meschenmoser, calls the book "the birth certificate of General Technology". In this booklet of only 72 pages Beckmann "normatizes Men and Machines", establishing a systematic classification for Technology, based on the systematic classification developed by Carl von Linné (1707-1778). Linnean taxonomy or systematics has a ranked hierarchy, with kingdoms (mechanical processes, chemical processes), divisions (or *phyla)*, classes, orders, families, genera, species. As an example, in the kingdom "chemical processes", there is an order "filling of imperfections" (of the bodies), which can be done by greasing, varnishing or glazing/vitrifying (these are three "families"). "Species" for greasing are bee wax, carnauba wax, candelilla wax; for varnishing, there is lacquer (shellac); for glazing, there is lead oxide. Before Beckmann, other technologists made use of binary classifications; Johann Georg Krünitz (1729-1796) qualified in his "*Oekono-*

mische Encyclopaedie" (1790) different types of coal in accordance with a binary system: *Carbo Anthrax* (= charcoal), *Carbo Lithoanthrax* (= hard coal), and others[42].

Beckmann's publications and teachings were rich and prolific. His rational work, derived from late Enlightenment, was very distant from the Romantic thinking then dominant in Germany. This dominance was another reason for Beckmann's oblivion in the German Romantic period. Otto Gekeler takes this text of 1806 as an obvious complement for the text published in 1777.

> It may be stated that "Beckmann's viewpoints are trivial and universal at the same time: one object can be made following different systems; one system can be used for different objects[43].

He was the first to mention what chemical engineers today call 'unit operations', a concept introduced by Arthur Dehon Little (1863-1935), professor at the *Massachusetts Institute of Technology.*

In his treatise from 1806, Beckman presents his "principle of completeness" (*Ganzheitsprinzip*), in the following words[44] (Beckmann, 1806):

> We must obtain the material and immaterial benefit from the commodity with a minimum of nature and human substance throughout the commodity's life – with due regards to health, political, ethical and other relevant aspects.

Multidisciplinarity hidden in the *Ganzheitsprinzip* unveils Beckmann's concern in producing science and technology 'for the people'. Quoting Gekeler[45] ,

> This conscious appreciation of all possible implications of technology and commodities, encountered at all stages of their existence (from production over usage and/or consumption to waste management) will be called the 'ganzheitliche Betrachtung' or contemplation in entirety.

This is clearly in the spirit of universal Enlightenment.

A group of Japanese researchers, leaded by Tetsuo Tomita, translated Beckmann's treatise from 1806 and the "History of Inventions" into Japanese (1976/1982), wishing to understand and better assess how technology was transferred from Europe to Japan[46]. Tomita writes:

> Our purpose was not necessarily to learn the history of technics of Europe but to compare the basic civilization and technics of Europe depending upon their climate and geophysical elements with those of Japan, particularly before the developments in the field of electricity and modern synthetic chemistry had been attained. Such trails will make it possible for us to find suggestions for analysis and prediction of conditions and reactions of technological transfer in future[47] .

Sometime before, in 1786, in Göttingen, and in the spirit of Enlightenment, Johann Friedrich Gmelin (1748-1804) published the first textbook on Chemical Technology, *"Grundsätze der Technischen Chemie"* (Foundations of Technical Chemistry); a second edition (1795) was titled "*Handbuch der Technischen Chemie*". Gmelin used terminology in the sense we mentioned, saying that *"Technical Chemistry is that part of Applied Chemistry which teaches the basics of factories, manufactures, arts and crafts, and the advantages of applying these principles to these activities*"[48] . Some of these crafts existed since remote times, in Gmelin's opinion, but others are unimaginable without technical chemistry. Among the oldest crafts related to chemistry, practiced since the thirteenth and fifteenth centuries, Gmelin mentions in his "*Geschichte der Chemie*" (1797, "History of Chemistry") activities like metallurgy, obtention of alum and vitriol, ceramics, glass, dyeing, pharmacy. In any case, also for Gmelin, Chemical Technology dates from the second half of the eighteenth century, the "great century" of chemistry, among other reasons because of the emergence of methodologically organised Chemical Technology.

Characteristic features of Beckmann's *Technologie* are, as mentioned by Guido Frison:

> - the object of Technologie corresponds to something which may be called "industrial work"; and the subject who is interested in Technologie is the ruler of the process of production.
> - Technologie is a science, or more accurately an analysis of production from a naturalistic perspective.
> - Technologie examines the productive procedures; i.e., what goes on between the social actor and his means of labour but not from a sociological point of view;
> - the knowledge of Technologie allows innovation [49].

Such characteristics, according to Frison, are still distant from an ideal productive procedure. At the same time Beckmann creates his '*Technologie*' as a discipline, his friend and colleague in Göttingen, historian August Ludwig von Schlözer (1735-1809), conceives a new form of presenting the *Universal-Historie*, a general and universal history, in which he considers Technics and Inventions (in the sense given by Beckmann) as driving factors for human and cultural development[50]. Schlözer suggests four "methods" for structuring History: the chronographic, technographic, geographic, and ethnographic methods. The chronographic method is a simple chronologic record, unable to analyse the relation between facts. The technographic method explains progress and retrogression of Humankind in terms of progress and retrogression of *Technologie* and inventions. The geographical method accounts a systematized harmony of the diverse geographical regions. In the ethnographic method, the inhabitants of the Earth are brought together on the basis of behavioural similarities, in groups, "peoples" or "populations" – although it remains unclear how many "peoples" would exist.

EVALUATION

The evaluation of Johann Beckmann has varied much according to place and time, sometimes viewed as positive, and sometimes not so much. It is not really an evaluation of Beckmann himself, but of the methods he proposes for the creation, management and improvement of technological processes or procedures. One same process can be analysed and explained in accordance with different stances: as a purely empirical sequence, disconnected from every theoretical association, as sequences of trial-and-error reactions; or, as a rigorous application of a "technological methodology", similar to a scientific methodology. The most emblematic example is the explanation of Leblanc's process for producing soda (1791): Charles Gillispie (1918-2015) suggests an artisanal and empirical sequence of trial-and-error reactions[51]; John Graham Smith suggests a typical case of rigorous application of a technological methodology[52].

Beckmann intended – and for this he is often criticised – to include in university teaching all aspects related to technology: raw materials, rationalisation of technological processes, use of by-products and many others.

In pioneering countries of the Industrial Revolution, like France and Great Britain, empiricism alone lead to satisfactory results with respect of quality and costs of products obtained, and theoretical concerns, as expressed by Beckmann, seemed to be irrelevant. As Frison observes, the notions of "technique" and "technology" are absent from the works of Adam Smith (1723-1790) and John Stuart Mill (1806-1873): terms like 'art', 'trade', industry', 'manufacture' are found instead[53]. In fact, as Ruy Gama observes, Beckmann does not exist in French or British technological literature, he is not cited in the monumental "History of Technology" by Charles Singer (1876-1960), or in the famous article about mills, which Marc Bloch (1886-1944) published in 1935 in the *Annales*. Authors less famous today, although fundamental for the evolution of this area of knowledge, as George Sarton (1884-1956), Lewis Mumford (1895-1990) or Edmund Oskar von Lippmann (1857-1940) attribute minor importance to Beckmann. Karl Marx (1818-1883) was a frequent reader of Beckmann and quotes him several times in his "*Capital*", as a source of factual data. Marx became familiar with Beckmann's works through one of the latter's students, the technologist Johann Heinrich Moritz von Poppe (1776-1854)[54]. He utilized as a definition of technology that used by Beckmann and J. H. Poppe. Marx was aware of the meaning and originality of this new discipline created by Beckmann[55] .

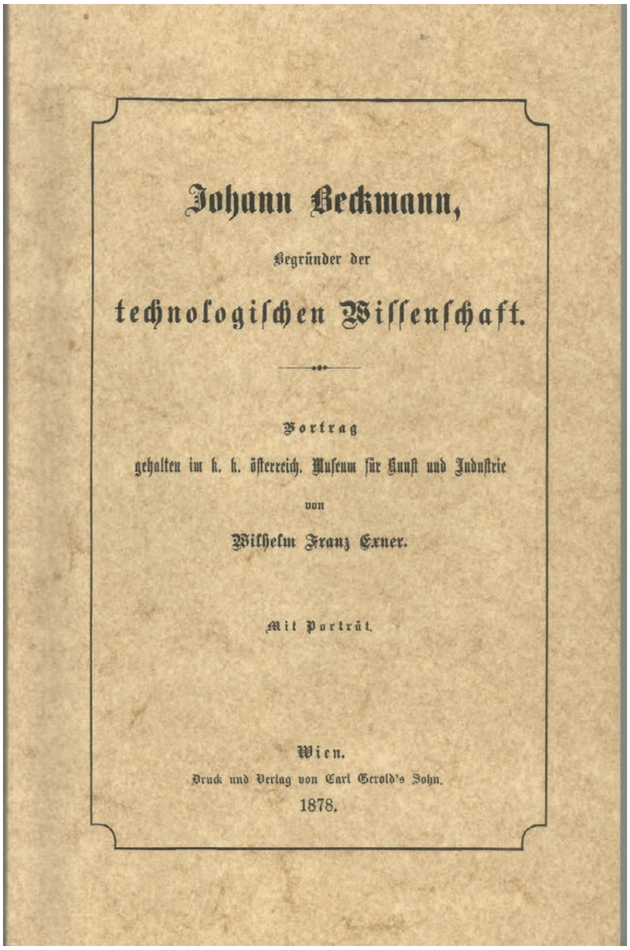
A renewed interest for Johann Beckmann arose in the 1970s in former German Democratic Republic. Marx's interest in Beckmann can be found in several essays and papers on techniques and technology. With the collapse of the socialist system of production in Eastern Europe the interest of historians and scholars even for this critical interpretation of the Marx-Beckmann relationship diminished.

Wilhelm Exner, in his presentations in Vienna in 1878, the centennial of the publication of "*Anleitung*", regretted the oblivion of Beckmann in his own country, for which there is, however, a plausible reason. Beckmann advocated during all his career at Göttingen the inclusion of technological matters into university teaching, an initiative which brought him many opponents. For the incredulous and sceptics, Beckmann wrote in the Introduction of the *Anleitung* *[56]*:

> To those who do not understand, and to those who do not want to admit, that Agriculture, Technology and Commerce can be taught with good results at University, I ensure that I know the contrary based on ten years of experience, and I could mention people who now occupy high positions, whose duties require such knowledge, and who would … confirm it.

It is obvious, he comments, that artisans learn their activity in workshops, merchants in their offices, but it would be ridiculous to assert they do not need any theoretical knowledge in their professional practice. Exner was too pessimistic. Industrialisation in Germany, an unified nation only since 1871 – "the nation which arrived too late" – began in the middle of the 19th century, and the contribution of universities to the productive process would be successful only with the involvement of a third partner: the State. The chemist August Wilhelm von Hofmann (1818-1892) was personally engaged in establishing this conjunction of factors. The equivalence of traditional universities and *Technische Hochschulen* was recognised formally in 1900, including the privilege to grant *Ph.D.* titles.

Technology is an inseparable and irreversible part of modernity. This realisation, from which one cannot



Johann Beckmann,
Begründer der
technologiſchen Wiſſenſchaft.

Vortrag
gehalten im k. k. öſterreich. Muſeum für Kunſt und Induſtrie
von
Wilhelm Franz Exner.

Mit Porträt.

Wien.
Druck und Verlag von Carl Gerold's Sohn.
1878.

Figure 5. Wilhelm Franz Exner's essay on life and work of Beckmann, 1878.

escape, gave origin to Philosophy of Technics or Philosophy of Technology, dedicated to, among other purposes, identifying the limits between the rational and the irrational, the artificial and natural, mechanization or "machinization" (in the sense of replacing the work of a person with that of a machine). From the inevitability of Technology in our context, good or evil, we derive the inevitability of ethical/normative questionings. To discuss these issues falls outside the scope of this paper. Our aim is to discuss the role of Beckmann in the history of Technology and social progress.

A common critique of Technology and of Beckmann suggests that technology or technical science is still a project, a project which tries to reshape the world according to machinery principles, and dreaming in turning its principles into the basis of a unified knowledge. This proposition is a denying one, and ignores the history of science. Leblanc's process for soda production is an example that technology is not a project, but that it advanced far beyond a project. Other examples are the Solvay process for soda production, the contact process for producing sulphuric acid, the electrochemical and the Haber-Bosch processes for ammonia production, among others. Artificial production of fertilizers is, as the chemist William Crookes (1832-1919) puts it as a follower of Malthus, a basic condition for maintenance of life in later days[57]. Beckmann's strategy can be seen in all of these processes, even for those who do not want to admit it: maximum utilization of raw materials, search for alternative raw materials, recycling raw materials and their rejects, usage of by-products, removal of environmental damage, reduction of costs. Obviously, this did not occur overnight, but is the result of a gradual ripening of a *technological project*. The gap between the "two cultures" – the scientific/technological and the humanist – of Charles Lord Snow (1905-1980), makes it impossible, or at least very difficult, to have a full understanding of problems like the importance of Beckmann.

Another kind of critique is presented by post-modern authors, as Bruno Latour (1947-2022), for whom the notion of science hold by scientists is irrelevant for scientific activity[58]. But without taking into account what scientists and technologists think about their activities, philosophers and sociologists of science could not explain how it was possible to technologists like Beckmann, or to chemists like Martin Heinrich Klaproth (1743-1817), to change from phlogiston theory to lavoisierian anti-phlogistic theory without any rupture in their work. Philosophers and sociologist of science would not be able to work out a methodology of scientific practice, nor decide about the scientificity or not of a theory.

Finally, it must be said that in Beckmann's time there was no distinction between a "scientific" culture and a "humanist" culture. In other words, the "two cultures" show the comprehensiveness of all their vast knowledge: historical, philosophical, educational, practical and technical. This was a time of optimism about technology, distinct from today's fears about possible (probable?) technological excesses damaging the fabric of society.

