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INTRODUCTION TO THE ENGLISH TRANSLATION OF "THE THEORY OF DISSOCIATION"

A Forgotten Classic of Chemical Thermodynamics

William B. Jensen, University of Cincinnati

It was originally intended that the *Bulletin for the History of Chemistry* should function as a vehicle not only for the publication of scholarly papers dealing with the history of chemistry and alchemy, but also for the publication of translations of key historical documents—a function which has so far been exercised in only a few cases (1, 2). Though the problem of the gradual disappearance of history of chemistry courses and its potential impact on history of chemistry as an academic discipline has been commented on several times in the past (3, 4), the increasing inability of modern-day American chemistry majors to access directly primary documents in the history of chemistry, due either to a lack of modern language skills or the absence of suitable English translations, has so far escaped notice. For most of the 20th century, doctoral programs in chemistry required at least a minimal reading proficiency in either German, French, or Russian. However, beginning in the early 1990s, this requirement was dropped from most of these programs and, as far as most current chemistry majors are concerned, the vast majority of 18th-, 19th-, and early 20th-century European chemical literature might as well be written in ancient Greek or Latin when it comes to their ability to read it in the original.

Ironically, there was a conscious effort to provide suitable English translations of many classic chemical papers during the period when most American chemists still had some reading knowledge of either French or German, though at present, when the need is far more pressing, the majority of publishers are no longer interested in such projects. Thus, beginning in the late 19th century, both Harper Brothers of New York and the British-based Alembic Club, under the leadership of Leonard Dobbin, issued English translations and/or reprints of classic scientific papers of chemical interest (5, 6), and a similar program was initiated by Dover Books in the 1960s (7). In addition, several collections containing translations of selected passages from key papers were also published—most notably the volumes by Leicester (8, 9), Farber (10), and Crosland (11) —as well as several collections of key papers in such specialized fields as colloid chemistry (12) and chemical kinetics (13).

Nevertheless there are still many notable exceptions. Thus it is only recently that an English-language collection of Mendeleev's key papers on the periodic law has been published - nearly 136 years after its initial proposal (14). The classic 1904 and 1916 papers by Abegg (15) and Kossel (16) on the electronic theory of chemical bonding still await translation, as does the famous 1867 paper by Pfaundler on the application of the kinetic theory to chemical reactions (17) and, until now, the foundational 1873 paper by Horstmann on the first application of the second law of thermodynamics to the theory of chemical equilibrium (18).

These latter two examples also illustrate a curious asymmetry in the translation record. More than four decades ago Stephen G. Brush published a three-volume collection of many of the basic papers dealing with the origins of the kinetic theory of gases (19); and several collections of classic papers relating to the establishment of both the first (20) and second laws (21-23) of thermodynamics have also been published, some of which date back to the 19th century. What is missing, however, in all of these collections are translations of the key papers in which these fundamental models and principles were first explicitly applied to chemical processes.

The foundational status of Horstmann's publication of 1873 for the discipline of chemical thermodynamics is justified in the paper which appears in this issue and which also serves as a commentary on the following translation (24). Consequently, all that is required here are a few comments on the basic mechanics of the translation process itself. In 1987 I commissioned Heike Ulmer, who was at that time a German exchange student in the Chemistry Department at the University of Cincinnati, to produce a preliminary translation of Horstmann's paper. This I have since extensively revised. In so doing, I have exercised my preference for a free, rather than a literal, translation in order to avoid what are, from the standpoint of the English reader, awkward sentence structures and word choices. In keeping with this, I have sometimes inverted the order of the various sentence clauses and have modernized some of the chemical nomenclature when I felt this did not introduce a serious historical anachronism. Perhaps more controversial is my decision to substitute the term "mole" for Horstmann's more awkward phrase *eines Molekulargewichtes* of substance. Though he actually used the abbreviation "Mol" in several places for this concept, this is not quite the linguistic equivalent of the Latin term *mole*, which was first introduced into chemistry by Ostwald sometime around 1900 (25). Likewise, I have taken the liberty of occasionally rendering the term *Zufälligkeiten* or "random accidents," which Horstmann uses when discussing Pfaundler's kinetic approach, as "fluctuations," as this term is more congenial to the modern reader and is certainly in keeping with Horstmann's intended meaning. The reduction of Horstmann's original equations to a single-line format has also required the introduction of various parentheses and brackets in order to maintain mathematical consistency. Likewise, in keeping with the style of the *Bulletin*, Horstmann's original references have been removed from the bottom of the various pages and have instead been collected together at the end of the translation.

In reprinting Horstmann's paper in 1903 for Ostwald's series, *Klassiker der exakten Wissenschaften*, van't Hoff noted a number of corrections which have been incorporated without comment in the present translation (26). Otherwise any additional editorial clarifications within the body of the translation have been enclosed in square brackets. Interestingly, a more serious problem, which passed unnoticed by van 't Hoff, was Horstmann's inconsistent use of the symbol x. In his first four equations he correctly uses it to represent the number of moles of reactant that have decomposed and thus to represent the degree of reaction or dissociation. However, he then immediately turns around and redefines it in his fifth equation as the moles of reactant which have not yet decomposed, thus negating his third equation for total entropy production as a function of x. Luckily, this inconsistency does not seriously mar the remainder of his paper and the modern reader is able to make the necessary adjustments.

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HISTORY OF CHEMISTRY LISTSERVE: chem-hist@listserv.uni-regensburg.de

CHEMICAL HERITAGE: http://www.chemheritage.org

HISTORY OF SCIENCE SOCIETY: http://www.hssonline.org

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PRIMARY DOCUMENTS

"The Theory of Dissociation"

A. Horstmann

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It is characteristic of dissociation phenomena that a reaction, in which heat overcomes the force of chemical attraction, occurs for only a portion of a substance, even though all of its parts have been equally exposed to the same influences. In the remaining portion, the forces of chemical attraction, which are the only reason for the reaction to proceed in the opposite direction, maintain the upper hand. Hence, for such reactions there is a limiting state which the molecular system in question approaches irrespective of the initial state and, once it is reached, neither heat nor chemical forces can produce further change so long as the external conditions remain constant.

The degree of dissociation, i.e., the size of the portion encompassed by the reaction in the limiting state, depends upon the following external conditions: the temperature, the pressure and volume, the relative quantities of the reacting substances, etc., and indeed the influence of these various factors varies with the state of aggregation and the nature of the substances in question.

A complete theory of dissociation has to explain in general why an equilibrium state, rather than a complete reaction, is possible and, for each individual case, which circumstances are able to influence the degree of dissociation. I believe I can demonstrate the basis for such a theory in the following.

W. Thomson was the first to take note of one of the consequences of the mechanical theory of heat (1) - namely that the entire world is continuously approaching, via the totality of all natural processes, a limiting state in which further change is impossible. Repose and death will then reign over all and the end of the world will have arrived.

Clausius (2) knew how to give this conclusion a mathematical form by constructing a quantity—*the entropy*—which increases during all natural changes but which cannot be decreased by any known force of nature. The limiting state is, therefore, reached when the entropy of the world is as large as possible. Then the only possible processes that can occur are those for which the entropy remains constant, e.g. stationary movements such as those which we attribute to the smallest particles of a body at constant temperature. The cause of the limiting state for dissociation phenomena is, in my opinion, identical; it occurs when the entropy has become as large as possible for the change in question. Hence our problem is solved if we know by what circumstances and in what manner the entropy of the process in question may be altered.

If we follow the approach of Clausius, we find, first of all, that the more the energy of the world takes the form of heat and the lower the temperature of that heat, the greater the entropy.

If a quantity of heat Q is produced at absolute temperature T, e.g. from mechanical work or chemical potential, then the entropy is increased by *Q*/*T*. The reverse process corresponds to an equal decrease in the entropy and, since the total entropy cannot decrease, this will never happen without an increase of equal or greater magnitude occurring at the same time.

From what has been said, it is apparent that the entropy will also increase if a quantity of heat *Q* is withdrawn from a body at temperature *T* and is transferred to another at a lower temperature *T'*, since then $Q/T < Q/T'$ if $T > T'$. From this follows the well-known theorem of Carnot that heat cannot be transformed into work without heat being simultaneously transferred from a hotter to a colder body.

However, this theorem is only valid for the production of mechanical work via so-called cyclic processes (i.e., via processes in which all of the participating materials return to their initial states) since, in the transformation of heat into mechanical work or chemical potential, the heat always causes an accompanying (3) alteration in the arrangement of the particles of a body and thereby overcomes the internal and external forces which oppose the change without this being associated with a transport of heat in the sense of Carnot's theorem.

The decrease in the entropy which corresponds to the transformation of heat into potential energy is accompanied in such cases only by a change in the arrangement of the particles of the respective body, and thus it can be seen that the entropy must also be dependent on this arrangement. It is increased by any change in arrangement in which the heat must do work and by at least as much as is required to compensate for the simultaneous decrease. Clausius (4) has described the arrangement of the particles in a body by introducing a new quantity—*the disgregation*—which is dependent on this arrangement and which specifies how large the entropy is for a given arrangement. For the details of how to determine this magnitude, the reader is referred to his original memoir.

Those changes in arrangement which correspond to an increase in disgregation are easily identified because, like those in which the entropy increases, they can occur by themselves without any other accompanying change. In contrast, a decrease in disgregation is only possible if the entropy is also simultaneously increased, e.g. via the conversion of mechanical work or chemical potential into heat.

The disgregation is increased by melting and vaporization, and by the decomposition of chemical compounds. It decreases in all chemical processes which occur with the release of heat.

But bodies can also undergo changes in disgregation without a change in their chemical composition or state of aggregation. This is recognizable by means of specific criteria, e.g. the disgregation of a gas increases when it occupies a larger volume. But at constant volume it will be constant and will remain so even if a second gas is introduced into the same space.

Like the density, the disgregation of a liquid is constant at constant temperature. It can only be changed by mixing it with other liquids. The disgregation of each of the two components depends on their ratio in the mixture.

Lastly, the disgregation of a solid body does not change upon mixing with other solids. At constant temperature it can differ only for allotropic modifications of the same solid. Thus one can conclude that the state of aggregation leads to intrinsic differences which also influence the phenomena of dissociation.

In general, save for a few exceptions (5), the disgregation of a body will increase whenever its atoms or molecules are further separated from one another. Hence one is now able to form a picture of the nature of the equilibrium state for dissociation. That is to say, one sees that the process of dissociation may be divided into a series of processes by means of which the entropy is partially increased or partially decreased. If we consider a particular case, e.g., the decomposition of a gaseous compound into gaseous products at constant volume, then the entropy:

1) decreases during the conversion of heat into chemical work;

2) increases as the separation between the atoms of the decomposed molecules increases;

3) increases because the remainder of the undecomposed molecules must expand to fill the same volume;

4) and 5) decreases because the number of molecules for the two decomposition products increases and they are thus forced closer together.

The entropy will therefore will be greatest when as many molecules as possible are decomposed but the least possible amount of heat is consumed, and when the molecules of each of the three gases are separated from one another as much as possible. This is generally not the case for complete decomposition and hence only a portion is decomposed.

A reaction, whatever its type, can only begin and proceed so long as the collective sum of the various entropy changes contributed by the individual processes increases, since, as we know, the total entropy cannot decrease. The reaction must therefore stop at the very instant when the decreases become larger than the increases, i. e. at that point when the total increase becomes zero. Thus one arrives at a mathematical expression for the condition for an equilibrium state for dissociation. This requires that $dS = 0$, where S denotes the entropy of the system. This equation contains the entire theory of dissociation. It says that, in general, the degree of dissociation will depend upon all those circumstances which determine the entropy of the system. In order to deduce yet further conclusions we must give this equation another form.

For this purpose let x denote the relative amount, in units of molecular weight [i. e. moles], of a substance that either decomposes or reacts with other substances. Then x can serve as a measure of the degree of dissociation and all other quantities that change during the reaction, such as the entropy, will become functions of x. Thus one can write the condition for the equilibrium state as follows:

$$dS = (dS/dx)dx = 0$$

or

$$(dS/dx) = 0$$

Furthermore, if Q denotes the quantity of heat required to decompose totally one mole of a compound, then for completion of the reaction the quantity of heat Qx is required which must be considered when calculating the entropy of the system. If T is the absolute temperature and Z is the disgregation of the system, then:

$$S = (Qx)/T + Z$$

and, if equlibrium occurs, then:

$$(dS/dx) = [Q + x(dQ/dT)]/T + dZ/dx = 0$$

This equation will be further elaborated only for individual cases, and especially for that case in which a single substance is decomposed into two others. If one mole of this substance is initially present and, at a given moment, x moles remain undecomposed, and if every molecule splits into r and s molecules, respectively, of the decomposition products, and if m moles of one of the products was present initially, then it follows that the relative amounts of the three reacting substances are x, $r(1 - x) + m$, and $s(1 - x)$, respectively, and that:

$$Z = xZ_1 + [r(1 - x) + m]Z_2 + s(1 - x)Z_3$$

where Z_1, Z_2 and Z_3 represent the disgregation per mole of each substance.

Assume that both the substance being decomposed and one of the decomposition products are solids but that the second decomposition product is a gas which obeys the law of Gay-Lussac and Mariotte [G-M]. Then Z_1 and Z_2 are independent of x, and Z_3 depends only on the volume that is available to the gas, i.e., on the density of the gas. If u is the volume per mole, then, according to Clausius, it follows that:

$$Z_3 = Z_3' + ARln(u/u_0)$$

where Z_3' is the disgregation for the same quantity of gas referred to a normal [i.e. standard] volume u_0, R is the constant per mole for the G-M law, and A is the caloric equivalent for work. Thus, if p is the pressure of the gas, one has

$$up = RT$$

In most cases, including that under consideration, Q consists of two parts, one being the actual heat of decomposition, q, which is transformed into chemical potential, and the other being the amount of heat required to generate the mechanical work used in overcoming the pressure p, which is equal to Apu or to ART. Both parts are independent of x. If one uses these data, then for the case under consideration, our basic equation assumes the following form:

$$q/T - ARln(u/u_0) + C = 0$$

where $C = Z_1 - rZ_2 - sZ_3'$ is the change in the disgregation when the newly formed gas occupies the volume u_0—a quantity which, like q, no longer depends on x but only on the temperature. Hence the equation contains only one variable, u, that can be altered by the reaction and requires that either u or (since $up = RT$) the pressure of the gas must assume a unique value at equilibrium.

This conclusion is confirmed by the well-known dissociation of calcium carbonate, ammonium chloride, and compounds containing water of crystallization. According to the observations of Debray, Lamy and Isambert, the pressure of a gas over solid compounds, like that in the vaporization of a liquid, depends only on the temperature, but not on the ratio of the compound being decomposed and its solid decomposition product (6), as is required in general by our theory

The maximum pressure at constant temperature can only change if, for some reason, q and C assume different values. This is the case, for example, with the above mentioned compounds if only a portion of the water or ammonia is set free because the remaining portion is perhaps bound in a different manner.

C and q may have different values in the decomposition of *aragonite* versus *calcite* [i .e., two polymorphs of $CaCO_3$], assuming that this difference persists at the high temperature of the experiment, and hence the pressure of the carbon dioxide may be different. (A difference in the vapor pressures for the two modifications of phosphorus, for which precisely the same considerations apply, was demonstrated by Troost and Hautefeuille).

In accord with the experiments of Joulin (7), yet another factor may disturb the process of dissociation for some metal carbonates. Because of the high temperatures, the oxides undergo a modification which makes it impossible for them to rebind the carbon dioxide upon cooling and consequently, bit by bit, a complete decomposition ensues. In keeping with our definition, these cases no longer qualify as dissociation phenomena.

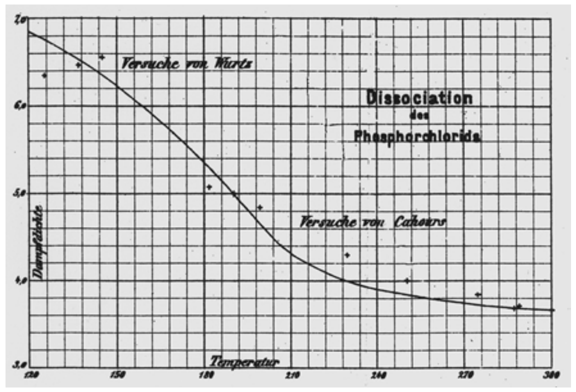
If q and C (which are actually temperature dependent) are treated, to a first approximation, as constant, one obtains the same relation between p and T as was observed earlier for the vaporization of a liquid under similar conditions using a different approach (8).

Looking at a second case—the decomposition of a gaseous compound into two gaseous components—Z_1 and Z_2 have the same form as Z_3 had earlier. Like the partial pressures of the three gases, the disgregations in the gas mixture are additive.

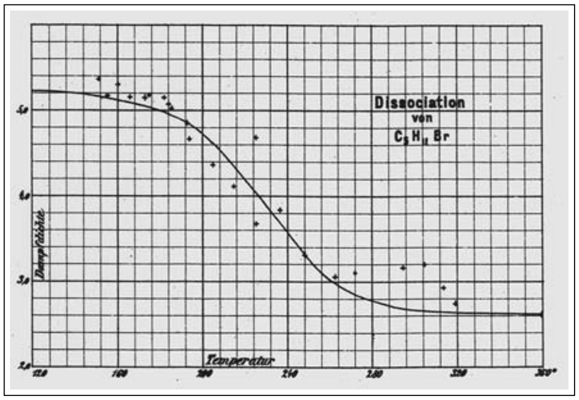
In experiments relating to this case, one mole of the initial compound decomposes by forming one mole of each of the decomposition products and during the decomposition the total pressure remains constant. Under these conditions our basic equation assumes the following rather complicated form:

$$q/T + AR\{1 + [2x/(2 - x + m] - \ln(1/u_0)[x/(1 - x + m)(1-x)]\} + C = 0$$

Here C is the change in disgregation when one mole is decomposed, provided that the gases have the molar volume u_0 before and after the reaction, C is independent of temperature, and the G-M law applies. All other symbols have the same meaning as before. If $m = 0$, then the equation is valid for the well-known experiments of Cahours with PCl_5 and Wurtz with $C_5H_{11}Br$. The degree of dissociation, which is known to depend on the vapor density, must be a function of T alone, as shown by experiment. Again, if one considers, as a first approximation, that C and q are constant, then, by examining the following graphs, it is possible to convince oneself that the form of the function also agrees with experiment (see Graphs 1 and 2).



Graph 1



Graph 2

I stress that the absolute pressure at which decomposition takes place does appear in our equation. Hence the curve for phosphorus pentachloride, whose constants are taken from Cahour's experiments at atmospheric pressure, must also be valid for Wurtz's observations at lower pressures (9). For purposes of comparison, the mean values are shown in the graph.

If m is not equal to zero, then a surplus of one of the decomposition products has been added and, at a given temperature, the value for x will be larger. The degree of dissociation has been decreased by "mass action," an influence which decreases as the decomposition increases, as shown in the following table. Since it is impossible to solve the above equation for x, this lists the temperatures at which x (and the vapor density d) have the same value with and without admixture.

m	x	d	$t°$
9	0.99	7.13	67
0.5	0.99	7.13	213
0	0.027	3.65	300
0.5	0.027	3.65	322

In the experiments cited above, Wurtz always added more than 0.5 mole of excess PCl_3, the temperature was always lower than 213°, and the average density was 7.2. It must be emphasized that, according to our theory, the addition of chlorine would have the same effect. Each of the gaseous decomposition products can alter the degree of dissociation via "mass action," but solid decomposition products cannot, as we saw in the previous case.

Dissociation phenomena are observed not only during decompositions but also in double displacements. Elsewhere (10) I have pointed out how one can imagine the mechanism by which heat counteracts chemical force in these cases. In my opinion, the effect of heat is always involved whenever an equilibrium is observed whose direction can be arbitrarily changed by external circumstances. In any case, our basic equation is valid for all systems which display an equilibrium since the cause of this equilibrium cannot be anything other than the maximization of entropy.

At this juncture the reactions of steam with iron, of sulfuric acid with sodium chloride in solution, and of potassium carbonate in solution with barium sulfate will be further examined, as all three reactions attain equilibrium before the reaction is complete and have been studied in detail.

Let Z_1, Z_2, Z_3, and Z_4 represent the disgregations for one mole of each reacting substance. In the first example, Z_1 and Z_3 have the form required for gases, whereas Z_2 and Z_4 refer to solids and are hence independent of the degree of dissociation. The external work cancels because for each volume of H_2O an equal volume of H_2 is formed. Hence $Q = q$ and the condition for an equilibrium in a closed space becomes:

$$q/T + ARln(p_1/p_3) + C = 0$$

where C once more stands for the change in the disgregation when the gases are in their normal states [i.e. standard states], and p_1 and p_3 are the partial pressures of the individual gases [*in the original Horstmann inconsistently used* p_2 *instead of* p_3]. The ratio of the two is constant at a constant temperature. The amount of one gas cannot be increased without increasing the density of the other in the same ratio. However, the equilibrium state does not depend on the relative amounts of the two solids. If q and C are considered constant, then this equation gives the approximate relationship between p_1/p_3 and T. These conclusions were all tested earlier (10) and were found to correspond to experiment. At that time the equation was deduced using another method, but the present approach provides a stronger justification for its application.

The other two examples cannot be as rigorously subjected to calculation since the relationship between the disgregation of a salt in solution and its concentration is not known. However, it is known, as mentioned earlier, that the disgregation changes with the concentration and this is sufficient to deduce an important conclusion.

When all four substances are in solution, as in the case of the interactions between Na_2SO_4, HNO_3, $NaNO_3$, and H_2SO_4, then the relative amounts of each must influence the degree of dissociation because the disgregation of each changes as the reaction progresses.

The investigations of J. Thomsen (11) confirm this. Each of the four substances can exert a mass action effect, and there is an equilibrium only at a certain ratio of the relative amounts of the reacting substances. The relation which must exist at equilibrium may be approximated, according to Thomsen, by the equation:

$$apq = p'q'$$

where p, q, p' and q' are the relative amounts and a represents a constant.

I want to mention that our theory would lead us to a relationship of this kind if one assumes that in dilute solutions the disgregation of a salt depends on the separation of its particles in a manner similar to that of a permanent gas, an assumption which is highly probable.

In the third example, only two of the reacting substances (K_2SO_4 and K_2CO_3) are in solution, the other two ($BaSO_4$ and $BaCO_3$) being solids, which, according to our theory, should have no influence on the degree of dissociation. This is confirmed by the experiments of Guldberg and Waage (12), who noted themselves that "the action varies only slightly upon increasing the amounts of these solids." I take the following numbers from their work, which show that the relationship between K_2SO_4 and K_2CO_3 in solution is independent of the relative amounts of the solids. Compared with the variation in the ratio $BaSO_4/BaCO_3$, the value of the ratio K_2SO_4/K_2CO_3 at the same temperature may be considered constant, which is what would be expected from our theory if the previously mentioned hypothesis concerning the disgregation of dilute salt solutions is correct.

Interactions Between $BaSO_4$, K_2CO_3, $BaCO_3$ and K_2SO_4 in Solutions Containing 1 Mol. of Salt per 500 Mol. of Water

Initial Conditions			*Final Conditions*	
$BaSO_4$	K_2CO_3	*Temp.*	K_2SO_4/K_2CO_3	$BaSO_4/BaCO_3$
1.0	0.25	100°	0.17	26.8
1.0	0.5	100°	0.19	11.5
1.0	1.0	100°	0.25	4.0
1.0	1.0	100°	0.21	4.7
1.0	2.0	100°	0.22	1.4
1.0	3.0	100°	0.23	0.75
1.0	4.0	100°	0.24	0.17
1.0	5.0	100°	0.24	0.08
1.0	5.0	15°	0.04	4.3

According to the table, the ratio K_2SO_4/K_2CO_3 also depends on temperature, as is generally required by our theory.

It must be noted here that it is possible that the influence of temperature on the degree of dissociation may become negligible if, for example, Q/T is very small in comparison with the other terms in the basic equation and if the disgregation of the reacting substances varies only slightly with temperature. According the work of Péan de St. Gilles and Berthelot (13), this may be the case for the reaction of organic acids with alcohols.

The theory of dissociation developed here may require yet further testing and verification, though it is in keeping with the examples that have been cited. It correctly predicts which circumstances determine the degree of dissociation in general and how in individual cases the degree of dissociation may be altered by changing these circumstance to the extent that we are able to control them. Summarizing the results of the theory, we find that, in addition to the chemical natures of the reacting substances, the most important influences are the temperature (though at times only to a small degree), as well as the volume which is occupied by the reacting substances, and the pressure to which they are subjected, especially when changes in these quantities affect the disgregations of the individual substances in different ways—for example, when some are liquids or solids and some are gaseous. Lastly, there is also the matter of the relative amounts of the reacting substances, but only when their disgregation depends on these relative amounts. It is primarily the state of aggregation of the reacting substances which determines whether they can or cannot alter the degree of dissociation by means of "mass action." Such "mass action" effects are always to be exerted by gaseous and dissolved reactants but never by solids and liquids that are immiscible, since they may be removed from the reaction without affecting the disgregation of the whole system. It seems to me that these conclusions concerning mass effects are the most important results of the theory and are worthy of further examination.

Until now one has attempted to explain the phenomenon of dissociation (14) on the assumption that the temperature of individual molecules is different from the average temperature which we measure and that, due to random fluctuations, the molecules of a substance capable of undergoing dissociation will, at a given instance, favor reaction in one sense or the other, and thus not all of the molecules will be able to react simultaneously in the same way.

The assumption of random fluctuations, which can cause the molecules to deviate more or less from the average condition, cannot be avoided given a variety of facts and our present views concerning the nature of heat. This is why I believed for a while that I could use it as a basis to develop a theory of dissociation (15). But one soon encounters contradictions with experiment. In particular, one cannot explain in a satisfactory manner the fact, mentioned earlier, that the mass of solids has no influence on the degree of dissociation. I do not wish to describe further the difficulties which discouraged me from pursuing this approach; rather I wish only to discuss how this fact agrees with the present theory. This employs to a certain degree a reversal of the approach used by statistics. The latter assumes a series of identical individual processes and must infer from their resultant in bulk the general laws for the whole, which also prevail for particular cases but which are masked by random fluctuations. In contrast, we know very little of what happens to the individual molecule, but we know the general laws which cannot be infringed upon by any particular process, and we must investigate how much scope remains for the operation of random fluctuations.

We know that there is no reaction between individual molecules which can lead to a lowering of the entropy. This is why, in general, only those changes can occur in which the entropy increases. If this happens, for example, during a decomposition, then in general the decomposition can only proceed if the individual molecules also continuously recombine under randomly favorable conditions.

It is possible to show that, at a certain stage of dissociation, every further change corresponds to a decrease in entropy. In this state as a whole further changes are no longer possible, however many fluctuations the individual molecules may undergo in one direction or the other. As mentioned previously, since the assumption of such random fluctuations cannot be avoided, one must imagine, like Pfaundler, that the state of equilibrium for dissociation phenomena is a stationary state in which the forward and reverse reactions are continuously and simultaneously occurring with the same frequency. However, the existence of these fluctuations and the equal number of reactions proceeding in both directions are no longer the reason for the stationary state, as assumed by Pfaundler.

The limits which a molecule can attain via random fluctuations are, in any case, of great importance for the reaction process and are mainly responsible for determining the velocity with which it proceeds. Probably many processes which are slow are only possible because some molecules deviate so far from the average. They would not occur if all of the molecules were in the average state. In contrast, many other reactions cannot occur, even though they would be accompanied by an entropy increase and the atoms would thereby attain a more stable state of equilibrium, because none of the possible molecular fluctuations are able to attain the necessary extremes.

Also with regard to the phenomenon of dissociation, there will be fluctuations which will, bit by bit, make the reaction possible for individual molecules, thereby driving the reaction, faster or slower, towards the stationary limiting state. However, when this limiting state is reached, it is not maintained by randomness, but rather by a general law which governs all individual processes, be they in limited molecular systems or in the world at large. The state remains stationary because the entropy can no longer increase.

Heidelberg, September 1873

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2. *Abhandlungensammhung II*, 34.
3. See Clausius, *Abhandlungensammlungen I*, 247.
4. *Ibid*., 248
5. See Clausius, *ibid*., 250.
6. This is contradicted by A. Weinhold, *Pogg. Ann*., 149, 217.
7. *Compt. rend*., 76, 1588.
8. *Annalen Suppl*., 8, 125 ff
9. *Berichte der deutschen chemischen Gesellschaft*, 6, 450.
10. *Berichte der deutschen chemischen Gesellschaft*, 4, 636.
11. *Pogg. Ann*., 238, 94 ff.
12. *Etudes sur les affinités chimiques*. Programm de l'université Christiana, 1867, 59.
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14. Compare Naumann, *Thermochemie*, 55 ff.
15. *Berichte der deutschen chemischen Gesellschaft*, 1, 210.

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The Society for the History of Alchemy and Chemistry (SHAC) would like to invite applications from Society members for its new award scheme. Two types of award are available: support for research into the history of chemistry or history of alchemy by New Scholars (up to £500) and support for Subject Development of either history of chemistry or history of alchemy (up to £1000). Closing date for applications: 31 May, 2010.

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AUGUST HORSTMANN AND THE ORIGINS OF CHEMICAL THERMODYNAMICS

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The Challenge (1)

Arguably the single most recognizable equation of modern chemical thermodynamics is that coupling the free energy (ΔG) of a reaction at constant T and P to its standard enthalpy change ($\Delta H°$), standard entropy change ($\Delta S°$), and reaction quotient (Q) (2):

$$\Delta G = \Delta H° - T\Delta S° + RTlnQ \qquad [1]$$

which, in the limiting case of equilibrium ($\Delta G = 0$ and $Q_{eq} = K$), gives us the equally famous equation:

$$\Delta G° = \Delta H° - T\Delta S° = -RTlnK \qquad [2]$$

If asked when these relations were first recognized and by whom, most chemists would probably plead ignorance or perhaps guess, given that ΔG is now known as the Gibbs free-energy function, that they were first derived by the American physicist, Josiah Willard Gibbs.

In fact, as we will see, they were first derived in a different, but equivalent form, in 1873 by an obscure German chemist, August Friedrich Horstmann, whose name has all but disappeared from the modern textbook. But before examining Horstmann's contribution, it is necessary to provide a context for his work by briefly reviewing the early history of both thermochemistry and chemical thermodynamics. This history has been extensively documented by previous historians and is the subject of numerous monographs, several of which are listed in the accompanying references. It is not our purpose here to repeat this history in detail, but merely to remind the reader of some significant names and dates in order to provide a chronological framework for our more detailed discussion of Horstmann.

The Thermochemical Context

As just suggested, it is necessary to distinguish between the older discipline of thermochemistry, which deals with heat alone, and the discipline of chemical thermodynamics proper, which deals with heat, work, and entropy. Indeed, the history of thermochemistry may, in turn, be further divided into what might be called the "caloric" phase and the "first law" phase (3).

In the caloric phase heat was regarded as a subtle, imponderable (i.e., weightless) fluid which could chemically combine with atoms to form an external atmosphere which rendered them mutually repulsive (4). As such, it worked in opposition to chemical affinity, which caused the atoms to mutually attract. Association reactions were assumed to be inherently exothermic because they decreased the accessible atomic surface area available to bind caloric, thus setting some of it free as sensible heat. In contrast, dissociation reactions were assumed to be inherently endothermic since they increased the accessible atomic surface area available to bind free heat as insensible combined caloric. No necessary relationship was postulated between heat release or absorption and the degree of chemical affinity. If anything, the preoccupation was compositional (i.e., measuring the caloric content or composition of various molecules) rather than dynamic.

The caloric phase began in 1784 with the work of Lavoisier and Laplace on heats of combustion. Its most productive practitioners were the French team of Pierre Favre and Johann Silbermann, who measured many heats of reaction, formation, and transition in the period 1844-1853, and its most important contribution was the law of constant heat summation, first proposed by the Swiss-Russian thermochemist, Germain Hess, in 1840.

As suggested by its name, the first law phase rested on the enunciation, in the period 1841-1847, of the first law of thermodynamics or the law of energy conservation—primarily by James Joule in England and by Robert Mayer and Hermann von Helmholtz in Germany—though there are many other claimants (5). It was first extensively applied to chemical systems a decade later, where it was most closely associated with the work of Julius Thomsen in Denmark in the period 1850-1886 and that of Marcelin Berthelot in France in the period 1864-1897 (6, 7).

Based on the equivalence of heat and work, it postulated, in contrast to the caloric theory, a direct relationship between heat release and the degree of chemical affinity via the so-called "principle of maximum work," which assumed that the greater the heat release, the greater the decrease in the potential energy of the atoms, and the more stable the resulting molecule. Direct application required that a distinction be made between the heat release due to chemical change (ΔH_{chem})—the quantity to which the principle of maximum work actually applied—and that due to the physical changes of state (ΔH_{phy}) which necessarily accompanied the reaction:

$$\Delta H_{rx} = \Delta H_{chem} + \Delta H_{phy} \qquad [3]$$

a distinction which proved impossible to apply in practice.

The Thermodynamic Context

The passage from thermochemistry to chemical thermodynamics proper is predicated on the enunciation of the second law by Rudolph Clausius in Germany in 1850 (using *Q/T,* not called entropy until 1865) and by William Thomson (Lord Kelvin) in Great Britain in 1852 (using the concept of energy dissipation) (2, 8). However, nearly two decades would pass before the second law was applied to chemical reactions (9). Early contributions of note then came from J. Moutier (1871) and H. Peslin (1871) in France, Lord Raleigh (1875) in Great Britain, J. W. Gibbs (1875-1878) in the United States, and, as we will soon see, from Horstmann in Germany (1869, 1873). The first monograph to deal with chemical thermodynamics proper was published in England by George Liveing in 1885, but it was based on the qualitative concept of energy dissipation rather than on Clausius' quantitative entropy function (10).