Beckmann looked at technology and its evolution in terms of his *Ganzheitsprinzip*, or, as a unified whole, including historical, cultural, social, political, ethical, and environmental aspects. For today's skeptics with respect to the environmental cause, let us see Beckmann's opinion on using ivory: "*aesthetics associate to artworks and objects made of ivory on one side, on the other side, the irrationality of pursuing animals for sake* *of aesthetics*"[59]. *Nil sub sole novum*. But this is a paper about the past and about Beckmann, for whom the advantages of Technology surpass in much the risks; but nowadays risks are greater day after day, so that George Sarton himself suggested caution with machines[60].

TRIVIA

I had the pleasure to be in correspondence, during several years, until his death, with Egon Max Beckmann (1925-2012), descendant of Johann Beckmann. His grandfather Adolf Beckmann (1861-1934) came as an immigrant to Brazil, and in 1887 founded in Joinville the *Hotel Beckmann*, a meeting point for voyagers and local people. Sold in 1915, it reopened later as *Hotel Palácio*. I stayed there for a few days in 1951, with my mother, during school holidays. Such incredible coincidences cannot be predicted....

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Historical Article

Kuroda Chika (1884-1968) – Pioneer Woman Chemist in Twentieth Century Japan

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Abstract. Kuroda Chika was the first Japanese woman to graduate in chemistry. This article describes her early education and subsequent career in chemical research in Japan from 1913, and includes two years in Oxford (1921-1923). Her career as a researcher in The Physical and Chemical Research Institute (RIKEN) and as a professor at Ochanomizu University in Tokyo is described. Kuroda's organic chemistry studies, specifically the identification of the constitution of plant dyes is described. The status of female education and female employment in Japan during the first half of the twentieth century are also considered. Later in her career the achievements of Kuroda Chika were acknowledged with prestigious prizes and awards.

Keywords: Kuroda Chika, organic chemistry, plants dyes, chemistry in Japan, women scientists in Japan, Ochanomizu University, Tohoku University, RIKEN.

Dedicated to the memory of Ms. Dr. Fukiko Tsuruki, biochemist, patent attorney and a good friend (1945-2020).

EDUCATION DEVELOPMENT IN KURODA CHIKA'S LIFE

Kuroda Birth to in Kyushu

Kuroda Chika was born in Saga, Kyushu Island, on 24 March 1884, the third daughter of her father Kuroda Heihachi and her mother Toku. Kuroda Heihachi 黒田平八 (1843-1924) participated in the samurai class rebellion known as the Saga Rebellion in 1874, and later served as a director of the Saga Rice Exchange 佐賀米穀取引所. He enabled his children, including his daughters, to receive a good education.

Education for girls in the late nineteenth-century Japan was rare. What drove Kuroda Heihachi to send his daughters to school in 1889? What was the social, educational and political situation in his town Saga in northwest Kyushu in those days?

The Need for a Better Education System

The realization of the need for a better, western influenced education, spread in Japan after 1853-1854 following the arrival of Commodore Perry's American party, which included the demonstrations of modern cannons in action and other technologies. The Japanese soon realised that they were far behind western countries in their technologies, and that they needed to acquire advanced techniques from the West in order to be able to compete with western countries and to prosper economically.

Kuroda Chika's life spanned the reigns of three Emperors. She was born during the Meiji Era (Meiji 1-45; 1868-1912) which stimulated the modernization of Japan; her education was during the Taisho Era (Taisho 1-15; 1912-1926); and her research and teaching was conducted during the Showa Era (Showa 1-64; 1926-1989). Those three eras, each one named after the corresponding emperors, represented the long road during which Japan progressed from a feudal country, with separate rulers in villages in remote domains, through changes in the national, military, political, and economic administration. After 1950 Japan became a world leader in its economy and several technological fields.

It is pertinent here to give a brief account of the major changes of the educational system.

Education System Revisions

In Edward R. Beauchamp's Introduction in *Japanese Education since 1945*, he observed that … "major attempts to implement basic educational systems occurred in the 1870s and again following World War II…."

In the section on "Japanese education, 1868-1945" Beauchamp explains that under the Meiji reformers "a highly centralized administrative structure with an emphasis on state-run normal schools was borrowed from France; a system of higher education rooted in a handful of elite public universities was the German contribution; the English model of Spartan-like, character-building preparatory schools stressing normal discipline which fit nicely into the Japanese context, and from the United States came the model of elementary education, a number of practical pedagogical approaches, and an interest in vocational education." (Beauchamp, 1994, pp. 3-4).

Beauchamp observed that "A second major reform period took place immediately following World War II as a key element of the Allies' determination to transform Japan from an aggressive military dictatorship into a peace-loving democracy (Beauchamp, 1994)." In the context of this reform, the Tokyo Women Normal High School in which Kuroda Chika studied and worked from 1907 became Ochanomizu University in 1949 and Kuroda was appointed a full professor of this university.

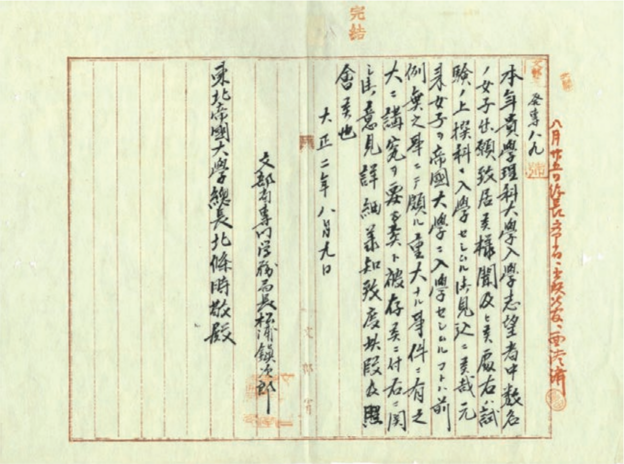
KURODA CHIKA'S LIFE HISTORY

Early Career

In 1899 (Meiji 22), aged five, Chika entered Saga town's Kanko Elementary School. She remained there until age 14 when she transferred to the Saga Girls Normal School (*Saga shihan joshi-bu*) for three years (in 化学史への招待 *Invitation to the History of Chemistry* 2019). During 1901 she served as a primary school teacher at another school in Saga and then moved to Tokyo.

In April 1902, Kuroda Chika entered the Division of Science of Tokyo Women's Higher Normal School (*Jokoshi*). Her chemistry teacher was Hirata Toshio. She graduated in March 1906. In the following month she was invited to teach at Fukui Normal School where she spent one year training teachers. Both Fukui Normal School and the Saga Normal Women's Department had the same principal who suggested that she should teach in Fukui, because he planned to establish a similar female science class at Fukui Normal School. She added that "the chemistry teacher was, of course, enthusiastic. The students were also enthusiastic, it was challenging, and it was fun and enjoyable." During 1907-1909 she completed her graduate course at the Tokyo Women's Higher Normal School and became assistant professor at the school. (Chika Kuroda Life History, Ochanomizu University digital research center p. 21).

She was first assigned to assist Professor Nagai Nagayoshi (1844-1929), who had studied chemistry and pharmacology in the laboratory of A. Wilhelm von Hofmann in Berlin.[1] Nagai's twelve years in Germany shaped his views in favor of women education. After returning to Japan in 1874, Nagai taught at the Department of Pharmacy, College of Medicine, Tokyo Imperial University, and at the Tokyo Women's Higher Normal School, where Kuroda Chika prepared demonstration experiments for his lectures. Nagai recommended that she take the entrance examination to Tohoku Imperial University in 1913, the year in which it opened its doors to women. She took the entrance examination with more than forty other people. Thirteen of them passed, including Chika and another woman, Tange Ume, both for chemistry studies. A director at the Ministry of Education sent a critical letter to the president of Tohoku Imperial University arguing against letting women start



完結

八月廿五日総長文部省ニ出張ノ際交渉済

発専八九

本年貴學理科大學入學志望者中數名ノ女子出願致居候處右試驗ノ上採科ヘ入學セシムル見込ニ候哉元来女子ヲ帝國大學ニ入學セシムルコトハ前例無之事ニテ頗ル重大ナル事件ニ有之大ニ講究ヲ要スト被存候ニ付右ニ関シ貴意見詳細承知致度此段及照會候也

大正二年八月九日

文部省専門學務局長松浦鎮次郎

東北帝國大學總長北條時敬殿

Figure 1. Hand written letter from the Ministry of Education to the President of Tohoku University 9 August 1913 (received from Tohoku University Library Archive 13.12.2020, publication permission 7.2022). On the right side of the letter, it is written in red letters that the President of Tohoku University went to the Ministry of Education to attend a meeting on August 25th. No record was made of what transpired at the meeting. (Courtesy of Tohoku University Archives).

Figure 2. Kuroda's photo legend: "Father and mother on their golden wedding anniversary and I (2nd row second from right) Tohoku Imperial University graduation commemoration." (Courtesy of Tohoku University and Kuroda Kotaro).

their education there, pointing out that it had never happened before (Fig. 1). However, Kuroda Chika was allowed to continue her studies and graduated in September 1916.

A copy of the hand written letter and its transcript is shown in Fig. 1.[2]

At Tohoku Imperial University, Kuroda Chika could choose from one of three chemistry professors: Ogawa Masataka (Inorganic Chemistry), Katayama Masao (Theoretical Chemistry), and Majima Riko (Organic Chemistry). Kuroda chose Professor Majima Riko as her instructor and advised him that she wished to study the constitution of natural coloring matters (Maeda Koko, Ochanomizu University digital research center publication p. 8).

In Kuroda Chika's memoirs written in 1957 she included a family photo taken in Saga in 1916, the year in which Kuroda Chika graduated (Fig. 2).

The photo (Fig. 2) shows everyone in traditional Japanese clothing. The father, Heihachi is sitting in the 2nd row, 4th from right, his wife Toku is next to him, 5th from right. Standing 5th from right is Kuroda Ryukichi 黒田龍吉, eldest son of Heihachi.[3] The parents are celebrating their golden wedding anniversary, which took place just after Kuroda Chika graduation of Tohoku Imperial University

After graduating from Tohoku Imperial University, Kuroda Chika returned to her alma mater, and taught at Tokyo Women's Higher Normal School. Concerning 1918 she wrote that "At that time, the influence of the First European War caused the status of science and engineering world in Japan to rise, and the chemical world was no exception." (Kuroda, 1957).

In another lecture in 1960, and article in 1961 she added:

> At that time, Professor Shibata Yuji took the lead at the University of Tokyo, saying, 'A Tuesday party was organized, and volunteers regardless of their university of origin held after their work, meetings once a month.' The venue was usually Enrakuken, in front of Todaimae, and the main purpose was to get to know each other.[4]

It was a lot of fun because it was both informative and encouraging, including discussions and souvenir stories." (Kuroda, (Ku-2012), 1961). This is a vivid description of the informal gathering organized by Professor Shibata with both young men and women from different universities; it was a relaxed and enjoyable social meeting.

Kuroda published her first article in 1918, in the journal of Tokyo Chemical Society (later the Chemical Society of Japan), presenting the results of her research under Majima's guidance. She managed to crystalize Shikon 紫根 *shikon/murasakine*, the purple root, gromwell root (of species *Lithospermum erythrorhizon*), and also established its structure (See Fig. 11 below). She named the color Shikonin. On 11 November 1918 she presented her findings in a lecture titled "About Purple Root Pigment" to the society. This was the first occasion when a woman addressed the society. (Kuroda, (Ku-1001), 1918). In 1918 she was appointed a professor at Tokyo Women's Higher Normal School.

THE OXFORD YEARS, MARCH 1921-AUGUST 1923

In 1921, Kuroda at age 37 was sent by the Ministry of Education to the University of Oxford in England, with the intention of working with Professor William Henry Perkin Jr. (1860-1929) on phthalonic acid derivatives. Perkin's response letter to Sakurai's letter of recommendation is kept in Ochanomizu University Archive. Perkin apologizes for not having a place for her, but nevertheless suggested that she should call for him later. Sakurai's letters to Perkin have so far not been found, but what is clear is that Perkin found a place for her to undertake research in 1921, apparently, in the new laboratory at Oxford (Appendix: Ku-4301).

Concerning Perkin's laboratory, Peter J. T. Morris quotes Jack Morrell's description of an organic chemistry laboratory built for Adolf Baeyer at Munich in 1877, which was a model for copying in England:

> …The [laboratory] system may have worked well, but it was probably liable to liberating volatile vapour into the atmosphere of the laboratory. It is perhaps not surprising that W.H. Perkin Jnr., a student of Baeyer who copied this arrangement in his laboratories at Manchester and Oxford, probably died of mercury poisoning. (Morris, 2015, Murrell 1993).

The transfer of the laboratory design to Manchester and Oxford is also mentioned in Kuroda's description of her conversation with Robert Robinson in Manchester prior to her return to Japan.

In her memories Kuroda tells how she enjoyed her time in Oxford and the hospitality of Perkin's family. During the two months' summer vacation she traveled to Europe. In Switzerland she climbed the Jungfrau Mountain and at the foot of Interlaken she gave a geography lesson at a primary school, telling the pupils "in a broken English" about Japan (Kuroda Memoirs 1957, (Ku-2006), -33- 72).

Japanese Students' Life Abroad in Nineteenth and Early Twentieth Century

Japanese students' stay in foreign countries involved overcoming a wide number of challenges concerning the difficulties of getting used to a different language, different food, daily customs and behavior (Cobbing 1998).

During Chika's stay in Oxford Albert Einstein was invited to Japan. In his recollections during the ship's sail to Japan he described his impression of the Japanese students in Berlin at that time:

> Never in my life have I been more envied in Berlin, and genuinely so, than the moment it became known that I was invited to Japan. For in our country this land is shrouded more than any other in a veil of mystery. Among us we see many Japanese, living a lonely existence, studying diligently, smiling in friendly manner. No one can fathom the feelings concealed behind this guarded smile. And yet it is known that behind it lies a soul different from ours… (Einstein, 1922, in Rosenkranz Ed. **2018**, 245).

Even though Kuroda Chika was a single Japanese woman in Oxford who had managed to come to terms with the different way of life in England, including accepting the way people looked at her, it seems from Kuroda's written memories that she had a pleasant stay in Oxford. It could be attributed to her good nature, as well as to that of her host, W. H. Perkin Jr.

Apart from a joint article with Perkin Jr. in 1923, very little can be found about her stay in Oxford in the English language. It is assumed that since her fellowship was paid by the Japanese Ministry of Education, she was not registered in Oxford University's records.[5] In her memories of 1957, in a photo taken at Oxford, Chika is dressed in a kimono, standing near a garden wall made of bricks, wood, and bushes (Fig. 3).

In Oxford, some months before Kuroda's return to Japan, one photograph (Fig. 4) shows in addition to Kuroda and Kato, sitting next to her, that there are six other Japanese men who were in Oxford at that time. In this case thirty-eight year old Chika is dressed in a western style and a hat. She wrote about her experience of putting on western clothes while she was on the ship going to England, sharing experience with her two younger cabin-mates. Kuroda Chika was elegantly dressed, in either kimono or western suit.

Kuroda recalled:

> Since Taisho 10 (1921), I spent two years in Oxford, England, supported by Prof. W. H. Perkin, who funded the research. In the research time Professor Robinson from Manchester University often visited Prof. Perkin. Just before I left England to return home I visited Professor Robinson at Manchester University. He invited me for a meal, I thanked him and I was told that the design of Prof. Perkin's laboratory in Oxford is the same as in Manchester. That was a comprehensive and an exceptionally memorable discussion (Kuroda (Ku-2012), 1961).

Kuroda included in her memoirs a photo of the boarding house at 139 Woodstock Road, Oxford, in which she resided (Fig.5). The boarding house owner was Mrs. Whitmarsh.[7]

Kuroda's memories from Oxford included:

Figure 3. (Ku-6016) Kuroda Chika in Oxford, Taisho11, 1922.

> Studying in the English Oxford University it is not easy to gain admission even for those who reside in the country. it is not easy to gain admission. But I am so grateful to Sakurai Jōji that I was enabled to undertake research. This was with the permission of Professor W. H. Perkin, the only professor of organic science at Oxford University, following a recommendation from Sakurai. For more than two years, I lived in the same room in a clean house in a scenic area; the laboratory faces the University Park next to Professor P [Perkin's laboratory]. I was able to continue my work in the room with an abundance of material, and I would like to thank Dr. P. [Perkin] for his generosity.

She concluded her memories, written in 1957, by adding: "During those two years, I had no time to become 'homesick'." Homesick she wrote in English, in katakana ホームシック (Kuroda、in Ocha. 1957 p.-33-72).

Figure 4. (Ku-6018). Taisho 12 January 26 (1923) in Oxford. Kuroda Chika and Japanese students.[6]

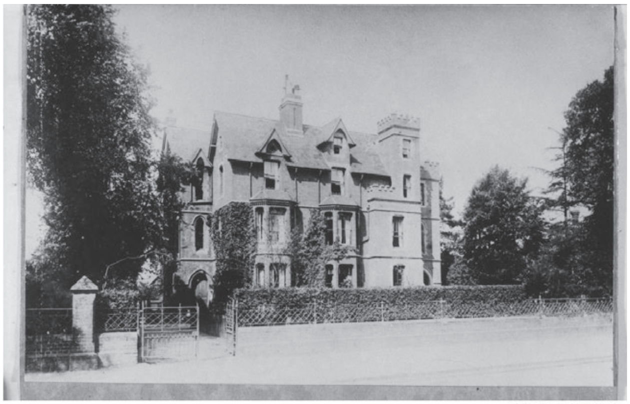


Figure 5 (ku-6017). Kuroda's boarding house on 139 Woodstock Road, Oxford (Ochanomizu University History Museum. Reproduced with permission).

BACK IN JAPAN

In August 1923, Kuroda's returned to Japan and her home in Saga, and then she reentered Tokyo Women's Higher Normal School. After the Great Kanto earthquake of September 1923 completely demolished the buildings of the school, Majima offered her a place in the Institute of Physical and Chemical Research (*Rikagaku Kenkyusho*, abbreviated RIKEN), founded in 1917.

Kuroda reflected: "Mr. Sakurai Norio (later, executive, doctor) guided me, but not only is the building and equipment comparable to those of foreign countries, but with air to each room pumped from a motor placed in the basement, etc. I was delighted to see that these standards in Japan had raised so much."

In RIKEN Kuroda continued her research and published her results under the title of "About the structure

Figure 6. Kuroda Chika, (Ku-6107), at age 40, at RIKEN, the Physical and Chemical Research Center, 1924. (Ochanomizu University History Museum. Reproduced with permission).

of safflower pigment" (Safflower (*Carthamus tinctorius L.*) (紅花の色素 *benibana no shikiso* 1929). This was her doctoral thesis. Original samples of her research materials are today held in Ochanomizu University Archives, (See Fig. 11).

Kuroda's Work Places: RIKEN > KAKEN > RIKEN

RIKEN was founded under a special government regulation and with financial support from the Imperial Household and private businessmen and companies. Facing financial difficulties after World War II it was reorganized in 1948 and was renamed KAKEN (*Kagaku Kenkyusho*, the Scientific Research Institute Ltd.). Kuroda Chika's affiliation was mainly RIKEN and then KAKEN for a few years (1949-1954). Further, after World War II, there was a new administrative reorganization, and in 1958 RIKEN assumed its original name *Rikagaku Kenkyusho*, and abbreviation, RIKEN (RIKEN, 1983). It seems that since the 1920s Kuroda held a professorial, mainly teaching, position at Ochanomizu University, and had no facilities for chemistry experimental research. She used her RIKEN affiliation, to undertake experiments, as did other researchers, having more than one post at a certain time. Interestingly, in a publication of 1967, Kuroda's almost last article, co-authored with Okajima Masae, her affiliation is shown as the Department of Chemistry, Faculty of Science, Ochanomizu University, contributed by Yubata Teijiro. In this article Kuroda presented absorption spectra in the UV and visible ranges, infra-red spectra, as well as NMR spectra. This in accord with the progress of techniques in physical organic chemistry that were developed and used in those years.

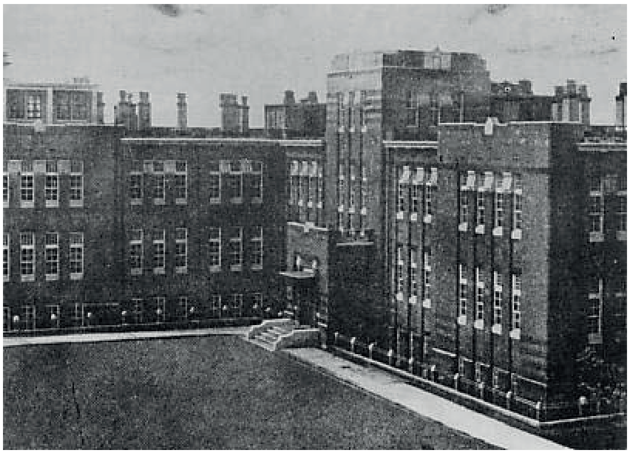


Figure 7. RIKEN building in Komagome, in northern Tokyo. (Reproduced with permission from RIKEN).

Kuroda Chika's home was in Sugamo 巣鴨, in the northern part of Tokyo on the Japanese National Railway (JNR) train line, east of Ikebukuro 池袋. The map of Tokyo City shows that she could easily reach RIKEN, which was then located at Komagome 駒込 just one station east of Sugamo JNR rail station, or to Ochanomizu University, South-east of Sugamo. (Kuroda Kotaro. in *Invitation to Chemistry History* 2019).

Kuroda's Research and Teaching Colleagues

Kuroda's Research Partners

Kuroda's partners in research deserve their rightful recognition: firstly with her host professors in Japan's RIKEN, Majima Riko (1922); and in Oxford with W. H. Perkin Jr. (1921-1923). Then she published eleven articles during the years 1929-1931, and other articles as the sole author during the subsequent years. She collaborated with the following researchers, according to her list of publications: Matsukuma Tokiyo (1932, 松隈ときよ 2 articles); Nakamura Teruko 中村照子 (1932, 2 articles); Mizu Wada 和田水 (collaborated during 1932-1938); Kisako Koyasu (1944); Umeda Masao (1949, 1951); Okajima Masae (1950, 1951, 1954, 1958, 1960, 1962, 1964, and 1967); and Harada Mie (1955). No students are mentioned who continued her line of research.

Kuroda's Career Progress and Teaching Colleagues

In 1929 (Showa 4th year) at 45 years of age, Kuroda Chika received the title Doctor of Science (D.Sc.), from Tohoku University. She received the 1st Majima Award from the Chemical Society of Japan in 1936. In 1949 Kuroda Chika became professor of the newly established Ochanomizu University, formerly the Tokyo Women's Higher Normal School (*Jokoshi*).

Kuroda's women colleagues at Ochanomizu University are shown in Fig. 8. The topics of higher education and of positions held by academic women in the first half of the twentieth century will be dealt with below. in 'Women Scientists in Early 1920s Japan'.

Kuroda's 1961 Speech (Ku-2012)

Kuroda's speech on the occasion of Majima's 88th birthday Showa 36 year, 21 May 1961. The 88th birthday is considered an important birthday in Japan. (Kuroda, (Ku-2012), 1961).

Figure 8. (Ku-6032). Faculty members of Ochanomizu University. Showa 25 about 1950. From right: 吉田武子 Yoshida Takeko, 黒田チカ Kuroda Chika, 保井コノ Yasui Kono 辻村みちよ Tsujimura Michiyo, 和田冨起 Wada Fuki. (Courtesy of Ochanomizu University).

In her speech and published article, "Rice from the same Pot," おなじお釜のご飯, following the Majima's birthday lecture, Kuroda outlined the history of chemistry in Japan, starting with Udagawa Youan, who wrote books about botany and chemistry during the first half of the nineteenth century. Kuroda mentioned Udagawa Youan's book *Seimi Kaiso*, 舎密開宗 (Introduction to Chemistry), in which the author used Henry's original research work as the basis for a chemical book translated into Dutch and referring to similar books, along with his own experiences.[8] The Japanese nineteenth century scholar Udagawa Youan started botanical and chemical research after books from Europe that were imported to Japan (Endo et al., 2014. For Udagawa Youan see Siderer, in *Substantia* March 2021; Kikuchi and Siderer December 2021).

Kuroda further recollected: "The Chemical Society of Japan 75th anniversary meeting in 1953 was a very meaningful occasion, with the visit of Sir R. Robinson to Japan and other important events as mentioned above.[9] In recent years, the annual meeting reflects current trends in the development of chemistry." Robinson gave a lecture and other talks that I attended. I was happy to meet him and became more nostalgic. While I was a student in Sendai, and researched 紫根 Shikon, gromwell root, since about Taisho 5 (1916), reading carefully a joint paper by Professor P. and Dr. R. on natural pigment research, deepens my interest in plant dyes."

Robinson sent her Christmas cards every year, a special one in the year 1960: "Last year (1960) was very dif-

Figure 9. (Ku-6033), Prof. Majima, Surrounding Prof. Katayama 片山先生 Showa 26 October 1951. Front row from left ：辻村みちよ Tsujimura Michiyo, 黒田チカ Kuroda Chika (67 years old), 眞島利行先生 Prof. Majima Riko, 片山正夫 Katayama Masao, 片山正夫夫人 Mrs. Katayama Masao. Back row from right: 伊達たまき Date Tamaki, 山西貞 Yamanishi Tei, 岡嶋正枝 Okajima Masae, 鈴木照子 Suzuki Teruko, 吉田武子 Yoshida Takeko, 一人おいて leaving out one person, 小林ハナ子 Kobayashi Hanako.

Figure 10. (Ku-2012), 1961, 1163. Yoshinomiya and the author [Kuroda Chika] at the completion celebration venue of the Chemical Society of Japan Chemistry Library (Courtesy of Ochanomizu University History Museum).[12]

ferent in taste, and it was Dr.'s [Robinson] personality, humorous, ironic and impressive, so I will post it here." Robinson's appreciation of Kuroda Chika's research is reflected by his inviting her to Manchester University before she left Oxford to return to Japan; by his sending her annual Christmas and New Year greeting cards;[10] and by their meeting upon his visit to Japan in 1953. At the National Library of Israel in Jerusalem there is a copy of Robinson's comprehensive book following his lectures which he delivered on the occasion of the first Chaim Weizmann Memorial Lectures in Rehovot, Weizmann Institute of Science, Israel, in 1953. In this book he cited Kuroda's articles (Robinson 1955).[11]

Kuroda cited several of Robinson's works, including "VI. Notes on the characterization of the anthocyanins and anthocyanidins by means of their color reactions in alkaline solutions" for the use of specific solutions to change the pH of the dye under study (Robertson and Robinson 1928).

Kuroda continued her greetings "…By the way, what I would like to mention specially is the celebration of the completion of the Chemical Society of Japan's library on December 2, 1960. The honor and gratitude for being invited was inspiring, but at the same time, I was impressed with the deep joy and recounting of the history of Japanese chemistry." Kuroda's modesty and politeness is evident at the end of her 1960 speech, and in all her writings. In Fig. 10, during the celebration she wrote about, Kuroda is surrounded by scientists and other guests. One may see their appreciation to her.

Summary of Kuroda's Research Life Story

In dozens of articles Kuroda described detailed processes for isolation, crystallization and determination of the construction of the isolated dye crystals, extracted from plants and sea animal that were traditionally found and used in Japan. In 1936 she concluded that many of the extracts were derivatives of anthocyanin. In her memoirs written in 1957 Chika acknowledged and included photos of those scientists from whom she benefited: R. Majima, W. H. Perkin Jr., his brother G. A. Perkin, and R. Robinson.