The Empirical Context

In addition to the above two conceptual threads we also have a final experimental thread based on the empirical concept of chemical equilibrium. First introduced by the French chemist, Claude Berthollet, in the period 1799-1803, the study of equilibrium reactions in solution was pioneered by, among others, L. F. Wilhemy (1850), J. H. Gladstone (1855), M. Berthelot and L. Péan de Saint-Gilles (1862), A. G. V. Harcourt and W. Essen (1864), and, most famously, by the Norwegian team of C. M. Guldberg and P. Waage (1864, 1867) (9, 11).

Empirical equilibrium studies entered a new phase (both literally and figuratively) when they were extended from solution reactions to gaseous dissociation reactions. Typical examples of this type of reaction include:

$$\text{Heat} + CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

$$\text{Heat} + NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$$

$$\text{Heat} + PCl_5(s) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Though some important early results were obtained by G. Aime (1837) and W. R. Grove (1847), it was the extensive efforts of Henri Sainte-Claire Deville and his colleagues, H. J. Debray and L. J. Troost, in France in the period 1857-1868 that really brought the experimental study of gaseous dissociation equilibria to the forefront by establishing important analogies between the pressure and temperature dependency of these equilibrium reactions and those observed for the vapor pressures of liquids (12).

Rationalizing Gaseous Dissociation Equilibria

Various attempts to rationalize theoretically these experimental results began to appear in the late 1860s and the 1870s, some of which were based on the newly emerging kinetic-molecular theory of gases and others on the laws of thermodynamics. The most important qualitative kinetic-molecular rationale was given by the Austrian physicist, Leopold Pfaundler, in 1867 based on the temperature and pressure dependence of molecular collision frequencies, the formation of transient collision complexes, and the requirement of threshold reaction energies—ideas which anticipated much of the conceptual basis of modern chemical kinetics (13).

Following the qualitative approach of Pfaundler, Horstmann initially attempted to develop a quantitative theory of dissociation using the kinetic theory of gases, but abandoned these attempts because they appeared inadequate to explain the absence of a mass action effect in the case of pure solids (14). Adopting an alternative thermodynamic approach instead, Horstmann first applied it to the thermal dissociation of ammonium chloride (the second reaction given in the previous section) in 1869 (15). Using the analogy with vapor pressures, he fit the data for the change in the dissociation pressure of ammonium chloride, as a function of absolute temperature, to an empirical equation first proposed by Biot for vapor pressures and then applied a rearrangement of the Clausius-Clapeyron equation:

$$(dP/dT) = \Delta H/(T\Delta V) \qquad [4]$$

in order to calculate the corresponding heat of dissociation:

$$\Delta H = (T\Delta V)(dP/dT) \qquad [5]$$

This was followed by three more papers on dissociation in the period 1871-1872, again based on the application of both the differential and integrated forms of the Clausius-Clapeyron equation (16).

In 1873, however, Horstmann returned to the subject once more in a paper entitled *Theorie der Dissociation*, in which he took an entirely new approach based on an explicit application of Clausius' new entropy function (17). Here he formulated the equilibrium condition for dissociation as a direct function of having maximized the change in the total entropy (dS) of the isolated system with respect to the degree of reaction or dissociation (dx):

$$(dS/dx) = 0 \qquad [6]$$

in which the total entropy production was given by the equation:

$$S = (Qx)/T + Z \qquad [7]$$

where Q/T is the heat of reaction per mole (Q) divided by the absolute temperature (T), and Z is the change in the "disgregation" of chemical reactants and products. This latter quantity was first introduced by Clausius in 1862 and was his rationale for the underlying molecular basis for entropy increase: namely, that it corresponded to a decrease in the degree of molecular aggregation and thus to a corresponding increase in the degree of molecular dispersion or disgregation (18). Similarly, Horstmann's requirement that $(dS/dx) = 0$ at equilibrium was nothing less than a direct mathematical expression of Clausius' famous 1865 reformulation of the second law: "Die Entropie der Welt strebt einem Maximum zu."

However, application of these equations to actual chemical reactions required a further elaboration of Eq. 7, which Horstmann then proceeded to do on a case by case basis. This may be illustrated with his simplest case: the thermal dissociation of a solid reactant to produce a single solid product and an accompanying gaseous product:

$$\text{Heat} + \text{AB(s)} \rightleftharpoons \text{A(s)} + \text{B(g)}$$

as exemplified by the thermal dissociation of calcium carbonate shown in the pervious section. Here the final equilibrium condition was given by the specific equation:

$$(dS/dx) = q/T + ARln(u/u_o) + C = 0 \qquad [8]$$

where q is the equilibrium value of Qx, A is the mechanical equivalent of heat, R is the universal gas constant, C is the change in the disgregation of the various reactants and products when in their standard states, and u/u_o is the ratio of the equilibrium molar volume (u) of the single gaseous product to that of its standard state (u_0).

In other words, the second term in this equation represents the manner in which the disgregation or entropy of a gaseous species varies as a function of its degree of dilution expressed as volume per mole (V/n). In deriving it, Horstmann made pioneering use of the ideal gas law written for the first time on a per mole, rather than a per gram, basis:

$$up = RT \qquad [9]$$

where u is the volume per mole of gas (19). Molar volume (V/n) is, of course, inversely related to both molar concentration (n/V) and partial pressure (p), the two variables usually employed when writing the reaction quotient.

In his third example, Horstmann derived the specific equilibrium conditions for the reaction of a gas with a solid to generate both a solid and gaseous product, as in the reaction of steam with hot iron to produce dihydrogen gas and iron oxide:

$$\text{H}_2\text{O(g)} + \text{Fe(s)} \rightleftharpoons . \ \text{H}_2\text{(g)} + \text{FeO(s)}$$

for which he obtained the specific result:

$$(dS/dx) = q/T + ARln(p_1/p_3) + C = 0 \qquad [10]$$

where p_1 and p_3 are the equilibrium pressures of the gaseous reactant and gaseous product, respectively (note their inversion relative to u_1 and u_3), and the other symbols have the same meaning as previously.

Lastly, Horstmann applied his approach to the solution-phase double-displacement reaction:

$$K_2SO_4(aq) + BaCO_3(s) \rightleftharpoons K_2CO_3(aq) + BaSO_4(s)$$

Using both the data and symbolism of Guldberg and Waage, he showed that his approach led to Julius Thomsen's conclusion that, at equilibrium, this reaction obeyed the relationship:

$$apq = p'q' \qquad [11]$$

where p and q are the equilibrium concentrations of the reactants, and p' and q' are the equilibrium concentrations of the products, not to be confused with Horstmann's earlier use of the same symbols for other quantities (2). The letter a in this equation represents our modern equilibrium constant K, but only if, as Horstmann noted, the concentration dependence of the disgregation for the solute species obeyed a law similar to that for ideal gases, and the values of q and q' for the insoluble barium carbonate and sulfate also remained constant. This first condition anticipated by more than a decade the later work of van 't Hoff on the theory of dilute solutions and his famous analogy between osmotic pressure and the ideal gas law (20).

In summary, we see that all of Horstmann's specific results at equilibrium can be generalized using the master equation:

$$(dS/dx) = q/T - ARlnK + C = 0 \qquad [12]$$

though he himself never took the final step of subsuming all of his specific concentration and/or pressure ratios for the gaseous- and solution-phase species at equilibrium under a single generalized symbol K.

A Comparison with the Modern Free-Energy Equation

To see the equivalence between Horstmann's result and our modern free-energy equation it is necessary first to divide the latter at equilibrium by $-T$:

$$-\Delta G/T = -\Delta H°/T + \Delta S° - RlnK = 0 \qquad [13]$$

and compare both this and equation 12 with a proper accounting of the resulting entropy changes (21):

$$\Delta S_t = \Delta S_e + \Delta S_s \qquad [14]$$

where ΔS_s is the entropy of change of the closed chemical reaction system, ΔS_e is the entropy change of the surrounding environment, and ΔS_t is the total entropy change for the resulting isolated system corresponding to their sum, whence it is apparent that:

$$\Delta S_t = -\Delta G/T = dS/dx \qquad [15]$$

$$\Delta S_e = -\Delta H°/T = q/T \qquad [16]$$

$$\Delta S_s = (\Delta S° - RlnK) = (C - ARlnK) \qquad [17]$$

The absence of a minus sign in front of q in equation 16 reflects a difference in sign conventions for heats of reaction, as formulated by Thomsen in the 19th century, and our modern conventions for enthalpy changes (6), whereas the presence of the minus sign in Eq. 15 accounts for why maximization of the total entropy corresponds to minimization of the free-energy and vice versa.

Who was Horstmann?

Since the life of Horstmann (Fig. 1 and 2) has recently become the subject of an excellent biographical monograph by Alexander Kipnis, all that is required here is a brief outline of its bare essentials (22). August Friedrich Horstmann was born on November 20, 1842 in Mannheim, Germany to a family of prosperous merchants. He entered the University of Heidelberg in 1862, where, despite the presence of such illuminaries of the future discipline of physical chemistry as Bunsen, Kopp, Kirchhoff, and Helmholtz, he chose instead to study organic and theoretical chemistry in the private laboratory of Emil Erlenmeyer. Receiving his D. phil. in 1865, he did postdoctoral work under Rudoph Clausius at Zürich, where he learned thermodynamics, and under Hans Landolt at Bonn, where he learned the techniques for the experimental study of the vapor pressures of volatile liquids. Following a brief visit to Paris, where he met Regnault and Silbermann, he returned once more to Heidelberg in 1867, where he presented a Habilitation thesis dealing with the relationship between the densities and molecular weights of

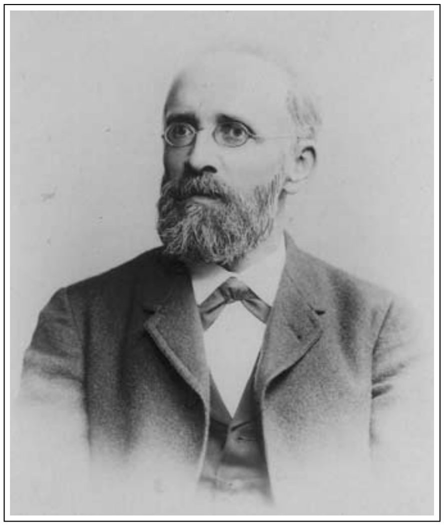

Figure 1

vapors and was appointed as a Privatdozent. There he remained for the rest of his life, eventually becoming Professor of Theoretical Chemistry. He was 26 when he wrote his paper on the dissociation of ammonium chloride in 1869 and 30 when he wrote his definitive paper on the theory of dissociation in 1873. His productivity in later years was increasingly hampered by diminishing eyesight, and he was essentially blind when he died at age 86 on October 10, 1929.

Why is He Forgotten?

By the end of the 19th century, Horstmann's work was already being routinely mentioned in various histories of chemistry (23). In 1903 his collected papers on the theory of dissociation were reprinted, under the editorship of van 't Hoff, as part of Ostwald's series *Klassiker der exakten Wissenschaften* (24), and he was afforded a 25-page obituary notice in the *Ber. Dtsch. Chem. Ges.* after his death in 1929, as well as numerous shorter notices in other journals (25). Yet unlike Gibbs, for example, his name has all but vanished from the 20th- and 21st-century thermodynamics literature.

One important reason for this neglect is that Horstmann did little to propagate his explicit entropy approach to chemical equilibrium. Thus, in an important dictionary article on "Dissociation," which he wrote for the 1876 edition of Fehling's *Neues Handwörterbuch der Chemie*, he described Pfaundler's kinetic theory in detail, but dismissed the reference to his own work of 1873 with the comment that it was not possible to describe in detail (26). Though he published at least eight more papers on the theory of dissociation between 1876 and 1884, he made no further mention of his entropy equation, but rather reverted once more to the approach he had originally used in 1869 based on the Clausius-Clapeyron equation (15, 16). Only in his 1885 textbook, *Theoretische Chemie,* did he once again make an explicit, albeit brief, mention of his entropy function (27). However, this book never went beyond the first edition and, to the best of my knowledge, was never translated into other languages.

The reasons for this neglect were simple enough. All of the parameters in the Clausius-Clapeyron equation could be quantitatively evaluated using available experimental data, whereas the same was not true of the standard disgregation term (C) in Horstmann's entropy function. It would not be until the early decades of the 20th century and the advent of the thermodynamic quantification program undertaken by G. N. Lewis and his associates at the University of California-Berkeley that both quantified entropy and free-energy data would become widely available (28).

However, a far more important reason for this neglect was the fact that the 19th- and early 20th-century chemical community was extremely uncomfortable with the entropy concept, which is precisely why Horstmann's approach was unique. Accustomed as we are today to a molecular interpretation of entropy as a measure of kinetic energy dispersion based on the quantum-statistical theory of thermodynamics, it is difficult for us to appreciate how little this physical point of view had permeated chemical and engineering circles by the end of the 19th century and how abstract the purely phenomenological definition found in typical textbooks of the period appeared to the average student of chemistry and engineering. As the engineer, James Swineburne, lamented in 1903 (29, 30):

> As a young man I tried to read thermodynamics, but I always came up against entropy as a brick wall that stopped my further progress. I found the ordinary mathematical explanation, of course, but no sort of physical idea underlying it. No author seemed to try and give any physical idea. Having in those days great respect for textbooks, I concluded that the physical meaning must be so obvious that it needs no explanation and that I was especially stupid in that particular subject ... After a few years I would tackle the subject again, and always I was brought up dead by the idea of entropy. I asked other people, but I never met anyone who could tell me, and I met one - an engineer - who admitted he did not know.

Figure 2

Initially, the free-energy function introduced by Gibbs in 1876, which also contained an explicit entropy term, fared little better (31). French and German translations of Gibbs' epic memoir were made available by Ostwald and Le Chatelier in 1892 and 1899, respectively (32, 33), but the succinctness and rigor of Gibbs' mathematical approach made his work largely inaccessible to the average chemist. Although he would become a virtual icon among physical chemists by the 1920s, this was, as Wilder D. Bancroft observed in 1926, largely a result of their having retrospectively uncovered in his memoir ideas and concepts which they had discovered independently via a much less rigorous and more tortuous path (34):

> The famous monograph on equilibrium in heterogeneous systems by J. Willard Gibbs is in some respects one of the most remarkable scientific articles that has ever been written. Gibbs was possessed of marvelous and apparently unerring insight, but the gift of expression was denied to him. It is not too much to say that Gibbs wrote in hieroglyphics and that a great part of his manuscript is still undeciphered. We know now that we can find in it the chemical potential, the phase rule, and the theory of osmotic pressure; the theory of electromotive forces, the Donnan equilibrium, and the theory of emulsification. We feel certain that some day we shall find in it theories in regard to all sorts of other things; but we do not know when we shall find them. It used to be popular to ascribe the negligible influence which Gibbs then had on the development of physical chemistry to the fact that his monograph was published in the *Transactions of the Connecticut Academy,* but this fiction cannot be maintained. Everyone knows about Gibbs now; but the only way that one can find anything new in Gibbs is to discover it independently and then look it up in Gibbs.

While it is true that Planck had used an explicit total entropy function in his 1897 textbook on thermodynamics (35), and both Duhem (36) and van Laar (37) had written early monographs arguing for the use of the Gibbs free-energy function (1886, 1906), most chemists of this period preferred instead to discuss the thermodynamics of chemical equilibrium in terms of the "Arbeit" or "Affinity" (*A*) functions and osmotic pressure analogs advocated in the influential writings of van 't Hoff and Nernst. Though mathematically equivalent to the functions of Horstmann, Planck, and Gibbs, these approaches completely disguised the role of the entropy function in chemical reactions by making it implicit rather than explicit.

Thus Nernst preferred to use "the more intelligible" notion of maximum work (*A*) or Helmholtz free energy and always used its temperature coefficient, (dA/dT), rather than -$\Delta S°$ when writing his Arbeit function (38):

$$-RT\ln K = A = U + T(dA/dT) \qquad [18]$$

Even more eclectic was van 't Hoff, who preferred an approach formally analogous to the standard equation for the interconversion of heat and work in a steam engine! (39):

$$-RT\ln K = A = q(P - T)/P \qquad [19]$$

where q is the heat of reaction, P is the equilibrium temperature for the reaction (i.e., the temperature at which $A = 0$), and T is the actual temperature at which the reaction is being run. At other times he preferred to use the gas law and his famous equation for osmotic pressure to calculate the work required to convert the initial system into one at equilibrium via a series of expanding and contracting pistons and selective osmotic membranes assembled in an imaginary device known as an "equilibrium box"(see Fig. 3) which calls to mind the famously sarcastic comment by Lewis and Randall concerning so-called "cyclic processes limping about eccentric and not quite completed cycles" (28).

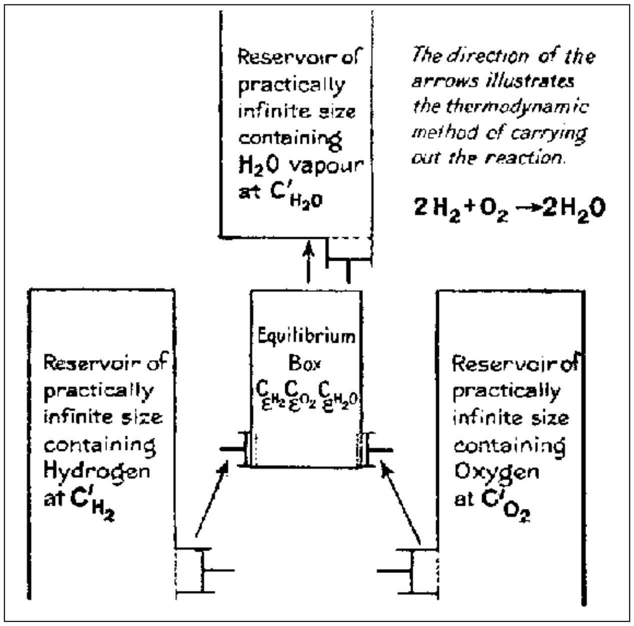

***Figure 3**. Van 't Hoff's "Equilibrium Box" (Ref. 39)*

Indeed, an informal survey of introductory physical chemistry textbooks and chemical thermodynamics texts published between 1893 and 1933 showed that 70% preferred the "Arbeit" or work approach of Nernst and van 't Hoff, 22% used either Gibbs or Helmholtz free energy with $\Delta S°$ explicitly given, 8% used neither, and 40% contained no index entry for entropy. It is, of course, the famous 1923 textbook of chemical thermodynamics by Lewis and Randall in the United States (28) and its advocacy by Hudleston in Great Britain (40), which are generally credited with having finally made ΔG and $\Delta S°$ inherent part of every chemist's thinking.

A third and final reason for this neglect lies in the descriptions of Horstmann's contributions found in the average history of chemistry text, whether written during his lifetime (23) or subsequently (41). Though all of these acknowledged his contributions to the theory of dissociation and often mentioned his use of the Clausius-Clapeyron equation, almost none of them, including the account of his life appearing in the prestigious *Dictionary of Scientific Biography* (42), called explicit attention to his pioneering application of the (dS/dx) function to the theory of chemical equilibrium in general. An exception is the 1952 history by Eduard Farber, which was, in fact, responsible for first drawing the present author's attention to this subject (43).

What Goes Around Comes Around

Given Horstmann's almost total disappearance from the 20th-century thermodynamics literature, it is somewhat ironic that several developments in this field during the past century strongly resonate with Horstmann's original approach:

1. The introduction by De Donder in 1920 of the extent of reaction parameter (ξ) and his replacement in certain situations of the ΔG symbol with the differential $dG/d\xi$ - a distinction which greatly clarifies the relationship between the ΔS_t and ΔG terms in Eq. 15 and Horstmann's own use of dS/dx (44):

$$\Delta S_t = -\Delta G/T = -(dG/d\xi)/T = dS/d\xi \qquad [20]$$

This unfortunate dual usage of the Δ symbol was characterized by Bent in 1973 as "a weed in the garden of thermodynamics" and has since become a subject of some interest in the chemical education literature (45).

2. The widespread use since the 1960s of a qualitative molecular disorder interpretation of entropy in introductory chemistry courses in order to address, like the original qualitative molecular disgregation interpretation of entropy used by Clausius and Horstmann, Swinburne's "missing physical basis" lament. Of course, neither the disorder nor the disgregation interpretations of entropy are absolutely identical to the more sophisticated energy dispersion picture provided by modern statistical mechanics and, as Lambert has repeatedly pointed out, the disorder picture, in particular, can lead to a number of incorrect conclusions if pressed too far (46).

3. The proposal by Rosenberg and Klotz in 1999 that ΔG be replaced by an explicit total entropy function, which they have called the "Planck function" in honor of Planck's use of such an approach in his textbook of 1897, and which they have also since incorporated into the most recent edition of their own popular thermodynamics text (47, 48). They seem unaware that this approach was already used by van Laar in his thermodynamics text of 1893 and that he had already dubbed it the "Planck potential" (37). Of course, both terms are, as we have seen, historically inaccurate and a more appropriate name choice would be either the Horstmann function or, perhaps, the Horstmann-Planck potential. As any historian is aware, such historical misattributions are rampant in the textbook literature, where they function as perfect examples of Stigler's famous law of eponymy (49). In addition, there are problems with interfacing this approach with the absolute rate theory of chemical kinetics, as it requires that activation barriers be replaced with entropy sinks (50).

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2. One of the difficulties in reading Horstmann is that his choice of symbols often conflicts with modern thermodynamic conventions. Thus the modern use of Q for reaction quotient will conflict with Horstmann's own use of this letter to represent heat of reaction at constant P, T, now symbolized as ΔH. Likewise Horstmann often uses the same symbol to represent more than one quantity. Thus he uses q not only for standard heat of reaction (ΔH°), but also, via Guldberg and Waage, to represent (along with q') the solution concentrations of various reactants and products, as well as p to represent not only pressure, but also (again via Guldberg and Waage) solution concentration, etc. Consequently the reader must always be aware of the immediate context in which a particular symbol is being used. It should be noted that similar examples of context related redundancies also occur in modern thermodynamics, such as the continued use of Q for heat in discussions of Clausius' original formulation of the second law in terms of the quantity Q/T.
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Teaching History of Chemistry

The report on "TEACHING HISTORY OF CHEMISTRY IN EUROPE," based on the information sent by many teachers of history of chemistry in Europe, has been a project of the Working Party on the History of Chemistry EuCheMs *http://www.euchems.org/Divisions/History/*

It has been coordinated by José Ramón Bertomeu-Sánchez, with the help of Ernst Homburg and Evangelia Varella, and is now available for download at:

http://www.euchems.org/binaries/Nov07TeachingHistReport_tcm23-108306.pdf

In order to update the information, please send your comments, additions and amendments to José R. Bertomeu, Departament d'Història de la Ciència i Documentació Facultat de Medicina Blasco Ibañez, 17 46010-València, SPAIN. bertomeu@uv.es .

A WOMAN IN BIOCHEMISTRY AND TOXICOLOGY: THE POLISH-BRITISH REFUGEE REGINA SCHOENTAL

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For over three decades from 1939, Polish-born Regina Schoental (1906-1995) studied, successively, at Oxford and Glasgow, syntheses and identification of polycyclic aromatic hydrocarbons (PAHs), metabolites of carcinogenic PAHs, and, at the Medical Research Council, Carshalton, Surrey, the carcinogenic action of pyrrolizidine (*Senecio*) alkaloids, and diazomethane and nitroso compounds. In particular she demonstrated the relationship between plant-derived hepatotoxic pyrrolizidine alkaloids and primary liver tumors. The role of Schoental and colleagues in the history of the development of synthetic methods for PAHs is also of interest because some are strong candidates for use in electronic devices.

Introduction

On February 2, 1995, the London *Times* recorded the death at the age of almost ninety of biochemist, cancer researcher, and toxicologist Regina Schoental. At that time I was preparing to travel from Jerusalem to London, where I had hoped to meet Dr. Schoental to discuss the transfer of her archive to the Hebrew University's Sidney M. Edelstein Center. It was to have been our first meeting; she had not long before made contact after reading my articles published in the *Biochemist*.

In the event, after arriving in London, I accompanied her solicitor and a member of the family to her apartment in Wallington, Surrey, to examine the archive. It filled at least one large room; there were notebooks, reprints, research notes, correspondence, conference programs and reports, trade and government literature, travel brochures, monographs, obituary notices on her former colleagues, manuals, textbooks, and slides and photographs, as well as exotic dried plants and shrubs and samples of chemicals. Subsequently this material arrived at the Hebrew University, and, after selective reduction, is now held at the Edelstein Center. Most of the manuscripts and publications deal with toxic substances in plants, mycotoxins, polyaromatic hydrocarbons (PAHs), and various other carcinogenic chemicals. These sources reveal that Regina Schoental's research, described in over 250 published papers, contributed to industrial hygiene, diet, including nutritional factors in carcinogenesis, the understanding of the relationship between structure and activity in natural and synthetic carcinogenic organic chemicals, and toxicology in general. Though the archival collection remains largely uncataloged, it includes many items of interest to the history of chemistry, particularly of a woman scientist struggling not only to survive in a mainly male-dominated field, but also in a harsh and changing world outside the laboratory. The following is a summary of her life and career, with an emphasis on chemical studies, based on fragments, some quite substantial, from the archive (1).

Among the many letters in the archive is an item dated September 26, 1983, in which Regina Schoental congratulates a former colleague, the cancer expert Isaac Berenblum, on reaching his eightieth birthday, and in-forms him that on November 11 of that year she would complete "45 years of my wanderings in the British Desert (2)." These few words spoke reams on her career as a scientist-refugee who survived through a series of appointments in England and Scotland, helped by some colleagues, used by others, but all the time contributing to new knowledge in aromatic chemistry, biochemistry, and toxicology. That she never gained a tenured academic post was, in the opinion of Berenblum, in large part a result of her constant and sometimes voluntary moves. Perhaps more likely was the general difficulty faced by women in gaining academic and leadership posts. Biochemistry, toxicology, and industrial hygiene—areas in which Regina specialized—certainly did offer decent openings for several women, some of whom, like Dorothy Hodgkin and Ethel Browning, were appointed to senior research positions or posts as government inspectors, respectively. The chemist Gertrude Belle Elion, after a difficult start, benefited from male staff shortages during World War II, which enabled her in 1944 to embark on drug development at Burroughs Wellcome; in 1988 she shared the Nobel Prize for Physiology or Medicine, and in 1991 was the first woman to be inducted into the National Inventors Hall of Fame. In most cases, however, in order to overcome career discrimination, outstanding women scientists not only had to rely on strong support from male colleagues in senior positions, but were also expected to conform to prevailing social and cultural norms. As for Schoental, an excellent scientist and world authority in two important areas of toxicology, and with considerable male respect, if not always support, her own tensions with colleagues, as also suggested by Berenblum, did not help her to gain advancement. That may also explain why she has remained hidden among the second rank of exceptional immigrant scientists whose contributions are frequently overlooked. Along with current interest in the role that skilled technicians, as well as ordinary scientists, play in research this makes her achievements of even greater interest. Here they are set into a context that highlights their significance.

Early Life

Regina Schoental was born on June 12, 1906, in Dzialoszyce, a small Polish town northeast of Cracow, where her Jewish family was engaged in industrial pursuits. Her mother was from Cracow and a cousin on this side of the family was the well known bacteriologist Phillip Eisenberg, who in 1914 had published on bacterial variability. Life in Dzialoszyce during the early 1900s was subject to constant political change, including in 1907, when the town was occupied by Russia. After 1914 Regina's private education was frequently interrupted, as the German and Russian armies fought over control of Polish land. In 1916 Regina left home for Cracow, probably to stay with her mother's family. In 1922 she "passed the Entrance Examination to the VIIth Form of the 1st Private High School for Girls." After two years at the school she passed the "Matura" examination that allowed her to study chemistry at Cracow's Jagellonian University, where she also attended classes in bacteriology and biology. The course lasted four years and was followed with postgraduate studies. In 1929 she was awarded the M.Chem., and in 1930 the degree of doctor of philosophy. Her thesis, on "a physico-chemical topic," was not published because of the death of her supervisor, Deodatus Szyszkowski, and, later, her departure from Poland. She spent 1931 in Paris at the Pasteur Institute and other clinical laboratories, gaining experience in clinical biochemistry and bacteriology (3).

Figure 1. *Regina Schoental, seen here front row at right, with her Ph.D. supervisor, Professor Deodatus Szyszkowski, seated at center, and colleagues at the Department of Physical Chemistry, Cracow, around 1930. Date and photographer unknown. Schoental Archive, Edelstein Center.*

During 1932-1936 Regina undertook postgraduate research at the Clinical Laboratory of the Military Hospital, Cracow, and also at the "Cancer Laboratories of the University Clinic." After this, she opened a private diagnostic laboratory and was a part-time researcher at the University of Cracow Institute of Forensic Medicine, associated with the medical academy (1936-1938). (Regina also stated that during 1933-1938 she was affiliated with the "Cancer Research Laboratory, Department of Internal Medicine, Cracow.")

In 1938 Cambridge biochemist and emerging historian of science, Joseph Needham, while visiting Cracow, encouraged Regina to pursue her research in the United Kingdom. At that time Needham was seeking out chemists to join his planned research program at Cambridge on the chemical basis of embryonic induction and probably considered Regina a good candidate, even though he did not have access to funds to support her. He was particularly anxious to bring in immigrants, both to assist them and also because their employment costs would be low, or they would be self-funded (4). A recommendation from the head of the institute of forensic medicine, J. Olbrycht, enabled Regina to obtain a "scientific passport" from the Polish authorities. With the promise of financial support from her parents, she wrote to the cancer expert (later Sir) Ernest Laurence Kennaway at the research institute of London's Royal Cancer Hospital. She may have chosen to write to Kennaway on the recommendation of Needham, who hoped that this would be a way of getting her to be close at hand, even if not immediately to join his team (in the event Needham abandoned his project for lack of funds and infrastructure). She was no doubt aware of Kennaway's work on carcinogenic natural tars and PAHs, including his synthesis in 1924 of carcinogenic tars by pyrolysis over hydrogen of isoprene and acetylene, and his demonstration that 1,2:5,6-dibenzanthracene (dibenz(*a*,*h*) anthracene) and its derivatives, and then 3,4-benzo(*a*) pyrene, produced tumors in mice (5). This followed the 1915 publication by Japanese workers K. Yamagiwa and K. Ichikawa of experiments that demonstrated the presence of carcinogens in coal tar; the tars were found to induce skin cancer. Regina Schoental later noted that Kennaway was the first to demonstrate that "a pure chemical can induce tumors in experimental animals." She appears to have done some work on polyaromatic hydrocarbons at Cracow, perhaps as a postgraduate, judging from reprints she retained of 1925 and 1927 papers authored by Karol Dziewoński and coworkers published in the *Bulletin de l'Académie Polonaise des Sciences et des Lettres*. She also retained mid-1930s reprints of work on natural products, including quinine, undertaken by Jerzy Suszko and others at Poznan.

Chemists and Cancer

It is pertinent here to introduce a little more background on chemists and others engaged in cancer research between the two world wars, particularly those with whom Regina Schoental would later work. The chemist (later Sir) James W. Cook had joined Kennaway at the London cancer hospital in the autumn of 1929, and during 1931-1932 they and coworkers isolated and identified a carcinogenic component in coal tar, namely 3:4-benzo(*a*) pyrene. This followed the observation by W. V. Mayneord in 1927 that the carcinogenic coal tar fractions showed a striking fluorescence. Subsequently Cook and colleagues synthesized various derivatives of 1,2-benzanthracene, several of which were cancer-producing. These carcinogenic derivatives exhibited fluorescence bands that, like the tar fractions, were shifted to longer wavelengths. Then in 1931, Israel Hieger (at the London hospital since 1924), obtained from two tons of gas-works soft pitch, via the picrate, 7g of crystalline hydrocarbon which proved to be 3:4-benzo(*a*)pyrene. It was highly carcinogenic, which correlated with the fluorescence spectrum. Independent synthesis from pyrene and structural determination, by comparison with synthetic 1,2-isomer, by Cook and C. L. Hewett, was crucial to confirmation of identity and further progress.

An undated note of Regina, alluding to the different personalities of Kennaway and Cook, written long after the death of Kennaway (in 1958), adds a slightly different slant to the story, and contributes to how Cook rose to fame. It is particularly interesting in view of the fact that Regina's most productive and probably happiest years in Britain before the mid-1950s were spent in Cook's Glasgow laboratory. Reminiscing on the time that she had sat in a lecture theatre with an unwell Kennaway towards the end of his life listening to Cook recount some of his own achievements, perhaps in Regina's mind not giving sufficient credit to others, she compared the "humility" of Oxford-educated Kennaway with the "self assurance and pride" of Cook (6):

> …a self made man—hence probably lacking this ease and certainty that appropriate upbringing in higher classes can give. He was neither in Oxford or Cambridge, but at John Cass College, University of London, not distinguished in any way…[Kennaway] turned to him for samples of PAH, for Hieger to examine their fl[uorescence] spectra to compare with those given by coal tar fractions. Hieger, who slaved with fractionation of coal tar for a long and laborious time, was deprived from his just record, crystallization of 3,4BY[Benzpyrene], because he was not enough of an organic chemist. So the honour and glory went to Cook.

Notwithstanding personal feelings over credit and priority (that were certainly not apparent at the time the work was reported), this identification of a carcinogenic factor in coal tar stimulated extensive synthesis and animal testing of PAHs. At the end of the 1930s, it was a novel and exciting area for original research in cancer, following concerns, particularly in England and Germany, over lung cancer caused by tars from cigarette smoking (7). Other notable workers in the fields of chemistry of PAHs, and PAHs and cancer, included in Czechoslovakia Erich Clar, in a private laboratory, in the United States Louis F. Fieser, at Harvard, and in Mandate Palestine Ernst David Bergmann and Chaim Weizmann at the new Daniel Sieff Institute (later the Weizmann Institute), Rehovot, who investigated anthracene and phenanthrene derivatives. Kennaway and Fieser independently led investigations into the correlation between chemical structure and carcinogenic activity. Cook had expanded on Clar's synthesis of various 1,2-benzanthracene derivatives, reported in 1929, during his first studies with Kennaway's group in London.