It should be emphasized here that Kuroda Chika's research and achievements were on topics similar to those of the leading organic chemists in England, though there was far less support for laboratory facilities in Japan, and less recognition of her work.

She continued part time research and teaching as an emeritus professor after her retirement in March 1952.

Kuroda Chika started her memoirs by writing "Since I've learned about the endless world of academic study and the joy of walking that path, I was just drawn to the joy of discovering something I hadn't seen yet; and before I knew it, I had reached the age of 72. I am grateful that I still have enough energy to continue my research."

> At the end of last year, the research on substances in onion skin that act against high blood pressure which I had been working on for a long time, finally came to fruition, and it was transformed into the blood pressure medicine "Keltin C"; I am incredibly happy that it will be useful to many people, it will be my honor. (Kuroda (Ku-2006), 「化学の道に生きて)」 1957).

Recognition of Kuroda Chika's Achievements

In 1959 (aged 75) Kuroda Chika was awarded the Medal with Purple Ribbon (紫じゅ褒章, *shiju hōshō*), a type of Japanese medals of honor conferred by the emperor of Japan since 1955. In 1960 she was declared honorary president of the Society of Japanese Women Scientists. In 1965 (Showa 40) she was awarded the

Order of the Precious Crown, Gold Rays with Neck Ribbon 勲三等宝冠章受章.(Ochanomizu University Chika Kuroda's Life History p. 22).[13]

Kuroda Chika died in Fukuoka City, Kyushu, on 8 November 1968 (Showa 43), at 84 years of age. Her memory is cherished in Japan as a pioneering woman chemist.

Kuroda's Legacy for Young Women Students

Kuroda and her friend, the first woman biologist Professor Yasui Kono (1880–1971) established a prize for young students. They donated the celebratory money received at their retirement ceremonies (1952) to the school as part of the "Yasui-Kuroda Scholarship," which continues to encourage young researchers to this day (Ochanomizu University Library Website 2022).

New award carrying Kuroda's name was declared by Tohoku University.

The Kuroda Chika Award

> Every year, the Aoba Society for the Promotion of Science awards a selected few of female graduates who have produced outstanding achievements during their scientific doctoral studies. This award is given to female students selected from the whole doctoral cohort across the Graduate School of Science and the Graduate School of Life Science at Tohoku University. Named after Dr. Chika Kuroda, the first female to receive a chemistry doctorate in Japan from the Faculty of Science, the award was founded in 1999 to encourage female researchers in their scientific endeavors and careers. Over the last 15 years, 45 female students have been honored. (Received a link from Tohoku University 18.8.2022).

A statue of Kuroda Chika stands on the main street of Saga, alongside statues of other dignities of the city.[14]

Kuroda's Memorial Collections

Kuroda Chika's memorial collections are mainly stored in three institutes: (i) Ochanomizu University in Tokyo, where she studied and later taught; (ii) Tohoku (formerly Imperial) University in Sendai, where she started her academic chemistry studies in 1913; Kuroda's family donated her belongings to the archive in 2013 (reported in Mainichi shinbun 5 July 2013); (iii) and in RIKEN, where she pursued her research and published here articles. "Unfortunately, Kuroda Chika's materials before World War II were burnt in the war and only a few remain" (Kuroda Kotaro email, 11-12.4.2021).

KURODA CHIKA'S RESEARCH OF NATURAL PIGMENTS IN PLANTS AND IN A SEA ANIMAL

Early Studies of Plants in Japan

The study of plants has a long history in Japan. Eighteenth century herbal studies in Europe and in Japan were broadly reported in "Dodonaeus in Japan" (Edited by W.E. Vande Walle, co-Editor Kazuhiko Kasaya. 1998). The difficulties in translating Dodonaeus were explained by W.E. Vande Walle (Dodonaeus p.17). Eighteenth century writing in Japan about plants by Ono Ranzan (1729-1810) still referred to a Chinese book about plants. The introduction of western botany into Japan began with Udagawa Youan (1798-1846) and Ito Keisuke (1803-1901). Organic chemist Professor Majima Riko (1874-1962) started modern organic chemistry studies in Japan at the Imperial University of Tokyo. Majima had graduated in 1899 and became a graduate student of the department under the supervision of professor Sakurai. His generation was the first to study fully within a modern educational system. In 1903 Majima was promoted to the position of associate professor and was then sent by the Ministry of Education to Europe for further study. He conducted research in Kiel under Carl Dietrich Harries (1866-1923) and in Zurich under Richard Willstätter (1872-1942). Majima returned to Japan in January to the chemistry department at Tohoku Imperial University, a newly established imperial university in Sendai, northern Japan, in March 1911 (Kaji, 2015). Kuroda Chika was Majima's first student and later an associate; she continued studying organic chemistry and extended the knowledge of chemical studies of plants, specializing in plants dyes.

It should be noted that Kuroda's professors and mentors, Nagai Nagayoshi, Majima Riko and Sakurai Jōji, spent some years studying in Europe and brought to Japan their experiences, approaches to scientific research and instruments, from which Kuroda benefitted.

Kuroda's Scientific Publications

In the introductions of her articles Kuroda wrote short explanations for the reason to choose a certain plant in order to study its coloring material. These were certain historical or cultural explanations, mainly showing the Japanese background and occasionally the use of a plant in other parts of the world. Kuroda describes the analyses themselves by an accurate and concise way, without explaining the reasons for choosing a specific test method. However, she relied on many publications that dealt with similar materials, thus justifying their application in her further research.

In the following section, several of Kuroda's publications in which she specified the processes of chemical analysis and then the choice of synthesis in order to confirm the identity and formula of a certain extracted plant material are summarized.

As stated above, Kuroda published her first article in 1918, the result of her research under Majima's guidance. She crystalized Shikon 紫根, purple root (*murasaki*), gromwell root (of species *Lithospermum erythrorhizon*), and established its constitution and named the color Shikonin.[15] Another paper she published on this topic was with Professor Majima (Majima R. and Kuroda, C. (Ku-1002). *Acta Phytochimica*, 1922. Cited by Maeda, Ochanomizu University website).[16]

Interestingly, she returned to study the constitution of Shikonin in 1936 (Fig. 11). In her article, together with her female colleague of many years Dr. Wada Mizu, they crystalized Alkannin, the coloring matter of the root of Alkanna. They discovered the optical isomer of Alkannin, and that of Shikonin, having an asymmetric carbon next to carbon 3 of the ring. They decided that the Shikonin substance is a naphtazarin derivative, and not a naphtopurpurin, as Majima and Kuroda have previously suggested. Kuroda and Wada offered a proof based on synthesis for the constitution by synthesizing iso-hexyl-naphtazarin that had not been synthesized previously. Their product and Shikonin had the same melting point of 100°C and very similar elemental analysis, i.e., the relative amount of carbon, oxygen and hydrogen. Kuroda and Wada described the synthetic routes and characterized the intermediate compounds. Kuroda returned to the same molecule some eighteen years later. The relations between chemical analysis and synthesis are addressed below, following B. Bensaude-Vincent (Kuroda and Wada, (Ku-1031), 1936), (Bensaude-Vincent lecture 2021).

The Constitution of Carthamin

During the years 1929 to 1930 Kuroda Chika published several articles on "The constitution of Carthamin", the coloring material of Safflower flowers. It is a celebrated color in Japan and the petals contain both a yellow and a red dye. Crude carthamin paste was washed, dried, recrystallized from pyridine, giving several derivatives in order to detect the exact location of the hydroxyl group, and the nature of the color forming reaction. UV spectral data of the derivatives were given. (Kuroda (Ku-1004) 1929, Kuroda (Ku-1005) 1929, Kuroda (Ku-1006), 1929).[17]

Figure 11. (Ku-5001). Research results specimen kept by Kuroda: Shikon and Carthamin. Crystals and structural formula of Shikonin, Carthamin and Murasaki, Benibana (dry), purple dyeing. Experiments Materials: Murasaki – Root of Murasaki including pigment. Shikonin Research: gromwell root (of species Lithospermum erythrorhizon). Taisho 5th year ~Taisho 7th year. Safflower (Carthamus tinctorius); dyer's safflower. Carthamin research: Taisho 13th year – Showa 4th year. (Photo courtesy of Ochanomizu University History Museum).

The Constitution of Awobana

In 1931 a preliminary report on "The Coloring Matter of 'Awobana'" published by Kuroda Chika, discusses the flowers of *Tsuyukusa* 露草**,** *Commelina communis.* They are a beautiful azure blue from which were extracted blue fabric colorants, named Tsuyukusa or Awobana, meaning dew grass or a blue flower, respectively, commonly known as Asiatic Dayflower . "It is one of the most well-known and the oldest of its kind in Japan and the uses has a historical interest." (Kuroda (Ku-1014), 1931). Although not practical as a dye, it was still employed for drawing patterns in the art of Yuzen silk print and Shiborizome (tied dyeing). It is grown in some regions and used for paper dyeing by painting the flower extract on sheets of paper and drying in the sun, (thus) labeled Awobana paper." (Kuroda (Ku-1014), 1931, and (Ku-1022), 1933). Kuroda did not find an earlier record of this coloring material. She used the Awobana paper for the studies of the coloring matter constituents. Further studies on Awobana reported recrystallization; needle crystals were obtained from methyl alcohol.[18]

Anthocyanin Pigments

In a series of articles Kuroda reported her studies on *Kuromame* (black beans), *Shiso* and *Nasu* (eggplant) and the constitution of each of the natural coloring matters that she named Kuromamin, Shisonin and Nasunin, respectively. By 1935 she combined her and Wada's research on these coloring materials. Kuroda states that she realized that the natural dyes that she studied were anthocyanins.

Anthocyanins are glycosides of anthocyanidins, the basic chemical structure of which is shown. (Wikipedia, accessed 24.3.2022).

Kuroda explained: "Kuromame", "Shiso" and "Nasu" are widely used vegetables in Japan, specially favored for their bright colors; therefore, the chemical study of their coloring matters is of great importance and of much interest. But almost no literature was found on the subjects. Kuroda and Wada were successful in isolating the main coloring matters in the crystalline states, and found that all three pigments were anthocyanins. Photographs of the different crystalline derivatives of each of the three dyes of Awobana were presented.[19] A detailed experimental section described all analytical steps, and color changes due to pH; Absorption spectra were measured. Following their earlier publication on each of those substances in 1933-1935 Kuroda and Wada combined their full findings in detail (Kuroda, (Ku-1030), 1936).

The Constitution of Kuromame, Black Soya Beans

> Kuromame, 黒豆, or black soya beans, belongs to *Glycine Soja Benth*, and is given the name because of its delicacy of taste and the especially deep bluish color of the seedcoat. It is used as a common food but is also served as one of the symbolic sweets in the typical ceremonial menu of the Japanese New Year. It is also favored as a medicinal substance, and especially recommended to vocalists Kuroda Chika and Wada Mizu (Ku-1030), 1936, p. 1). The black pigment was at first belived to be an anthocyanin. Kuroda and Wada gave the pigment the name Kuromamin to the crystalline glucoside of the pigment. In the mid-1930s, because it was suggested that different samples from different sources might have different derivatives as a result of their different appearances, the two researchers studied beans samples that they received from Manchuria (Mukaden and Shing Tai Tzu), which were under Japanese rule in those years, and showed that "the coloring matters of "Kuromame", regardless of the varieties and the localities, belong to the same kind of compound.[20] (Kuroda (Ku-1030), 1936).

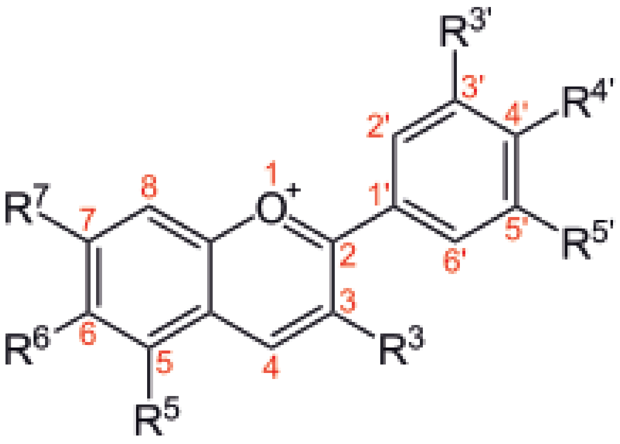


Figure 12. Anthocyanin.

Shisonin, the Coloring Matter of "Shiso"

The pigment of shiso 紫蘇 leaves (*Perilla Ocimoides L. var Crispa Benth*) (Japanese special name *Chirimen Shiso*) is extensively used in Japan for coloring "umeboshi", a kind of plum pickle. Kuroda and Wada studied the anthocyanin pigment obtained from the leaves cultivated in Tokyo. Following treatment with several solutions they found two substances that they labeled Shisonin A and Shisonin B. Shisonin was shown to be a mixture of two glucosides, Shisonin A and Shisonin B. Shisonin A was crystalized as its chloride; Shisonin B chloride was confirmed to be a compound of Shisonin A chloride and *p*-coumaric acid: the two components were isolated when Shisonin B chloride was treated with cold alkali in an atmosphere of hydrogen. (Kuroda and Wada (Ku-1030), 1936).

Nasunin, the Coloring Matter of Nasu (the Japanese name of eggplant)

Eggplant (*Solanum Melongena* L. *var esculentum Ness*) is a popular and useful vegetable food from summer to autumn in Japan; the color of its epidermis is noted for the beautiful dark purple which was used as a standard in dyeing in earlier times, called "Nasu blue." Kuroda and Wada were attracted to the study of its pigment. They found that it belongs to the anthocyanins and used the methods they have previously used for analyzing anthocyanin derivatives. "The isolation of the Nasu pigment in a crystalline state was extremely difficult; however, after several experiments a new crystalline glucoside which was named Nasunin by the authors who successfully obtained it as picrate, and finally as chloride. The Nasunin was shown to be 3-bio-di-glucoside of delphinidin", that is, an anthocianidin with two glucose derivatives attached to it.[21] (Kuroda and Wada, (Ku-1030), 1936, p. 283).