Kennaway was interested in cancers caused by other aromatic molecules, particularly the so-called aniline cancer, named after the aniline dye industry, which used a variety of aromatic amines in dye manufacture. The most potent carcinogens were found to be β-naphthylamine and benzidine, both in use as intermediates for dye manufacture since the 1880s, and since the 1930s known to cause tumors in humans (8). These amino compounds were investigated by Kennaway from the mid-1920s and soon after by Isaac Berenblum and G. M. Bonsor at Leeds. In August, 1932 Berenblum published a comprehensive review of "Aniline Cancer," focusing on bladder cancer (9). During the mid-1930s investigations into bladder cancer caused by dye intermediates were carried out by George H. Germann and Wilhelm C. Hueper at DuPont in the United States (10).

Cook and Kennaway coauthored reports on the literature related to "Chemical Compounds as Carcinogenic Agents" for the *American Journal of Cancer*. These were predecessors of the *Survey of Compounds Which Have Been Tested for Carcinogenic Activity*, which first appeared in 1941, compiled by Jonathan L. Hartwell for the National Cancer Institute. Of the 696 compounds listed in the survey, 129 were reported as active. The second edition appeared a decade later, with 1,329 compounds listed, of which 322 were active (the survey was reprinted in 1963 by the U.S. Public Health Service).

At the end of 1938 Regina's interest was drawn to Kennaway's several lines of research in cancer. However, as she later reminisced (11):

> I wrote to Kennaway and without waiting for his reply arrived in London on the 10th November, 1938, only to learn that Kennaway wrote that he is not able to accept me; the Chester Beatty Institute [the expanded research facility at the hospital] was then under construction).

The Chester Beatty Research Institute (now the Institute of Cancer Research) opened in 1939.

Figure 2. *Ernest L. Kennaway. Date and photographer unknown. Schoental Archive, Edelstein Center.*

Cambridge, Oxford, Glasgow, and Chicago

Regina arrived in England with fifty pounds sterling, all she was allowed to take, little knowledge of English, and no research position. She managed, perhaps through Needham, to spend a few weeks in Cambridge, at the Molteno Institute, with biologist and discoverer of cytochromes David Keilin, also of Polish-Jewish origins, who sympathized with her plight. It was through registration at Chelsea Polytechnic "so as not to be returned to Poland" and this brief unpaid post that her visa was extended. Regina then joined, as a volunteer researcher, funded by her parents, the Sir William Dunn School of Pathology at Oxford, directed by Howard W. Florey. After the Nazis marched into Poland in September 1939, she was forced to remain in Britain as a refugee. She later recorded, "The outbreak of the war interrupted [my] cancer research." Regina found herself "cut off from my people and resources." She considered joining the Hebrew University in Mandate Palestine, which was also engaged in cancer research involving studies on PAHs, and was accepted by Leonid Doljanski of the university's cancer laboratories, department of experimental pathology. The war put an end to plans for going to Palestine.

However, "Thanks to the unforgettable kindness of Professor (now Sir) H. W. Florey, F.R.S.…I was given a grant from the Nuffield Trust, and this enabled me to remain in the Department (12)." Her good fortune from this time was to undertake research with outstanding, and later leading, biochemists, toxicologists, chemists, and cancer researchers. At Oxford she worked with

Ernst Chain, who left Nazi Germany in 1933, biochemist Norman George Heatley, who from the late 1930s, after working with Needham at Cambridge, had been engaged in the investigation of metabolism of cancer tissues, and Isaac Berenblum (whose Polish-Jewish family had left Bialystock in 1906 following Tsarist pogroms). Chain, Florey, and Heatley were then developing penicillin. "Florey and Chain suggested that I try to isolate the antibiotic substances from Ps. Pyocyanea, which according to Trueta had beneficial effects upon the wounds (13)." Joseph Trueta, former professor of surgery in Barcelona, and from early 1939 a refugee from Franco's Spain, was, with the support of Florey, at the Sir William Dunn School during 1939-1941. Regina published her research on this topic in 1942, though her main interest was in cancer. By then she had become a member of the Oxford University Research Centre of the British Empire Cancer Campaign, under Berenblum's direction (1938-1948). The research staff consisted of just three members: Berenblum, experimental pathologist, Chain, chemical adviser, and Regina Schoental, "Biochemist—Part-time voluntary worker." In 1942, Berenblum and Regina began to publish jointly on 3:4-benzo(*a*)pyrene (benzpyrene) and its toxicity. They isolated and identified phenolic metabolites of the benzpyrene, chrysene, and 1:2-benzanthracene (14). At Oxford, the mechanism of carcinogenesis was investigated on two fronts: Berenblum's biological approach based on three separate steps, using croton oil; and, through collaboration with the Dyson Perrin Laboratory, Sir Robert Robinson's chemical approach, an attempt to correlate chemical structure with carcinogenic potencies. Robinson and colleagues synthesized sulfur-containing derivatives of PAHs as part of the contribution to Berenblum's research.

Regina, supported with grants from the cancer campaign, remained with the Oxford cancer center until 1946. On behalf of the center, she was at the chemistry department of Glasgow University during 1943-1944, engaged in collaborative research. At Glasgow, Regina was associated with James Cook, since 1939 Regius Professor of Chemistry and Director of the Chemical Laboratories. This brought her into both carcinogenesis and the synthesis and characterization of novel PAHs, an endeavor that would continue until at least the late 1950s. The facilities were excellent, a dedicated chemistry building (the first in Britain) comprised of two substantial wings opened in 1939 (a third, according to the original plan, would be added after 1945), directed by the leading British chemist engaged in the synthesis of carcinogenic aromatic hydrocarbons. Regina's work at Glasgow was originally stimulated by interest at Oxford in the possible inhibition of tumor growths by metabolites of carcinogenic substances, and the need to synthesize a number of metabolites. The facilities were also attractive to the Admiralty that had commandeered a large laboratory for wartime research.

A reprint of Cook's 1942 review of "Polycyclic Aromatic Compounds," in the *Annual Reports of the Chemical Society*, the first such review since 1933, was no doubt a treasured possession of Regina, since it still retains the carefully applied protective wrapping. One of her notebooks, marked "Department of Organic Chemistry, University of Glasgow, Syntheses of Hydroxy-derivatives of Polycyclic Hydrocarbons," with entries for October 1943-December 1945, shows that she maintained close contact with both Kennaway and Berenblum. This suggests that Regina's post at Glasgow may have come about through Kennaway's connections, or, probably more likely, Berenblum's own interest in PAHs. Either way, at a time of depleted ranks among male researchers called away for war-related work, her efforts were invaluable. Various reference compounds for the study of biochemical actions were synthesized mainly by Regina in Cook's laboratory and forwarded to Berenblum at Oxford. At Glasgow, Regina and Cook established the structures of metabolites of the benzpyrene. Regina showed considerable interest in another aspect of Kennaway's work, primary cancer of the liver, as a result of her own pre-war study of such cancers at the Cracow university clinic through measurement of the lactic acid content of blood in normal subjects and those with various diseases.

Regina returned to Oxford late in 1944, probably at her own request, but she must have soon had second thoughts. Personal difficulties, particularly with Berenblum in 1945, prevented concentration on her work. No doubt concern over the absence of contact with her family in Poland was a cause of deep distress. Regina thought of leaving the Oxford group and joining Kennaway, who in March, 1945 offered her a short term post in London. "It was very hard to make a decision," she wrote to Cook on March 20, 1945, "the more so, as Prof. Kennaway prefers me to finish the synthesis of the 8-benzpyrenol in Oxford. In spite of all that I decided however in favour of London, realizing that this is my last chance to work with Prof. Kennaway (15)." Regina, desperate to leave Oxford, advised Cook: "A lot of work remains to be done (I am expected in London in June), in order to finish some of the problems I have been concerned with—but I shall try to concentrate in the first place on the synthetic work, as the prospects of continuing it later are rather bad (unless you would care to take me back to Glasgow at some later date!).” Regina added notes in pencil to her draft, suggesting that she was not at all happy, even with a post in London, and yearned to return to Glasgow (16):

> In this fine weather—Oxford often painfully beautiful—obviously does not induce much enthusiasm for work.

Kennaway, however, though highly sympathetic, particularly towards a Jewish refugee, expressed concern over the lack of future employment prospects. Regina was prepared to accept the temporary post in London since her intention was to join the Hebrew University. Cancer research in Jerusalem, where conditions were very difficult in other ways, seemed to be a strong option now that the war was entering its final phase (17). This, however, did not materialize, due to lack of facilities for chemical research and animal experiments, restricted research opportunities, and her failure to obtain a grant from the British Empire Cancer Campaign, notwithstanding support from Berenblum, Florey, and Kennaway. Regina had even suggested that the chemical problem could be overcome through collaboration with Ernst David Bergmann. In the event, Regina decided not to take the London post. Kennaway, who always showed great kindness to Regina, would in any case retire one year later from directorship of the Beatty.

Still at Oxford, Regina undertook the further synthesis of various benzpyrene derivatives, particularly 10-methoxy-3,4-benzpyrene, while maintaining close contact with Cook (18). The work was highly challenging, and the product elusive. “I think we got the real 10-MeO-BP,” wrote Schoental to Cook on one occasion, though the product could not be fully characterized (19). Separation of chlorinated benzpyrenes “proved a rather difficult job,” though it eventually afforded an “embarrass[ment] of riches,” namely, four products (20). There was also work on the hydroxyl derivatives, stimulated by the belief that they were important intermediate metabolites of benzpyrene during carcinogenesis. Progress, however, was increasingly hampered by growing personal difficulties at Oxford. Regina considered obtaining a position in the United States, but in October, 1945 wrote to Cook that “My prospects for the USA seem rather bad,” and ended her letter: “I do not know what to do. Why did I ever agree to leave Glasgow, all my troubles started since (21)!”

A practical problem was the absence of a stock of benzpyrene, at least until 30 g were obtained in January, 1946. Regina, discovering that IG Farben had filed a patent for benzanthrone-1’-aldehyde, asked Cook whether there was any way of procuring a supply from Germany, which Cook thought unlikely. Both were interested in the forthcoming availability of C-13 for research purposes from the Medical Research Council (22).

After many enquiries for a research post, including with Albert Claude at the Rockefeller Institute in New York, had led nowhere, Regina requested, or at least suggested to Cook, a post back in Glasgow. Hinting again of her dissatisfaction with Oxford, on February 6, 1946, Regina wrote to Cook (23):

> The new scheme you put forward for the two hydroxybenzpyrenes is certainly most interesting and I would be only too anxious to undertake it. I feel however that my continuing synthetic work in Oxford, somehow as a side line besides other problems, without your advice on the spot, is not quite satisfactory; it would certainly give quicker results if I could be in your Department, if this would suit you.

Cook immediately offered her a vacant bench in a small research laboratory. His space and resources were extremely limited, so much so that had Regina’s letter arrived one day later the position would already have been filled. Cook expressed the hope that the large laboratory previously occupied by the Admiralty would be made available for research later in the year. Early in April, not long before her departure from Oxford, there was another indication of frustration (24):

> Oxford is now so incredibly beautiful with the pink almond trees etc., as if it tried to make me sorry for leaving it, which I am not.

At the end of April, 1946 Regina began working in Glasgow, funded with her existing grant. Later in the same year she published with Berenblum a paper in which they showed that metabolites of 3:4-benzo(*a*)pyrene were 8- and 10-hydroxyphenolic derivatives (benzpyrenols) and benzpyrenequinones (25). By April, 1947 her funding was transferred from Oxford, extended, and increased, for a period not exceeding three years (26). Despite the personal problems in 1945, Regina maintained a close connection with Berenblum, who invariably offered her support with funding; they remained on first name terms, the affectionate “Gina” and “Berry,” respectively.

Now back in Scotland, Regina must have been delighted, even though she was probably aware of the limited long term prospects, particularly for women. The increasing numbers of women recruited into laboratories during the war did not immediately improve their status, irrespective of their qualifications. They were far more poorly paid than men. Kennaway’s wife, Nina, even undertook research in close collaboration with her husband as a volunteer, a situation that lasted over thirty years! Furthermore, cancer research was less prestigious than drug design, and less likely to attract substantial research funds. At a more mundane level, for women at least in British laboratories, there were even restrictions on dress, including on the wearing of trousers, except in the winter (27). The wartime winters, and that of 1947, were particularly severe, though cold laboratories did sometimes favor recrystallizations. It is not without interest that of three issues of the *Chemical Bulletin* that Regina retained after a visit to Chicago in 1953, one highlighted the "Professional Problems of Women Chemists (28)."

At Glasgow there were major compensations. The international standing of the chemistry department was maintained by its first-rate scientists, including the X-ray crystallographer John Monteath Robertson, who not only solved the phase problem that enabled the determination of structures of biological macromolecules, including proteins, but also for Cook undertook bond length measurements on naphthalene, anthracene, and other aromatic hydrocarbons and their hydroxyl derivatives. Prominent guests included, in 1948, Linus Pauling. Regina appears to have enjoyed her time back at Glasgow. She participated in social events and took an interest in the chemistry department's Alchemists Club that catered mainly to undergraduates. She retained just one issue of the club's newsletter, *The Alchemist*, perhaps because it included the article, "Devils, Drugs, and Chemists," that noted (29):

> Penicillin was an English discovery, i.e. the greater part of the work was done by Fleming, a Scotsman; Florey, an Australian; and Chain, a German of Russian descent.

In late 1946 Erich Clar, pioneer in synthesis and identification of polycyclic aromatic hydrocarbons and leader in the field, had joined the chemistry department at Glasgow. In the 1920s Clar had studied at the technical institute in Dresden, from around 1930 he was at the Ronzini chemical institute in Milan and by the end of the 1930s had opened a private laboratory in the Sudetenland at his home town of Herrnskrestchen, southeast of Dresden. He continued to publish in Germany during World War II, including, in 1941, *Aromatische Kohlenwasserstoffe* (30). After the war prior to joining Glasgow he was at the central laboratory of Rütgerswerke A.G. At Glasgow he was supported with an ICI research fellowship.

Cook and Regina, using oxidation with osmium tetroxide as described in 1942 by R. Criegee, B. Marchand, and A. Winnowius, found that benzpyrene and ten other carcinogenic PAHs afforded novel products, since they were attacked at positions not sought by other oxidizing agents. Moreover, in the case of the benzpyrene derivatives the products were, unlike those from oxidations with the usual reagents, close analogs of metabolic products (31). Following the extensive use of fluorescence spectra in PAH studies, Cook and Regina drew upon Clar's studies to survey UV spectra in order to establish relationships between bond structure and the longest UV absorption of various PAHs (32). Significantly, many compounds prepared and characterized by Clar have in recent years proved important in the development of pentacene (five fused linear rings)-based semiconductors.

In 1945 Regina Schoental discovered that most of her family had perished in the Holocaust, including Phillip Eisenberg (d. 1942). A sister-in-law and her thirteen-year-old daughter survived, by escaping to the Soviet Union, where they were sent to Boukhara. Regina's brother, Wincenty, died there in 1942, of typhus. After the war the child was repatriated to Poland and placed in a clearing camp for orphans at Lodz. At the end of 1946, Regina brought the girl, Marya (Matylda Maria Ludwika [Marion]), to Britain and arranged for a home and education; in the early 1950s Marya studied medicine at the University of Glasgow. The trauma brought on by the loss of family led Regina after 1948 to develop close contacts with colleagues in Israel, where from the mid-1950s she attended conferences dealing with cancer, diet, toxic plants, and related topics. Regina, incidentally, never recorded her attitude toward Clar, who during the war had remained in Nazi-occupied Sudetenland, where he continued his research. However, he appears to have had little interest in politics and no sympathy for the Nazis. Regina's professional connection with Clar was certainly congenial.

Regina was awarded the D.Sc. by Glasgow University in 1950 as a result of her syntheses of PAH derivatives and study of the metabolic products of PAHs. This work was continued, for example, with Friedel-Crafts succinoylations of anthracene. At that time she began looking for more permanent employment. In 1950, she joined the Glasgow Royal Cancer Hospital Research Department (from 1952 the Cancer Research Department, Royal Beatson Memorial Hospital), directed by Peter R. Peacock, and continued studies mainly on the metabolic fate of carcinogenic and related PAHs in mice and rats. Tobacco alkaloids were another topic. As a result, during 1951, Regina published a note on the dangers of cigarette smoke in the *Lancet* (33). Much of her research was carried out in close collaboration with Cook (34).

From September 1952, Regina spent just over one year with the Oncology Department, Chicago Medical School, working on the synthesis and metabolic fate of C-14 labeled 8-methoxy-3:4-benzpyrene. Since on her arrival the laboratories were not complete, she took the opportunity to travel to research institutes on both the east and west coasts. Later she wrote up her impressions of the trans-Atlantic trip for a lecture before an audience of British biochemists. The draft reveals humor and amazement, as she emphasized bigness, the overriding role of instruments and even casual dress (35).

> The thing that strikes immediately a visitor from [Britain] is the terrific activity in Scientific Quarters. Enormous research laboratories are either under construction or have just been finished everywhere you go. The American approach to expanding research is a bit different from what it is here. Once they have the money for an institute they build one which obviously has to be bigger and better than any other; then they equip it with the most modern instruments and gadgets available on the market, then they start to think what actually to do with all this, and whom to appoint for the work. This last item, to find appropriate research workers, causes a lot of headache to directors and administrators. So many new laboratories, Scientific and Industrial, have grown up like mushrooms in the last few years, that there are not enough people to go round and staff them.

As for the obsession with instrumentation:

> During my stay in Chicago I isolated an impurity present in starting material used for the manufacture of detergent which was suspected of being carcinogenic. Naturally the manufacturers became alarmed and sent their chemists to discuss the matter with me. In the course of our discussion, on the possibilities of the identification of this substance, these industrial chemists just casually said: "We shall have a couple of x-ray analyses done, some infra-red and ultra-violet absorption spectra, and then see what more is needed." No one suggested that a simple oxidation or reduction may give a lot more information.

Woods Hole on Cape Cod produced some surprises, especially for a European lady accustomed to somewhat formal sartorial standards (35):

> All wear just jeans and short sleeve shirts or blouses, men, women and children, young students, or Nobel prize winners, half a dozen of whom you can find there any time of the summer.

Regina also found time to attend a Gordon Research Conference on cancer at New London, New Hampshire, a symposium on organic chemistry at Ann Arbor, Michigan, and three major scientific meetings in Chicago.

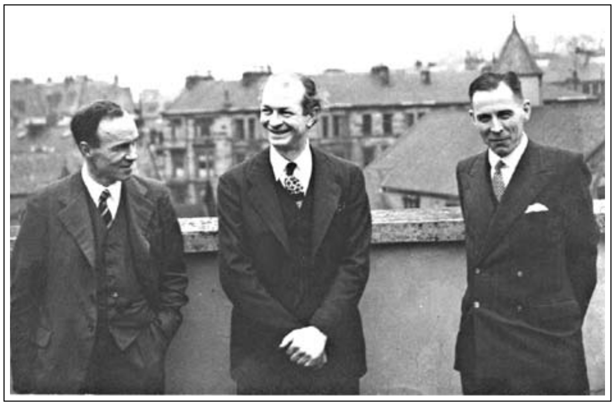

Figure 3. *From left to right: John M. Robertson, Linus Pauling, and James W. Cook, on the roof of the chemistry building, Glasgow University, April 1948. Photographer unknown. Schoental Archive, Edelstein Center.*

Pyrrolizidine Alkaloids

In 1953 Regina returned to the Beatson, but in January 1955, either because funding from the British Empire Cancer Campaign ran out, or of her own accord, she left the Glasgow hospital. One reason was that the cancer campaign would not support her work on a new topic, toxic pyrrolizidine alkaloids and liver disease, in which she had taken a serious interest in Cook's laboratory. There in 1949, Regina and Cook, in collaboration with E. Duffey of the Glasgow hospital, investigated the connection between alkaloids extracted from the weed ragwort and primary liver tumors. An undated draft research report noted (36):

> This would be the first instance of a natural product exhibiting carcinogenic action (all the known carcinogenic substances are synthetic chemicals or products of chemical industries), and would obviously open new fields for further investigation.

By early 1955, as a result of this change in research interests, Regina was again seeking a new post. During April and May, residing at The Brangwyn Hotel in London, she was in touch with Derek H. R. Barton, then at Birkbeck College, University of London, and about to take on the regius professorship at Glasgow, with a research proposal based on the toxic alkaloids to be undertaken in Glasgow (in 1954, after Cook became principal of University College Exeter, his former post was split; Robertson became head of the chemical laboratories). Barton could gain no support for her proposal in Glasgow. When Regina advised him that she intended to apply for a Council of the Royal Society Tropical Fellowship, as advertised in *Nature*, she received his endorsement (37). This research work, however, would have to be done elsewhere. The tentative proposal, a topic connected to the alkaloids, was entitled "The Chemical and Biological Study of Herbal Medicines Used in Tropical and Subtropical Countries for the Treatment of Women and Infants, with Special Reference to the Hepatotoxic Constituents in Such Herbs." Regina's research application was based on statistical information of liver disorders, particularly liver cirrhosis, in Israel, that showed significant increases with the immigration of Jews from "oriental" countries (Yemen, Iraq, Iran, and North Africa). These immigrants had brought with them various herbal remedies that Regina wished to study as potential hepatotoxic agents. It was a unique opportunity, though it did not suit the needs of Glasgow's chemistry department, that would couple Regina's interest in Israel with a medical problem there that was relevant to many other countries in the Near East, Africa, and Asia. She had on her first visit to Israel in February, 1955, shortly after leaving Glasgow and at the invitation of Berenblum, attempted to stimulate interest into herbal remedies, but without success. Regina later noted that despite this lack of interest in Israel, as well as from the Medical Research Council and Colonial Office in England, a Palestinian Arab in Kuwait and Egyptians had recognized and studied the problem of toxic herbs.

The successful award of the fellowship marked the beginning of a change in the direction of Regina's research; at least, until around 1960, it opened a second branch. On July 1, 1955 Regina joined the Medical Research Council (MRC) Toxicology Research Unit, at Carshalton, Surrey, directed by toxicologist John M. Barnes. The unit was established by Barnes, who had served as a Royal Army Medical Corps officer associated with the Biology Department, Porton Down, during World War II, at the Porton site in 1947; the unit was moved to Carshalton in 1950. Regina, initially funded with the Royal Society research fellowship, was "very happy to have left the Peacock's Department—there is so much more scope and facilities for work here (38)."

Carshalton, "Epping Jaundice," Australia, Africa, and London

In addition to her new research topic, Regina continued with aromatic chemistry, mainly on PAHs, at Carshalton, collaborating with colleagues at Glasgow University and at the Beatson. In 1957 she isolated 3,4:9,10-dibenzpyrene from coal tar. Fortunately, it had been prepared in 1939 by Clar, and his assistance enabled identification. Interest in its carcinogenic activity was stimulated by the fact that in 1956 it had been reported as a constituent of cigarette smoke. In 1964 Regina, now a world authority on the toxicity of carcinogenic PAHs, published an extensive review of carcinogenesis caused by PAHs in Clar's new book, *Polycyclic Hydrocarbons*. In her historical introduction dealing with the discovery of coal-tar carcinogens, rather than engage in polemics over the matter of where most credit was due she simply noted, with references, that (39):

> The story of the exciting and successful discovery of the first carcinogenic constituent of coal tar, 3,4-benzopyrene…has been told by Cook and Kennaway, who recorded the contributions of each individual worker associated with this problem.

Toxicological problems associated with industrial hygiene and cancer in general led to appointments on various committees. Her assignments included the investigation of an outbreak of poisoning known as "Epping jaundice" in February, 1965. Regina established that the cause was contamination of bread in the Epping district of London by the epoxy resin hardener 4,4'-diaminodiphenylmethane, used in the CIBA resin araldite. The hardener, during transport by road, had escaped from containers and mixed with flour later used to make whole meal bread. Some 84 people were hospitalized after they had consumed the affected bread. The results were published in *Nature* (40). Other aromatic amines investigated included β-naphthylamine, benzidine, and azo dyes. Unlike carcinogenic PAHs, whose effects were at the site of application or injection, the target organs for aromatic amines, mainly the bladder, were distant from the place of administration.

The emphasis on aromatic hydrocarbons declined as novel areas of research became available through association with the prestigious MRC unit and its wide ranging contacts outside Britain. As a result, the pyrrolizidine (*Senecio*) alkaloids, those found in the herbal remedies, particularly in the tropics and subtropics, featured increasingly in Regina's research interests from the late 1950s. They were also available from products sold by herbalists in Britain. The study of their carcinogenic action, particularly their ability to induce chronic lesions and tumors in the liver, pancreas, etc., was often undertaken in collaboration with Peter N. Magee at the MRC unit (Magee later moved to the Courtauld Institute of Biochemistry at Middlesex Hospital). Pyrrolizidine alkaloids are phytotoxins prevalent throughout the plant kingdom. Ingestion by animals of these "pyrrole" derivatives in plants is a common cause of poisoning. Over 150 members have been isolated and identified, including their structural determinations. Most are toxic after both acute and chronic exposure, and have continued to stimulate research in toxicology.

Opportunities for work-related travel, including attendance at conferences and convenient stopovers on long haul flights, aided considerably the interest in toxic substances in plants. For five months in 1960, Regina was at the Commonwealth Scientific and Industrial Research Organization (CSIRO) chemical research laboratories in Melbourne, Australia. On the outward journey she visited African countries and on return, early in 1961, several Asian countries, including India, where she lectured on hepatotoxic plants and liver disease (41). In 1963 she produced liver disease in experimental animals comparable to those encountered in humans. During 1964-1967, with Björn B. Afzelius of Stockholm, Regina collaborated in studies on the toxic action of retrorsine, an alkaloid found in certain South African *Senecio* species. Some of this work was done while Afzelius was on sabbatical leave at the University of St Andrews, Scotland, in 1964. The contacts made during the 1961 trip were of tremendous importance in gaining information for a comprehensive review of liver disease and its connection with both natural and synthetic hepatotoxins. Studies on human toxicity following the ingestion of pyrrolizidine alkaloids in foods and folk medicines took Schoental back to African countries, where she was warmly welcomed. During 1970-1971 she was in Ethiopia and East Africa (Tanzania, Uganda, Kenya), mainly in search of plants used as herbal medicines, beverages or foods, in order to continue and broaden investigations into the role of hepatotoxic plants in liver disorders. The health hazards connected with the herbal remedies, particularly in Ethiopia, were of great interest to her.

Regina also studied, from around 1960, the toxicity of diazomethane ("the simplest alkylating agent," and among carcinogens "the simplest of them all"), and certain nitroso compounds (42). Around 1965 she investigated human nasal tumors, particularly in furniture workers and wood machinists. This followed her work (with S. Gibbard) on carcinogens in Chinese incense smoke, again as a result of the MRC's international standing, and which, since the products were derived from wood, was extended to a study of cancer of the nasopharynx in English furniture workers (43). Among the Chinese population, the highest incidence of cancer of the nasopharynx was found in the south, in Kwangtun Province, Hong Kong, and Macao. Several PAHs, including 3:4-benzo(*a*)pyrene, were isolated from incense smoke by thin layer and column chromatography, with detection by UV. The benzpyrene was estimated fluorimetrically. In the search for suitable aldehydic constituents of lignins, as an extension of this work, samples of tannins were procured from the British Dyewood Company, Glasgow, in 1969. This was an example of Regina's special interest in different pathological conditions that appeared to be prevalent in certain countries. In this case the study of a Chinese problem was found to be applicable to conditions in a sector of British industry, as well as in Kenya (44). There were also studies on metabolites of *Fusarium* and other microfungi (45). In 1967 Regina supplied Stephen Mason at the University of East Anglia samples of high-polymer DNA and the methylated DNA for optical rotatory dispersion (ORD) and circular dichroism (CD) measurements. Other topics around 1970 included the carcinogenicity of oestrogens. Her work on the possible impact of tricothecene toxins in human diseases attracted considerable interest in the early 1980s.

At the end of September, 1971 Regina reached statutory retirement age and left the MRC toxicology unit. In the same year she joined as a visiting worker, at first without research funds, the Department of Pathology, Royal Veterinary College, University College, London, where she continued research into pyrrolizidine alkaloids and nitroso compounds until final retirement in 1988. The publication in the same year of *Pyrrolizidine Alkaloids* by the World Health Organization clearly demonstrated her pioneering role in the understanding of these toxic natural products (46). She maintained contact with colleagues in Africa and Israel, including Isaac Berenblum (who had joined the Weizmann Institute at Rehovot in 1950 to inaugurate its cancer research program).

Berenblum and Schoental

Isaac Berenblum's correspondence with Regina hinted at the professional tensions and rivalries at Oxford in the mid-1940s, and the breakup of the group of cancer researchers there. By early 1947, he was considering taking up a post at the Sieff Institute in Palestine (from 1949 the Weizmann Institute), after spending two months in the United States (47). However, in October, 1948 he joined the National Cancer Institute, National Institute of Health, in Bethesda, Maryland, as visiting special fellow, working on skin cancer induced by 9,10-dimethyl-1,2-benzanthracene. In September 1949, shortly before he emigrated to what had now become Israel, Berenblum told Regina that he was glad that she enjoyed a conference at Cambridge, "if even the presence of Chain did not put you off…," a reference to Chain's volatile and abrasive personality, as much as cultural differences (48). (Chain had also left Britain in 1948, for Italy, after declining the post at the Sieff Institute that was taken up by Berenblum, returning in 1961 to Imperial College.) In 1949 Regina had wanted to test the carcinogenecity of 8-benzpyrenol at Oxford, but she was advised by Berenblum that the cancer unit was being closed down: "Florey made this decision when he heard that I was not coming back. I always knew, and told you myself, that he never had any love for keeping cancer going (48)." Regina had also enquired about the possibility of joining Berenblum at Rehovot, but their own strong differences around 1945 no doubt influenced Berenblum's decision (48):

> On the matter of the possibility of your joining me at Rehovoth, I wished you had not put me in the position of having to answer it. You know that I think highly enough of your work, and that I have always tried to fight your battles against those who were prejudiced against you, and even those who pretended to be your friends but never went out of their way to help you. But you must surely remember the last year of our collaboration. I remember it only too well, and cannot see myself doing anything that might lead to a repetition of it. Please believe me that I am not harbouring any grievances; I really do hope that, from a distance, we could forget the unpleasantness of that association and only remember the years of amicable and fruitful collaboration.... Please let us forget it all and continue as friends.

Certainly they remained good friends, often exchanging information about scientific and family matters, and making use of their several contacts. In 1955, for example, Regina arranged for pure anthracene to be sent to Rehovot by Cook, who had generously provided samples to several research groups.

As mentioned at the outset, Berenblum opined that Regina's constant travels and moves, sometimes as a result of her own preoccupations, particularly with liver disorders, including cancer, in many ways prevented her from gaining a tenured or senior academic post. There were also the personal difficulties, hinted at by Berenblum, and by colleagues at the MRC. Nevertheless, she was very highly regarded, particularly by Berenblum and Cook, while Barnes appreciated her as an extremely competent scientist and a valuable member of his MRC team.

Regina Schoental contributed a chapter to *Chemical Carcinogens* (ACS Monograph no. 173) (49), edited by C. E. Searle, and to the enlarged two-volume work (ACS Monograph no. 182) (50), and co-edited, with T. A. Connors, *Dietary Influences on Cancer: Traditional and Modern* (51). She was Member of Council, Royal Society of Medicine, Section of Oncology, during 1979-1982 and a member of both the Chemical Society and Biochemical Society. In later years she spent much time applying scientific theories, often based on her toxicological studies, to speculate, for example, on the causes of catastrophic events recorded in the Bible, George III's attacks of madness, the deaths of homosexual lovers of great musicians, and HIV infections and AIDS.

Regina Schoental's portrait appeared on the cover of *Cancer Research* in February, 1988 and again on September 1, 1991, this time accompanied with a one-page review of half a century of research, written by biochemist and cover editor Sidney Weinhouse of Philadelphia (52). She published widely in leading international journals, including *Journal of the Chemical Society*, *British Journal of Cancer*, *Lancet*, *Nature*, *Biochemical Journal*, and *Cancer Research*, as well as in journals published in Poland, Australia, East Africa, India, and Israel. Regina Schoental never married. She passed away on January 29, 1995 and is buried in Jerusalem.

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1. Much of the information for this article has been taken from CVs and research proposals drawn up by Regina Schoental and now held with the Schoental Archive, Sidney M. Edelstein Center for the History and Philosophy of Science, Technology and Medicine, The Hebrew University of Jerusalem, Israel (hereafter SA).
2. Schoental to Berenblum, September 26, 1983 (SA).
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An ACS Councilor since 1972, Jack was Chairman of the Division of the History of Chemistry in 1990, ACS Representative to the Chemical Heritage Foundation (CHF) Council, and a dedicated member of the Bolton Society. At the family's request, memorial gifts in Jack's name can be sent for Project SEED Scholarships to ACS Office of Development, 1155 16th St, NW, Washington, DC 20036.

SOME NOTES ON THE EARLY HISTORY OF NITRIC ACID: 1300 – 1700

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Introduction

Nitric acid is one of the compounds that have played an important role in alchemy, chymistry, and crafts. The first clear European recipe for its preparation is in the Latin treatise *Liber de inventione veritatis*, which appeared around 1300. Together with four further works, this treatise formed a corpus initially considered to be of Arabic origin, compiled by Jābir ibn Hayyān, known in Europe under the Latinized form of his name Geber. In the medieval Arabic world doubts had already been expressed as to whether this alchemist had actually ever lived. Confusion concerning the authorship of the works under Jābir's name continued well into modern times. H. Kopp, who dealt extensively with the history of nitric acid, originally considered Jābir to be the author of the corpus and thus of *L. de inventione veritatis*. It has been recognized subsequently that these books are of European origin, influenced by Arabic sources. Called the Pseudogeberian corpus, it was then generally accepted as a source that had introduced nitric acid in Europe.

This compound brought deep changes in alchemy and in crafts, especially what concerned new approaches to assaying, because it allowed the separation of gold from the rest of metals in a wet process. Simultaneously, reactions of nitric acid with these metals led to new compounds and thus to the broadening of knowledge that gradually contributed to the development of chemistry (1). Yet, further studies of alchemy and early chemistry have revealed that the history of nitric acid is more complicated. As will be shown, a serious obstacle in this study is old terminology, which makes it difficult to decipher texts with sufficient reliability. With these problems considered, there appear signs that nitric acid could have been known before 1300 and not only in Europe. The history of this compound is therefore not a closed chapter.

In Search of Nitric Acid

Nitric acid was no exception in the confusing language of early-modern chemistry. There are two principal problems in analysis of old chemical terminology (2). In some cases, one name was assigned to several different substances; in the particular case of nitric acid it was, for example, the term *aqua corrosiva* that reflects the ability of this compound to "corrode" or dissolve metals. Yet, other mineral acids posses this same property as well. As a result, "corrosive water" sometimes stood for sulfuric acid, but this expression could also denote mixtures of mineral acids that originated from a combination of various compounds.

The second problem is the use of many different terms, sometimes chosen arbitrarily, for one substance. This too is the case with nitric acid: the earliest known recipe calls it *aqua nostra dissolutiva* ("our dissolving water"), but during the subsequent centuries a variety of terms appeared. Some of these are summarized in the table. They can be roughly divided into three groups.

The first of these includes the word "aqua," an allusion to one of the quartet of Aristotelian elements. The second, more complex group includes three terms. "Spirits" denoted vapors in general and also various volatile substances (such as mercury). Thus, fumes escaping from an acid were also considered to be spirits. "Oleum" referred to the consistency of a liquid compound, which could resemble that of oil. Eventually the term "nitri," derived from *sal nitrum* (known as saltpeter, mostly potassium nitrate), was introduced as the ingredient from which nitric acid was made (3). The term "aqua nitri" therefore belongs in both the first and second groups.

The third group comprises the potentially confusing code names that alchemists often used in their texts. For example, *aqua mercurialis* seemingly hints at mercury rather than at nitric acid, but was used for this acid (4) and sometimes for $SbCl_3$ (the latter compound was also known as *butyrum antimonii*, for its butter-like consistency).

Table. Names of Nitric Acid as they appear in Old Sources

- Aqua fortis
- Aqua acuta
- Aqua calcinativa
- Aqua caustica
- Aqua dissolutiva
- Aqua gehennae
- Aqua gradatoria
- Aqua mercurialis
- Aqua nitri (sometimes used for sal alcali, K_2CO_3)
- Aqua nostra dissolutiva
- Aqua solvens
- Aqua stygia (sometimes used for a. regia)
- Aqua valens
- Oleum nitri
- Rubigo nitri
- Spiritus acidus nitri
- Spiritus fumans Glauberi
- Spiritus nitri
- Chrysulca
- Draco
- Protheus
- Roter Löwe
- Salamanderblut
- Stomachus
- Struthionis
- Sudor hermaphroditici

European Origins

The oldest known unambiguous European recipe for nitric acid is found in the *Liber de inventione veritatis,* a part of a corpus originally assumed to be translations of the works of Jābir ibn Hayyān, Arabic alchemist known as Geber in Latin Europe (5). However, it has been suspected since the late 19th century that these works are of European provenance, compiled by an unknown author sometime around 1300. The authorship of this corpus was consequently attributed to an anonymous Pseudogeber (6), and speculations as to the exact dates and authorship of these works continue today (7). According to Newman, *Liber de inventione veritatis* was written shortly after *Summa perfectionis* as a commentary on this book (8). A more precise dating of these works is problematic, as is the dating of the discovery of nitric acid. As will be shown, this is not the only confusion in the early history of this compound.

The recipe in *L. de inventione veritatis* is as follows (9):

> In the first place I will speake about our solvent [*aqua nostra dissolutiva*] that I had mentioned in our 'Summa,' there, where I had spoken about dissolving with strong liquids. First take one pound of vitriol [$CuSO_4.5H_2O$], one half of a pound of saltpeter [KNO_3], and one quarter of a pound of alum [$KAl(SO_4)_2.12\ H_2O$]. Prepare this liquid with red [color ?] of alembic, because it has a high solvent action. Use it, as was given in the preceding chapters. It will be yet much stronger if thou dissolveth a quarter of a pound of sal ammoniac [NH_4Cl] in it. This liquid then dissolves gold, sulfur, and silver.

The reference to *Summa* was obviously an intentional attempt to link both treatises, but there is no mention of any "strong water" in the *Summa* (10). In fact, the cited recipe leads to two potent solvents: the beginning describes the preparation of nitric acid, whereas the subsequent addition of sal ammoniac turns it into *aqua regia*, a mixture of hydrochloric and nitric acid, which indeed dissolves gold. The expression "red [color ?] of alembic" suggests that a high temperature is necessary, that the alembic (distilling apparatus) should glow red. With the discovery of *aqua regia*, gold ceased to be the "immortal" metal that it had long been considered to be because of its low chemical reactivity. Yet, the formulation of this recipe does not suggest that its author had discovered the acid.

It should be stressed that the recipe for nitric acid in *L. de inventione veritatis* is currently accepted as the first unambiguous one, which had appeared in

Europe. Discovery of strong mineral acids, particularly nitric acid and *aqua regia* derived from it, had likely occurred repeatedly as independent acts, but this knowledge did not spread; it remained unnoticed or maybe it was not understood correctly. Nitric acid could have been prepared unintentionally since the necessary ingredients, potassium nitrate and iron or copper sulfate, had been known from ancient times, and alchemists especially used distillation as one of their essential techniques (11).

It is difficult to trace these discoveries, because before introduction of nitric acid in mediaeval Europe no special term for this compound was used. The allusions to "strong waters" that occur sometimes in old texts could be confusing. They could stand both for acid and alkaline solutions. These "waters" could also denote such solutions produced by hydrolysis of suitable salts. Furthermore, the passages in question could be later insertions into an older text.

According to Multhauf (12), mineral acids were not implied in the meaning of this word, but they have been gradually recognized over two centuries beginning *at least* as early as 1300. He points out that neither Albertus Magnus (before 1200-1280) nor Roger Bacon (1214/1220-after 1292) knew of these substances, in spite of the fact that it was Bacon who was the first to mention saltpeter, Albertus also did not mention Pseudogeber's work — what is considered a sign that it appeared later, and its dating around 1300 can be accepted as correct. These facts, however, do not prove unequivocally that mineral acids had not been prepared before this time.

On the contrary, Multhauf supposed that alchemists were familiar with mineral acids earlier. According to this author these substances had appeared in their treatises in a broad span of time, from the twelfth-century *De aluminibus* (attributed to Pseudorhazes) to Pseudolullian *Testamentum* that in Multhauf's words appeared two centuries later (13). Nitric acid in more or less pure form could have been prepared incidentally as a byproduct or intermediate substance in some process. Only later properties of this substance were sufficiently recognized, and the technique was worked out for its production. The technical problem of preparation of nitric acid was obviously the obstacle that slowed down its introduction into wider use (14). Although the earlier occurrence of this acid might sound plausible, this statement remains hypothetical unless new information is uncovered.

Occasional references to nitric acid appeared soon after 1300. For example, the cardinal Vitalis de Furno (1260-1327) is also supposed to have prepared this acid (15). According to his recipe *sal petrae* and *corprosse* (copper sulfate) mixed with *aqua ardens* (alcohol) should be distilled. This process should be repeated and the "water" made in this way was said to dissolve all metals. The recipe is problematic, because gold, too, is mentioned among these metals; but no further ingredients are given in the text that could have produced *aqua regia*. Nevertheless, the original inorganic ingredients and description of the effect of the product make it quite plausible that it was nitric acid. The date of Furno's death helps narrow the possible time when nitric acid appeared in Europe, if *L. de inventione veritatis* were really the first account of it.

As Multhauf further added, from 1350 onwards references to some mineral acid appear more frequently in alchemical literature. In *Rosarius minor*, attributed to Arnald of Villanova (16), "the key to seven gates" of the rose garden should be actually *aqua fortis* produced from vitriol, saltpeter, and alum, denoted as "three herbs" in the text. In his search for "sulphur of philosophers" John of Rupescissa (active around 1350) alluded to nitric acid and concluded that this substance is humidity or spirit drawn from saltpeter and Roman vitriol (copper sulfate).

A later account appeared in *Das Buch der Heiligen Dreifaltigkeit*, an anonymous German alchemical manuscript, the oldest version of which was compiled between 1410 and 1415/17. Nitric acid is mentioned here as *aqua fortis*. This treatise was influential especially because of its symbolical approach to alchemical topics (17).

These references document that nitric acid entered alchemical laboratories first; only later did craftsmen, too, employ this substance. Because of technical problems, originally only small amounts of this compound were prepared.

Possible non-European Origins

The Indian alchemical treatise *Rasarnava* is supposed to have been compiled around the twelfth century A.D., but this dating is doubtful. Because of their philosophical views, Indians were not especially concerned with time, and therefore did not often date their texts. If the age of *Rasarnava* were accepted, any discussion about mineral acids should be more complex. The text in question is a dialogue between Bhairava (the god Shiva) and his consort Parvati, both of whom are crucial figures in Indian alchemy (18). Bhairava first lists the metals known to him: gold, silver, copper, iron, tin, and lead. He adds that their resistance to waste decreases in that order. He continues (19):

> Hear attentively as I shall now speak of the killing of metals. There is no such elephant of a metal which cannot be killed by the lion of a sulfur.

In the language of European alchemy "killing" denoted a process in which metals lose their metallic appearance through their transformation into some compound (20).

Bhairava gives the following recipe ingredients: "Green vitriol, rock-salt, the pyrites, stibnite (21), the aggregate of the three spices (black pepper, long pepper, and dry ginger), sulfur, saltpeter" and some plant juices, which surely did not play any real role in the process. But when this mixture was processed in the proper way, "…it makes a vida, which would kill all [the metals]" (22). It is not easy to decipher this text, because the crucial information about how this mixture was to be treated is not described. If it were distilled, then, pepper and ginger aside, the product would have resembled the mixtures that European alchemists used for the process of gradation (discussed below).

In the same treatise, there is also a recipe entitled "killing of gold" (23):

> Saltpeter, green vitriol, sea-salt, rock-salt, mustard, borax, sal ammoniac, camphor, the pyrites – all these are taken in equal parts. The crucible is to be smeared with the milky juice of *Euphorbia neriifolia* and *Asclepia gigantea*; then having added the power of the aforesaid 'vida,' the gold is to be killed, my beloved!

Killing of gold could be comprehended as its dissolution. Depending on the quantity of the combined substances and their processing, the Indian recipe could indeed have led to *aqua regia*, even though it would likely have contained other compounds as well. Indian scholars (24), careful in their conclusions, nevertheless admit that although the old texts do not mention mineral acids explicitly, it cannot be excluded that they had been prepared (25). Otherwise, the intentional use of these acids for dissolving metals seems not to have appeared in India before the sixteenth century. The "vida" thus remains a mystery.

The allusion to a substance that could dissolve wood, gold, and iron already appeared in the Chinese account written by Tuan Chhêng-Shih in 863 A.D. (26). According to this source, an Indian prince captured by the Chinese claimed to know the *Pan-Chha-Cho Shui* (Punjab "water" or "liquid") that must be handled with extreme care since it "melts and destroys hands." The old accounts should be taken cautiously; yet in this particular case the "water" able to dissolve gold could have been *aqua regia*. On the other hand the Indian prince could have exaggerated in his statements. In any case, the Chinese source points to India.

In the Arabic world, too, some early allusions appear that could be explicated as recipes for nitric acid or *aqua regia*. A recently analyzed work entitled *Kitāb Thahīrat Al-'Iskandar* ("The Book of the Treasure of Alexander"), supposed to be of Harrānian origin, was compiled probably in the 9th century A.D., but the oldest known manuscript is from 904 A.D. (27). Among various alchemical recipes dealing with typical procedures for purification of different substances or transmutation of metals, there is a text under the heading "Recipe for the grand softening water which Hermes called Kāliānūs, meaning the one that removes dryness" (27):

> A mixture of horse-hooves scraps, donkey-hooves scraps, scraps of goat horns, and similar ingredients should be buried in dung for two days. On the third day vitriol and sal ammoniac were to be added dissolved beforehand in water, and finally this mixture was distilled in a cucurbit. The obtained water of golden, bright color allegedly softens "white copper.

The recipe is not quite clear, but as the authors of this study suggest, it could have produced *aqua regia*. Decomposition of organic matter (hooves, horns) could result in nitrates if the process took longer than a few days. Subsequent addition of vitriol and sal ammoniac could then lead to a mixture from which a strong mineral acid could be isolated by distillation. Problematic is "white copper;" should it be copper or one of its alloys, this material would likely dissolve in *aqua regia* rather than be softened, unless "softening" would denote dissolution.

Mansur al-Kamily, chief chemist at the Egyptian mint at Cairo in the 13th century, wrote a practical handbook on the extraction, purification, and assaying of gold. According to Holmyard (28) who mentions this person, Arab chemists were already well acquainted with parting of gold and silver by nitric acid by that time, a century before *L. de inventione* was compiled.

Two Nitric Acids?

In 1735 the Scottish scientist William Cullen (c. 1710 – 90) remarked (29):

> It is certainly improper to support… different names where there is no real difference of the thing. How really these different names mislead may be observed from hence that in almost every table of specific gravities there occur in two distinct articles the specific gravities of spirit of nitre and aqua fortis.

Both terms stood for nitric acid, but in former times two basic kinds of this compound were distinguished.

This distinction depended on the ingredients used for their preparation, as Johann Rudolf Glauber (1604-1670) had introduced it. He called *salis nitri spiritus* (later only *spiritus nitri*) nitric acid prepared from saltpeter and alum, whereas this same acid made from saltpeter and vitriol was *aqua fortis* in his terminology (30). Glauber, however, noted that both acids serve the same purpose — dissolution of metals — and concluded that they are obviously "almost one thing and have the same effect" ("bey nahe ein Ding [sind] und gleiche würckung haben").

Later he worked out a method of direct production of relatively concentrated nitric acid by distillation of saltpeter with sulfur; yet he did not publish this process. It was said that he communicated it only by word of mouth in exchange for payment (31). In this process sulfuric acid is formed, which reacts with saltpeter to produce nitric acid and *nitrum vitriolatum* (potassium sulfate). According to other sources (32), Glauber performed this reaction directly with sulfuric acid and sodium nitrate. As a byproduct he obtained sodium sulfate, later known as Glauber's salt (33).

In his textbook *Cours de chymie,* Nicolas Lemery (1645-1715) described the preparation of both *spiritus nitri* and *aqua fortis* (34). The first procedure took about 14 hours (35), the second only eight to nine hours; but as Lemery stated, in this process the resulting product was a mixture of *spiritus nitri* and *spiritus vitrioli* (nitric and sulfuric acid) (36). In Lemery's opinion, the vitriol and the earth added in the second process only served to separate the particles of *sal nitrum* tightly bound together in the original substance.

Reconstruction of Nitric Acid Production

In the 1950s Schröder (37) attempted to reproduce the preparation of nitric acid according to some original recipes. To simulate the conditions of the old laboratories, he preferentially used minerals from deposits mined in the past, or substances preserved in old collections. The joints of the laboratory apparatus were "luted," tightened with a mixture including clay, straw, horsehair, egg white, and other substances, as was common practice in earlier centuries. The temperature regime closely simulated the heating produced by wood- or charcoal-burning furnaces. In this way, Schröder followed two basic procedures described in old literature and paraphrased below (38):

> *Aqua fortis*: The dry distillation of a mixture of 150.0 g of saltpeter, 150.0 g of vitriol, and 50.0 g of alum was performed in an earthen vessel at approximately 800°C. The resulting 70.0 g of HNO_3 corresponded to 74% of the theoretical yield, but subsequent analysis demonstrated that the product contained nitric acid of 51% concentration and a small admixture of nitrous acid of 0.4% concentration. The solution had a blue color when fresh, due to dissolved N_2O_3, but this color eventually disappeared.
>
> *Spiritus nitri*: The dry distillation of a mixture composed of 50.0 g of saltpeter and 150.0 g of bolus alba (hydrated aluminosilicate, white clay, kaolin) was performed in an earthen vessel at 800-1000°C. This procedure produced 8.0 g of blue-green distillate corresponding to 32% of the theoretical yield when calculated as pure HNO_3. The product was, in fact, nitric acid (concn. 53.2%) with a small admixture of nitrous acid (concn. 0.6%). The blue-green color of this solution eventually changed to a light yellow.

Soukup and Mayer (39) later performed a similar experiment in the interest of explaining its chemistry. They tested a procedure from Agricola's *De re metallica* (40), using 4 pounds of vitriol, 2 ½ pounds of saltpeter, ½ pound of alum, and 1½ pounds of spring water. In this process, "a blue or intermittently green liquid could be observed in the condenser, which drops into the receiver with vigorous evolution of gases." This gas was N_2O_3 produced by the following sequence of reactions:

$$2\ CuSO_4 \rightarrow 2\ CuO + 2\ SO_2 + O_2$$

$$KNO_3 + SO_2 \rightarrow KO_3SONO$$

$$2\ KO_3SONO \rightarrow N_2O_3 + K_2SO_4 + SO_3.$$

If the cooling is insufficient, N_2O_3 decomposes:

$$N_2O_3 \rightarrow NO + NO_2$$

In the opposite case, this oxide dissolves in water to produce nitrous acid

$$N_2O_3 + H_2O \rightarrow 2\ HNO_2,$$

which disproportionates:

$$3\ HNO_2 \rightarrow HNO_3 + 2\ NO + H_2O.$$

Nitrogen (II) oxide reacts with the oxygen produced by the decomposition of $CuSO_4$:

$$2\ NO + O_2 \rightarrow 2\ NO_2$$

and the NO_2 formed in this step leads to further nitric acid:

$$4\ NO_2 + 2\ H_2O + O_2 \rightarrow 4\ HNO_3$$

At higher temperatures and insufficient cooling, side reactions accompanying this basic sequence may produce nitrosylsulfuric acid, sulfuric oxide, and water vapor. In these cases, N_2O_3 does not always form, and both nitric and sulfuric acids can result. This mechanism explains Lemery's assumption that *aqua fortis* is a mixture of two acids; the French chemist had apparently deviated from the appropriate conditions of his experiment. Furthermore, the contamination of saltpeter by potassium chloride leads to a small amount of hydrochloric acid.

If the vitriol is dehydrated prior to the experiment, the entire process can be expressed by the summary reaction:

$$2\ KNO_3 + CuSO_4.3H_2O \rightarrow 2\ HNO_3 + K_2SO_4 + CuO + 2\ H_2O.$$

Agricola's Acids

In Book X of *De re metallica*, Georgius Agricola (1494-1555) deals in detail with the parting of gold and silver (40) "by means of aqua valens, and by powders which consist of almost the same things as this aqua." Agricola first describes what this "aqua" is made of and subsequently provides ten recipes. As he states: "almost all these ingredients contain vitriol or alum, which, by themselves, but much more when joined with saltpeter, are powerful to part silver from gold." Yet, there is confusion even in the first recipe, because "one libra of vitriol and as much salt, added to a third of a libra of spring water" would yield hydrochloric, not nitric acid, upon distillation. However, most of recipes he cites would produce more or less pure nitric acid, such as the fourth one, in which the mixture "consists of two librae of vitriol, as many librae of saltpeter, one quarter of a libra of alum, and three-quarters of a libra of spring water."

The tenth composition is difficult to interpret in modern terms. Agricola points out that the mixture lacks both vitriol and alum, but (41):

> …it contains three librae of saltpeter, two librae of stones which when thrown into a hot furnace are easily liquefied by fire of the third order, half a libra each of verdigris, of stibium, of iron scales and fillings, and of asbestos, and one and one-sixth librae of spring water.

The fusible stones mentioned in this process are not specified, and the indication of the degree of heat as a "fire of the third order" is too vague a characterization.

Agricola concludes that all these *aquae* cleanse gold of its impurities, but there are "certain compositions which possess singular powers." One of the four recipes for such powerful waters runs as follows:

> The second composition is made from one libra of each of the following, artificial orpiment [As_2S_3], vitriol, lime, alum, ash which the dyers of wool use, one quarter of a libra of verdigris, and one and a half unciae of stibium..

Depending on temperature and other conditions (such as the variously impure compositions of the ingredients), the distillation of this mixture could have produced sulfuric and perhaps even sulfurous acid containing various volatile contaminants (such as compounds of arsenic, and maybe of antimony).

Although the examples in this section are from Agricola's *De re metallica*, the works of alchemists abound in similar recipes. Vannoccio Biringuccio (1480-1539), the first of three important metallurgists of the European Renaissance (the other two are G. Agricola and L. Ercker) already noticed this variation of ingredients in alchemical recipes for acids (42). In the first chapter of the eighth book of his work *De La Pirotechnia* (1540) he describes the preparation of "common parting acid" from saltpeter and vitriol, or from alum, which was a more expensive ingredient. Then he turned attention to approaches in which various further ingredients were added (42):

> Alchemists make infinite varieties of acids for their solutions and the aforesaid minerals are the basis of all. It is indeed true that they add sublimates and various salts and other corrosive materials according to their opinion

Yet, he does not elaborate with further details. Various recipes given by Agricola thus stem from other sources, although he drew substantially from Biringuccio.

Indeed, Agricola appears to have copied these recipes from experienced persons and written sources, and is not thought to have necessarily tested them himself. This raises an important point as to who made such mixtures, and what were their uses. The explanation lies in procedures utilized by alchemists and craftsmen alike; in early-modern Europe there was often no hard and fast distinction between the two, with 'alchemical' and 'metallurgical' activities being performed sometimes in the same laboratory, especially in connection with the processing of precious metals (43, 44).

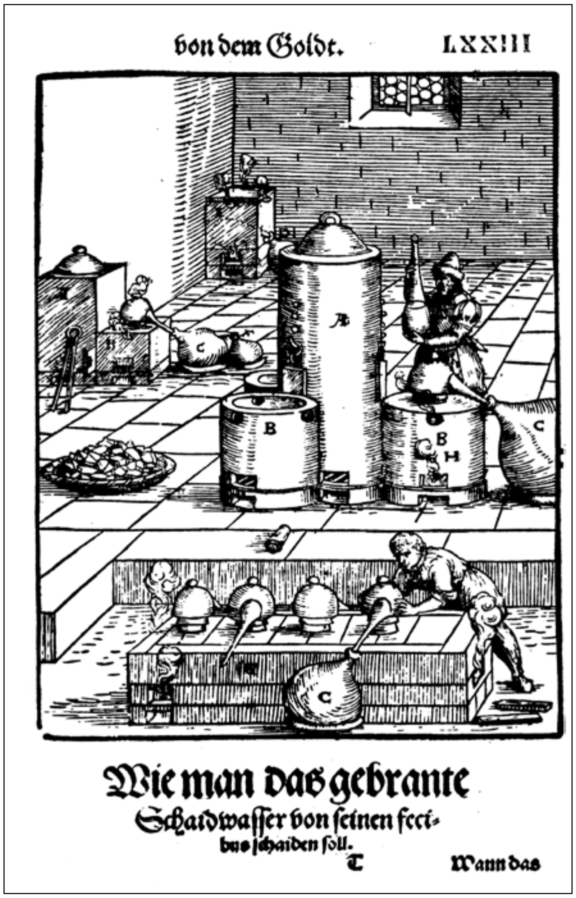
Nitric Acid in the Parting of Gold

Nitric acid is notable for its ability to dissolve all metals except gold, and this property makes it ideal for the separation of the precious metals. The origin of this understanding cannot be dated reliably, but it seems that alchemists were pioneers of this approach. The preparation of nitric acid was not easy, and as mentioned above, it is likely that originally only small amounts of this compound were available, thus allowing only small-scale experiments in laboratory conditions.

Increasing nitric acid production to quantities sufficient for the large-scale isolation of gold was a question of time. Numerous *Probierbüchlein*, assayers manuals, which began to appear from the beginning of the 16th century, indicate that this process became standard practice (45,). Later metallurgists described the isolation of gold in greater detail; Biringuccio's *De La Pirotechnia* was the first example of such works. Two points concerning the processes described by Biringuccio are particularly significant. First, he recommended building a large furnace "for holding three or four pairs of cucurbits or as many as you wish." This clearly reflects that a large-scale production of nitric acid was already common by his time. He also brought attention to safety concerns, remarking that the vessels must be of high quality, and their glass must be without bubbles, "for they would be dangerous" if they broke (46). This warning indicates why the production of larger amounts of nitric acid appeared only gradually.

The second point concerns the subsequent cleaning of the product "if you wish this acid to be good." Pure silver should be added and "you will see the acid begin to grow turbid." This step had the effect of removing traces of hydrochloric acid that were often present because of the contamination of saltpeter by potassium chloride. In this way, hydrochloric acid was precipitated as silver chloride (47).

A quarter century after Biringuccio's treatise Lazarus Ercker (? 1528/30-1594) published his work, *Beschreibung Allerfürnemisten Mineralischen Ertzt* devoted to assaying (48). In the second book of this treatise the most detailed contemporary account on making of both nitric acid and *aqua regia* appears. The preparation of starting substances, vitriol and saltpeter, is described first. Vitriol should be calcined (heated to remove crystal water), whereas saltpeter must not be heated, but it should be cleaned of impurities as described in the fifth book of Ercker's treatise. A typical contaminant was common salt; quite a simple technique was employed based on different solubility of potassium nitrate and sodium chloride in a hot, almost saturated aqueous solution of the former (49).



The equipment for nitric acid production as shown in Ercker's Beschreibung (Fig. LXXIII). The furnace in the center was known as "Heinzen."

Ercker describes various materials suitable for reaction vessels, glass, clay, or iron, and specifies conditions for distillation. He gives two basic recipes. According to the first procedure, four pounds of saltpeter and four and a half pounds of calcined vitriol are used (50). For "remarkably strong Scheidewasser" three pounds of both calcined vitriol and saltpeter, one pound of calcined alum, and two pounds of “burnt silicious stone” (*gebrannte kisling* in the original, perhaps roasted iron pyrite, which surely contains sulfates) should be selected (51). One recipe describes preparation of *aqua regia*. Removal of hydrochloric acid by silver, as described by Biringuccio, appears in Ercker’s treatise as well.

Separation of gold became one of the techniques alchemists employed for the alleged transmutation of metals. The alchemist Wenzel Seiler (? 1648-1681) successfully applied this approach in a famous transmutation performed in 1677 (52). He dipped an allegedly silver medallion weighing 4200 grams into a colorless liquid “tincture,” after which the immersed part seemed to become gold. An analysis of this artifact performed in the twentieth century revealed it to be composed of a gold-silver-copper alloy (53), which resembles silver, even though it has a yellowish hue. The tincture was most likely diluted nitric acid, which dissolved all the metals from the surface except for the gold. This spectacular experiment attracted wide attention, and even Robert Boyle inquired in his letters about details of this supposed transmutation (54). It can thus be seen that both alchemists and craftsmen made use of the same processes.

Graduatio and Gradatio

In Agricola’s description of the “parting” of gold, he briefly mentions that it can be done with a powder. This is an allusion to a method of gold refining that had been known to the ancients (55), but the confusing terminology of European craftsmen and alchemists has led to the result that two terms, *graduatio* and *gradatio*, have sometimes been used interchangeably. However, these were actually two separate processes, both of which employed nitric acid.

Graduatio: The specificity of this technique was the addition of another metal to the gold. Two distinct approaches existed, denoted as a dry (a) and wet (b) process in the present article. Nitric acid was used only in the wet process.

a) The oldest known European description of this process occurs in the treatise *De diversis artibus* (approximately 12th century A.D.) attributed to Theophilus Presbyter (56). Impure gold was hammered into thin sheets and cut into square pieces with a hole in their center. These sheets were interlayered with a powder made of clay and salt, moistened by urine, and placed in an earthen crucible. This is the powder mentioned in *De re metallica*. The filled crucible was closed by placing another one on top, dried, and strongly heated day and night. Then the gold was removed, hammered again, and the process was repeated (40):

> After another day and night take it out again, mix a little copper with it, melt as before, and put it back in the furnace. And when you have taken it out for the third time, wash it carefully and dry.

This is actually a cementing process that, in its typical form, had been performed without the addition of another metal.

b) The principle of adding another metal to estimate the purity of gold was introduced sometime after the discovery of nitric acid. In this method, three parts of silver were added to one part of gold, and it was these proportions that gave the process the name *quartatio*, or *analysis per quartam* (57). *Quartatio* is mentioned in numerous sources, such as the “Testimony of Helvetius” (58), but we will consider the brief description of this process that occurs in Agricola’s *De re metallica* (59). Gold weighed at the beginning was refined by cupellation during which a threefold quantity of silver was added, and to which was later joined a small amount of copper. If necessary, this operation was repeated to obtain a pure alloy of both precious metals. The resulting buttons of the alloy “are hammered and flattened out, and each little leaf is shaped in the form of a tube, and each is put into a small glass ampulla. Over these there is poured one uncia and one drachma of the third quality aqua valens.” When heated, “small bubbles resembling pearls in shape will be seen to adhere to the tubes. The redder the aqua appears, the better it is judged to be; when the redness has vanished, small white bubbles are seen to be resting on the tubes, resembling pearls not only in shape, but also in color.” The nitric acid had to be replaced several times, and finally the sheets were washed and weighed. The difference between the original and final weight reflected the amount of impurities in the gold.

The success of this operation depended on the skill of an assayer, the crucial factors being the gold content of the original sample, the amount of added silver, and the quality of the nitric acid. This method worked by allowing maximum contact between the alloy and the acid: the silver dissolved, and the resulting cavities in the alloy allowed the acid to enter and dissolve more silver, eventually leaving behind mostly gold. As Agricola mentioned, a small amount of silver remains undissolved, and therefore a correction should be introduced into the final assessment. The recipe of Theophilus cited above also works by maximizing the access of reagent to the inside of an alloy by a small admixture of copper, though in that case the reagent was common salt.

Gradatio. According to the *Alchemia* (1597) of Andreas Libavius (? 1560-1616), *gradatio* was one of two processes that are kinds of *exaltatio* (Erhöhen) (60). In alchemy, *gradatio* was sometimes used to denote the alleged transmutations in which the appearance of metals was changed to look like gold or silver. One of these techniques (61) employed various mixtures containing nitric and sometimes also sulfuric acid among other ingredients (62). Such mixtures appear in Agricola's tenth *aqua fortis* recipe, and especially in the separate group of four "compositions."

Libavius describes *gradatio* as the "raising of metals" to a higher degree of quality, which concerns their weight, color, and durability. However, he emphasizes that *gradatio* does not have the power to "transfigure" a substance, despite the opposite claim made by Paracelsians. In Libavius' opinion, such a claim would be mendacious and fraudulent. He goes on to mention examples of the capabilities of *gradatio*, such as the reddening of white gold, the fixing of a volatile substance, and the purification of an impure one (63). Purification, however, is an allusion to the process known as *graduatio* (or *cementatio*) described above. This further documents the degree of confusion that could exist in using such terminology. Libavius, nevertheless, admits that the treating of common metals by *gradatio* can so closely approach transmutation that it can be even considered as such a change. Moreover, in this we can see the difficulty that even he faced in defining what constituted a true transmutation, as it is supposedly only by the "exalting" of metals (*exaltatio*) that "matter is made nobler in its substance," i.e. transmuted.

Libavius gives a recipe for nitric acid (64), but he states that there are other known kinds of *aqua fortis* as well. Together with the standard ingredients, such as vitriol and saltpeter, further substances are also used in the preparation of *aqua fortis*: "once it is any salt, another time hydrargyrus sublimatus, cinnabar, 'rust of copper,' gypsum, burnt lime, arsenic, 'federalaun,' colcothar, fel vitri, red sulfur, etc." (65) It is hardly possible to judge what the product would have been after adding such diverse materials, but it is likely that in some cases the resulting mixtures could have dyed the base metals to resemble precious ones.

Conclusions

As has been shown, nitric acid played an important role in both alchemy and crafts. Still, various questions concerning its history remain unanswered. It is sometimes claimed that nitric acid had been discovered earlier than in the Middle Ages, or that it was not discovered in Europe, or not only in Europe, as the Indian treatise suggests. In fact, the widespread technique of distillation could have led to this product even in the more distant past, as the crucial ingredients, vitriol and saltpeter, were certainly available. It would also be of interest to investigate in deeper detail the alchemical technique of *gradatio*, and to determine what the products of these processes could have been. Likewise, it would be important to explore the relations between the impurities that were often present in the original ingredients and in the final products. It could be that impure nitric acids led to reactions that were subsequently explained in terms of metallic transmutation.

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REFERENCES AND NOTES

1. The history of nitric acid is dealt with in several works, among others H. Kopp, *Geschichte der Chemie*, Dritter Theil, Braunschweig, 1845, 225; E. O. von Lippmann, *Entstehung und Ausbreitung der Alchemie*, G. Olms, Hildesheim, 1978 (reprint of the J. Springer edition, Berlin, 1919), 363; J. M. Stillman, *The Story of Alchemy and Early Chemistry*, Dover, New York, 1960, 276ff.; R. J. Forbes, *A Short History of the Art of Distillation*, E. J. Brill, Leiden, 1948, 86-87. The modern use of nitric acid with a brief excursion into its history is covered in T. H. Chilton, *Strong Water. Nitric Acid: Sources, Methods of Manufacture, and Uses*, The MIT Press, Cambridge, MA, 1968.
2. M. P. Crosland, *Historical Studies in the Language of Chemistry,* Heinemann, London, 1962.
3. The term *sal nitrum* descended from ancient Egyptian n^e-t^e-r, which had originally denoted impure sodium carbonate; later, in mediaeval Europe it began to be used for potassium nitrate. Modern terms *nitric acid* and *nitrogen* stem from the ancient Egyptian word. This history is briefly described in M. R. Feldman, "N and Na – The Egyptian Connection," *J. Chem. Educ*., **1980,** *57*, 877-8.