A beautiful, realistic drawing of Nasu was presented by the Japanese nineteenth century scholar Udagawa Youan, as depicted in his book of drawings (宇田川榕菴写生植物図譜).[22] As mentioned above, in her article “Rice from the same Pot” Kuroda mentioned Udagawa Youan’s book *Seimi Kaiso*, 舎密開宗 (Introduction to Chemistry), “in which he used William Henry’s original work as the basis for a chemical book translated into Dutch and referring to similar books, along with his own experiences.” (Kuroda Ku-(2012), 1961).

Studies on the Derivatives of Naphthoquinone

Kuroda Chika’s published articles include a series on “Studies of the Derivatives of Naphthoquinone”, numbered from I- XVIII. Their subtitles refer to several sources of naphthoquinones, such as the pigments of Sea-urchins I-XIII, published during 1940-1967. Kuroda and her co-workers studied, analyzed and named seven different naphthoquinone derivatives that differed from each other by hydroxy or methoxy groups on the naphthoquinone rings or as side chains that determined the color, melting point, elemental and dissolution in different solvents. The long synthetic routes and the study of several kinds of sea-urchins received separate studies (Kuroda (Ku-1035) 1940, Kuroda (Ku-1048) 1953, Kuroda (Ku-1056) 1967).

In the final article in this series, published in 1967, Kuroda concentrated on *Pseudocentrotus depressus* (Ag.), the Japanese Aka-Uni or Hirata-Uni, a kind of sea-urchin unique to Japan. The shell, spine, and tube-foot of the sea-urchin are colored in dull red. The structures of four pigments labeled Spinochrome A to Spinochrome D were analyzed and presented. They were separated by column chromatography which gave three zones, colored violet, brownish red and green. They were examined by spectroscopic methods, including UV, visible spectra, infrared as well as NMR spectra. The use of NMR instrument method was not previously reported by Kuroda (Kuroda (Ku-1056), 1967).

The Outer Skin of the Onion Bulb, (1949, 1951)

Kuroda Chika’s first article on “The Pigments and the Related Compounds in the Outer Skins of Onion Bulb” was published in 1949 (Kuroda, (Ku-1040), 1949).

The onion skin was used for dyeing yellow Easter eggs in Germany, and also alum dyeing of woolen, linen and cotton materials. “It was also used for dyeing in Japan in the home industry, giving brilliant golden yellow to commercial “alumite” (aluminum covered with its oxide).” (Kuroda (Ku-2006), 1957). Kuroda and co-author Umeda Masao stated that they wanted to continue and improve the earlier chemical study of Arthur George Perkin and John James Hummel (1896). After a tremendous amount of work they suggested that the yellow crystalline pigments obtained were quercetin, and continued the analytical identification of this matter. As described below, this research led Kuroda to the development of Keltin C, a drug used to treat high blood pressure. [23]

During research using the waste material of the outer skin of onion they confronted extraction difficulties, before they managed to obtain 100g of quercetin crystals, in December 1952. Kuroda filed four patents describing the process of extracting quercetin from the onion skin and making it into tablets, Showa 28- Showa 34 (1953-1959) (See appendix 2). Clinical trials were officially conducted, and it was confirmed that there were no side effects. In 1956 (Showa 31), a commercial product was released as “Keltin C” by the Japan-US Pharmaceutical Co., Ltd. In Kuroda Chika’s memories she was thankful for the successful production of that drug (Kuroda (Ku-2006), 1957. Kuroda Kotaro 2019).

Concerning Kuroda’s work, of which only some parts are mentioned here, the following questions come to mind. Were the methods that Kuroda Chika used the most recent methods of her time? In order to be able to answer these questions this author reviewed articles on similar topics of the same period.

KURODA CHIKA’S RESEARCH AND WOMEN IN SCIENCE IN JAPAN

In the following sections attention is given to two topics that arise from Kuroda Chika’s career. They are: (1) Kuroda Chika’s research in organic chemistry within the realm of organic chemistry in her time. (2) Women in science in Japan during the first half of the twentieth century.

Organic Chemistry

The following is a summary of the processes in chemical analysis and then the choice of synthesis in order to confirm the identity and formula of certain extracted plant’s materials.

Organic Chemistry until 1960

Organic chemistry in the first half of the twentieth century was based on wet and dry methods, mainly analysis, degradation and synthesis. Only after 1960 did instruments such as NMR, and mass spectra began to change the style of laboratory work.

The general approach is presented in Reinhard W. Hoffmann's book *Classical Methods in Structure Elucidation of Natural Products*. In his preface Hoffmann explains: "The structures of many natural products are depicted in standard textbook of organic chemistry as 'established facts.' But how certain are the experimental data that predicate a particular structure given for a natural product. In the case of natural products, the structures of which were elucidated in the period 1860-1960 by classical chemistry methods, the lines of evidence are frequently buried under a plethora of degradation studies, that is, investigations that repeatedly led into culs-de-sac and to revised structure assignments (Hoffmann 2014)."

Hoffmann's observation is reflected in Kuroda's approach, her extraordinary efforts and experiments to establish the correct identification of a substance.

A further example is Todd, on the work of Robert Robinson (Todd 1976). There are sections on anthocyanidins and anthocyanins. The chemical steps for elucidation the precursors of these molecules are described. Many years passed and many teams worked in order to decipher the constitution of materials, natural materials in this case, before the introduction of spectroscopic methods.

As for Japan, organic chemist Nakanishi Koji (1925- 2019), in *A Wandering Natural Products Chemist*, observed: "Organic chemistry in Japan in the early 1950s was undeveloped, and it would take 20 years before it reached a level approaching that of leading western countries. Monographs in Japanese on the electronic theory had just started to appear, but spectroscopy was still mostly unused." (Nakanishi 1991. p. 30). Nakanishi was working at Nagoya in early 1950s, and his description indirectly adds confirmation to the methods reported on in Kuroda's articles.

Analysis and Synthesis

For the various steps in isolations of a specific material one should bear in mind the importance of purity in order to enable identification. Indeed, there is no theoretical explanation by Kuroda as why she chose any route in her experiments. Her choices were based on intuition, knowing the relevant literature, and experience. Kuroda used synthesis in order to confirm her identification and characterization of the material she purified from plants' leaves. In order to validate the molecular structure she used synthesis in order to reach a molecule that resembles the molecule that she analyzed. Starting with molecular building blocks the synthesis progressed by steps until reaching the target product. This approach was used by Robinson and others (cited by Todd 1976, pp. 460-462).

It is of interest to refer to Bernadette Bensaude-Vincent 2021 reflection on analysis and synthesis: "The difference between synthesis and analysis rather emphasizes the significance of empirical knowledge, skills, tacit knowledge and tours de force. If synthesis complements analysis it is more as an exploratory method for discovery than as a method of proof to establish the true value of a hypothesis" (Bensaude-Vincent 2021).

In summary, the characteristics of laboratory life shed light on the work and results of Kuroda Chika's scientific research in her time, from 1916 to 1968: purity; crystallization; taking photos of various crystals' derivatives of the same parent molecules; [24] measuring melting points; elemental analysis; absorption spectra; and analysis and synthesis as complementing each other.

WOMEN SCIENTISTS IN EARLY TWENTIETH JAPAN

The following considers briefly the issue of women in science in Japan in the first half of the twentieth century. Kuroda Chika was a lecturer at Ochanomizu University and undertook her research in RIKEN. Even though it was a very successful career, one may wonder why the laboratory in RIKEN during those entire years was Majima's laboratory, even when he was engaged in Tokyo and only occasionally visited RIKEN. Kuroda's articles were submitted to journals by Majima or others. It is not clear whether this was a regular procedure.

Harrington on Women's Education

In 1987, Ann M. Harrington presented detailed documented information on the development of Imperial regulations concerning women's studies, starting in the Meiji era; the difference between the supporting rules that existed for lower level girls' studies, and hindrances of higher education for women. (Harrington. 1987).

Harrington shows that from 1871, there were several debates on the suitability for higher education for women, and though their conclusions were that even if it was favored, there was not Imperial regulation in support.

> In 1926, the question of women's education was dealt with in the House of Peers (upper house 1871-1947). It was argued that children possessed little economic sense because they were educated by mothers who do not have

> these skills. …Because of shortage of money… it was suggested again that co-education be tried. Against this suggestion there was "the assumption that men's and women's spheres are too different. Japan was not yet ready, it was argued, for a sudden change such as co-education. (Harrington 1987).

How are those events related to Kuroda Chika's career? We have seen that she could receive early education in her home town Saga, and a medium level education in Tokyo. As an intelligent and industrious student, she was recommended by Prof. Nagai to apply for the Tohoku Imperial University entrance examination in 1913. She was accepted and completed her studies, in spite of the Ministry of Education critical letter cited above. Nevertheless, Tohoku University did not enroll women to study for the next ten years. She undertook research in RIKEN for many years, but did not have a designated laboratory of her own. Perhaps this is the reason that we do not know of any student who worked with her and continued her work. So far, this author has not found any reference to Kuroda's complaining about this situation. On the contrary, in several instances Kuroda praised and was most thankful to those who helped her to pursue her research.

Scarcity of Research Positions for Women

The lack of higher studies by women implied fewer chances to undertake research. In 2008, Otsubo Sumiko described and analyzed women scientists' education, family, mentors, employment, and social activism. In the chapter on employment Otsubo states: "In the 1930s, talented women like Yasui (Kono), Tange (Ume) and Kuroda were all recruited by the women's schools from which they graduated. Although they were able to teach and earn a living, these schools more often than not lacked the facilities and funds to support their research. Thus, the women had to make special arrangements, such as using equipment at such institutions as Tokyo Imperial University and RIKEN, in the capacity of unpaid or poorly paid adjuncts." (Otsubo 2008. See also Kozai Y. et al. 2001). Significantly, the specific arrangements for Kuroda Chika in RIKEN during the years of her employment there are not described.

More recently, Furukawa Yasu has gathered information on seventy women who were born before 1920. He followed their educational history in Tokyo Women's Higher Normal School and Japan Women's College, and the role of RIKEN as a place for research. Furukawa considers the mechanism by which women could advance as researchers in the education system. Furukawa gathered statistics of those female studies: by birth, increasing in number from 1870 (2 researchers listed) to 1910-1920 (29 researchers listed); the school or university in which they attended, and the topics studied, e.g. logic, agriculture, humanities and sciences, science and technology and medicine. Furukawa mentions gender perspectives for specific topics chosen by female for their studies, but he gives no further elaboration on this point in these articles. (Furukawa 2020).[25]

Reports by the Chemical Heritage Japan (CHJ) Program

The Chemical Heritage Japan (CHJ) program of the Chemical Society of Japan was established in 2008. Its mission is to recognise world-class chemistry as part of the cultural heritage in Japan, from 2009, and disseminate information about its history, starting with Udagawa Youan's "chemistry –related materials including *Seimi Kaiso*" since 1820. By 2020 fifty seven reports related to academic, technical (manufacturing chemistry) and people had been published. About half of those are related to individuals. Arai Kazutaka thoroughly analyzed those reports. (Arai, in *Kagakushi*, The Journal of the Japanese Society for the History of Chemistry, 2021). Kuroda Chika's biography is briefly told on report no. 19, including her photo (Kuroda 2013). Kuroda Chika is the only woman who is included in these fifty seven short publications. While this certainly reconfirms her acknowledged achievements, one may wonder why there were no other successful women included in that list. For example: Sechi Kato (1893-1989), in 1931 she received a doctorate of science from Kyoto Imperial University, becoming the third woman to receive this degree. In 1942, at the height of the war, she was appointed to be a full-fledged research scientist, performing work on airplane fuels. In 1951 she became RIKEN's first female chief scientist, a position she held until her retirement in 1954 (RIKEN 2019 p.17); Michiyo Tsujimura (1888-1969), who became the first Japanese woman to earn a doctorate in agricultural science. She was appointed to a research position at RIKEN and later went on to become a professor at the newly established Ochanomizu University, a national university for women (RIKEN 2019 p.18); Ume Tange (1873-1955), an expert in food and vitamin chemistry (Furukawa 2021 p.315). More of their scientific career achievements are told in RIKEN's 2019 publication. Were their names considered for getting a CHJ report and dismissed or not considered at all is not known to this author.

NOTES

1. “Nagai Nagayoshi (1844-1929) was a pioneer elder of chemistry and pharmacology in Japan. He was a student at the University of Berlin, where he studied physics, botany and chemistry, and then undertook research in A. W. Hofmann’s laboratory on organic chemistry, between 1870-1884; In Meiji 17 (1884) after 14 years in Germany he returned to Japan. In Tokyo Imperial University Nagai joined the physics and medicinal chemistry departments, and was in charge of teaching. Moreover, in Meiji 34 he was in charge of home chemistry at the Faculty of Home Economics, Japan Women’s College.” (*The Chemical Society of Japan, 2003. A 125-year Quest for Excellence 1873-2003*. Kikuchi and Siderer, 2021).

2. Transcript of the hand written letter and its printed version (received with thanks from Tohoku University Library Archive; and email from Tohoku University Archives):
本年貴学理科大学入学志望者中数名ノ女子出願致居候様聞及ヒ候処右ハ試験ノ上撰科ニ入学セシムル御見込ニ候哉　元来女子ヲ帝国大学ニ入学セシムルコトハ前例無之事ニテ頗ル重大ナル事件ニ有之大ニ講究ヲ要シ候ト被存候ニ付右ニ関シ御意見詳細承知致度此段及照会候也
大正二年八月九日 Taisho 2nd year (1913) 9 August
文部省専門学務局長　松浦鎮次郎
Ministry of Education Specialized Academic Affairs Bureau Director Matsuura Shigejiro
東北帝国大学総長　北条時敬殿 President of Imperial Tohoku University Houjou Tokiyuki.