4. This term appears in *Testamentum novissimum*, attributed to Ramon Lully (ca 1232 – 1315/16), in reality a spurious work by unknown Pseudolully (On Lully see A. Clericuzzio, *Lullus, Raimundus (Lull, Ramon),* in C. Priesner and K Figala, *Alchemie. Lexikon einer hermetischen Wissenschaft*, C. H. Beck, München, 1998, 224). Alchemical writings under Lully's name are briefly analyzed and listed in M. Pereira, *The Alchemical Corpus Attributed to Raymond Lull*, The Warburg Institute, London, 1989. Pseudolully gives a recipe for nitric acid in which he used cinnabar in place of alum (Kopp, *Geschichte*, p 227).
5. A detailed analysis of the Jābir problem can be found in P. Kraus, "Studien zu Jābir ibn Hayyān," *Isis*, **1931**, *15*, 7-30; P. Kraus, *Jābir ibn Hayyān: Contributions à l'Histoire des Ideés Scientifiques dans l'Islam*, Mémoires de l'Institut d'Égypte, Cairo, 1942; some corrections are in Syed Nomanul Haq, *Names, Natures and Things. The Alchemist Jābir ibn Hayyān and his Kitāb al-Ahjār (Book of Stones)*, Kluwer, Dordrecht, 1994, Ch. I. Doubts concerning the very existence of Jābir had already been expressed in the medieval Arabic world. See J. W. Fück, "The Arabic Literature on Alchemy According to An-Nadīm (A.D. 987)," *Ambix*, **1951,** *4*, 81-144.
6. The Pseudogeberian corpus comprises five treatises: *Summa perfectionis magisterii*, *Liber de investigatione perfectionis, Liber de inventione veritatis, Liber fornacum,* and *Testamentum Geberi*.
7. For example, Holmyard had proposed several explanations for the origin of this corpus. He did not exclude the possibility that it is a genuine translation of Jābir's works, or a translation of the works of other Arabic authors. As another explanation, this author proposed that these works could be summaries of Jābir's books compiled in Europe or medieval European forgeries written by an unknown author (E. J. Holmyard, *Makers of Chemistry*, Oxford University Press, Oxford, 1953, 63; E. J. Holmyard, *Alchemy*, Penguin, Harmondsworth, 1957, 79).
8. W. R. Newman, *The Summa Perfectionis of Pseudo-Geber*, E. J. Brill, Leiden 1991, p 81.
9. A German translation of the whole Geberian corpus, with commentary, occurs in E. Darmstaedter, *Die Alchemie des Geber*, Springer, Berlin, 1922, 113. The recipe cited is translated from this book.
10. The preparation of nitric acid is briefly mentioned in the *Liber fornacum*, a later work of the Pseudogeberian corpus. In Chapter 18, titled "Dissolution of Prepared Metals," the unknown author states, "Our method is: dissolve granulated or filed metal in our solvent that is prepared from sal nitrum and vitriol …" This formulation indicates that preparation of nitric acid was known by that time and, therefore, the author did not go into the details of the process. The dating of the *L. fornacum* is problematic; it appeared after *Summa* (Ref. 9, p 118).
11. Leicester briefly mentions a Byzantine manuscript from the end of the 13th century that describes the preparation of nitric and sulfuric acids (H. M. Leicester, *The Historical Background of Chemistry*, Dover, New York, 1956, 77). The same statement appeared earlier in G. Fester, *Die Entwicklung der chemischen Technik bis zu den Anfängen der Großindustrie*, Springer, Berlin, 1923, 75.
12. R. P. Multhauf, *The Origins of Chemistry*, Franklin Watts, New York, 1966, 179.
13. Multhauf's statement should be corrected, because *Testamentum* appeared later, after 1300. No known Pseudolullian alchemical manuscript dates back to the 14th century (see Ref. 4, Pereira, *The Alchemical Corpus*, 22).
14. Ref. 12, pp 196, 197.
15. Ref. 12, p 207, n. 23.
16. Another problematic personality in the pantheon of alchemy, Arnald (ca.1240-1311) was a physician and diplomat; but according to some modern authors he was not an alchemist, and alchemical works under his name would be later forgeries (G. Keil, *Arnald von Villanova*, in C. Priesner, and K. Figala, *Alchemie*, 62; see Ref. 4).
17. W. Ganzenmüller, *Beiträge zur Geschichte der Technologie und der Alchemie*, Verlag Chemie, Weinheim, 1956, 234.
18. P. Ray, *History of Chemistry in Ancient and Medieval India*, Indian Chemical Society, Calcutta, 1956, Ch. III.
19. Ref. 18, p 138.
20. It could be achieved, for instance, by strong heating (calcination) or by various chemical reactions and later by using mineral acids.
21. Green vitriol generally corresponds to $FeSO_4$. The pyrites cannot be reliably identified, but they were probably mostly sulfides of iron and/or copper. Stibnite, named also antimonite, is Sb_2S_3.
22. Ref. 18, pp 138-139.
23. Ref. 18, pp 139.
24. D. M. Bose, S. N. Sen, and B. V. Subbarayappa, Ed., *A Concise History of Science in India*, Indian National Science Academy, New Delhi, 1971, 307.
25. The products could have contained sulfuric acid as well; in the first recipe cited in this paragraph "lion of a sulfur" is claimed to be able to "kill" metals. The term "killing" was used to express the transformation of metals into their salts by sulfuric and/or nitric acid. Some sulfates are less soluble in water.
26. T'sao T'ien-Ch'in, Ho Ping-Yü, and J. Needham, "An Early Mediaeval Chinese Alchemical Text on Aqueous Solutions," *Ambix*, **1959**, *7*, 122-155.
27. A. M. Alfonso-Goldfarb, and Safa Abou Chahla Jubran, "Listening to the Whispers of Matter Through Arabic Hermeticism: New Studies on the *Book of the Treasure of Alexander, Ambix*, **2008,** *55*, 99-121.
28. See Ref. 7, Holmyard, *Makers of Chemistry*, 77.
29. L. Dobbin, "A Cullen Chemical Manuscript of 1735," *Ann. Sci.*, **1936,** *1*, 147-148.
30. J. R. Glauber, *Furni novi philosophici*, Johann Fabel, Amsterdam, 1647, Bd. II, 38, 65ff.
31. U. Klein, *Verbindung und Affinität*, Birkhäuser, Basel, 1994, 143.
32. See Ref. 1, Chilton, *Strong Water*, 14.

33. Glauber was apparently the first to prepare sodium sulfate from common salt (NaCl) and *oleum vitrioli* (sulfuric acid); he named his product *sal mirabile*. To keep the process secret he used dispersion of knowledge, common in alchemical works: he wrote this recipe in two parts published separately, and in each part he used different names of reactants (Ref. 2, p 39).
34. The first edition appeared in 1675; the present text is cited from N. Lemery, *Cours de Chymie, Oder vollkommene Chymist*, J. J. Winckler, Dresden, 1726, 522ff.
35. In the German translation of Lemery's textbook, this product is named "Salamanderblut" (blood of salamander).
36. The terminology in Lemery's textbook seems to reflect the problem of the composition of *spiritus nitri*. In Ch. 2, entitled "Silver-crystalls, which are called Vitriolum Lunae," the method of preparing such crystals is described: "This operation is dissolution of silver that is reduced into a kind of a salt by acid spikes of spiritus nitri." The product, silver nitrate, is nevertheless called "vitriol" which name was usually applied to what are today recognized as sulfates. It is as if Lemery interchanged both kinds of salts in this case (Ref. 30, p 142).
37. G. Schröder, *Die pharmazeutisch-chemischen Produkte deutscher Apotheken im Zeitalter der Chemiatrie*, Herbig, Bremen, 1957, 59ff.
38. According to this author, the thermal decomposition of potassium nitrate occurs at high temperatures. Not only are nitrogen oxides formed in this process, but also oxygen is directly produced. If an earthen vessel were to be used, potassium nitrate would react with the silicates. This reaction also produces both oxygen and nitrogen oxides, while the surface of the vessel acts as a catalyst and contributes to the processes leading to the formation of nitrogen oxides. These reactions generally occur when earthen distillation apparatus is used.
39. R. W. Soukup and H. Mayer, *Alchemistisches Gold. Paracelsische Pharmaka*, Böhlau, Wien, 1997, 137ff.
40. G. Agricola, *De re metallica*, transl. by H. C. Hoover and L. H. Hoover, Dover Publ., New York, 1950, 439ff.
41. Verdigris denoted a green copper compound, usually basic copper (II) acetate; stibium was antimony (III) sulfide; and asbestos was apparently the substance currently known by this name.
42. *The Pirotechnia of Vannoccio Biringuccio*, transl. by C. S. Smith and M. T. Gnudi, Dover Publ., New York, 1966, 188.
43. T. Nummedal, *Alchemy and Authority in the Holy Roman Empire*, The University of Chicago Press, Chicago, IL, 2007, Ch. 3 and 5.
44. R. W. Soukup, *Chemie in Österreich*, Böhlau, Wien, 2007, Ch. 5.
45. E. Darmstaedter, *Berg-, Probir- und Kunstbüchlein*, Verlag der Münchner Drucke, München, 1926; see also A. G. Sisco and C. S. Smith, Ed., *Bergwerk- und Probirbüchlein*, The American Institute of Mining and Metallurgical Engineering, New York, 1949.
46. Soukup and Mayer (Ref. 39, p 138), point out that gases (especially NO and NO_2) evolving in this reaction could cause the explosion of the vessel. The old sources recommended leaving a small hole closed by a piece of wood between the vessel and helm. The pressure inside the vessel would push this wooden stopper out when it became too high.
47. According to H. Kopp, *Geschichte der Chemie*, Vieweg, Braunschweig,1843-1847, Dritter Theil, 228, Paracelsus already knew this technique.
48. Lazarus Ercker, *Beschreibung Allerfürnemisten Mineralischen Ertzt / und Berckwerckarten / ...* Prag, 1574.
49. Ref. 48, fol. 137v. Solubility of potassium nitrate increases with the temperature, whereas solubility of sodium chloride, which is lower from the beginning, remains almost constant. If a mixture of both salts is dissolved at increasing temperature, sodium chloride collects on the bottom of a vessel, whereas potassium nitrate continues to dissolve. Then, solution enriched in potassium nitrate results. The solubility of these salts is [at 10°/ 100°C in grams per 100 g of H_2O]: NaCl 4/56.2, KNO_3 21.2/245.
50. Soukup and Mayer (Ref. 46) point out that Ercker's recipe (Ref. 48, fol. 67v) is more comprehensible and leads to stronger acid.
51. Ref. 48, fol. 70v/70r.
52. V. Karpenko, "Witnesses of a Dream: Alchemical Coins and Medals," in S. J. Linden, Ed., *Mystical Metal of Gold*, AMS Press, New York, 2007, 117-160.
53. Microanalysis of four samples from the surface and from the edge revealed the following average composition (in %wt.): Au 47.55, Ag 43.37, Cu 7.56, with traces of tin, zinc, and iron. See R. Strebinger and W. Reif, "Das alchemistische Medaillon Kaiser Leopold I., " *Mitt. der Numismatischen Gesellschaft in Wien*, **1932**, *XVI*, 209-218.
54. L. M. Principe, *The Aspiring Adept*, Princeton University Press, Princeton, NJ, 1998, 95.
55. A. Ramage and P. Craddock, *King Croesus' Gold*, The British Museum, London, 2000.
56. *Theophilus, On divers arts*, transl. by J. G. Hawthorne and C. S. Smith, Dover Publ., New York, 1979, 108.
57. It appears in Martin Ruland's (1569-1611) lexicon of alchemy as "Quartura" (*Lexicon Alchemiæ sive dictionarium alchemisticum … auctore Martino Rulando*, Frankfurt, 1612, 400); nitric acid is named *aqua stygia* here.
58. F. S. Taylor, *The Alchemists*, Paladin, Frogmore, 1976, 143.
59. Ref. 40, p 248.
60. *Exaltatio* denoted the process in which "a higher stage of a substance and its action can be achieved by maturatio (ripening), or gradatio." The latter of the aforementioned processes can be performed by such techniques as *cementatio*, *extinctio* (Ablöschen, quenching), and *coloritium* (coloring). See *Die Alchemie des Andreas Libavius. Ein Lehrbuch aus dem Jahre 1597*, Verlag Chemie, Weinheim, 1964, Ch. LVI, 99.

61. V. Karpenko, "The Chemistry and Metallurgy of Transmutation," *Ambix*, **1992**, *39*, 47-62.
62. Ref. 60, p 107: "There is gradatio … [performed] by means of spirits of 'sharp waters.'"
63. This sentence is a verbatim citation from Ruland's *Lexicon*, the entry "Gradatio" (Ref. 57, p 245).
64. Ref. 60, p 459.
65. "Rust of copper" could be any copper compound probably prepared by the "corrosion" of this metal. Naturally occurring basic copper (II) carbonate seems to be more probable than artificially prepared basic copper (II) acetate, which was also known as verdigris (Ref. 41). Arsenic needs to be specified; it could be an oxide or any sulfide of this element. "Federalaun" was one of several names of alum, and colcothar was usually impure Fe_2O_3.

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BRITISH WOMEN AND CHEMISTRY FROM THE 16th TO THE MID-19th CENTURY

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Introduction

We have shown elsewhere that a significant number of women chemists were active in Britain between 1880 and 1949. In fact, during that period a total of 896 women were members of the Royal Institute of Chemistry and/or the Chemical Society (1). Prior to that period, much has been published about the 17th-century chemistry researcher, Elizabeth Fulhame, author of *An Essay on Combustion* (2) and about the 18th-century chemistry popularizer, Jane Marcet (1769-1858), author of *Conversions on Chemistry* (3). Though it is certainly true that Fulhame and Marcet have exalted places in the history of women in chemistry, in our view, it is important to show that they were not the only women who developed an interest in the subject before the late 1800s. Here we will introduce some other women who had an involvement in the chemistry of their time, and then we will survey the avenues by which women of the late 18th and early 19th century could (and many did) acquaint themselves with advances in chemistry.

Mary Sydney Herbert painted by Nicholas Hilliard (ca. 1590), National Portrait Gallery painting number NPG5994 (reproduced by permission)

The Scientific Lady

The earliest recorded account of a society woman whom we could find with an interest in chemistry was Mary Sydney Herbert, Countess of Pembroke (1561-1621) (4). The Countess pursued all aspects of learning: languages, literature, poetry, music, and needlework, which were common for an intelligent aristocratic woman; more unusual were her studies of embryology, medicine, and chemistry. Herbert's biographer, John Aubrey, noted (5):

> Her Honour's genius lay as much towards chymistrie as poetrie. ... She was a great Chymist, and spent yearly a great deale in that study. ... She kept for her Laborator in the house Adrian Gilbert (vulgarly called Dr. Gilbert) halfe-brother to Sir Walter Raleigh, who was a great Chymist in those dayes.

Of course, in that period, it was more of a combination of alchemy and pharmacy than 'modern' chemistry. Unfortunately, as far as is known, Herbert did not keep a diary and thus her actual experiments are unknown. Herbert's chemical interest seems to have focused on the extraction of substances from plants by chemical procedures. This was certainly the pursuit of Lady Margaret Clifford (1540-1616), daughter of Henry Clifford, 2nd Earl of Cumberland. Her own daughter Anne recorded (6):

> She was a lover of the Study and practice of Alchimy, by which she found out excellent Medicines, that did much good to many; she delighted in the Distilling of waters, and other Chymical extractions, for she had some knowledge in most kinds of Minerals, herbs, flowers and plants.

A few years later, Dorothy Moore (c. 1612-1664) became a chemical experimenter. It was following her marriage to John Drury that she entered an intellectual circle centered around Samuel Hartlib but also involving Robert Boyle and his sister, Katherine Boyle, Lady Ranelagh (7). Moore had a particular interest in chemistry and pharmacy, and there are many references to her recipes and experiments in Hartlib's records (8). For example, Moore worked with Katherine Boyle on distillation in 1649 and with Dr. (Arnold or Gerard) Boate on "Paris chemistry" in 1654 [the Paris school, espousing modernistic chemical ideas for the time, had been founded six years earlier (9)]. Moore's extractions of essential oils from herbs and spices led her husband, Drury, to enquire from friends about the possibility of setting up a shop; but it was suggested that in view of the Drurys' position in society, private sales to a select clientele was more appropriate.

Lady Margaret Clifford

The socialite, Margaret Cavendish, Duchess of Newcastle (1624-1674), devoted many spare hours to working in the family laboratory where, among her studies across the sciences, she learned the process of chemical distillation and the dissolving power of strong acids (10). She insisted on attending demonstrations by famous scientists, such as Robert Boyle, at the most prestigious scientific institution of the day, the Royal Society (11). In fact, Cavendish was the first woman to be admitted to a meeting of the Royal Society, which she attended on May 30, 1667; but her success was a reflection of her own social position and influence rather than a breakthrough for her gender.

Margaret Cavendish

Samuel Pepys attended the meeting and took more note of her clothing than her scientific intellect (12):

> After dinner I walked to Arundell House [the Royal Society meeting place], ... where I find much company, indeed very much company, in expectation of the Duchesse of Newcastle, who had desired to be invited to the Society; and was, after much debate, pro and con, it seems many being against it; and we do believe the town will be full of ballads of it. Anon comes the Duchesse with her women attending her...The Duchesse hath been a good, comely woman; but her dress so antick, and her deportment so ordinary, that I do not like her at all, nor did I hear her say any thing that was worth hearing, but that she was full of admiration, all admiration. Several fine experiments were shown her of colours, loadstones, microscopes, and of liquors among others, of one that did, while she was there, turn a piece of roasted mutton into pure blood [by dissolution in concentrated sulfuric acid], which was very rare. ...

Over 100 years later another Duchess, Georgiana, Duchess of Devonshire, had an equal fascination for science, particularly mineralogy and chemistry. On October 23, 1793, Lady Sutherland described Georgina's routine in a letter to Lady Stafford (13):

> ... the Duke has got the gout, & the Dss is "at home" every night at 12 o'clock, afterwards she sits with him till 3. She is busy studying Chemistry, and goes out a little, she is going this morning to a chemical lecture.

Georgiana became the patron of promising scientists, including Dr. Thomas Beddoes, who is credited with the discovery of laughing gas, dinitrogen oxide.

Alic has written about the growing scientific interest by women as the 19th century progressed (14). For these upper middle class women, mathematics, biology, geology, and astronomy were relatively easy to practice for they required little in the way of facilities or expenditures. As Weldon commented in 1825, the pursuit of chemistry could only be accomplished by professionals and the very wealthy (15):

> [Chemistry] requires such an appropriation of time and property; such a variety of expensive and delicate instruments; such an acquisition of manual dexterity; and so much thought and attention to its successful prosecution, as will necessarily confine the *professed pursuit* of it to a few professors, and enthusiastic amateurs, whom fortune and opportunity favour.

Georgiana, Duchess of Devonshire

Elizabeth Fulhame (mid-1700s to 1800s) was the one exception. She not only practiced chemistry but also received recognition among the chemists of her time. For example, the Chemical Society of Philadelphia elected Fulhame a corresponding member (16) and, in an oration, stated that (17):

> Mrs Fulhame has now laid such bold claims to chemistry that we can no longer deny the sex the privilege of participating in this science also.

Though little is known about Fulhame's life, Fulhame had an advantage that her husband, Thomas Fulhame, was an affluent physician and that she was acquainted with some of the scientists of the time, such as chemist Joseph Priestley (18). In addition, a quote in the preface of her book suggests that she was goaded into commencing experimentation (19):

> The possibility of making cloths of gold, silver, and other metals by chymical processes, occurred to me in the year 1780; the project being mentioned to Doctor Fulhame and some friends, was deemed improbable. However, after some time, I had the satisfaction of realizing the idea in some degree by experiment.

The lack of chemical laboratory facilities is probably why Mary Somerville (1780-1872), hailed at her death as "The Queen of Nineteenth Century Science," contributed little to chemistry (20). Her sole venture, performed in collaboration with Michael Faraday, was a study of light absorption by different materials using the degree of darkening of silver chloride (21).

Public Lectures

Even if women (with very few exceptions, such as Fulhame) were unable to practice chemistry, they were eager to learn about it, and the 'scientific lady' became an accepted term in the vocabulary of the time (22). Higgitt and Withers have extensively reviewed the participation of women at the British Association for the Advancement of Science (BAAS) meetings (23). The BAAS meetings had a dual role of professional discourse and of popularization of scientific discoveries, two very dissimilar and often conflicting objectives. At first women were allowed to attend only the social functions, though the scientific interest of some of the women became apparent at the 1831 meeting at York, when the *Yorkshire Gazette* reported that there was "... an *elementary* lecture on magnetising at which there were present perhaps not less than a hundred fashionable ladies!!" (24). There was much concern among the organizers of the Oxford meeting the following year that Mary Somerville would attend (25). Fortunately for them, she did not, relieving them of the anxiety of what to do with a woman who was also a *bona fide* scientist.

Women were first formally admitted into the geology and botany sections in 1837 and then into other sections, including chemistry, by 1838 (23). However, admission was subject to the availability of space in the galleries and in women-only parts of the rooms. At the Newcastle meeting held that year, of the 3,530 attendees, 1,100 were 'ladies.' A very high proportion of the women were wives or daughters of scientists and they were at the meeting ostensibly for the social events; nevertheless, many women did attend and enjoy the sessions.

The most important venue for women to learn about chemistry was the Royal Institution (RI). Though the first public lecture at the RI took place in 1800, it was Humphry Davy's charismatic chemistry lectures during the 1802-1812 period that brought the affluent to the institution's premises on Albemarle Street (26). Notably, about half the audience was made up of women, which pleased Davy. However, Davy believed that women should absorb scientific knowledge and transmit it to their offspring but certainly not practice science (27).

There are several accounts of the audience reactions at these lectures (26), but unfortunately none is by a woman. What is particularly interesting in all these reports is the gender difference in attitude: the males feigning boredom, while the women were assiduously paying attention and often note-taking. Among the several accounts of this difference was that of Robert Southey (1774-1833). Southey, an English poet, wrote in 1807 an extremely penetrating and accurate account of English life of the period, including a description of a Royal Institution lecture (28):

> Part of the men were taking snuff to keep their eyes open, others more honestly asleep, while the ladies were all upon the watch, and some score of them had their tablets and pencils, busily noting down what they heard, as topics for the next conversation party.

The apparent boredom of the male audience during such fascinating presentations seems paradoxical. However, Myers (29) has offered an explanation in terms of public lectures as being seen as the trivialization of science at which the gentlemen had either to pretend that chemistry did not count as worthwhile knowledge or that the chemistry was already familiar to them. For ladies to find the knowledge so gripping and noteworthy only further trivialized the subject. From the perspective of this work, however, it is the obvious interest of the women in chemistry that is striking.


Caroline Fox

One of the women who attended a lecture at the Royal Institution during the time of Davy's successor, Michael Faraday, was Caroline Fox (1819-1871). Daughter of the amateur scientist Robert Were Fox, she kept a journal from 1835 until shortly before her death. She grew up in a household surrounded by her father's science as her mother's relative, Mary Anne Schimmelpenninck, commented (30):

> Imagine the back drawing-room strewn with reflectors, and magnets, and specimens of iron, and borax, cobalt, copper ore, blow-pipes, platina, &c., &c.; deflagrations, fusions, and detonations on every side; whilst we were deeply interested in watching the fusions of the ores, or their assaying; only that now and then I, having a house of my own, had a fellow feeling with Maria [wife of Robert Fox], at seeing a certain beautiful zebra-wood table splashed with melted lead or silver, and the chased Bury Hill candlestick deluged with acids.

According to her journal, Caroline Fox attended many of the BAAS meetings. In addition, she visited the Royal Institution on June 13, 1851 to watch Faraday's chemical experiments. She reported (31):

> We went to Faraday's Lecture on "Ozone." He tried the various methods of making Ozone which Schönbein has already performed in the kitchen, and he did them brilliantly. He was entirely at his ease, both with his audience and his chemical apparatus; he spoke much and well of Schönbein, who now doubts whether Ozone is an element, and is disposed to view it simply as a condition of oxygen, in which Faraday apparently agrees with him.

It was not only London women who were intrigued by chemistry. At the University of Edinburgh, Thomas Charles Hope, Lecturer in Chemistry, introduced in 1826 "A Short Course of [Chemistry] Lectures for Ladies and Gentlemen" (32). The presence of women on campus was not appreciated by many academics; for example, Lord Cockburn wrote to a T. F. Kennedy (33):

> The fashionable place here now is the College; where Dr Thomas Charles Hope lectures to ladies on Chemistry. He receives 300 of them by a back window, which he has converted into a door. Each of them brings a beau, and the ladies declare that there was never anything so delightful as these chemical flirtations.

Printed Resources

In addition to scientific lectures for women, some women's magazines in the 18th and early 19th centuries carried articles on science (34). There were three short-lived women's magazines in the early 18th century that contained scientific essays (22a): *The Female Spectator* (1744-1746) and *Epistles for the Ladies* (1749-1750), both edited by Eliza Haywood, and then *The Lady's Museum* (1760-1761) by Charlotte Lennox. Longer surviving was *The Ladies' Diary: or, The Woman's Almanack, Containing many Delightful and Entertaining Particulars, Peculiarly Adapted for the Use and Diversion of the Fair-Sex* (1704-1840), which focused on science, philosophy, and mathematics (35).

Shteir (36) has examined three other journals: the *Lady's Magazine* (1770-1832); the *Lady's Monthly Museum* (1798-1828), and the first volume of the *Lady's Companion at Home and Abroad* (1849-50). At the beginning of the 19th century, the *Lady's Magazine* frequently carried articles on science, as Shteir noted (37):

> For a short time, the *Lady's Magazine* included scientific excerpts drawn from contemporary publications, such as an essay on the "Progress and Utility of Chemistry" from the recently founded *Quarterly Journal of Science* and a portion of Sir Humphrey Davy's 1821 address to the Royal Society on "the present State of Science."

However, the ownership of the magazine changed in 1822, and the new editor eschewed "the abstruse mysteries and tedious details of science." When the topic of science for ladies was discussed in 1831, botany was considered the most suitable because (37):

> …ladies will not, in pursuing botany, have to discolour their fingers in trying chemical experiments on substances which they may have previously risked their necks to obtain.

The first editor of the *Lady's Companion at Home and Abroad* was Jane Loudon, who believed her task was to educate her readers and provide mental stimulation – or 'mental cultivation' as she called it. Included in this goal was a steady stream of scientific articles. Again, quoting Shteir (38):

> In 1850 one of the male contributors presented a series of articles about fermentation and combustion under the title 'Chemistry and Everyday Life.' Edward Solly, a teacher and lecturer on chemistry who was associated with the Royal Institution and the Horticultural Society, joined Loudon's crusade to bring science into general female education. Applauding the increased 'desire for knowledge,' he celebrated the importance of the sciences.

After Loudon gave up her position as editor in June, 1850, the direction of the magazine changed dramatically. When a long-standing subscriber expressed her dismay that drawings of flowers were now ornamental rather than botanical, the new (male) editor expressed his opinion that the designs of bonnets and sleeves were more important for women's minds than the mysteries of the botanical world.

Books were the primary means for women to learn about science (39), for writing about science enabled women to participate in the scientific enterprise without violating gender norms (40). The first book on chemistry specifically for women was *La Chymie charitable et facile, en faveur des dames*, authored in France by Marie Meudrac in 1666 (41). This was sufficiently popular that it was reprinted in 1674 and again in 1711. However, for British women, it was through Jane Marcet`s book, *Conversations on Chemistry: in which the Elements of that Science are familiarly explained and illustrated by Experiments* (42), that they were able to comprehend the mysteries of chemistry and, from edition to edition, keep up with the latest discoveries (43).

Marcet had developed an interest in chemistry by attending some of Davy's early lecture-demonstrations at the Royal Institution. Finding them confusing, she decided to write a fictional account of a discourse on chemistry between a teacher, Mrs. B, and two students, Emily and Caroline. Initially for her own understanding, the book was first published in 1806. Marcet considered the conversational style particularly appropriate to women readers (44):

> Hence it was natural to infer, that familiar conversation was, in studies of this kind, a most useful auxiliary source of information; and more especially for the female sex, whose education is seldom calculated to prepare their minds for abstract ideas, or scientific language.

In addition, as Myers has discussed, Marcet's adaptation of chemical discovery to a work of fiction set in a country house gave women readers a sense that chemistry was also part of their own world (29).

Marcet's book was read by at least three well-known women of the time. Helen Hamilton Douglas (c.1768-1837), wife of the Scottish geologist and chemist, Sir James Hall Douglas, wrote to Jane Marcet explaining her reasons for reading *Conversations on Chemistry* (45):

> I was at that time keen to improve myself by reading and attending lectures, keen to acquire knowledge, for the pleasure of conversing with my husband and communicating instruction to my young family.

A reader of the French translation of *Conversations on Chemistry* was Anne Louise Germaine Necker, Madame de Staël (1766-1816). Necker wrote to Jane Marcet's husband, Alexander Marcet (46), "I have proposed the study of chemistry in the dialogues of Mrs. Marcet ... the beginning [is] most clever and the work admirably clear."

The novelist Maria Edgeworth (1767-1849) also read *Conversations on Chemistry* (47). In fact, her chemical knowledge, acquired by reading Marcet's book, possibly saved the life of Edgeworth's younger sister. The sister had swallowed acid and Maria recalled from the text that milk of magnesia was an effective antidote. Following the incident, Edgeworth wrote of the benefits for women of studying chemistry (48):

> ... chemistry is a science particularly suited to women, suited to their talents and to their situation. Chemistry is not a science of parade, it affords occupation and infinite variety, it demands no bodily strength, it can be pursued in retirement, ... there is no danger of its inflaming the imagination; ... [because] the mind is intent upon realities, the knowledge that is acquired is exact; and the pleasure of the pursuit is a sufficient reward for the labour.

Commentary

In this account, we have endeavored to show that there have been British women interested in, and involved in, the chemical scene at least since the late 1500s. Unfortunately, we will never know the full extent of this involvement as women's history in this context is so fragmented. Likewise, we are unlikely to learn much more about the hundreds who viewed chemistry from the sidelines at the Royal Institution lectures or the thousands who purchased a copy of Marcet's book.

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AN 1815 PERSPECTIVE OF CHLORINE AS A CHEMICAL AGENT USED IN BLEACHING - A SECTION FROM JAMES RENNIE'S ESSAY ON BLEACHING

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Introduction

Among publications concerning the chemical properties and bleaching aspects of chlorine in early bleaching is included the analytical testing of bleaching solutions, as described in a manuscript entitled "An Essay on the Improvements in the Art of Bleaching by the Application of the Principles of Chemistry" by James Rennie (1787-1867). The manuscript is held by Birmingham City Archives within the James Watt Collection, and it is thought to have been written in 1815-16, very probably shortly before Rennie was awarded a first prize for this essay in the same period. The authorship is indicated by a pencil insertion in an apparently different hand. An edited but incomplete version was published as a series of articles titled "Essays on Bleaching, By James Rennie, A.M. Lecturer on Philosophy, &c. &c., London," in *The Glasgow Mechanics' Magazine; and Annals of Philosophy* during the period 1825-1826. For this present short article Rennie's section entitled "Chlorine and its Compounds," part of Chapter IV, "Chemical Agents used in Bleaching," has been fully transcribed; and it is within this chapter that Rennie covers his main chemical considerations within the entire essay.

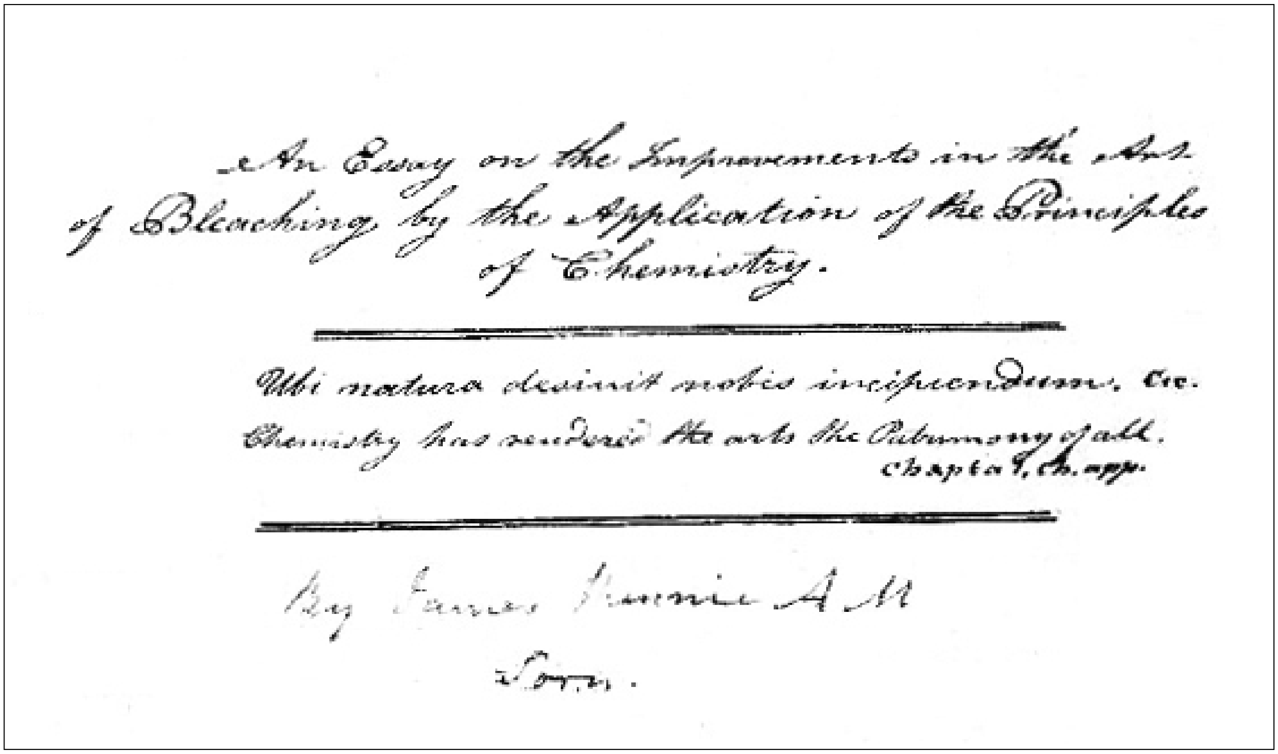
This author first encountered Rennie when seeking evidence for the use of indigo in a test method to determine the bleaching strength of chlorine water solutions in the early bleaching industry in Britain. Such evidence was found in the essay mentioned above. Useful though this was, the present assessment will show little original material by Rennie, whose strength lay more in his accurate and wide reporting from established published sources of the period rather than from practical knowledge of the burgeoning Scottish industry. This single section of Rennie's *Jugendwerk* provides a systematic presentation of material, the whole of which qualifies the work more as a treatise than essay. This perhaps explains the several citations made by Musson and Robinson (1), these being the only modern historians of science to draw from this long forgotten, obscure manuscript. An account of Rennie's quite extraordinary life in Britain until his departure to Australia in 1840 is given elsewhere; but for contextual reasons some brief notes are presented here about his life up to the time of his writing the essay (2).

The Essayist: James Rennie (1787-1867)

The *Oxford Dictionary of National Biography* correctly describes Rennie as a naturalist, born February 26, 1787 (3), son of Thomas Rennie (or Rainey) of Alderholm, Sorn, Ayrshire, Scotland. Nothing is known of James' early years until his matriculation at Glasgow University in 1810 (4). He appears to have studied the standard arts curriculum, which included Greek, Logic, Ethics, Physics, and Latin; and it was during these undergraduate years that he won prizes for essay writing (5). After graduating in 1815 (6), he gained two further prizes: one for an essay on bleaching, the other for an essay on the use of steam in navigation (7). For each of these he was awarded the Watt Prize of £10. The only known complete copy of Rennie's bleaching essay is among the papers of James Watt, held by Birmingham City Archives. James Watt wrote to George Jardine of Glasgow College regarding essay prizes "to be given annually as a premium for the best Essay (by any student in the College) upon any subject in Natural Philosophy, Mechanism or Chemistry or the arts ... which shall be appointed by the faculty yearly ..."(8). Apparently, Watt proposed to donate prize money and suggested a five-yearly cycle of topics (9):

1. Bare mechanics, its machines & arts
2. Statics, its machines & arts, Equilibrium of forces, weighing machines, Bridges, Carpentry, etc. etc.
3. Pneumatics, Statical and Chemical, Windmills, Sails, Bellows, Barometers, etc. etc.
4 Hydraulics and Hydrostaticks, Machines & Arts, canals, sea ports, mills,
5. Chemistry in general, & its processes & apparatus.

There is no evidence that Rennie continued as a registered student at Glasgow University after 1815, but it is possible that he may have taken classes on an informal basis. His essay writing in order to win financial reward appears to have been an acceptable activity of graduates of the period.



An Essay on the Improvements in the Art
of Bleaching by the Application of the Principles
of Chemistry.

Ubi natura desinit nobis incipiendum, &c.
Chemistry has rendered the arts the Patrimony of all.
Chaptal, Ch. app.

By James Rennie A M
[illegible].

"Chlorine and its Compounds:" Section 8 of Chapter IV, transcribed from the original manuscript.*

*Boldfaced endnotes in parentheses within the essay refer to those of the present author, as do square bracketed insertions.

Chlorine and its Compounds

Next to oxygen Chlorine is perhaps the most interesting of all the chemical agents. The theoretical researches to which it has given rise are the most profound and the least satisfactory of all the subjects of Chemistry. With these at present we have nothing to do; but we shall find its use in manufactures and chiefly in Bleaching no less interesting and surely more important than the ingenious theoretical discussions which it has produced (**10**). This substance has been called an acid, but it wants one of the most marked properties of this class of bodies, namely, the power of converting vegetable blues to red. Chlorine discharges all vegetable colours and renders them white; hence its use in Bleaching and its distinction from acids.

In the gaseous form it is of a greenish yellow colour, whence its name; and, although it supports combustion, it cannot be respired without great injury to animal life.

For the purposes of Bleaching it is made by an apparatus invented by Berthollet and subsequently improved by Henry, Des Charmes, Fisher, and others **(11).** A description of the latest improvements in this apparatus has already been given: I shall now briefly state the process. - The black oxide of manganese and muriate of soda are mixed together in the proportion commonly of 2 to 3, and after moistening them with water they are wrought till the mixture is of the consistence of moist dough, in order that the manganese may unite more intimately with the salt. The mixture is perfect when it is uniformly black. In this state they are put into the retort. There is now gradually added in conformity to the above proportions 2 2/7 [two and two sevenths] parts of sulphuric acid diluted with its own weight of water and allowed to cool in order to prevent accidents. This immediately without the application of heat disengages chlorine from the mixture in the state of gas. As soon as the quantity of gas thus disengaged diminishes, a fire is kindled under the water bath in which the retort is placed and continued till all the procurable gas comes over. This gas impelled by its expansive force passes from the retort to the large leaden receiver where it is combined with water, with lime, or with some of the alkalies. The rationale of this process is, that the sulphuric acid having a greater affinity than muriatic acid for the soda of the muriate, combines with the soda and sets free the muriatic acid which according to Davy parts with its hydrogen to the manganese; - according to the old theory attracts the oxygen of the manganese, - forming chlorine gas. This gas it was, which was formerly used in Bleaching pure and without admixture; but this is now, I believe, wholly laid aside: and a combination of it with water - potash - soda - magnesia - or lime; is preferred. These it will be necessary to discuss in their order.

1. The chlorine diffused through water was the mode of using it invented by Berthollet, and still followed in some old establishments. The Bleaching liquor formed in this way may be either made of the proper strength for use at first, or it may be made stronger and more concentrated by putting in a smaller quantity of water into the receiver or a larger proportion of ingredients into the retort; in which case it can be afterwards diluted to the proper strength. When the liquor is much concentrated it has, like the gas, a greenish yellow colour or what Werner calls a siskin green **(12).** It has also like the gas a very penetrating and offensive smell arising indeed from the disengagement of the gas. It cannot be breathed even for a few instants, without the danger of a most obstinate and violent cough; and it sometimes causes the workmen to fall down senseless. Asthmatic affection of the breast, headache, tears and smarting of the eyes, bleeding at the nose, pains in the small of the back, and spitting of blood are the ordinary symptoms which its respiration induces. So that unless the most careful and unremitting attention be paid to the lutes, it is impossible even for a strong man to support for several successive days so unhealthful an employment. Des Charmes (Page 65.) **(13)** was so much affected by the violent expectoration this produced, that he could retain no food on his stomach; he was deprived of sleep and exceedingly afflicted with acid humours flowing from his nose and eyes so that he could not bear the light, while he suffered great pain in his back and thighs. These consequences are very serious and they soon called forth the genius of invention to contrive preventives. One of these was to introduce carbonate of potash or soda into the water in the receiver in the proportion of one fourth to one of the muriate of soda employed. Even the sprinkling of a solution of any of those carbonized alkalies upon the surface of the Bleaching liquor previously to using it, will in a great measure neutralize the disagreeable effluvia. By this method however the alkali was not only totally lost and the expense in consequence greatly increased, but the detergent power of the liquid was supposed to be considerably diminished which was attempted to be proved by Mr. Rupp of Manchester from numerous experiments **(14).**

To obviate the primary evil, and to avoid the expense of its proposed cure he contrived a very simple apparatus for exposing the goods equally to the liquid and preventing the escape of the noxious gas, a description of which has already been given in its proper place. The application of Chlorine condensed in water however may now be considered as one of the nearly obsolete agents in Bleaching, although it is unquestionably more powerful than any of the oxymuriates.

2. When the simple gas, and also water impregnated with it were mostly given up, oxymuriate of potass or soda came to be used as we have already seen in the history. The preparation of the Bleaching liquor with these is precisely similar to that employed in the impregnation of water: the leaden receiver being in the former case filled with a solution of one of these alkalies. The experiments of Mr. Rupp and others, to prove that the detergent power of Chlorine is diminished by neutralizing it with an alkali, have been found practically erroneous. It is not unlikely

indeed that they were deceived by the circumstances of the oxymuriates not producing so sudden an effect as the pure chlorine, but this is rather an advantage than otherwise, for the chlorine is disengaged so slowly and gradually from these salts that time is given it to act equally and effectually on every part of the cloth. Little is lost consequently by the escape of gas which is so copiously emitted in the former case; and the operation is also rendered more healthy to the workman. Lately, the combination of Chlorine with the mineral alkali has been much used in the Calico manufacture for clearing the whites of maddered goods, and it has almost superseded, in this department of the art, the tedious and expensive process of crofting. It is used in a state of great dilution; for although a strong solution would clear the whites more rapidly and more effectually, yet care must be taken not to make it strong enough to affect the colours which are to remain fast in the piece. The strictest attention ought to be paid to the purity of the alkali used for making oxymuriates, as if it be contaminated with neutral salts, the chlorine is not all taken up, and that which is left in an uncombined state being greatly stronger than what unites with the alkali, it will attack the colours of the printed goods, and in all probability discharge them.

3. Sir Humphrey [*sic*] Davy found by experiment (Elem. of Chem Phil. I. 242-3.), that the texture of linen was considerably injured when immersed in a hot solution of chlorine and water by the corrosion as he supposes, of the muriatic acid **(15).** Now this he justly thinks decreases considerably the advantage of the speedy and effectual Bleaching which is thus produced. To remedy this he instituted a set of experiments and was so fortunate as to discover a substitute wholly free from this inconvenience, namely, the oxymuriate of magnesia. This may be produced by the method already described, by diffusing the magnesia through the water in the receivers with which the chlorine combines and becomes condensed. It acts much more slowly and gradually than any of the other compounds of chlorine employed for the same purpose **(16),** and consequently must produce a more equal detergency. At Sir Humphrey [*sic*] Davy's suggestion, it was employed to some extent for clearing the whites of printed calicoes, in the large establishment of Mr. Duffy of Dublin **(17),** and with great success, for it was not found to injure in the least even reds and yellows which had been fixed by mordants. While the oxymuriate of lime not only changes all the colours and renders them of a duller hue, but also particles of the lime attach themselves so intimately to the cloth that it acts as a discharge and effaces the colours altogether **(18).** The oxymuriate of potass again, although not so strong an alternative changes red to pink and gives to purple and lilac a bluish shade; the alkali always diminishes the intensity and brilliancy of all colours. The oxymuriate of magnesia seems free from these imperfections. Sufficient quantities of magnesia can be procured for this purpose from sea water or from the residual liquor of salt works; and perhaps the act which grants a drawback on salt to the makers of chlorine (38th Geo. III. c.89. s.89,) **(19)** may be found to extend to this use of sea water, or if not, that a similar act may be procured to pass when the advantage becomes manifest. It is not unlikely, if the oxymuriate of magnesia shall come into general use, that a similar method will be taken to manufacture it in the dry state as is now successfully practised with respect to the oxymuriate of lime, in order to facilitate its conveyance to a distance.

4. Lime was impregnated with chlorine for the purposes of Bleaching at an early stage of the improvements we are now detailing, by Watt, Henry, and Cooper, but it does not appear, that it was by them brought into their general practice, as they seem to have preferred the simple water or oxymuriate of potass. It was reserved for Mr. Charles Tennant of Glasgow to improve the process of making it so as to render it both a cheap, convenient, and efficacious agent in Bleaching. The oxymuriate of barites and strontites, which were also mentioned in his patent, were found to be too expensive for practical purposes, as the latter substance could not be procured in great quantity and the former could with difficulty be separated from the sulphuric acid, with which it is usually found combined. The first process which he adopted for the purpose was to dissolve 30 lbs. of muriate of soda in a receiver which contained 140 winegallons of water for this purpose of giving greater specific gravity to the water. The muriate being dissolved 60 lbs. of quicklime were added in the state of an impalpable powder. For the production of the gas, a retort was charged with 30 lbs. of pulverized manganese mixed with an equal weight of muriate of soda to which 30 lbs. of sulphuric acid, previously diluted with 18 lbs. of water, were added. The distillation was then conducted in the usual way, care being taken constantly to agitate the materials during the process. Mr. Tennant was deprived of the patent he had for the manufacturing of this substance in consequence of a decision of the court of session. The loss of his patent stimulated him to new efforts of ingenious invention, and he succeeded in combining chlorine with lime in the dry way, which renders it so easily portable to any distance at a small expense. In consequence of this his business

has increased very much, while the Bleaching processes have received great improvement. The expense also is greatly lessened, as lime is so much cheaper than the alkalies which wont to be consumed for this purpose to a prodigious amount.

In order to produce this important agent, the chlorine gas is sent into a receiver similar to that formerly described, which contains in a pulverized form the dry hydrate of lime, that is, lime slaked with the least possible quantity of water. The powder, during the influx of the gas from the distilling apparatus, is continually agitated and the gas combines with it to a certain amount or till the hydrate becomes saturated. The salt so formed is a soft white powder which possesses little of that intolerable smell so characteristic of the gas. It is partially soluble in water and its solution is little different from that obtained by the process in which the combination is formed in the solution of lime in water. So great has been the reduction of expense from the introduction of this agent, that it was proved upon oath, that by using it the consumption of ashes in a single Bleach-field has been reduced £3000 in value in one year.

The concrete oxymuriate of lime or Tennant's salt, as it is called by the Bleachers, is, when prepared for immediate use, diffused by agitation in a quantity of water. This is allowed to stand for some time till any insoluble matter contained in the lime be precipitated and the supernatant liquor remain transparent. The liquor thus clarified is drawn off and diluted with a considerable proportion of water, when it is ready for the immersion of goods. This salt differs remarkably from most others, that it cannot be procured from the solution either in a dry mass or in crystals by evaporation; for when such a solution is evaporated part of the acid escapes and the rest is mostly converted into muriatic acid; so that instead of oxymuriate of lime, muriate of lime is obtained. The dry salt can only be obtained by Mr. Tennant's process of using dry hydrate of lime in the first instance.

In treating of the other agents of Bleaching, we have seen of how much importance it is to the Manufacturers to be able to ascertain the quantity of efficient matter in any of the substances of commerce which he has occasion to purchase. With respect to oxymuriate of lime, this ought perhaps to be still more attended to, in so much as it is the principal agent for producing pure whites. But I am not aware that any method has come into general use among Bleachers, by which the quality of a given quantity of this substance can be ascertained. They are under the necessity indeed of ascertaining the Bleaching power of the diluted liquid previous to immersing their goods which is commonly done by an indigo test, and in this way by observing the quantity of salt and the proportions of water used they may make a crude guess concerning the strength of the salt when purchased, but this at best must be an inaccurate method of proceeding. To remedy those inconveniences, the ingenious Mr. Dalton instituted a course of experiments in which he was successful in obtaining a test of easy application for ascertaining the purity of Oxymuriate of lime. Of these experiments I think it of some importance in an essay of this kind to give a full and distinct account: I shall do so *in the author's own words*, promising that his explanations of the Phenomena are made upon the old theory that oxymuriatic acid (chlorine) consists of muriatic acid and oxygen **(20).**

> Experiment. 1. One Hundred Grains of recent dry oxymuriate of lime were exposed to a low red heat in an iron spoon: The loss was 32½ grains. To the residuum water was added, and a solution of 535 grain measures of 1.055 sp. grav. was obtained, and further an insoluble residuum of 30 grains. The solution was found to be muriate of lime, and consequently consisted of 16 muriatic acid and 18 of lime. The residuum was dissolved in muriatic acid, and formed a solution indicating 21 lime; a small portion of carbonic acid was given off, but not of any amount. No trace of oxymuriatic acid could be found after the salt had been heated. Hence we learn, that 100 grains of dry oxymuriate of lime contains 39 grains of lime, combined and uncombined; and that by a low red heat, all the oxymuriatic acid is either driven off or converted into muriatic acid.
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> Experiment. 2. One hundred grains of the same specimen of oxymuriate were added to upwards of 1000 grains of water; after being stirred for some time, the liquid was filtered, and 1000 grain measures were obtained of the sp. grav. 1.034; I got also a residuum, which, dried in a moderate heat, gave 33 grains. This last treated with muriatic acid was dissolved, and indicated 18½ lime. The liquid, which contained a mixture of oxymuriate and muriate of lime, was treated with carbonate of soda, which converted the whole of the lime into carbonate of lime. From the quantity obtained, it appeared that the combined lime in the liquor was also 18½ grains. From this experiment the total quantity of lime in 200 grains of dry oxymuriate was 37 grains. In the former it was 39 grains. The quantity of lime in the solution being thus found, it remained to find the quantities of muriatic acid and oxymuriatic acid with which it was combined. The muriatic acid was determined as follows.
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> Experiment. 3. Two hundred grain measures of a solution of the sp. grav. 1.034 were taken; to these a

given quantity of muriatic acid test was added, such as previous trials had shown was more than sufficient to expel all the oxymuriatic acid from the lime. The new compound was well agitated in a bottle, and the oxymuriatic acid gas was blown away as long as any continued to be given out. The liquid solution was then tested, and found to be acid, but not to destroy colour. Nitrate of mercury was then added, as long as any calomel was thrown down. The calomel, when dried, weighed 31 grains; one ninth of this was muriatic acid equal to 3.44 grains; and from this deducting the quantity of 2.14 grains added to the liquid there remain 1.3 grains of muriatic acid previously in combination with the lime. Now we have seen that the lime in 200 measures of liquid was 3.7 grains, which would require 3.5 grains of muriatic acid; it had previously only 1.3 grains; therefore the lime in combination with oxymuriatic acid must have been so much as would require 2.2 grains of muriatic acid to saturate it. Hence it appears, that nearly 1/3 of the lime in the solution was engaged by muriatic acid, and the remaining two thirds by oxymuriatic acid. But the quantity of this last was still undetermined.

The usual way of comparing the values of any two Bleaching liquids has been, I believe, to find how much of any given coloured liquid a given portion of the acid liquor would saturate. The experiment serves well for the purpose of comparison; but it does not inform us of the precise quantity, either of volume or weight, of the acid gas which the liquor contains. We might expel the acid gas from a given weight, either of the dry or liquid oxymuriate, by means of an acid, in a graduated tube, over mercury or water; but unfortunately both these liquids act upon the acid: no doubt the analysis might be accomplished this way; but it would require an apparatus expressly for the purpose. I have succeeded however another way in discovering a very excellent test of the quantity of oxymuriatic acid in any compound. This test is a solution of green sulphate of iron. As soon as green sulphate of iron comes in contact with oxymuriatic acid solutions, the black oxide is converted into red, at the expense of the oxygen of the oxymuriatic acid; if the sulphate is deficient, a strong smell of oxymuriatic acid accompanies the mixture; whence more sulphate must be added, till the mixture, on due agitation, ceases to emit the fumes of the oxymuriatic acid; if too much sulphate be put in, then more of the acid liquor must be added by degrees, till its peculiar odour be developed & a very few drops of either liquor are sufficient to give the mixture a character when near the point of saturation. I found that 40 grain measures of a solution of sulphate of iron of the sp. grav. 1.149 were sufficient to saturate 100 measures of oxymuriate of lime of 1.034 sp. grav. In order to understand more clearly the relative weights of oxymuriatic acid and oxide of iron, which are required for mutual saturation, I made the following experiment.

Experiment. 4. A graduated tube was filled with oxymuriatic acid gas. This was then plunged into a dilute solution of green sulphate of iron and the whole of the gas was by due agitation immediately absorbed by the liquid. If any smell of oxymuriatic acid remained, the experiment was repeated on a stronger solution of green sulphate; but if no smell remained, then it was repeated with a weaker solution; till in a few trials the strength of the sulphate was found, which was just sufficient to cover the smell of the gas; or in other words to saturate the acid. This was when the solution was 1.0120 sp. grav. or nearly 1/12 of the strength which I commonly use as a test solution, as mentioned above. Now 100 measures of oxymuriatic acid gas weigh .29 of a grain, reckoning its specific gravity at 2.46; and 100 measures of the sulphate contains (as I find by experience) 1.32 gr. of real dry salt, of which 68 pts are sulphuric acid and 64 pts oxide of iron; of which 50 are iron and 14 oxygen, as is well known. The red oxide of iron is known to contain half as much more oxygen as the black; hence 64 pts. of black oxide will become 71 of red, or the black oxide receives 7 pts. of oxygen from the 29 of oxymuriatic acid, and reduces it to 22 of muriatic acid. These numbers perfectly accord with those deduced as the weights of the respective atoms. (Dalton's Phil. of Chem. P.^{t} II.). [Dalton wrote "in the 2d part of my chemistry." *Rennie leaves out a small section here of Dalton's paper and now quotes only selectively.*] We conclude that dry oxymuriate of lime contains in 100 parts, 13.5 muriate of lime, 26 oxymuriate of lime, 18.5 lime, and 42 water **(21).**

Mr. Dalton adds, that age diminishes the value of a solution of oxymuriate of lime, by converting it partially into muriate; but this effect is also produced in some degree on the dry salt when kept in a bottle. He had kept some in this manner for 6 years which was at first about the same value as that whose proportions have just been stated: he found it so far depreciated as to contain only 1/4 or 1/5 of the requisite quantity of oxymuriatic acid. (Ann. of Phil. I. 20.) **(22).**

Although however the green sulphate of iron appears from these experiments to be by far the best test of the oxymuriate of lime, yet as the indigo test does tolerably well in ascertaining the strength of the diluted liquor, and as it is very generally used, I cannot well omit detailing the manner of its application. Prepare a very dilute solution of indigo by dissolving in the usual way a pound of the best Spanish in four pounds of concentrated sulphuric acid, which proportions will generally be sufficient to produce saturation. When all the indigo is dissolved one part by measure of this solution is to be diluted with sixteen parts by measure of water, when it will be fit for use. To

> obviate any deception which may arise from the difference of strength in the indigo, it is best always to preserve some of a former preparation to compare with the new, when by a little management it may be made equal. The quantity of water used is not material provided that the same Bleacher keep always to the same proportion. The strength of the Bleaching liquor is determined by the quantity of it which is required to destroy the colour of any given portion of the test. In practice it is usual to have two graduated glass tubes, one for the test the other for the liquor, by which arrangement the efficient quantities are seen by inspection **(23).** Berthollet says (Ann. de Chim. II.) he was informed by Mr. Watt, that the indigo test will not accurately show the strength of either oxymuriate of soda or of potass, and recommends a decoction of cochineal as not being so liable to inaccuracy or deception **(24).** From what I can learn however, this has not been found so convenient in practice as the indigo test: Mr. Dalton's test from sulphate of iron will soon, I imagine, supersede all others. (see Page, 172-3) **(25).**

Concluding Remarks

In this article only 18 pages from Chapter IV of Rennie's essay, consisting of 213 pages (26), have been considered. Any cautious conclusions therefore arise from this small sample only. It is clear that the writer drew extensively upon published works for his information. Source acknowledgments are not consistent and in some instances are completely missing. His choice of subject was fitting, particularly if only because the role of chemistry in industry was becoming apparent in the rapidly expanding field of bleaching.

Elsewhere in the essay Rennie stated that he did not envisage its publication, although he probably wrote the work in the hope of financial reward. Such hope was realized for it has been shown that the prize of £10, a considerable reward, was gained,. The author was a highly educated and well read postgraduate, well-versed in the art of successful essay writing. His two other prize-winning essays attest to this ability and to his potential as a future writer. That potential was indeed realized but is outside the scope of this article.

The manuscript of the essay bears no date, but the fact that it is headed "By James Rennie A.M." suggests it was composed in 1815 (his graduation year) or shortly afterwards; and this is further confirmed by the award of a prize in 1815–1816 (27). Thus Rennie was 28 years old and unmarried when he wrote it. Whether or not he aspired to a career in writing and lecturing cannot be ascertained, although this proved to be his main employment some years later. He held the professorship of natural history at King's College, London from 1830 to 1834.

For this essay he drew freely on other contemporary authors of reputable standing, particularly in matters of chemistry. It should be noted that textbooks of that time often contained sections devoted to the art of bleaching. For example, Parkes's *Chemical Essays* contains a considerable treatise entitled "Bleaching," which most certainly assisted Rennie in writing his essay (28). His several references elsewhere in the essay to Thomas Thomson are noteworthy. Clearly *A System of Chemistry* (29) was very well known and Rennie appears to have held its author in the highest esteem by recalling, many years later, of the …"'highly distinguished chemist, Dr. Thomson, whose pupil I also had the good fortune to be" (30). The entry on bleaching in *Encyclopaedia Britannica* (1803), possibly by Thomson, may have induced Rennie to take this subject as the basis for his own essay (31). Rennie's evident plagiaristic use of the *Edinburgh Encyclopaedia* (1811) has been noted in earlier sections of the essay and interestingly, though not reported by Rennie, it is from this source that we first learn of Watt's full scale trial involving chlorine bleaching of 500 pieces of linen (32).

As a future professor of natural history the essay-writer was also a reputable chemist, having clearly informed himself of many aspects of the subject. It seems a pity that he chose to quote verbatim such large tracts of other people's work, sometimes without giving specific acknowledgment. Nevertheless, this points to his unquestionable knowledge of the standard and most recent literature. Certainly Rennie's *Jugendwerk* on bleaching remains an exemplar of what was known (chemically) and practiced in the period before its writing in about 1815 and clearly points to his abilities and potential as an author.

This small chapter about chlorine points to Rennie's close use of contemporary textbooks and journals. For example, bleachers' dependence upon elemental chlorine, often generated on their own premises, had probably diminished at the time he wrote the essay—a point not yet evident in published books of the time—although Rennie recognized the process as being obsolete. The new bleaching powder available from the developing manufacturing of Charles Tennant Company of Glasgow (33) was reported by Rennie, but he failed to present this as a far more satisfactory means of obtaining a bleaching solution. So by 1815 the generation of elemental chlorine gas and its dissolution in water or alkaline solutions by individual textile firms had greatly diminished. Bleachers were turning to the use of bleaching powder. Though discussed by Rennie, particularly the methods used to determine its strength in bleaching operations, he nevertheless presented the older methods of using elemental chlorine in some detail.

Regarding Rennie's analytical observations, it is difficult to see why he chose to give John Dalton so much attention. Dalton's analytical methods, accurate though these were, must nevertheless have been quite inappropriate to the limited laboratory resources and chemical knowledge of the time. The lengthy and complicated methods offered no advantage in an industrial context at a time when faster volumetric determinations were becoming popular. Furthermore, through the introduction of solid bleaching powder, a measured weight or volume would result in a roughly judged bleaching strength, the bleaching operative merely needing confirmation by the simplest of tests: the indigo test.

During the twenty-five years following the appearance of this essay Rennie continued a successful writing and lecturing career in Britain, before leaving for a new life in Australia in 1840. The essay and the small section considered in this article concerning chlorine bleaching remain as testament to his early abilities.

REFERENCES AND NOTES

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2. F. G. Page, "James Rennie (1787-1867), Author, Naturalist and Lecturer," *Arch. Nat. Hist.*, **2008,** *35,* (1), 128-142.
3. J. Hodge, "James Rennie (1787–1867)," *Oxford Dictionary of National Biography*, Oxford University Press, Oxford, 2004. http://www.oxforddnb.com/view/article/23375, accessed Sept. 20, 2006].
4. W. I. Addison, The *Matriculation Albums of the University of Glasgow from 1728-1858,* J. Maclehose, Glasgow, 1913. In this year, 1810, he was in the class of John Young, Professor of Greek. His father's name is given as Thomas, an Ayrshire farmer.
5. Noted in the University Prize Lists for the period 1777-1833, compiled by W. I. Addison, Glasgow University Archives (GUA) R7/1/1. Logic 1811-12, Ethics and Logic 1812-13, Mathematics and Physics 1813-14; these were class prizes, value unknown but probably less than £10. It was during 1814-15 that he gained a prize for a geology essay, "A Comparative View of the Huttonian and the Wernerian Theories of the Earth," handwritten, signed by James Rennie, A.M., Glasgow. 1815; [George Neilson Collection of MS, author of *Trial by Combat* and joint editor of *Acta Dominorum Concilii*, *1496-1501*, Edinburgh, 1918.] The National Library of Scotland (hereafter NLS) acquired the collection in 1927, and there is no indication in the MS as to how Neilson obtained the copy of the essay. The essay contains a pasted page (vi) insertion: "To the Most Noble The Marquis of Douglas and Clydesdale with J. Rennie's most grateful and respected Compliments - Glasgow College 18th April 1816." The hand does not appear to be that of Rennie. This essay gained second prize, donated by a Mr. Coulter. The first prize, donated by Dr Watt of Birmingham, was awarded to George Oswald Sym of East Kilpatrick.
6. W. I. Addison, *Roll of Graduates of the University of Glasgow 1727-1897*, Maclehose, Glasgow, 1898. The Register of Masters of Arts for 1764-1888 (GUA 26676) records Rennie's graduation on July 20, 1815. The listing also noted: 'Professor of Natural History at Kings College London, 1830-34; emigrated to NS Wales, 1840, born at Sorn, Ayrshire 26 February 1787; died at Adelaide, 25 August 1867.'
7. "An Essay on the Improvements in the Art of Bleaching by the Application of the Principles of Chemistry," [Birmingham City Archives (BCA), MS 3219/4/295, formerly JWP/C4/C8.] This was followed by another prize winning essay: "Essay on the Application of Steam to the Purposes of Navigation," 1816, [NLS, MS 9352.] Both essays were awarded the Watt prize (£10).
8. BCA James Watt Papers, Private Letters 1803-10, p 219, to Geo Jardine Esq., Coll., Glasgow April 26, 1808.
9. Ref. 8, p 225, to James Young, Coll. Glasgow, June 4, 1808. It is not clear into which part of this cycle Rennie's essay fitted.
10. Rennie could be referring to the lengthy controversy over whether chlorine contained oxygen and was truly elementary. Davy had argued in 1807 that chlorine (oxymuriatic acid) contained no oxygen, but others, such as Gay-Lussac and Berzelius, believed otherwise. One strong voice supporting the nonelementary nature of chlorine was that of John Murray (d.1820), to whom Rennie had referred in an earlier section of his essay. Rennie appears to show little regard for these theoretical arguments and places the value of chlorine entirely in its practical bleaching properties.
11. Berthollet's first publication about chlorine and its bleaching effects was reported to the Académie Royale des Sciences in 1785 followed by a more practical article in *Ann. Chim.*, **1789**, *2*, 151-90. Berthollet's apparatus is fully described in the translation by R. Kerr, "Essay on the New Method of Bleaching by means of Oxygenated Muriatic Acid...from the French of Mr. Berthollet*,"* Edinburgh, 1790, published by Order of the Trustees of the Linen and Hempen Manufacture, unnumbered page preceding, p 130 and pp 130-139. In 1794 Peter Fisher of Glasgow designed the apparatus described in *Edinburgh*

Encyclopaedia, 1811, Vol. 3, 579. A footnote indicates that Fisher's apparatus was essentially the same as that of Charmes and Berthollet.