3. Kuroda Kotaro email to Y. Siderer, 4 February and 21 November2021.

4. Enrakuken was a fashionable western-style restaurant situated diagonally across from the red gate of Tokyo Imperial University.

5. “The only reference I have been able to find to Dr Chika Kuroda is in a pamphlet entitled ‘The Development of Organic Chemistry at Oxford, Part 1’ by JC Smith where two Japanese students are mentioned as under the supervision of ‘Clemo’…. As far as I have been able to discover, Clemo may refer to George Roger Clemo, a DPhil student within the department at the time.” (Correspondence with the Bodleian Library, Assistant Keeper of the University Archives 30 March 2021).

6. (Ku-6018) Members in Fig. 4. 加藤文雄 Kato Bunyuu is in the center, near Kuroda, celebrating his going to Manchester University as a foreign student. He was apparently a foreign student of Nichiren Buddhism. Other persons in the photo, from left to right:田中寛一（Tanaka Kanichi) Tokyo Higher Normal School (Presently University of Tsukuba); 神保格 (Jinbou Kaku) Tokyo Higher Normal School; 手塚 ？ (Tezuka ?) army major; 皆川正禧 (Minagawa Masaki) Mito High School (Presently Ibaraki University) 島村盛助 (Shimamura Morisuke) Yamagata High School (Presently Yamagata University); 田中秀央 (Tanaka Hidenaka) Kyoto Imperial University. Hidenaka Tanaka appears to have studied at Oxford, but we do not know about the others. (Ochanomizu University History Museum, email, 6 June 2022)

7. The address of the dormitory is verified in the Lodging House Delegacy list held by the Bodleian Library of Oxford University. “I have now had a chance to look through our records of the Lodging House Delegacy with mixed success. The records confirm that Mrs. Whitmarsh was a lodging house keeper at 139 Woodstock Road but we do not hold any records which list the names of the tenants who resided there at any period.” (Correspondence with the Bodleian Library, Assistant Keeper of the University Archives. Another source revealed that the house is no longer standing there (Anne and Phillip Harries, email of 26.8.2021).

8. In this article Kuroda outlined the history of chemistry in Japan, starting with Udagawa Youan of Tsuyama domain, who, she continued, “from a translation of an original book from the Englishman [William] Henry and also added his own experience he compiled his chemistry book *Seimi Kaiso*. However, he was not teaching in school.” She wrote about the distinguished Japanese scholars and important events during the years.

“However, the content seems to have been extracted from the writings of Sakurai Jōji and Majima Riko.” (Email correspondence with Information Development Section librarian, Ochanomizu University Library. 4.11.2021).

9. A photo of Robinson presenting his lecture in Japan in “around 1953” is included in Nakanishi’s book, **1991**, 31.

10. Kuroda received New Year greeting cards from Robinson each year; she reproduced the cover image of the 1956 card and the 1960 card, in her 1957 and 1961 memoirs, respectively. The 1956 image is a drawing of a large building; on its reverse is in hand “Sir Robinson laboratory”, with laboratory written in kanji. It is not clear which laboratory it was. The 1960 greeting card that Kuroda refers to shows a monk with a simple telescope looking out through a window. Three more cards were recently found in Tohoku University archive, and will be discussed elsewhere. Robinson sent his cards to her university or home address: Dr. C. Kuroda 5-990 Komagome Toshsima-Ku, Tokyo, Japan.

11. In his 1955, book following his 1953 lecture, Robinson referred to Kuroda Chika’s work by her name on p. 42. He cited her work on Carthamin (XLIII drawing)

from *Carthamus tinctorius* (Safflower) on p. 39: Ref. 87 p. 130 Kuroda C. Proc. Imp. Acad. Tokyo, 1929. **5**, 32, 82, 86.

12. "The library was closed in 2002 because the number of users decreased due to the improved availability of books in various universities." (Kuroda Kotaro email, 8.3.2022).

13. The Order of the Precious Crown (宝冠章, *hōkanshō*) is a Japanese order, established on January 4, 1888 by Emperor Meiji of Japan. Since the Order of the Rising Sun at that time was an Order for men, it was established as an Order for Women. (Wikimedia 29.10.2022)

14. Link to Monument of Great Figures (Spot 8) Pioneers of engineering and scientific fields Shida Rinzaburo/Kuroda Chika: http://saga-travelsupport.com/en/spot/detail.html?id=1163

15. Ocha 1. 学術論文リスト論文 p. 32. Ref. (Ku-1001), (in Japanese), 紫根の色素について、 Concerning purple root pigment 東京化学会誌、 **1918**, 39, 1051.

16. A list of Kuroda's publications in Ochanomizu University website numbered (Ku-x0yz). https://www.lib.ocha.ac.jp/archives/en/researcher/kuroda_chika.html?grid=txtlink

17. Carthamin is a natural red pigment derived from safflower (*Carthamus tinctorius*), earlier known as carthamine. It is used as a dye and a food coloring. Safflower has been cultivated since ancient times, and carthamin was used as a dye in ancient Egypt. It was used extensively in the past for dyeing wool for the carpet industry in European countries and to create cosmetics for stylish women, geisha, and kabuki artists in Japan, where the color is called Beni (紅). After 1859-60, it competed with the early synthetic dye fuchsine as a silk dye. (Wikipedia 30.10.2022).

18. *Tsuyukusa* 露草. A photo of the flower is shown in Ran Levy's book *Wild Flowers of Japan*, *A field Guide* **1995**, p. 150. Recently, the author of this article found the same flower in her garden.

19. In Kuroda's article on The Constitution of Awobanin and Awobanol (1936), (Ku-1029), p. 267 she included crystals' photos of: Fig.1 Awobanin picrate; Fig. 2 Awobanin A chloride; Fig. 3 Awobanin aglucone.

20. "The 'Kuromamin' was found to be identical with chrysanthemin, namely, cyaniding 3-monoglucoside. It took a long procedure. … Melting point 182°C and several methods used to decide the place in which the glucose molecule is attached. Absorption spectrum of Kuromamin chloride and chrysanthemum chloride also proved to be quite identical**...**" (Kuroda and Wada, (Ku-1026), 1935).

21. For the formula of delphinidin, see: https://www.frontiersin.org/files/Articles/746881/fnut-09-746881-HTML/image_m/fnut-09-746881-g005.jpg

22. In Udagawa Youan's album of plant drawings 榕菴写生植物図譜 *Youan shasei shokubutsu zufu* the eggplant, called Nasu in Japanese, and its flowers are beautifully depicted. One can appreciate the strong purple color that attracted Kuroda Chika to investigate the chemical nature of its pigment.

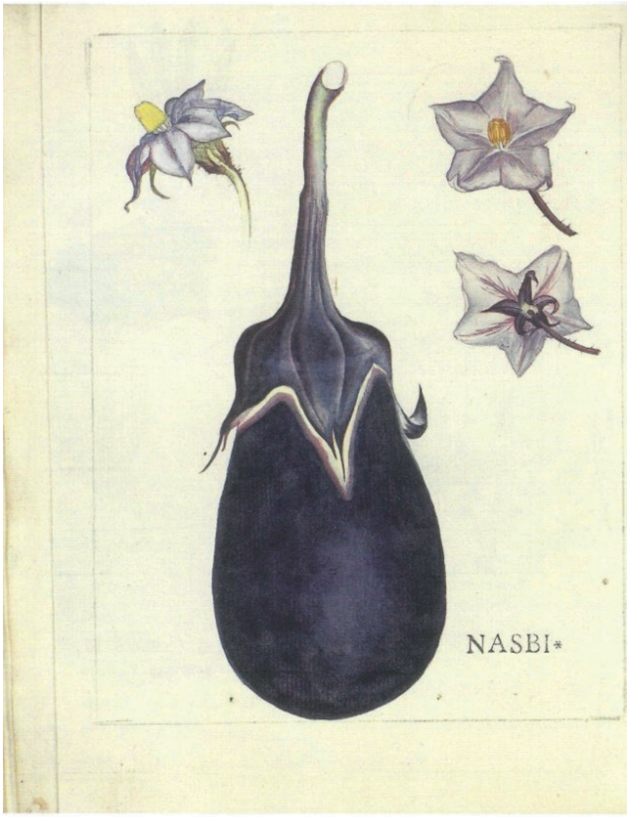


図 74（38b）ナス（*Solanum Melongena* L. var. *esculentum* Nees　ナス科）
「NASBI ＊」と印字（木活字）されている。

Figure 13. Udagawa Youan's eggplant painting (Endo et al. 2014, p. 611) (Photo courtesy of Takeda Science Foundation).

23. Kuroda's description of the steps to produce Keltin C.

"After re-examining the literature, I read that A.G. Perkin found that the onion skin contained 2% crecetin. Onion skin has long been used as a dye in Europe. Ruthin contained in buckwheat, etc. It was known that the glycoside of crecetin was effective in treating hypertension, but the November 1951 issue of Pharmaceuticals, which was read during the New Year holidays in 1952 (Showa 27), from a report in the magazine, I intui-

tively thought that crecetin obtained from onion skin would be used as a hypertensive agent…."
"Although 1 kg of skin was used every day in the experiment, it was only 10g in a basket cup, and it was extremely difficult to obtain multiple outer skins every day, but there was also the effort of many collaborators at this time." (Kuroda Ku-2006, 1957).

24. For instance, in her article on "The Constitution of Awobanin and Awobanol" (1936), (Ku-1029) p. 267) Kuroda shows photos of crystals of: Fig.1 Awobanin picrate; Fig. 2 Awobanin A chloride; Fig. 3 Awobanin aglucone.

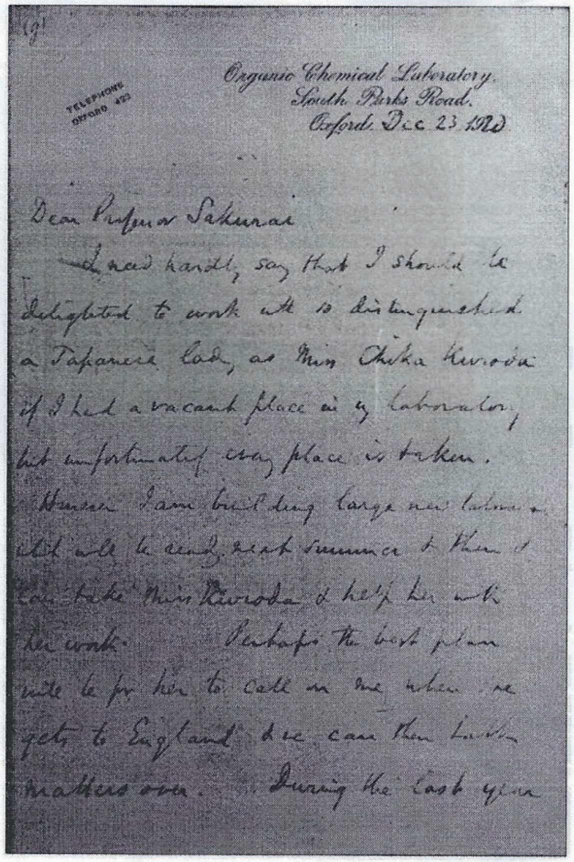
25. Furukawa Yasu seminar handout of 8 December 2020, titled: 東工大火ゼミ 2020.12.8 資料 日本における女性科学者の誕生：戦前期研究者の経歴からの一考察 古川 安 *Birth of Female Scientists in Japan: A Study from the Career of Prewar Researchers* (in Japanese).

APPENDICES

Appendix 1. W. H. Perkin Jr.'s Letter to Professor J. Sakurai concerning Kuroda Chika, Oxford, 23 December 1920

Transcription of Prof. W.H. Perkin writing to Professor J. Sakurai Oxford December 23 1920:

Organic Chemical Laboratory
South Parks Road
Oxford Dec. 23 1920
Telephone
Oxford 423
Dear Professor Sakurai
A new hurdle, sorry that I should be
delighted to work with so distinguished
a Japanese lady, as Miss Chika Kuroda
if I had a vacant place in my laboratory
but unfortunately every place is taken.
However I am building a large new laboratory
It will be ready next summer and then I
can take Miss Kuroda and help her with
her work. Perhaps the best plan
will be for her to call on me when she
gets to England & we can then handle
matters over. During the last year
[page ends]

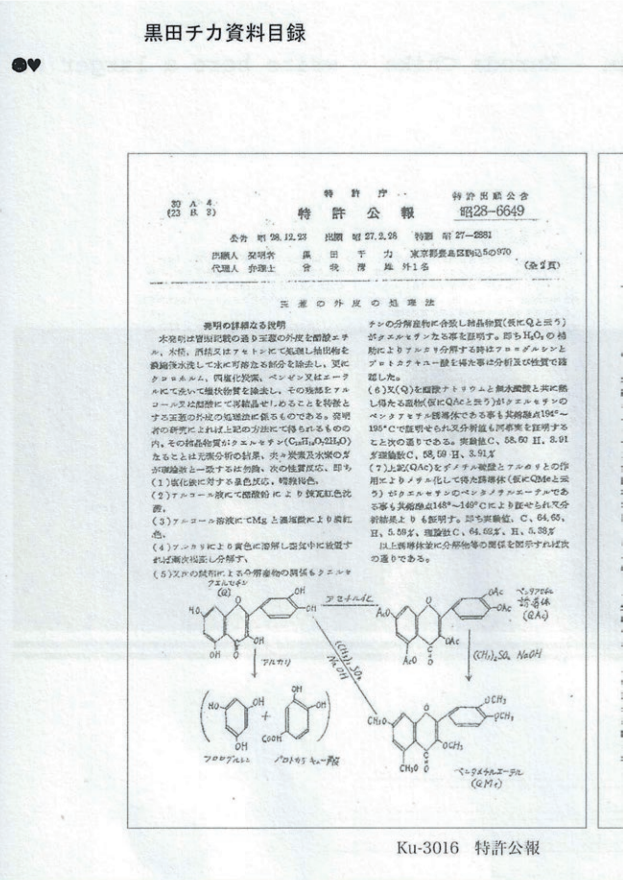


(9)
Organic Chemical Laboratory,
South Parks Road.
Oxford. Dec 23 1920
TELEPHONE
OXFORD 423
Dear Professor Sakurai
I need hardly say that I should be
delighted to work with so distinguished
a Japanese lady, as Miss Chika Kuroda
if I had a vacant place in my laboratory
but unfortunately every place is taken.
However I am building large new laboratories
which will be ready next summer & then I
can take Miss Kuroda & help her with
her work. Perhaps the best plan
will be for her to call on me when she
gets to England & we can then talk
matters over. During the last year

Ku-4301 パーキンの手紙

Figure 14. (Ku- 4301), W. H. Perkin Jr.'s Letter to Professor J. Sakurai concerning Kuroda Chika. December 23 1920.

Appendix 2. Kuroda Chika's first patent for the extraction of material from the outer skin of onion, 1953. Chemical structures in the patent seem to suggest how chemicals in an onion skin change in the baking process



黒田チカ資料目録

30 A 4
(23 B 3)

特許庁
特許公報
特許出願公告
昭28-6649

公告 昭28.12.23 出願 昭27.2.28 特願 昭27-2881
出願人 発明者 黒田チカ 東京都豊島区駒込5の970
代理人 弁理士 [illegible] 外1名 （全2頁）

玉葱の外皮の処理法

発明の詳細なる説明

本発明は冒頭記載の通り玉葱の外皮を酢酸エチル、木精、酒精又はアセトンにて処理し抽出物を濃縮後水洗して水に可溶なる部分を除去し、更にクロロホルム、四塩化炭素、ベンゼン又はエーテルにて洗いて蠟状物質を除去し、その残部をアルコール又は酢酸にて再結晶せしめることを特徴とする玉葱の外皮の処理法に係るものである。発明者の研究によれば上記の方法にて得られるものの内、その結晶物質がクエルセチン($C_{15}H_{10}O_7 2H_2O$)なることは元素分析の結果、夫々炭素及水素の%が理論数と一致するは勿論、次の性質反応、即ち

(1)塩化鉄に対する呈色反応，暗緑褐色。
(2)アルコール液にて醋酸鉛により鮮紅色沈澱。
(3)アルコール溶液にてMgと濃塩酸により深紅色。
(4)アルカリにより黄色に溶解し空気中に放置すれば漸次褐変し分解す、
(5)又他の試薬による分解産物の関係もクエルセチンの分解産物に合致し結晶物質(仮にQと云う)がクエルセチンなる事を証明す。即ちH_2O_2の補助によりアルカリ分解する時はフロログルシンとプロトカテキュー酸を得た事は分析及び性質で確認した。
(6)又(Q)を醋酸ナトリウムと無水醋酸と共に熱し得たる誘導体(仮にQAcと云う)がクエルセチンのペンタアセチル誘導体である事も其熔融点194°～195°Cで証明せられ又分析値も同事実を証明することと次の通りである。実験値C、58.60 H、3.91%理論数C、58.59 H、3.91%
(7)上記(QAc)をヂメチル硫酸とアルカリとの作用によりメチル化して得た誘導体(仮にQMeと云う)がクエルセチンのペンタメチルエーテルである事も其熔融点148°～149°Cにより証せられ又分析結果よりも証明す。即ち実験値、C、64.65、H、5.59%、理論数C、64.52%、H、5.38%

以上誘導体並に分解物等の関係を図示すれば次の通りである。

Ku-3016 特許公報

Figure 15. (Ku-3016) Kuroda patent 1953 玉葱【たまねぎ】の外皮の焼瑾法 "the way to bake an onion [and make it] like a beautiful ball".

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Book Reviews

Review of *A Cultural History of Chemistry*. Peter J. T. Morris and Alan Rocke, eds., Bloomsbury Academic: London, 2022

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When presented with a new multivolume series on the history of chemistry, one cannot help but compare it to J. R. Partington's masterful four-volume *A History of Chemistry*. The new six-volume *A Cultural History of Chemistry* reviewed here, however, is really a different beast and should not be viewed as a simple attempt to update Partington's previous series. As highlighted by series editors Peter Morris and Alan Rocke in the Series Preface that begins each volume, "This is not a conventional history of chemistry, but a first attempt at creating a cultural history of the science." As such, this series brings together 50 contributors in an effort to present the first detailed and authoritative survey of the impact of chemistry on society, as well as how society has influenced and impacted chemical practice and thought. Spanning from the earliest applications of the chemical arts in antiquity up through the present, this cultural history is split into six volumes, each covering a specific time period, with the structure of each volume consistent throughout the series. As such, each volume begins with an introduction, followed by the identical chapter titles: Theory and Concepts; Practice and Experiment; Sites and Technology; Culture and Knowledge; Society and Environment; Trade and Industry; Learning and Institutions; Art and Representation. As a result, this gives the reader the choice of focusing on a specific time period within a single volume, or following a chosen theme across history by reading the corresponding chapter in each of the six volumes. Each volume concludes with both a Bibliography and an Index, with all six volumes providing a combined 1728 pages of material. Separate reviews for each of the six volumes are given below, followed by some concluding remarks about the overall six-volume effort.

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Volume 1: *A Cultural History of Chemistry in Antiquity.* Marco Beretta, ed. (review by S. C. Rasmussen)

The initial volume covers by far the largest timespan, tackling nearly 4000 years over the period from 3000 BCE to 600 CE. The challenge of this task is highlighted by editor Marco Beretta in the introduction, particularly considering the limited surviving written sources from this period of history. Beretta argues that it is this scarcity of literary sources, in comparison to the wealth of archaeological objects, that has led to the focus on the material background of the chemical arts in previous attempts to cover this period by authors such as Partington. Still, in addition to the many practical achievements evidenced during antiquity, Beretta gives a good overview of the literary genre available that can be used as a lens into this period of time. The following chapters are then collaborations between the four contributors of this volume, with each author covering one of the primary cultures of focus: Egypt by Sydney Aufrère; Mesopotamia by Cale Johnson; Greco-Roman by Matteo Martelli, with Beretta providing overarching conclusions. This uniform structure for each chapter thus provides additional consistency throughout the various subjects discussed. Chapter one attempts to make connections between mythology and chemical theory, particularly within the Egyptian civilization. While the natural philosophies of the Greeks and Romans were more independent of such mythological influences, they did incorporate ideas and concepts from the older civilizations. Chapter two then delves into the technical practices during this period, including the wealth of chemical species applied, with discussion of the names and symbols used to distinguish the reagents, species, and products involved. Chapter three goes on to analyze the state of laboratories and the technological advances found within antiquity. For those that have studied the history of chemical technology of this period, this chapter is perhaps the most traditional of those offered in the volume, and offers a good overview of technical workshops and their products. Chapter four then reflects on the influence of religion on chemical practices, with focus on connections between the gods of a given culture and various activities of the craftsman. Chapter five then discusses the impact of the growing chemical technology on the local environments, both in terms of overexploitation of resources and the effects of toxic byproducts released during various operations. For a topic so prevalent in the discussion of modern chemical practice, it was very eye-opening to see these relationships mapped onto practices in antiquity. Chapter six covers the processes of trade between neighboring societies as a result of progresses made in the production of goods via chemical processes. This of course included not only the products themselves, but minerals, ores, and other reagents needed for their production. Chapter seven then discusses the development of recipes and the production of recipe books, which served the dual purpose of transmitting knowledge to future generations, as well as providing better control to the access of this knowledge. The final chapter then discusses the relationship between various practices and their artistic representation, both visually and in words (poems, songs, etc.). As illustrated by the quick summary given above, this volume brings much that is new to the study of this period of chemistry, providing new context to consider when reflecting on the processes and technologies developed during antiquity. While it would have been nice to have included aspects of the Far East, Beretta makes good arguments for why this was not included in the current effort. Regardless, this volume is highly recommended for anyone with an interest in this earliest period of chemical practice.

Volume 2: *A Cultural History of Chemistry in the Middle Ages.* Charles Burnett and Sébastien Moureau, eds. (review by R. H. Crabtree)

Sébastien Moureau's introductory chapter sets out the geographic scope of volume 2 as the Islamic South, the Orthodox East and the Latin West over the period 400-1500 C.E. It also outlines the grave difficulties facing students of the period, such as widespread pseudepigraphy, shifting nomenclature, allegorical symbolism and coded language. Applications to medicine, dying and transmutation are discussed and linked to alchemical principles and classifications, such as the familiar four element theory. The operations chapter that follows highlights the difference between craft and alchemy: both sought useful products but the latter also sought theoretical understanding. Various types of distillation, calcination, dissolution, coagulation and sublimation are also covered along with the equipment needed for each. Difficulties arise in interpreting the texts because they embody unstated 'know-how' that is hard to reconstruct. The third chapter on laboratories contrasts the abundance of relevant images in Latin sources with their paucity from Arabic ones, and even where they do exist in the latter they are often allegorical. There is also a useful extended discussion of archaeological finds with diagrams and images. Another avenue for exploration of the topic, although still too rarely used, is experimental, by design of historical replications. As for laboratories, domestic spaces seem to have been most common, but artists' depictions of them may owe more to invention than to reality. Archaeology indicates that abbeys may have housed workshops for preparation of inks for the scriptorium although this may have been a craft rather than a true alchemical tradition. Castles and noble urban dwellings have also provided similar evidence. Various specific tools, types of furnace and items of apparatus are listed or described, with the helpful addition of their Arabic and Latin names. Chapter 4 provides an interesting discussion of alchemy's relations with other natural philosophic efforts along with contemporary criticism of the practice. Already in Arabic mss., alchemy is not always listed among the sciences and its validity can be disputed. Because it had not existed in Aristotle's time, so not discussed by him, this had the effect of giving alchemy a secondary standing. Its relationship to the occult sciences of astrology and magic also hurt its standing, although many continued to hold the occult sciences as authentic. The close association of alchemy with medicine, especially in connection with Paracelsian doctrines and the analogy between an elixir curing people and the philosophers stone 'curing' metals is noted. The interconnection with religious ideas, so important in the period, is not neglected, as in the discussion of the quintessence and the special affinity of alchemy with Shiite Islam. In the Latin West, both detractors and supporters of alchemy are found among religious scholars, Roger Bacon being a notable adherent, Ramon Llull taking the opposite position. Mary the Jewess is identified as a rare female adept, remembered today in the French term 'bain Marie' for an aqueous heating bath. Chapter 5 discusses the place of alchemy and the alchemist in Society. For example, as a supposedly purely practical art without theoretical underpinning, Buridan thought it had no place in a monastery, but some monasteries did have alchemical connections. Numerous Arabic and European royal courts also encouraged alchemical efforts. A major concern was economic: currency minted with false alchemical gold would be equivalent to counterfeiting. The next chapter discusses medieval chemical technologies with case studies on metal and glass production, thus going beyond pure alchemy into trade and commercial concerns. Educational concerns follow next with a discussion of oral and manuscript transmission of the art, noting the problems posed by semantic fluidity of alchemical terms and the problems with later alchemists composing alchemical texts falsely attributed to well-known scholars, such as Llull, who in reality opposed the art. Perhaps the most original chapter is the final one on art, in which the images, often allegorical, found in the manuscripts are discussed and illustrated. In summary, this volume will be a valuable addition to institutional and personal scholarly libraries.

Volume 3: *A Cultural History of Chemistry in the Early Modern Age.* Bruce T. Moran, ed. (review by A. Greenberg)

The third volume traverses the sixteenth and seventeenth centuries. Paracelsus, born in 1493, revolutionized the medical paradigm; in 1597, Libavius published the first chemistry textbook; in 1697 Stahl published the phlogiston theory of combustion. The Introduction, by volume editor Bruce T. Moran, outlines historical and technical upheavals during the Renaissance. The cabinet of medicines enriched by discovery of New World plants and animals; Luther and the Protestant Reformation; Dutch East India Company and economic growth of Europe; Becher, chemist, and commercial advisor to the Holy Roman Emperor. Chapter One (Theory and Concepts…), by Lawrence M. Principe, seemingly "squares the circle" by accessibly contextualizing the four chemical theories of this era: Aristotle's hylomorphism: "forms" imposed upon "prime matter"; four elements; mercury and sulfur; and a "quasi-particulate conception of the structure of matter". To add to complexity, Principe describes variations and overlaps of these theories. William Newman and Principe reintroduced the archaic term "Chymistry" to remove the artificial barrier between serious alchemy and chemistry. Practice and Experiment… by Joel A. Klein emphasizes the development of chymistry as a practice and theory of analysis and synthesis. Beginning with pseudo-Geber, continuing with the sixteenth-century works of Agricola and Brunschwig, technologies of assaying and distillation became widely available to artisans and adepts. Indeed, Paracelsus considered the human body as a process of spagyria, a disassembly and reassembly of the tria prima (mercury, sulfur, salt). Sennert chemically separated gold-silver alloy, precipitating a silver salt and then recovering the pure metal. The gravimetric work of van Helmont began to make analysis quantitative. Laboratories and Technology…, by Donna Bilak, beautifully describes and illustrates the laboratory technology of the mid-seventeenth century with woodcuts of apparatus from LeFèvre's Compendious Body of Chemistry (1662) and a painting by David Teniers the Younger. But the foibles, failures and road to poverty of gold makers are illustrated by Bruegel painting engraved by Galle, and allegorical secrets illustrated in Atalanta fugiens (1618), by the musical alchemist Maier, in which a washerwoman launders philosophical matter to remove impurities.