12. Rennie's reference to A. G. Werner is not unexpected although of little importance in this instance. The bleaching essay and a further prize winning essay, "A Comparative View of the Huttonian and the Wernerian Theories of the Earth," (see Ref. 5) were written in the same period. He clearly had some knowledge of Werner's writings, but it is impossible to decide whether Rennie had referred to Werner's own German publications or the translations by Robert Jameson, "A Treatise on the External Characters of Minerals," 1805 and 1816, by several publishers, Edinburgh and London. In the 1805 edition on p 11: "*Siskin green* is emerald green mixed with lemon yellow and a little white. It makes the transition to the yellow colour…" Interestingly, the *OED* ascribes the first use of this color description to James Robertson in 1805.
13. C. Pajot des Charmes, *The Art of Bleaching Piece-Goods Cottons and Threads...*, G. G. & J. Robinson, London, 1799, a translation by W. Nicholson of *L'Art du Blanchiment des Toiles, fils et cotons de tout genre*, Paris, 1799. Charmes' vivid description of the results of the toxicity of oxygenated muriatic acid (p 64) states: "It cannot be breathed even for a few instants, without the danger of a most obstinate and violent cough. Its action is sometimes so strong that the operator will fall down senseless…"
14. T. L. Rupp, "On the Process of Bleaching with the Oxygenated Muriatic Acid; and a Description of a New Apparatus for Bleaching Cloths with that Acid Dissolved in Water, without the Addition of Alkali," *Mem. Manchester Lit. Philos. Soc.,* **1798**, *5*, 298-313. Rupp reported that the addition of alkali increasingly reduced the decolorizing property. This was a misleading statement, but it appeared to support Berthollet's ideas. See also J. G. Smith, *The Origins and Early Development of The Heavy Chemical Industry in France,* Clarendon Press, Oxford, 1979, 136-139.
15. H. Davy, *Elements of Chemical Philosophy*, 1812, J. Johnson, London, Vol. 1 (pt.1),; Davy mentions a warm solution only (p 242).
16. Ref. 15. This is an exact quotation from p 243, and the following sentence is almost word-for-word the same as Davy's text.
17. Duffy, Bryne, and Hamil Company, a staining and printing firm active into the early decades of the nineteenth century.
18. This sentence is word-for-word the same as in the *Edinburgh Encyclopaedia,* Blackwood, Edinburgh, 1811, (pt. III & IV), Vol. 3, 577-591 (587, note 64).
19. 38th George III. cap. 89. (1798) "An Act for Transferring the Management of the Salt Duties to the Commissioners of Excise," is a major Act embracing the entire salt duties legislation. It includes the use of salt in the production of synthetic alkali and chlorine for bleaching and their byproducts, and extends to 30 pages. Section 89 refers to "A drawback of duties to be allowed on British salt used in making Oxigenated Muriatic Acid for bleaching linen," and contains the statement that salt had to be "mixed with vitriolic acid, manganese and water, in the presence of the proper Officer of Excise...nor should any such drawback or allowance be granted to any person not being an actual bleacher of linen or cotton;" section 89 appears to have no relevance to sea water or residual liquor of salt works (bittern).
20. This is indeed full credit to Dalton; however, Rennie has drawn word-for-word from John Dalton, "On the Oxymuriate of Lime," *Ann. Philos.* **1813,** *1,* 15-23. Rennie's remark about Dalton's adherence to "the old theory" of the composition of oxymuriatic acid gas is noteworthy insofar as their writings were separated by only two years. It is this paper that contains Dalton's method of determining the strength of oxymuriate of lime by using the reaction with ferrous sulphate solution (Experiments 3 and 4), a method supported by Rennie in his closing remark (but probably rarely used).
21. Ref. 20, p 19.
22. Dalton reported on a further three experiments, but Rennie has ignored them. The case for using the ferrous sulphate test, rather than one based on a simple color change, is strongly argued by Dalton.
23 Rennie gives no credit to F. A. H. Descroizilles as the inventor of this important analytical test. The method was first brought to public notice by Claude Louis Berthollet, *Essay on the new method of bleaching, by means of oxygenated muriatic acid; with an account of the nature, preparation, and properties, of that acid. ... From the French of Mr. Berthollet. ...* by R. Kerr, ..., Trustees of the Linen and Hempen Manufacture, Dublin, 1790, 80. A quotation from the 2nd ed. (Edinburgh, 1791), p 131, is as follows: "Mr Decroisille [Descroizilles] has contrived a test, or gauge, by means of a solution of indigo in sulphuric acid. He takes one part, by weight, of indigo, reduced to a fine powder, with eight parts of concentrated sulphuric acid, and digests this mixture in a matrass, exposed to a sand heat for some hours, until the indigo is completely dissolved by the acid. This solution is then diluted with one thousand part of water, and is to be employed for measuring the force of the oxygenated liquor,…"I have not identified from where Rennie obtained his information. Spanish indigo, usually from Guatemala or Mexico (both countries were part of the Spanish empire), regarded as superior to African or SE Asian indigos, was widely available, if expensive. It was not however specified by Descroizilles. Furthermore, why Rennie suggested an indigo concentration of more than 1% is difficult to explain when Descroizilles had recommended 0.1%. Descroizilles' own account of this first volumetric method appeared as "Description et usages du Berthollimêtre," *J. Arts Manufactures*, **1795, 1**, 256-276, although the underlying idea had been mentioned earlier by Berthollet.
24. There is little evidence to show that cochineal was ever used in preference to indigo. Watt's first recommendation

for its use appeared in a letter dated February 15, 1788 to his father-in-law, Mr. McGrigor (MS 239, Birmingham City Archives); but the suggestion was not pursued and the indigo test continued to be used. Berthollet's report on Watt's suggestion appeared in *Ann. Chim.*, **1789,** *2*, 151-190 (188).

25. There is little evidence that this test gained common use. It was mentioned by S. H. Higgins, *A History of Bleaching*, Longmans, Green, London, 1924, 93, who described the Stockport bleach works of Sykes & Co: "Bleaching powder was tested at Sykes: in 1845 by titrating with sulphate of iron until the liquor changed red to yellow prussiate of iron." See also F. Szabadváry, *History of Analytical Chemistry*, Pergamon Press, Oxford, 1966, 217: "This rather uncertain method, however, was used for quite a long time,.."
26. The dimensions of the hand written volume are as follows: height 250 mm., width 205 mm., depth 21 mm. It contains 114 leaves and the volume consists of page numbers 1-213, along with an introduction page, contents pages, and the title page. The paper used is of a good heavy quality and is watermarked "J Budgen 1815."
27. W. I. Addison, *Glasgow University Prize Lists 1722-1833*, Carter & Pratt, Glasgow, 1902.
28. S. Parkes, *Chemical Essays,* Baldwin Cradock and Joy, London, 1815, Vol. 4, 3–177.
29. T, Thomson, *A System of Chemistry,* Bell & Bradfute, Edinburgh, 1802, 4 vol.
30. *Alphabet of Scientific Chemistry for the Use of Beginners*, W. Orr, London, 1833, xi.
31. T. Thomson, "Bleaching," *Supplement to the Encyclopaedia Britannica*, Thomas Bonar, Edinburgh, 1803, Vol. 1, 80-88.
32 *Edinburgh Encyclopaedia*, Ref. 18, Vol. 3, footnote on p 578.
33. See E. W. D. Tennant, "The Early History of the St. Rollox Chemical Works," *Chem. Ind. (London)*, **1947**, 667-673 (669). In the period 1799-1800 Tennant produced 52 tons of bleaching powder and in the following five years the amount trebled. By the time Rennie wrote the essay, output was probably approaching 300 tons annually or more. Clearly the change from chlorine water/alkali solutions to solid powder was underway by 1815.

ABOUT THE AUTHOR

Dr. Frederick G. Page, Wychbourne Kington Herefordshire HR5 3AQ. UK, after gaining a doctorate under the supervision of Professor William H. Brock at University of Leicester in 1999, has continued to publish and research topics related to his thesis regarding early analytical chemistry in the bleaching and alkali industry. He is currently transcribing the essays of James Rennie, author, naturalist, and lecturer; a small section of one of these being the subject of the above article.

ON TWO LETTERS FROM CASPAR NEUMANN TO JOHN WOODWARD REVEALING THE SECRET METHOD FOR PREPARATION OF PRUSSIAN BLUE

Alexander Kraft, Gesimat GmbH, Berlin

Introduction

Prussian Blue (ferric hexacyanoferrate(II)) was discovered accidentally by Johann Jacob Diesbach (1) and Johann Konrad Dippel (2) in Berlin in 1706 (3). As the first synthetic pigment, Prussian Blue received its name from the country in which its discovery occurred. It revolutionized the use of the color blue in artwork because it was less expensive and/or more stable than other blue pigments of the time.

In February, 1707, soon after the discovery of the Prussian Blue, Dippel fled Berlin to the Netherlands to avoid a second imprisonment (3). In the following years, Prussian Blue was produced and marketed by Diesbach and Johann Leonhard Frisch (4) in Berlin (3), at least until 1716, and for a certain time also by Dippel in the Netherlands (3). Next to nothing is known about Dippel's Prussian Blue production in the Netherlands prior to his departure from that country in 1714. The Prussian Blue manufacture in Berlin, on the other hand, was a great commercial success (3). Throughout Europe, people were interested in the secret to its production; but for obvious reasons, the manufacturers tried to protect their process. Frisch reported to Leibniz in a letter dated October 29, 1712 that some Italians wanted to buy the secret of the Prussian Blue production (5), but their offer was too low to match the high profits he realized with the production monopoly. Suddenly, in 1724, John Woodward (6), from London published a detailed description of the preparation process for Prussian Blue in the *Transactions of the Royal Society* (7). This production method had been sent to him from Germany. Until recently, the identity of the sender has been unknown, but this information is to be found in the archives of the Royal Society in London.

The Two Letters from Caspar Neumann to John Woodward

In the archives of the Royal Society, the excerpts of two communications from Caspar Neumann in Germany to John Woodward from the year 1723 can be found (8, 9). In the excerpt of the first letter, written in English in June, 1723, the following writing of Neumann to John Woodward is recorded (8):

> I am Still A Debtor to the Royal Society, to recommend my Self to them by Something or other that may be curious or usefull. For which reason I have been continually hitherto thinking on some way or other of discharging my Obligation in that Respect; but still nothing presented itself for my said Purpose. however now I have thought on a certain blew die of as deep a Colour as that of the flower Gentianella is. It is a Product of Alum and Sal Alkali precipitated by certain Knacks or manual Operations. Painters may use it with great advantage instead of Ultramarine. The first Inventor of it lives in Berlin; his name is Mr. Frisch, Conrector of the school of that Town, who is the onely Man that prepares it, and Sells a great quantity of it for Italy, and Germany, and I don't know but for England too.

> This Arcanum I should be willing to communicate to the Royal Society, provided it might prove acceptable to them: for else, if they should not value it, I should be loath to divulge it, and so make this pretty art known to the world, and thereby deprive that Gentleman of the Advantage and profit he draws from it, he being a good friend of mine. Indeed he never taught it me, nor did I ever exchange one word or Letter with him about it; but whatever Inkling or hint I had concerning some of the Ingredients, I by my Self found out the preparation thereof, by many Trials, and by my own Industry, with great cost and charges; So that I am able to prepare the Colour bright, dark, violet or purple, and yet all these of one and the same Stuff, the manual Operations do differ, and therein chiefly the Art consists. Yet I am not willing to communicate it under mine own Name, but Shall be content, if somebody else be said to be the Communicator of it. Wherefore if this Secret be not already known in England, I intreat you to acquaint me by your next, if the Communication thereof would prove acceptable or no, and then the Process, with all the several manuals, Shall be imparted, as soon as possible, by the Post.

Obviously, Woodward wrote back to Neumann that his information on the Prussian Blue manufacture would be welcome for the Royal Society because the above extract of the first Neumann letter is followed in the Register Book of the Royal Society by the production method for Prussian Blue sent by Neumann and dated 'Lips. 17. Nov. 1723,' written in Latin (9). Interestingly, both Neumann texts were sent or at least are shown to be sent from 'Lipsick' or 'Lips.,' i.e., Leipzig, a city in the German state Saxony about 150 km south of Berlin. Perhaps Neumann chose Leipzig to conceal that the sender of the Prussian Blue production method was located in Berlin.

***Figure 1**. Caspar Neumann, apothecary and chemist from Berlin, who revealed the heretofore secret production method of Prussian Blue to John Woodward in 1723 (© Leopoldina, Halle, Germany).*

From the extract of the first letter, it can be deduced that Neumann thought Frisch was the inventor of Prussian Blue and that he was not aware that Diesbach and Dippel were the two original inventors. In 1723 Dippel was still imprisoned on the Danish island of Bornholm (from 1719-1726). The existing information on Diesbach ends in 1716 with a letter from Frisch to Leibniz (5), and so it is not clear whether Diesbach was still working together with Frisch in 1723 on the Prussian Blue production in Berlin.

The Production of Prussian Blue According to Neumann

The preparation procedure for Prussian Blue which Neumann sent to Woodward (9) was the following (English translation after H. M. Powell (10):

> Preparation of Prussian Blue sent from Germany to John Woodward, M.D. Prof. Med. Gresh., R.S.S.
>
> Take 4 ounces of crude tartar (potassium hydrogen tartrate) and 4 ounces of dried crude nitre (potassium nitrate); powder them minutely and mix. Detonate them with charcoal, and you then have 4 ounces of extemporaneous alkali. While this salt is still hot it is finely powdered and 4 ounces of well dried and finely powdered ox blood is added.
>
> These well-mixed components are placed in a crucible so that it is two-thirds filled. After it has been covered with a lid it is put on a fire and the crucible is piled round with coals so that it gradually begins to glow and the material takes fire and begins to burn without any violent outburst. The material is kept in this degree of fire until the flame and eruption slacken. The fire is then increased until the substance glows intensely and little further flame emanates from the crucible. Then remove the crucible from the fire and grind the material gently in a mortar; have ready 2 pints of boiling fresh water into which the material is thrown while still glowing and boil for the space of half an hour. The decoction is passed through a piece of linen and the remaining black material, on to which a further

> portion of water is poured, is once more placed on the fire, boiled, and filtered. This procedure should be continued until the saltiness and all bitterness have been washed out and the water remains insipid. Well press out all the liquors remaining in the linen and the material and when you have collected them all together, place again on the fire and evaporate down to 3 1/2 pints and keep for later use. (No. 1).
>
> Then take 1 ounce of green vitriol, calcined gently to whiteness, and dissolve it in 6 ounces of fresh water; filter through paper and call this No. 2.
>
> Then take 8 ounces of crude alum ($KAl(SO_4)_2 \cdot 12H_2O$). Treat it with 2 pints of boiling water until complete dissolution of the alum and when this has been done, add it to the solution of vitriol No. 2 which is taken, boiling, from the fire, put into a pot of sufficient capacity and combined with the well boiling lixivium No. 1, previously set apart. There is a great effervescence of the contents and a green or greenish-blue colour appears. The liquid is poured alternately from one vessel to another during the effervescence, until it stops; then let it stand. It is then transferred to a piece of linen so that the liquors may flow through and the coloured substance remain on the linen. When no further water drips through it is removed from the linen with the aid of a wooden spatula into a fresh, smaller pot. Pour on to it 2 or 3 ounces of spirit of common salt and at once there appears a most beautiful blue colour. All is well stirred and allowed to settle overnight. Then a large quantity of fresh water is added and stirred with a spatula. After the material has settled the water is decanted and a fresh lot of water is poured over it, and this operation is repeated until all bitterness has been washed away and the water which flows out is insipid. When this has been completed, transfer the intensely blue precipitate to a taut piece of linen so that the water may gradually drain away. The pigment is dried in a gentle heat, and is then ready for use.
>
> N.B. - In this procedure the calcination is of great importance because the sea-blue colour and the hidden sky-blue arise according as the calcination of the dried blood with the alkali is light, medium, or strong, and hence there is a diversity of colour.
>
> The well-boiling lixivia are to be mixed one with the other in the most rapid manner.

According to his first letter to Woodward, Neumann discovered this procedure for the manufacture of Prussian Blue by his own experiments after he had acquired some knowledge about the principal reagents; and therefore, it is not necessarily the same method that Frisch and Diesbach used for their production in Berlin. An obvious difference from the procedure of the first Prussian Blue production by Diesbach and Dippel reported by Stahl (11) is that Neumann used a so-called extemporaneous alkali instead of potash for the calcination step with blood.

The Effect of Neumann's Letters

Woodward presented the contents of the second Neumann letter to the Royal Society on January 9, 1724. Obviously, the chemist John Brown (12), FRS initiated experiments to verify the production method for Prussian Blue and to perform some additional tests. He presented his results to the Royal Society on April 2 and April 16, 1724. Woodward published Neumann's Latin production method (9), without naming Neumann and without any further changes in the technique, in a paper in the *Transactions of the Royal Society* (7). Directly following this is a paper by John Brown, who describes his own experimental observations with this method and includes some new findings (13).

In 1725, one year after the publications by Woodward (7) and Brown (13), the French chemist Étienne-Francois Geoffroy reported that Prussian Blue was being produced in London in large amounts and that this Prussian Blue was of better quality than that which was

***Figure 2**. John Woodward, physician, geologist and naturalist in London, who in 1724 published the production method for Prussian Blue sent to him from Caspar Neumann (© The Royal Society).*

produced by the Messrs of Berlin (14). He also published the details of Woodward's and Brown's publications in French, together with some of his own experimental results (14, 15).

Therefore, by the mid 1720s the knowledge of the manufacturing process for Prussian Blue was publicly available in Europe. A production monopoly was no longer in existence.

The Life of Caspar Neumann

Who was Caspar Neumann? Biographical information on Caspar Neumann can be found in several sources (e.g. Ref. 16), the most detailed and comprehensive in a German doctoral thesis from 1938 (17). A short summary of this information is given here, accompanied by some additional material from the archives of the Royal Society in London.

Caspar Neumann was born on July 11, 1683 in Züllichau (since 1945 the Polish Sulechov), a small town in the very eastern part of the German state Electorate of Brandenburg not far from the Polish border. The area on both sides of the boundary had a mixed German and Polish population. Therefore, Caspar Neumann was fluent in both German and Polish. His father was the merchant Georg Neuman (died 1695), his mother Rosina Neuman née Weichert (died 1693). After the early death of his parents, he was raised by his godfather Johannes Romke, the apothecary of Züllichau. He later became an apprentice of the apothecary profession under Romke. He finished his apprenticeship in May, 1701. During and after his apprenticeship he worked in and later also managed the apothecary shop of Romke in the small Polish town Kargowa (with the German name Unruhstadt) just across the border from Züllichau. Because of the Great Northern War (1700-1721), which in large part was fought in Poland, he left Kargowa in 1704 for Berlin, the capital of the Electorate of Brandenburg and, after 1701, also of the new Kingdom of Prussia.

In Berlin he began working for the apothecary Christoph Schmedicke (apothecary shop Black Eagle at the Kings Gate) in 1705. Soon afterwards he changed his employer and became a traveling apothecary of King Friedrich I (18) and served in this position until 1711. He was proposed for this post by the former traveling apothecary Conradi, who accepted a job directly in the Court Apothecary Shop. Neumann accompanied the king as an apothecary during his travels. During the time the king stayed in Berlin, Neumann worked in the Royal Court Apothecary Shop (19). Neumann was also an accomplished pianist and was required to give private concerts for the king. Through this endeavour, he became personally acquainted with the king. In 1711 Friedrich I sent him on an extended trip through Europe to improve his chemical and pharmaceutical education in several countries. After traveling through various parts of Germany, he moved to the Netherlands. There he visited Leyden, Utrecht, and Amsterdam. He stayed for an extended time with Boerhaave (20). In early 1713 he arrived in London. Shortly after his arrival he received a letter from Berlin informing him of the death of Friedrich I, whose successor, King Friedrich Wilhelm I (21), did not need his services anymore and would terminate any further payment.

He sought a new job in London and was fortunate to become employed by Abraham Cyprianus (22), a famous and wealthy surgeon and hobby-chemist with a private chemical laboratory. Caspar Neumann worked for the next three years, until 1716, in this laboratory. He also lived in the household of Cyprianus. In addition, he gave public lectures in chemistry. He became well acquainted with several English scientists, among them Newton (17) and Hans Sloane (23), as can be deduced from a later letter sent from Neumann in Berlin to Sloane in 1733. In this letter he wrote (24):

> ... I am sensible, Hon. Sir, how much I owe to you, for I gratefully remember that it was by your Recommendation not only that I was received into Your Illustrous Society, but also, that during the 5 years which I lived at London in the House of Dr. Cyprianus, when I became acquainted with the family of Mr. Hadleys, I had leave to see your famous Collection of Natural Curiosities; for which favours bestowed upon me I find myself under eternal obligation.

Perhaps more importantly, during this time he also became acquainted with John Woodward, to whom he later sent the Prussian Blue letters. The content of this letter to Sloane, the help he received from several fellows of the Royal Society, and the fact that he was allowed to take part in meetings of this Society can explain Neumann's sense of being a debtor to the Royal Society, as he stated in his first Woodward letter in 1723.

Because he had a good and secure income now, Neumann decided to stay in England. To settle his affairs, he returned to Berlin in 1716 for a short time. Here he met the famous and influential Georg Ernst Stahl, physician and chemist, today best known for his contributions to the phlogiston theory. Stahl had been living in Berlin since 1715 and had been invited by King

Friedrich Wilhelm I to serve as physician to the King. Stahl wanted to hire Neumann for the Court Apothecary Shop in Berlin. Therefore, he arranged with the king for Neumann to be offered a substantial position in the shop. First, however, Neumann would be allowed to finish his educational travels through Europe with his expenses again paid by the king. Caspar Neumann agreed. He then moved back to London, where he completed his studies. While still in London at the end of 1717, he received the news of the death of the second apothecary, Johann Caspar Conradi, of the Court Apothecary Shop. Half a year later, Memhard, the Royal Court Apothecary, also died. At this point, Neumann returned to Berlin by way of France and Italy, where he completed his educational travels at a rapid pace.

In early 1719 he arrived in Berlin and was immediately appointed as new Royal Court Apothecary, a post Neumann held until his death. At the beginning of his tenure in the Royal Court Apothecary Shop, located in a side wing of the Berlin palace, Neumann was responsible for delivering drugs and remedies to 8,000 persons at no cost or for a reduced fee. By 1732 this number had risen to about 20,000 (17). Caspar Neumann greatly improved the technical and organizational conditions of the Court Apothecary Shop.

Neumann became a member of the Royal Prussian Society of Sciences in 1721. In the same year he married Cornelia Maria, the widow of the former second apothecary Conradi. He had no children of his own but raised the two children of his wife and Conradi.

In 1723 the Collegium Medico-chirurgicum (25) was founded in Berlin. Neumann was appointed professor of pharmaceutical chemistry here in the same year. His lectures were delivered in German, not in Latin because he was (26):

> being by a Royal Mandate are ordered to instruct the Youth here in what regards our institution in their mother-Tongue, which is the German: perhaps because the greatest part of the Students in Pharmacy and Surgery are unacquainted with the Latin.

Among his pupils at the Collegium Medico-chirurgicum was Andreas Sigismund Marggraf (27), who in 1751 first described a method of detection of iron in water by using the formation of Prussian Blue that occurred after the addition of hexacyanoferrate (so called blood lye) to water samples (28). In addition to instructing students, Neumann also gave public lectures in chemistry: "publick Lectures in Chymistry which I am oblig'd to make," as he wrote to Sloane (26).

It was also in 1723 that Caspar Neumann wrote his letters on Prussian Blue to Woodward. In 1724 Neumann was appointed to the new higher Collegium Medici and was thereafter responsible for all apothecaries in the kingdom of Prussia. Proposed by Hans Sloane, he was elected to be a Fellow of the Royal Society in 1725. In 1728 he was elected to be the 400th member of the Leopoldina academy (29) with the cognomen Synesius. He was promoted in 1733 to the title Privy Councillor (Hofrat). In May, 1735 his wife died at the age of 48. About two years later, on October 20, 1737 he died at the age of 54. His stepson, Johann Caspar Conradi, was his successor as Court Apothecary.

Caspar Neumann was a typical apothecary-chemist of 18th century Germany (30). As a chemist, he concentrated on pharmaceutical and food chemistry. In his lifetime he wrote 24 publications, mostly in Latin but some also in German, in scientific journals or separately. He is not remembered as a discoverer of new elements or substances or as a very creative chemist. Rather, he was someone who collected the contemporary chemical knowledge and brought order to this collection.

For several decades after his death Neumann was still influential in the chemistry community, especially in Germany, because of his widely read books (31, 32). The content of these books, published posthumously, was an extensive summary of his lessons on chemistry. They were valuable because they contained the complete chemical knowledge of the time with a critical examination of many facts; and they were widely accessible because they were written in German instead of Latin. In England William Lewis (33) translated and rearranged these collected chemical works, which were subsequently published with additional material containing later discoveries and improvements in 1759 (34) (first edition). Dutch and French translations were also published.

Conclusions

The secret production process for Prussian Blue was revealed in two letters sent from Caspar Neumann in Germany to John Woodward in London. Extracts of these letters are preserved in the archives of the Royal Society. Soon after receiving the information from Neumann, Woodward published the description of the manufacturing process in the most prestigious scientific journal of the time. After Woodward's publication, Prussian Blue manufacture began in various European countries.

REFERENCES AND NOTES

1. Johann Jacob Diesbach was a Swiss pigment and dye producer living in Berlin at least between 1701 and 1716. Further information on him has yet to be discovered.
2. Johann Konrad Dippel (1673-1734) was a pietist theologian, physician, and alchemist. Between 1704 and 1707 he lived in Berlin and between 1707 and 1714 in Maarsen, Netherlands.
3. A. Kraft, "On the Discovery and History of Prussian Blue," *Bull. Hist. Chem.*, **2008**, *33*, 61-67.
4. Johann Leonhard Frisch (1666-1743) was a teacher at the Berlin gymnasium of the Grey Monastery from 1698, when he arrived in Berlin after several years of travel through Europe. Besides being a school teacher until his death, he was also very active in scientific studies. He joined the Berlin Society of Sciences in 1706. His scientific studies included works on mulberry trees and silk production, linguistic studies (e.g. German-Latin and German-French dictionaries), encyclopedic books on insects and birds, and, last but not least, for a certain time chemical studies including the improvement, manufacture, and sale of Prussian Blue.
5. L. H. Fischer, Ed., J*oh. Leonh. Frisch's Briefwechsel mit G. W. Leibniz,* Georg Olms Verlag, Hildesheim, New York, 1976 (reprint of the book from 1896).
6. John Woodward (1657-1728), a physician, naturalist, and geologist, was appointed professor of medicine in Gresham College in London and Fellow of the Royal Society from 1693.
7. J. Woodward, "Praeparatio Caerulei Prussiaci ex Germania missa ad Johannem Woodward," *Philos. Trans. R. Soc.*, **1724**, *33*, 15-17.
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9. "Caspari Neumanni Praeparatio Caerulei Prussiaci ex Germania missa ad Joannem Woodward Prof. Med. Gresh. R.S.S.," November 17, 1723, Archive of the Royal Society, Register Book of ye Royal Society Vol. XI, 1722-1724, pp 403-405 (Ref. No. RBO.11.403).
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11. G. E. Stahl, *Experimenta, Observationes, Animadversiones, CCC Numero Chymicae et Physicae,* Ambrosius Haude, Berlin, 1731, 280-283.
12. John Brown or Browne (?-1735) a chemist in London, Fellow of the Royal Society from 1721.
13 J. Brown, "Observations and Experiments upon the Foregoing Preparation," *Philos. Trans. R. Soc.*, **1724**, *33*, 17-24.
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16. "Kaspar Neumann," *Allgemeine Deutsche Biographie*, **1886**, *23*, 535.
17. A. Exner, Der Hofapotheker Caspar Neumann (1683-1737); Ein Beitrag zur Geschichte des ersten pharmazeutischen Lehrers am Collegium medicochirurgicum in Berlin, D. Phil. thesis, Friedrich-Wilhelms-Universität, Berlin, Triltsch & Huther, Berlin, 1938.
18. Friedrich von Hohenzollern (1657-1713) was the son of the Elector Friedrich Wilhelm (1620-1688) of Brandenburg (the Great Elector). In 1688 he succeeded his father to become Elector Friedrich III of Brandenburg. In 1701 he crowned himself in Königsberg (the modern Kaliningad in Russia) as the first King in Prussia (Friedrich I). He died on February 25, 1713 in Berlin.
19. The Court Apothecary Shop (Hofapotheke) in Berlin was founded in 1598 by Electress Katharina (1549-1602), the wife of the Elector Joachim Friedrich (1546-1608) of Brandenburg. It was responsible for delivering drugs and remedies gratis or for a reduced price to the elector (or later the King) and his family, to court employees, soldiers, all church and school employees, and to the poor, widows, orphans, prisoners etc. in Berlin.
20. Herman Boerhaave (1668-1738), a professor of medicine, botany, and chemistry at the university in Leyden. He was one of the most famous scientists of his time.
21. Friedrich Wilhelm von Hohenzollern (1688-1740) was the son of the first King in Prussia, Friedrich I. In 1713, he became king himself (Friedrich Wilhelm I). Popularly known as the Soldier-King, he practiced rigid economy during his reign.
22. Abraham Cyprianus (~1656-1718), a Dutch surgeon and physician, living in London from 1696, a Fellow of the Royal Society from 1700, and Licentiate of the Royal College of Physicians.
23. Sir Hans Sloane (1660-1753), a physician, scientist, collector, Fellow of the Royal Society since 1685, and president of the Society from 1727 to 1741.
24. "Casper Neumann, dated at Berlin, to Hans Sloane," Berlin, April 16, 1733, Archive of the Royal Society, Early letters EL/N2/4.
25. The Collegium Medico-chirurgicum was an institution for the control and education of physicians and surgeons and for all other medical professions in Prussia. It was founded in 1723 in Berlin.
26. "Concerning Ambergris by Caspar Neumann," Berlin, October 15, 1729, Archive of the Royal Society, Classified papers Cl.P/11ii/20.
27. Andreas Sigismund Marggraf (1709-1782) was an apothecary and chemist. From 1726 to 1731 he was apprentice at the Royal Court Apothecary Shop in Berlin. He also attended lectures on chemistry by Neumann in the Collegium Medico-chirurgicum. He is still well known for his discovery of sugar in beet roots in 1747.
28. A. S. Marggraf, "Examen Chymique de l'Eau," *Histoire de l'Académie Royale des Sciences et Belles-Lettres de Berlin*, **1751**, 131-157.

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33. William Lewis (1709-1781), physician and chemist, Fellow of the Royal Society, received the Copley Medal for his work on platinum in 1754.
34. W. Lewis, *The Chemical Works of Caspar Neumann, M.D. Professor of Chemistry in Berlin, FRS etc., abridged and methodized: with large additions, containing the later discoveries and improvements made in chemistry and the arts depending thereon*, Printed for W. Johnston, G. Keith, A. Linde, P. Davey and B. Law, T. Field, T. Caslon, and E. Dilly, London, 1759.

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FUTURE ACS MEETINGS

March 21-25, **2010**—San Francisco, CA

August 22-26, **2010**—Boston, MA

March 27-31, **2011**—Anaheim, CA

August 28-September 1, **2011**—Chicago, IL

March 25-29, **2012**—San Diego, CA

August 19-23, **2012**—New York, NY

April 7-11, **2013**—New Orleans, LA

September 8-12, **2013**—Indianapolis, IN

March 16-20, **2014**—Washington, DC

September 7-11, **2014**—San Francisco, CA

March 22-26, **2015**—Denver, CO

August 16-10, **2015**—Boston, MA

March 13-17, **2016**—San Diego, CA

August 21-25, **2016**—Philadelphia, PA

April 2-6, **2017**, San Francisco

September 10-14, **2017**, St. Louis

THE BIOGRAPHY OF A PERIODIC SPIRAL: FROM CHEMISTRY MAGAZINE, VIA INDUSTRY, TO A FOUCAULT PENDULUM

Theodor Benfey, Guilford College and the Chemical Heritage Foundation

Introduction

Biographies have been written of people, chemicals, and devices like zippers. Here is the biography of a periodic table. The spiral table in the student magazine *Chemistry* was introduced in 1964 to emphasize the complex yet beautiful periodicity in the properties of the chemical elements. It was modified as new elements were discovered or predicted. The laboratory equipment company, Instruments for Research and Industry, added color when it used the spiral in its calendar. The table began appearing in textbooks and was included in a history of chemistry. Franklin Hyde, creator of silicones, modified it to emphasize the central significance of carbon and silicon. It found its way to a Max Planck Institute in Germany under the swings of a Foucault pendulum.

In 1963 the American Chemical Society, having acquired from Science Service a magazine *Chemistry,* of the size of the old *Readers Digest,* asked me to serve as editor. The reason for the acquisition was mainly to prevent any one else from owning a magazine with that name. What to do with it was left to be decided. On October 4, 1957, the Soviet Union had launched Sputnik, spurring the United States vastly to improve its science education. By 1963 two national curricular programs for high school chemistry had been underwritten by the US National Science Foundation, first The Chemical Bond Approach Project (CBA), and soon thereafter, since CBA seemed to some too radical, The Chemical Education Materials Study (CHEMS). It was then felt that high school chemistry students and teachers, once raised to a new level of interest and competence, deserved an extra-curricular tool purely for their enjoyment and continuing stimulation. For this purpose the ACS's *Chemistry* was to be dedicated and I was asked to design and edit it. The magazine was to be pitched to the top 40% of high school chemistry students and their teachers, but I insisted that its aim be broader, speaking to the abler beginning college chemistry student as well. I also requested that I spend the first year of my editorship in Washington at ACS headquarters. This was generously granted, and it allowed me to work closely with Richard L. Kenyon, director of publications, and with Joseph Jacobs, art director, who took personal responsibility for the overall layout and for the individual artwork for each issue of the new monthly magazine in its enlarged format.

Periodicity

The periodic law and table are at the heart of all of chemistry—comparable to the theory of evolution in biology (which succeeded the concept of the Great Chain of Being) and the laws of thermodynamics in classical physics. However, the standard periodic table as displayed in classrooms and used in textbooks always seemed to me thoroughly unsatisfactory. With its mammoth gaps in the first and second periods and the unattached collections of lanthanides and actinides floating below the table, the last impression a student would gain would be a sense of element periodicity. It was therefore with great excitement that I came across an oval periodic table resembling a football field (1), which showed no gaping holes or floating strings of elements. All elements had their place in a continuous spiral from hydrogen inside to the outer loop. The only annoyance I felt was that the lanthanides were all squeezed in a space elsewhere reserved for just three elements. The *Life* table appeared as a two-page spread (pp 82-83) in an unsigned section of its issue entitled “The Atom: A Layman’s Primer on what the World is made of.” It is a carefully multi-colored rendition of a black and white diagram published by John D. Clark (2). (Fig. 1) *Life* states that it received assistance for the article from William F. Meggers, Glenn T. Seaborg, and Clark. Since the lanthanide compression occurred in the outer loop, I decided it should not be difficult to give these elements a decent space simply by creating a protrusion – the resulting shape not surprisingly being nicknamed that of a snail. My unhappiness with the conventional table was probably not superficial. I had always been interested in geometry as well as in the arithmetic patterns often discovered in nature. The ancient Pythagoreans already had been fascinated by numbers which they felt were at the basis of all physical reality, and Johannes Kepler was clearly guided to his laws by his belief that God thought as a mathematician. In the 1960s I was teaching at Earlham College in Indiana and for some years Reino Hakala was a chemistry colleague. He developed one of the early diagrams showing the amazingly orderly progression in the filling of the *s, p, d, f* electronic subshells. Eric Scerri includes a similar diagram in an article on Mendeleev’s legacy (3).