Culture and Science…, by Andrew Sparling, describes the communication of chymical information by peripatetic chymists, including Paracelsus and Kunckel, a century later. During this period books and pamphlets found avid readership. Boyle described, in print, witnessing transmutations and Newton was an avid reader of the Harvard-trained alchemist Starkey. Chemistry and Environment…, by William Eamon, is a very ambitious, wide-ranging chapter emphasizing the role of distillation, from purely commercial to charitable, pigments, mining, domains of women, the exponentially-increasing role of books including books of secrets, chemical imagery, warfare, the environment among topics. Trade and Industry…, by Tilmann Taape, returns to the economies of distillation, including woodcuts of apparatus from the fifteenth and sixteenth centuries. Plat's Jewell House of Art and Nature (1594) is cited for the clarity of presentation of works culled from many sources. In Learning and Institutions…, Margaret D. Garber offers examples of the roles of European noble courts and universities, in fostering theory and practice. Physicians played an important role as liaisons between the courts and universities such as those in Prague, Jena, Wittenberg, and Leiden as well as in France and England. Arts and Representation…, by Elisabeth Berry Drago, employs a woodcut, an engraving and eleven paintings (in black and white), as well as excerpts of poems in order to illustrate the chymical mysteries, glories, foibles, and frauds, as imagined by the artists of the period. This third volume, although replete with names, theories, processes and historical perspective, is a must for any institutional collection as well as for individual libraries of those interested in a truly interdisciplinary approach to the history of chemistry.

Volume 4: *A Cultural History of Chemistry in the Eighteenth Century.* Matthew Eddy and Ursula Klein, eds. (review by A. Greenberg)

According to its cover, this fourth volume in the series covers the period from 1700 to 1815. Emerging as a modern science, chemistry achieves respect in cultural and academic circles and contributes to material wealth as laboratory and workplace skills improve agriculture, pharmacy, medicine, manufacture, and the fine arts. The Introduction, by the editors, describes the institutionalization of chemistry in eighteenth-century Europe in the context of the Enlightenment. A major school of thought attributes the chemical revolution largely to Lavoisier and his contemporaries. Another school conceives Lavoisier's breakthroughs in a wider context that developed gradually throughout the eighteenth century. Chapter One (Theory and Concepts…), by Ursula Klein, navigates readers through the complexities of the earliest chemical theories which maintained their hold into the eighteenth century: Greek atomists, Aristotelian philosophers, and Paracelsians. Stahl is a crucial link blending mechanical-corpuscular theories with theories based upon four principles comprising matter, transforming Becher's seventeenth century theory into phlogiston-explaining combustion and calx formation as one. Stahl linked his chemistry with affinity tables. The concept of the chemical element was critical and Macquer (1753) was an important pioneer anticipating Lavoisier's definition of a chemical element. Even so, Lavoisier conceived of gaseous oxygen containing the element oxygen with the imponderable element caloric, the latter released as heat when oxygen combined with, say, mercury. In Chapter Two (Practice and Experiment…), Victor D. Boantza defines eighteenth-century terms of chemical operations, most still familiar but some obscure (e.g., collature, filtration through a hair sieve) and illustrates apparatus from the 1757 edition of Lemery's Cours de chymie. Plants were exploited using "wet chemistry", e.g., solvent extraction, and more often by "dry chemistry", e.g., distillation, to produce medicines. Mineral chemistry led to Geoffroy's affinity table (1718), devoid of theory but the first ordering of chemical (and some physical) properties. Pneumatic chemistry, pioneered by Hales, Brownrigg, Cavendish and Priestley "set the table" for Lavoisier. Chapter Three (Laboratories and Technology…), by Marco Beretta, makes the important point that even university laboratories started with close ties to artisans, businesses and industries. Pharmacies had the greatest initial impact on laboratory techniques. A plate from the 1763 Encyclopédie depicts a mid-eighteenth-century laboratory. Beretta emphasizes Macquer's impact on theory and experiment including his 1766 Dictionnaire. The remainder of this chapter is devoted to pneumatic chemistry including illustration of Lavoisier's complex gasometer. Beretta describes Scheele's contributions, surprisingly little mentioned elsewhere in this volume. Chapter Four (Culture and Science…) by Bernadette Bensaude-Vincent describes the increasing fascination of professionals and the lay public with chemical demonstrations (no longer "the mere province of 'sooty empirics'") and lectures by Shaw, G.-F. Rouelle, and Cullen. Venel's essay and the illustrations in the Encyclopédie further popularized chemistry. At Edinburgh, Cullen's successor Black trained a generation of chemistry professors including those at the best American universities. The concluding section examines chemistry-inspired philosophies. In exploring Chemistry and Daily

Life, Matthew Daniel Eddy (Society and Environment…) takes an amazingly inclusive approach describing Patronage, Sociability, Consumerism, Politics, The Environment and Ecology. Particularly illuminating was the discussion of the interplay between chemistry and consumerism in European attempts to uncover the secrets of Chinese porcelain. Pott's unsuccessful attempts to crack the Meissen Company's formulation of porcelain led to the first widely-recognized chemical classifications of the earths. Chapter Six (Trade and Industry…) by Leslie Tomory begins with the mechanization of textile production during the industrial revolution, increasing the demand for innovation in and production of chemicals for bleaching, dying and fixing dyes to fabrics (salts termed mordants). In the section on metallurgy, we learn that Europe was initially dependent and eventually inspired by Indian technology as a source of high-quality zinc for making brass. A section on domestic goods is followed by one on chemical industries including gunpowder buoyed by Lavoisier's encyclopedic research on saltpeter. John C. Powers (Learning and Institutions…) describes the evolution of didactic chemistry from artisan chemists in the early eighteenth century toward university professors, noting that in 1720 there only six chemistry professorships in German universities that increased to twenty-eight in 1780. Apprenticeships were common in the early eighteenth century, but the quality of training was highly variable, and the increasing sophistication of chemical science demanded sounder didactics including theory. There were public lectures, for example G.-F. Rouelle, at the Jardin du Roi, that were often open free to the public and private instruction for those who could afford it. Boerhaave, at Leiden, presented a fairly modest course for university students but a more comprehensive course for paying customers. Throughout the eighteenth century, textbooks evolved from purely practical to incorporate theory, culminating in Lavoisier's 1789 Traité. Art and Representation…, by John R.R. Christie, illustrates the growing fascination among growing urbane middle and upper classes, depicting fascination with the science as well as opportunities for satire from such as Gillray. Perhaps the apex in chemical artwork is the very large, much-analyzed portrait by David of the Lavoisiers in the Metropolitan Museum of Art. Among literary representations, considerable emphasis is placed on the radical English poet Anna Letitia Barbauld, who remained Priestley's correspondent well beyond his emigration to America following the 1791 "Priestley riots" in Birmingham. As Christie comments: "Priestley's appearances in Barbauld's poetry received gentler and more positive handling than from the carricaturists of the 1790s."

Volume 5: *A Cultural History of Chemistry in the Nineteenth Century.* (Edited by Peter J. Ramberg, ed. (review by R. H. Crabtree)

The introduction to Volume 5 notes the high points of a century, the 'long' 19th, that may mark the high point for chemistry as a whole. This takes us from debates on atomism to the puzzling phenomenon of radioactivity. Whether Dalton's atoms were real, as he thought, or merely useful concepts, remained a continuing debate throughout. The middle of the century saw both Mendeleev's Periodic Table and the rise of organic chemistry and the dyestuff industry dependent on it. By the end of the century, professionalisation of the field was far advanced with universities creating laboratories for teaching and research, especially in Germany where the chemical industry also flourished, for example in dye production. A theory chapter follows that traces the development of the ideas of atoms, equivalents and formulas and argues that Berzelius and Davy were the most influential figures of the early period. The finding that Liebig's silver fulminate and Wöhler's silver cyanate had the same chemical composition led Berzelius to coin the term isomerism and explain this result in terms of a differing atomic arrangement. The rise of physical chemistry in the same period is discussed, including such figures as Gibbs, foreshadowing the rise of the US as a scientific power in the next century. Ostwald, denying physical atoms, used thermodynamics as a replacement scaffold for discussion of the experimental facts. Spectroscopy came into being with an early application of elemental analysis of the solar atmosphere by comparison of the solar spectrum with laboratory standards. Chapter two charts the development of experimental practice, including analysis, lab equipment, the representation of molecules, a section that includes an image of Kekulé's own molecular models. The next chapter contrasts the relative simplicity of the chemical laboratory in 1800, often in a private space, with the vastly more complicated situation by the end of the century when labs were almost always institutional and used not just for research but also for teaching, Germany taking the lead. Oxford resisted adding experimental sciences to its curriculum perhaps because most of its graduates took up clerical appointments. Chemistry, it was also felt, did not fit with the intellectual activities of the University. Activity also spread to the Americas: by the end of the period, Harvard had a Chemistry Department with 14 teaching staff and more than 300 students engaged either in undergraduate or graduate studies, thus approaching closely to the modern pattern. The next chapter more directly justifies the cultural history orientation of the whole work by looking at the influence of chemistry on the wider world. Jane Marcet's 'Conversations on Chemistry' popularized chemistry in 16 British editions from 1805 to 1853; public lectures, such as ones by Tyndall, Frankland and Faraday, were very well attended, including by Marcet herself. Faraday published his 'Chemical History of a Candle' in 1861, a work that, remarkably, is said to have never been out of print since. Applications to agriculture were the topic of several books in the period intended to encourage scientific farming, such as Liebig's 'Agricultural Chemistry'. Anaethesia in medicine also depended on chemistry, for example Queen Victoria much appreciated being given chloroform in her last two confinements. Advances in forensic medicine included the celebrated Marsh Test for arsenic and Orfila's test for blood stains. Religious influences were still evident--Prout, for example, pointed to Dalton's Laws as examples of divine wisdom. Mary Shelley's celebrated novel, 'Frankenstein', published as early as 1818, includes references to then-current popular science. The rise of photography from the 1840s relied on chemistry for development of the images and of course the dye industry led to much brighter clothing becoming available. The next chapter continues the theme of the influence of chemistry on society with a discussion of the numerous ways in which this was felt. For example, how the supply of clean water, and pure food and drugs was assisted by analytical chemistry. As for industry, we are told that chemists were only employed in significant numbers after 1870, because prior industrial practice differed little from traditional craft procedures. Chemical industry was strongly represented in the trade fairs that followed the Great Exhibition of 1851. Explosive manufacture was perfected in the same period, an advance that was to have a big impact in both peace and war. Thanks to the the foundation of women's colleges, such as Girton at Cambridge in 1869 and Vassar in 1865, women made significant contributions to research late in the century, but were sadly still excluded from many professional bodies. Chapter 6 covers chemical industry, with a close look at pharmaceuticals and fertilizers. The next chapter covers learning and institutions, with special attention to popularization and the role of chemical societies and their journals. The final chapter takes the 'mad scientist' as its theme, not a particularly appealing one to this reviewer. As a general point, a common problem with edited volumes is evident here: some material is duplicated in different chapters but otherwise this work provides a view of chemical history from an original viewpoint and will be a valuable addition to institutional and personal scholarly libraries.

Volume 6: A Cultural History of Chemistry in the Modern Age. Peter J.T. Morris, ed. (review by R. H. Crabtree)

The final volume has the formidable challenge of covering the period from 1914 to the present. Some of the themes include the rise of mechanism and of computational chemistry in explaining the course of reactions and of X-ray diffraction and of the common spectroscopic techniques for determining structures. The development of oral contraceptives influenced cultural behavior and demography and the rise of chemical engineering and green chemistry had a direct influence on industrial practice. Links with biology and physics were formed with the rise of molecular biology and chemical physics and links with industry came from natural products, polymers, silicones, solid state chemistry and catalysis. Isotope dating gave human development an absolute timescale and even determined the age of the Earth. Some of the themes of prior volumes are taken up again here, such as professionalization and internationalization. Adverse trends are also noted in the closure of some UK chemistry departments, and the possibility that the field might be largely absorbed by neighboring disciplines.

The major theoretical advance of the early period, the understanding of bonding and reactivity, led to mechanistic thinking that in turn fed into structure and synthesis with such advances as the hemoglobin structure and the Coenzyme B12 synthesis. Late in the period, nanoscience came to the fore with such novelties as Bucky Ball and carbon nanotubes. Research, education and policy form the core of chapter two, with emphasis on numerous advances, many of which affected the wider world. The next chapter examines the evolution of the laboratory over the period. A radical shift that started in the 1950s involved the introduction of major electronic instrumentation on a grand scale that displaced prior practices such as organic structure determination by chemical means. The advent of these costly machines greatly increased the costs of research but enhanced its output. Mass spectroscopy, gas chromatography and NMR spectroscopy are discussed in detail and the importance of timely books is illustrated by Roberts' 'Nuclear Magnetic Resonance' of 1959 that made NMR sufficiently understandable so the general bench chemist could use it. One point that could have had greater emphasis in this series as a whole is the importance of textbooks as both influencers of the field as well as providing evidence of its evolution over time. Chapter four shows how chemistry's earlier good public reputation was put in question in the 1970s by rising attention to such negative outcomes as industrial pollution and the undesired side-effects of pesticides and drugs; items later added to the list include halocarbon refrigerants and perfluorinated 'forever chemicals'. Chapter 5 continues the same theme with the international regulation of pollution, climate change and efforts to ban chemical weapons, and introduces a new one with the rise of women in the field. Chapter 6 traces the rise of the chemical industry with special reference to its globalization and internationalization during the century. Beginning with Japan in the 1950s and more recently with China, the rise of East Asia as a scientific center is documented but the 1990s are considered to bring in an era of global science, facilitated by the new methods of communication across the globe. The final chapter on art and representation continues the theme of the 'mad scientist', mentioned in the last volume, as well as tracing the representation of scientists in general literature such as children's comics. In summary, this volume does a fine job of selecting telling aspects of the century's development in the field and providing a useful bibliography for further study.

SUMMARY OF THE REVIEWERS

In conclusion, we collectively believe that the cultural history covered in the six volumes presented above provides a fresh view of the history of chemistry, with analysis and discussion that surpasses the frequent presentation of notable individuals, chemical processes, and discoveries. By considering the full impact and interplay of society with chemical practice, a much more complete representation is achieved. As such, this series marks a valuable addition to the study and knowledge of the history of chemistry.

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