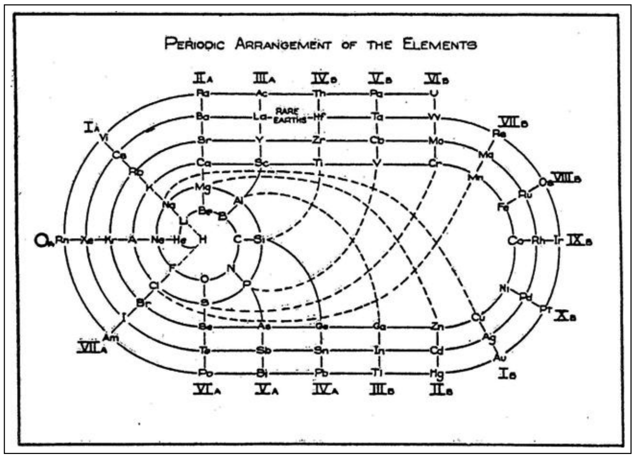

***Figure 1**. The Clark oval, the basis for the Life magazine periodic table. Used with permission of the Journal of Chemical Education. Copyright © Division of Chemical Education, Inc.*

I outlined the significance of Pythagorean thinking in the ordering of elements, at the Boston AAAS meeting as part of the Mendeleev commemorative symposium Decermber 29, 1969, but it was only published more than twenty years later (4).

I took my sketch of the modified *Life* oval to the ACS design department, and Joe Jacobs proceeded to convert it into a publishable image which after discussions and modifications appeared in *Chemistry* in 1964. (Fig. 2) It was first used to highlight the position of plutonium in the periodic table within a Seaborg article (5) on that element. My concern at the time was purely pedagogic. I needed a design that showed periodic patterns more clearly than in the tables students were used to. Jacobs, a professional artist still today, contributed the aesthetic appeal.

From the time of the spiral’s first appearance, whenever we carried an article dealing with an element or a group of related elements, we published a section of the spiral, often a pie slice, in the margin where we often added comments that looked as if scribbled in pencil.

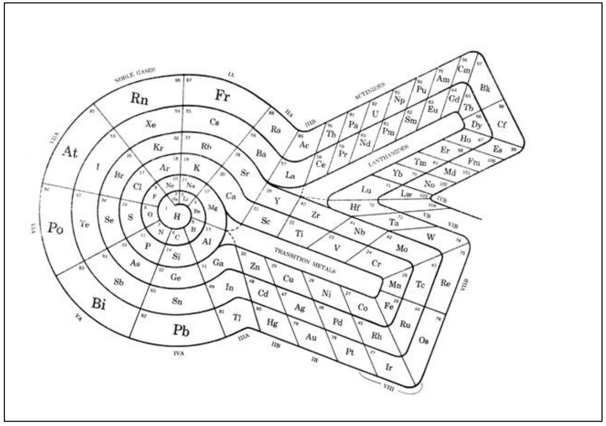

***Figure 2**. First image of the periodic snail in Chemistry.*

In correspondence with Philip Stewart I learned that I was not alone in starting on my quest when I saw the *Life* oval. For the Festival of Britain in 1951, the artist Edgar Longman based his large mural on it, and this in turn inspired Stewart’s ‘Chemical Galaxy’ (6). All three spirals are shown by Scerri (3). Scerri also included Stewart’s and my spiral in an article on newer developments in depicting the elements (7).

Glenn Seaborg

Chemistry reprinted or commented on several speeches Seaborg had given while heading the U.S. Atomic Energy Commission, as well as articles he published, and we were particularly interested in his speculations as to the expansion of the periodic table to accommodate new transuranic elements as they were being discovered. An unsigned Research Reporter piece (8) summarized and commented on an article by Seaborg (9)**,** in which he suggested where the transuranics would appear in future tables. He placed elements 93 to 103 (neptunium to lawrencium) to complete the actinide series, elements 104 to 121 as new members of existing groups, and then placed elements 122 to 126 as the beginnings of a third group of 14 elements analogous to the lanthanides and actinides. We accordingly expanded our spiral table with the extra elements clinging to our previous design with no new protrusion. This prompted one of *Chemistry*'s readers, a high school student Herbert Weiner, to object. In a letter to the editor (10) he pointed out that the rules for introducing new subshells (*s, p, d, f, g*, etc.) demand that a new subshell be introduced after two cycles containing a previous subshell. Thus after two periods of eight elements (containing *s* and *p* subshells) there are two periods of 18 (*s, p*, and *d*) followed by two of 32 (*s, p, d, f*). The next period should contain 2 + 6 + 10 + 14 + 18, or 50 elements and involve a new *g* subshell of 18 elements. If we follow earlier patterns, the 18 *5g* elements should precede a new lanthanide/actinide series and should begin with element 121, contrary to Seaborg's earlier placement of this element. To follow this suggestion we modified our spiral table further, introducing a second protrusion, thereby producing a black and white version of the spiral as currently known and widely reproduced. (Fig. 3) We published this with the Weiner letter, but we first sent the letter to Seaborg, whose answer appeared on the same page. Seaborg defended his earlier placement. He recognized the likely appearance of the *5g* series but felt doubtful that the g series would be completely filled before the *6f* series began. However, in 1969 Seaborg published in the Russian journal *Chemistry and Life* an article entitled "From Mendeleev to Mendelevium and Beyond," in commemoration of the hundredth anniversary of Mendeleev's formulation of the periodic table. The article was later reprinted in *Pravda* and in *Chemistry*, and in it he proposed the name "superactinide" for the 32-element combined series of 18 *5g* and 14 *6f* elements (11)**.**

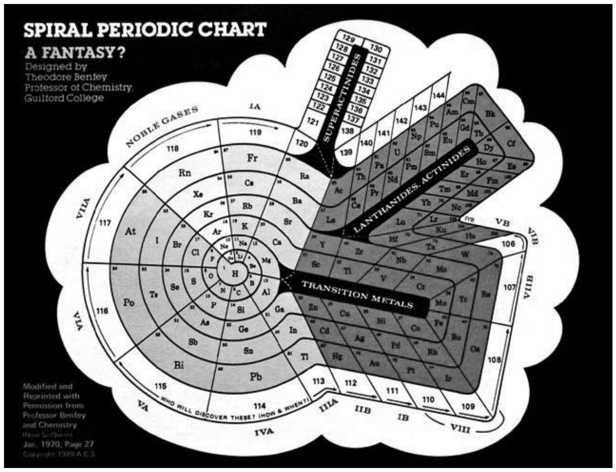

Figure 3. *Final shape of snail in a colored version as it appeared in an I^2R calendar*

After we had developed our own spiral design, we found that E. G. Mazurs had published a spiral with a separate protrusion for the lanthanides (12) which, under the image, he misleadingly ascribed to Charles Janet in 1928, the same year that Janet had published a simple circular form also shown by Mazurs. The Mazurs diagram with the lanthanide protrusion was reprinted in *Chemistry* (13). However, Stewart informed me that the Mazurs figure bears no resemblance to the Janet diagram he indicated nor to any other of his designs (14). Detailed references given a few pages later by Mazurs suggested correctly that the spiral derives from Stedman (15) and is so identified and depicted by van Spronsen (16). The Mazurs diagram is a mirror image of the Stedman spiral, updated to include elements discovered since 1947.

Enter the Calendar

Instruments for Research and Industry (I^2R), a company specializing in safety equipment for the chemical sciences laboratory, was founded in 1957 by Daniel Conlon. He had become dissatisfied with the scant recognition he received for innovations he had introduced while working at Rohm and Haas. Early in the new company's history, a suggestion was made for publicizing the company through a calendar. This bore fruit when the theme was identified as humorous scenes in the laboratory, a cartoonist was located, and the decision was made that each cartoon would show use of one or more of the company's products. However, one of Conlon's friends sought to publicize a new periodic table through the calendar. It was used as the September illustration because September was the school year's beginning. The search was on for periodic tables for future Septembers. Conlon was a Quaker interested in Quaker education and not infrequently donated minutely defective and hence not sellable versions of his company's offerings to Earlham and other Quaker college chemistry departments. In my teaching at Earlham I thus became acquainted with such I^2R products as curved shields, glove bags, and lead doughnuts for steadying Erlenmeyer flasks. At the same time Conlon must have become acquainted with *Chemistry*, and hence with the spiral table, the periodic snail. As a result the table, expertly colored by his company's artists, appeared in the 1966 I^2R calendar, and it reappeared in various forms in subsequent years, once together with one of Janet's circular versions, more than once in its expanded form with the extra "feeler" accommodating the superactinides (Fig. 3). Single copies of the September periodic tables were offered free of charge on request and could also be purchased in class-size quantities. Also the spiral table was offered as a 22" x 24" wall chart, silk screened on PVC. In addition to the 30,000 or so recipients of *Chemistry* magazine, a large new community of chemists and others on the company's mailing list were now exposed to the spiral snail.

The snail of course was not the only periodic table appearing on the calendar's September pages. Many alternative, often humorous versions such as the Boron Chemist's Concept which unduly blew up the space for boron, Industry's view which made Fe enormous with further attention to other industrially important elements, the organic chemist's chart with C at the center and with only elements prominent in the biosphere attached, and charts that could be cut and pasted to make cubic blocks ("of particular interest to cement chemists"), pyramids, and fancier helices. Some of us became unofficial scouts and consultants, seeking new tables, advising as to their suitability, and suggesting modifications (17). I^2R was acquired by the Glas-Col company in 2005.

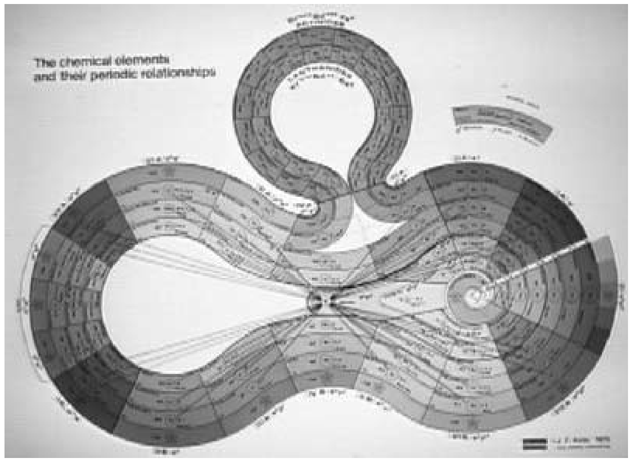

Figure 4*. Franklin Hyde's periodic table highlighting the pivotal importance of carbon and silicon.*
Copyright Dow Corning

The Hyde Spiral, Silicones, and Dow Corning

J. Franklin Hyde is widely considered the father of silicones. At Corning Glass Works he had created fumed silica used in fiber-optic cables, spaceship windows, and for sophisticated telescope lenses such as in the Hubble. Threatened by the mushrooming plastics industry, Corning asked Hyde whether there was a way to compete through the combination of properties of silicon with the diverse possibilities available among organic chemicals. Silicones resulted as well as the creation of Dow Corning as a joint venture of Dow Chemical and Corning Glass. Silly Putty was a minor by-product. Hyde's immersion in silicone chemistry made him realize the remarkable properties of carbon and silicon because of their centrally located position in the fourth group of the periodic table, between electropositive and electronegative elements. Whereas carbon is the essential element of the biosphere, silicon is central to the lithosphere. Having seen the spiral snail, no doubt through the I^2R calendar, he proceeded to modify it by creating a horizontal axis originating with hydrogen and going through carbon and silicon. It was printed by Dow Corning and was published in *Chemistry* (18). (Fig. 4). Aesthetically, it is a signal improvement over the lowly snail.

Subsequent History

The questioning of the final authority of the rectangular periodic table has slowly made its way into high school chemistry textbooks. Davis, Metcalfe, Williams, and Casca, authors of *Modern Chemistry* (successor to the classic Dull, Metcalfe, and Williams texts) chose the periodic snail as the opening image for its Chapter 5, "The Periodic Law" (19). It reached a spectacular display at the college level by appearing on the front and back hard covers of *Descriptive Inorganic Chemistry* by Rayner-Canham (20). It was ushered into chemical history by being the only periodic table shown among the 23 photographs between pages 360 and 361 in The Fontana/Norton History of Chemistry by Brock (21). Brock chose it because it clearly shows the location of the superactinides.

Finale: The Snail under a Foucault Pendulum

In 2003, an email brought news that the spiral had been installed in place of a simple circle or compass rose under a German Foucault Pendulum. Wolfgang Hönle, of the Max Planck Institute for Chemical Physics of Solids in Dresden, wrote that his institute had received a Foucault pendulum as a gift from another MPI and looked for a chemical form to place under the seemingly circling bob. He found the spiral snail easily enough at the website of Chris Heilman, Phoenix College, Arizona [*chemlab.pc.maricopa.edu*] by searching the internet under "periodic table." However, other than my name no indication as to source was given. Via the literature, the Deutsches Museum, and the Chemical Heritage Foundation, he tracked down the source. The pendulum is 11.50 m (37.7 feet) long in the entrance hall of the MPI. I trust the periodic snail is content, resting on a revolving piece of earth under the periodic swings of a pendulum. (Fig. 5).

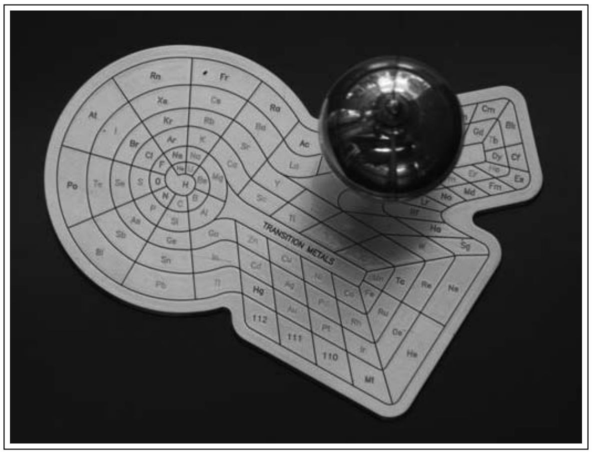

***Figure 5**. The periodic snail under the Dresden Foucault pendulum. Courtesy Max Planck Institute for Chemical Physics of Solids, Dresden, Germany*

ACKNOWLEDGMENTS

My thanks go to Philip Stewart for helpful correspondence, and to Cyril Harvey for preparing the image of the colored and black-and-white spiral.

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BOOK REVIEWS

Chemistry at Oxford: A History from 1600 to 2005. R. J. P. Williams, J. S. Rowlinson, and A. Chapman, RSC Publishing, Cambridge, 2009, x + 291 pp, ISBN 978-0-85404-139-8, £54.95.

How does one review an encyclopedic volume covering 400 years of Oxford chemistry that after sporadic starts blossomed and flourished? How can I evaluate the story of a chemistry department that I have never seen, in a city in which I stayed only a few days to attend a Quaker Conference, and that over fifty years ago? I did live in an Oxford college and sensed some of its charms; and the TV series *Brideshead Revisited* gives something of its flavor.

The founder of history of science in America, George Sarton, recommended that reviewers read their book pretty fast, draft an outline review, and then modify it as they delve into the details. Well, this book could not be perused rapidly, or should I say, even a rapid perusal took me a long time. The only justification for agreeing to be the reviewer is that I spent ten years in England and received bachelor and doctoral degrees there before moving to the States. My alma mater was University College, London, where I completed both degrees in a total of four years, thanks to the pressures imposed by war conditions. There were no tutorials—the characteristic mark of an Oxford education. And unlike Oxford, we did have examinations before the final one that counted; in fact we had one at the beginning of each term, designed to spoil our vacations. Perhaps ours was a war-time aberration.

Of the book's three editors, the significant research of two of them, Williams and Rowlinson, is described in the book and there is a hint of the latter's contributions as a science historian. His skills in that field are made abundantly clear in his 2008 Edelstein lecture published earlier this year in this *Bulletin*. The third editor, Chapman, is the author of "England's Leonardo: Robert Hooke and the Seventeenth-Century Scientific Revolution." He does not appear in the Index of Names. Yet I may have missed mention of him. Charles Coulson also is not indexed, yet he appears in the book as a significant chemist *and* as a significant human being on pages 221, 244, and 258.

The book is divided into seven chapters, beginning with an outline by Williams. Then Chapman covers Oxford chemistry to 1700, including a welcome appreciation of recent research on the significance of alchemy; this is followed by Peter J. T. Morris on "The Eighteenth Century: Chemistry allied to Anatomy." Next comes Rowlinson's "Chemistry Comes of Age: The 19th Century;" and he also is the author of a brief but important chapter on chemists at war. Before the latter, Jack Morrrell covers 1912-1939, and Williams concludes the book with "Recent Times: 1945-2005: A School of World Renown." In spite of this chapter's title, a concluding section describes "Oxford Chemistry Today, 2008." There are appendices on laboratories and on finances, and "Notes on Oxford University." Morris's coverage of the 18th century startled me. He and I had co-edited the volume of Robert Woodward's papers, where his contribution was the explication of detailed ultramodern synthetic pathways. Fortunately for this book's editors, Morris's 1978 Part II thesis (see below) was on "Education of Chemists in the Eighteenth Century."

Covering a subject chronologically has its drawbacks, because many strands overlap the chapter boundaries. This becomes particularly aggravating in the last chapter of 80 pages, which is further subdivided into the periods 1945-1965, 1965-1980, and 1980-2005. Since a number of chemists remained loyal to Oxford for many years, there are constant cross references to prior and later sections. Three of the most significant chemistry professors with long Oxford tenure were Cyril Hinshelwood, Robert Robinson, and Nevil Sidgwick.

Robinson I had encountered twice in my career, first when I was a student of Christopher Ingold, and much later in connection with Woodward. In both cases the impression relayed to me of Robinson was negative. He had proposed an alternative description of electron movements in organic reactions, but Ingold's terminology won out. Oxford called Ingold's scheme the Ingoldsby legend. In Ingold circles it was rumored that, as a Nobel laureate, Robinson had blackballed Ingold, who never got a Nobel. And Robinson's proposed structures for penicillin and strychnine were proved wrong by Woodward. The present work gave me a much more balanced view. Robinson's natural-product researches clearly justified his Nobel, yet the authors also point out his limitations. He stayed with classical structure determination in spite of the huge new power that instruments might have given him.

What delighted me about Robinson as revealed in this book was the humanity of the man. He helped Fritz Arndt and Arnold Weissberger get out of Germany and sought new positions for them. He tried to find ways to aid several others, including Richard Wilstätter. To my great surprise, he successfully found funds to make possible Dorothy Crowfoot-Hodgkin's X-ray crystallographic work, in spite of his own lack of interest in instrumental methods

Robinson had been recruited from Manchester, and he was not alone. His predecessor William H. Perkin jr., and his successor E. R. H. Jones also came from that city, and they brought a most un-Oxonian mood with them. They consulted for industry and received funds from industry and saw no gulf between pure and applied science. They were looked down on as "tradesmen" (p 7-8) by the traditional Oxford academics, including some in chemistry. Perkin, who was president of the Chemical Society 1913-15, appealed to his colleagues in his second presidential address—during the war—not only to devote themselves to applied research, but to "cooperate with industry, however distasteful these practices might be to some Oxonian academics." (p 137)

The recurring theme of the book or, perhaps more aptly, the background noise of the book, is the extraordinarily chaotic arrangement in which chemists had to operate. In places it is called the tension between the bottom-up forces—control by the colleges—and the top-down force exerted by the University. The professors were appointed by the university; but their freedom to operate and exert their will was largely circumscribed by the independence of college appointees. There were Fellows appointed by colleges, and Demonstrators appointed by professors. Fellows were given research space within the organic, inorganic, or physical chemistry laboratories; and the university-appointed professors, even though they were heads of these laboratories, had no jurisdiction over them. Professors attempted, with more or less success, to convince colleges to appoint Fellows of the professors' liking. Nobel laureate Frederick Soddy was treated abominably and slowly moved into writing on social and economic problems and the social responsibility of scientists. He had been appalled by the horrors of World War I, forever symbolized for chemists by the senseless death of Henry Moseley. Rutherford famously called it "a striking example of the misuse of scientific talent." Moseley's image appears on page 119, the only photograph of a scientist in the book. Nevil Sidgwick had to wait endlessly for a laboratory specifically assigned to inorganic chemistry. Slowly the increasing cost of doing quality chemical research shifted control and influence towards the university.

The fact that, in spite of this confusing set-up, Oxford became a world class center for chemical research might find an explanation in Renaissance Italy. It has been argued that it was precisely the fragmentation of Italy into independent fiefdoms that led each to aim for supremacy, whereas Chinese science, having achieved so much in an autocratic, bureaucratic system was resting on its laurels. But it turns out that there are several ways to achieve excellence in science, and the book mentions the Cambridge MRC, Harvard, and the University of London.

One major innovation needs to be mentioned. In 1916 Perkin moved into the new organic chemistry laboratory, the Dyson Perrins. That same year he convinced the authorities to include a year of research in the undergraduate chemistry curriculum. It became known as Part II, and Perkin hoped he would thereby gather a cohort of Perkin-type researchers to follow in his footsteps, as he had done in Manchester. But it did not work out that way. The undergraduates came from the colleges and were controlled by the chemistry Fellows who were not Perkin appointees, so they tended to do their Part II research in the inorganic and physical laboratories.

What makes the book refreshing, and lifts it out of an endless descriptive mode of 400 years of changes, is the authors' willingness to make judgments: for instance, harsh criticism of the way Soddy was treated after being lured to Oxford and criticisms of Robinson for not using the newer instrumental techniques. They have also exercised humor. When Oxford tried unsuccessfully to change Prime Minister Margaret Thatcher's cuts in funds for universities—Thatcher, after all, was an Oxford chemistry graduate—the author comments "The lady's not for turning," by analogy with the Christopher Fry play "The Lady's not for Burning." It seems that Thatcher first used the phrase herself, not knowing where it came from. A speech writer had put it there. Thatcher never received an Oxford honorary doctorate.

Some time earlier, when funds were needed for a chemistry laboratory, the obvious source was the profits from Bible sales, although there was some objection that the sciences were an "ungodly subject to benefit from the sale of God's word."(p 94). The resulting laboratory, the "Abbot's Kitchen," attached to the new Museum in 1860, appears on the front cover. It is a square building with a rather squat octagonal spire in the center and four slender spires at the corners, which in fact were exhaust chimneys for noxious gases.

A word about the hurdles in the way of getting into Oxford. It took the usual time for women to enter those august halls. Knowledge of Greek was required for entrance until 1918, Latin until 1946. I took Latin all through high school just in case I ended up in Oxford or Cambridge. I have never regretted that exposure to the Latin tongue. Dissenters, Quakers, and others were long barred from Oxford and Cambridge because they would not assent to the Church of England's 39 articles. However, in 1831, in a burst of remarkable magnanimity, Oxford conferred honorary doctorates on four dissenters, John Dalton and Michael Faraday among them (p 88).

A final footnote: in its later years, Oxford chemistry kept clear of geology, biology, and medicine, even though chemistry had emerged from those fields. Biochemistry, whose emergence could not be avoided, ended up as a separate discipline outside the parameters of this book.

To produce this book was an ambitious undertaking and to do it in such perceptive detail was remarkable indeed. My guess is that no one will attempt to improve on it. Specialized studies on parts of the story no doubt will appear; one in fact was published last year: *The Dyson Perrins Laboratory and Oxford Organic Chemistry 1916-2004* by R. Curtis, C. Leith, J. Nall, and J. Jones (reviewed in this issue). *Theodor Benfey, Guilford College and The Chemical Heritage Foundation.*

The Dyson Perrins Laboratory and Oxford Organic Chemistry 1916 – 2004. Rachel Curtis, Catherine Leith, Joshua Nall, and John Jones. John Jones, Balliol College, Oxford, 2008, john.jones@balliol.ox.ac.uk, 134 pp, ISBN-978-0-9512569-4-7, £16.

England is a country where sentiment and tradition mean so very much. Organic chemistry is a discipline which builds upon and treasures its past. For both England and organic chemistry, the recent disappearance of the Dyson Perrins Laboratory, the home of organic chemistry at Oxford for 87 years, is a great loss. This was the place of Waynflete professors William Henry Perkin jr., Sir Robert Robinson, Sir Ewart Jones, and finally Sir Jack Baldwin, along with thousands of scholars and their achievements. The student roster included such eventual luminaries as Lord Todd, Sir John and Lady Cornforth, Arthur Birch, Michael Dewar, and Jeremy Knowles, among many, many others.

Today, the DP, as it was and is affectionately known, is a Historic Chemical Landmark by the Royal Society of Chemistry. A plaque on the old front door serves as witness of the DP's history and this worthy Landmark designation. The building is now mostly used by Oxford University's Geography Department, hardly aware of the research accomplishments attained therein over its nearly 90-year history and the scientific careers molded therein, including my own (my sabbatical during the 1983—1984 academic year).

Not only has the DP disappeared from Oxford University but so have its other *completely* independent chemistry laboratories. I am told by the book's senior author that the Inorganic Chemistry Laboratory (ICL) and the Physical Chemistry Laboratory (PCL, now called the PCTL) "are very much there and still semi-independent. The only real change is that there is an overall Chairman Professor."

Step across South Parks Road, and you will find Oxford's 17,000-sq. meter state-of-the-art Chemical Research Laboratory, which Her Majesty The Queen opened on February 20, 2004. The newly combined Department of Chemistry is under the active stewardship of Stephen G. Davies, current Waynflete Professor of Chemistry. A virtual tour of this facility can be found at http://www.chem.ox.ac.uk/oxfordtour/crl/# . Several of these videos, when the perspective is turned 180° away from the new facility, focus lengthwise on the old DP without even any notice of that fact: see, for example, http://www.chem.ox.ac.uk/oxfordtour/crl/movies/05.html.

Thanks to John H. Jones and three of his post-DP Part II students, an abbreviated yet memorable story of the DP has been documented in this glorious book. Just as great scientific discoveries are often made in several laboratories at the same time, books on the same or similar subjects also frequently appear somewhat simultaneously. [See the accompanying review by Theodor Benfey.] Jones, a Fellow of the Royal Historical Society, is himself no stranger to the DP. He received his degrees in chemistry (B.A., M.A. and D. Phil.) from Oxford University which was followed by 40 years as an official Fellow of Balliol, jointly with a University of Oxford lectureship..

Nine chapters are graced with numerous photographs, ten appendices, and many pages of thoughtful and fact-filled references. The chapters are organized chronologically by era, appropriately focused on the Professor of Organic Chemistry of that particular era. The first chapter, "Oxford Organic Chemistry before the Great War," sets the context for the entire book. The following chapters are: "The Foundation and Construction of the DP," two chapters dealing with Perkin and his era (1912 – 1929), three chapters to the decades of Robinson (1930 – 1954), one chapter to the Jones years (1955-1978), and one to the Baldwin Years (1978-2004). According to the senior author's preface:

> We have not set out to catalogue the people of the DP . . . an exhaustive survey would be a very turgid book indeed . . . There is not enough History in it, and too much Chemistry, for this book to conform to the conventional pattern of writing about the History of Science . . . because between disciplines was where I aimed. And it was an engaging exercise with which to conclude my career, the experimentally active part of which was spent entirely in the DP.

The authors fully meet their goals and provide the reader with a tremendously interesting and enjoyable experience as well. Jones further states that the book "contains no Philosophy at all." Here he is, most fortunately, entirely wrong. Apparently without intent or perhaps British understatement, the book is absolutely swarming with anecdotes, reflections, and judgments that individually are captivating and, in total, provide a deeply thoughtful reflection on the progress of organic chemistry, the nature of academic research at its best, and the peculiarities of human conduct that especially reside in the discipline's greatest thinkers and practitioners.

Benjamin Brodie the Younger was in the mid- to late 1800s, Oxford's first organic chemist. A member of Balliol College, Brodie's:

> ..laboratory is now part of the Balliol student bar. [He] was engrossed in the development of a highly original but abstruse 'chemical calculus' which sought to describe Chemistry using mathematical symbolism and operations, without atoms. . . . Interest in his calculus had faded away by the time he died, since when it has been in oblivion except as a challenge for philosophers of science.

In 1888 and in 1913, J. E. Marsh, another Balliol man,

> seems to have been the first to appreciate that the criterion for optical activity was simply that a whole structure should not be superimposable on its mirror image.

The eventual construction of what became Oxford's organic chemistry domain was accompanied by tension between Oxford's powers – its more than 20 autonomous colleges, the Dons, the autonomous Heads of Departments, and eventually the University administration, as is vividly described .

> It was and is a constantly evolving maelstrom of administrative complexity, which nobody of sound mind would ever have planned.

The DP's benefactor was Charles William Dyson Perrins, "grandson of William Henry Perrins, a pharmacist who had made the family's fortune by developing, in partnership with John Wheeley Lea, the recipe for the well-known piquant [Lee & Perrins] Worcestershire sauce."

Arriving just before World War I broke out, Perkin—along with N.V. Sidgwick—played a major role in organizing and advising research related to WWI needs, including a novel process for the preparation of acetone, work related to TNT and related explosives, and the preparation of both phenol, a precursor of picric acid, and in the preparation of phenol itself. In addition to superb science contributions to the war effort and in peacetime, Perkin's DP provided the first organic chemistry patent at Oxford, the first engagements with industry, the introduction of the Oxford D.Phil. in 1917, and a novel undergraduate degree regulation: the Chemistry Part II which required a fourth year devoted entirely to full-time research concluding with a dissertation and oral examination.

Perhaps Perkin's greatest legacy—surely, his greatest student and collaborator—was Sir Robert Robinson, who followed Perkin with the Professorship, first at Manchester and then the Waynflete at Oxford, to which he was elected "in almost indecent haste." Robinson dominated the DP (1930–1954) and British organic chemistry if not all of organic chemistry for over 25 years. His contributions in natural products including alkaloids, plant pigments, and steroids, were recognized with the Nobel Prize in 1947. "Many found him a difficult man to deal with. All held him in awe, and some in affection."

One highlight of Oxford chemistry during WWII was the invention of the Birch reduction, not named the Robinson reduction because the Professor chose to have nothing to do with the research—other than order Birch not to do it, a command that Birch failed to follow.

Oxford was one site of intense investigation of penicillin:

> The investigation of penicillin . . . was initiated in the Sir William Dunn School of Pathology in Oxford by Howard Florey in 1938 . . . Collaboration with Robinson, Wilson Baker, and then J.W. Cornforth in the nearby DP began in late 1942.

In fact, the β-lactam structure of penicillin was not unambiguously determined until after the end of the war—and even then, not accepted by Robinson, who held to his alternative thiazolidine-oxazolone structure The E. R. H. Jones era was initiated by strong support from Robinson though Jones did not respond in kind. Regarding the support, Robinson was in favor of his replacement who, like himself, had been the professor of organic chemistry in Manchester. The other likely candidate was the future Nobelist Derek H. R.Barton. Jones exhibited his own independence by denying the retired but not retiring Robinson to occupy a wing of DP.

The authors discuss perhaps Jones's most important accomplishment, the improvement and expansion of the DP's facilities and improvement in its condition. The interplay between the various stakeholders—the DP and its chief, the Waynflete Professor Jones; the University and its money; and the colleges and their autonomy—is described. To understand Oxford chemistry is to understand the changing dynamics of these interactions, affected substantially by the powerful personalities of the protagonists – and especially the personality and behavior of The Waynflete Professor.

Only three pages of text are dedicated to the 26-year period of the Baldwin era. Given that the rate of chemical research has increased dramatically with time (and the development of modern instrumentation and computer technology), the Baldwin era's absolute if not relative contributions to science exceeded any previous 26-year period in the DP's history. The authors, however, make it clear (in a note in the reference section to the last chapter) that

> This Chapter does not attempt to be much more than an epilogue to those it follows. Balanced history cannot be written without an interval for things to settle into place, and while the fact that most of the protagonists simplifies the fact-gathering, it inhibits the making of judgments. And no relevant files have aged enough to be open . . .

The Baldwin era and the Dyson Perrins Laboratory closed somewhat simultaneously in 2003 with the opening of The Chemical Research Laboratory, known as the CRL. To me, this just does not have the ring or appeal as the "DP." Perhaps in 70 years, or even sooner, it will.

This book has many virtues. It is an easy read, yet it covers the development and progress of organic chemistry for 150 years through the lens of Oxford, the Waynflete professors, and the DP. The numerous people and personalities are presented, almost in real life, by wonderful descriptions and aptly chosen photographs and illustrations, all lovingly presented by its authors.

The book has several minor and one major weakness. The List of Illustrations that appears just after the Table of Contents contains full captions of the illustrations, which do not appear in the main body of the text. And there is no index. As the senior author says, "It is hoped that the extended Contents goes some way towards offsetting the lack of an Index; an electronically searchable version will in due course be made available." The book's major weakness is, indeed, related to its major strength. It is a story of Oxford and the DP. The chemistry is not placed into its appropriate worldwide context. But then, the authors specifically state that:

> our purpose [w]as simply to tell the story and highlight what seemed to me the most interesting and important Organic Chemistry worked out in Oxford . . .

For example, R. B. Woodward does not appear in the sections dealing with the structure determinations of either penicillin or strychnine. Woodward and Robinson held opposite views in the penicillin-structure debate, the younger being right, the established leader holding sway and resilient way beyond reasonableness. But then, Robinson was at the height of his powers, being just a few years from receipt of his Nobel, and Woodward was not even 30 (and two decades from his Nobel).

The book ends with a quote from the Oxonian Jeremy Knowles:

> Those of us who were brought up with the D.P.'s unique combination of smells, its extravagantly high ceilings, the staircase that millions of undergraduate feet could never wear away, the horrors of Room 33, and the open drains that made minor explosions in the teaching labs so much more interesting, will be nostalgic but not truly sorry. The Dyson Perrins has served Oxford well, but a bright new era begins. (J. Knowles, "The Dyson Perrins Laboratory at Oxford," *Org. Biomol. Chem.*, **2003**, *1*, 3625-3627.)

Well, there is another major weakness in this book. It is simply too short for my own appetite. And the same goes for the lifespan of the Dyson Perrins Laboratory. *Jeffrey I. Seeman, University of Richmond, Richmond, VA 23173.*

The Invention of Air: A Story of Science, Faith, Revolution, and the Birth of America. Steven Johnson, Riverhead Books, New York, 2008, xvi + 239 pp, ISBN 978-1-59448-852-8, $25.95.

First, what this book is not. It is not a standard biography of a great man. Steven Johnson is not interested in the usual "Life and Times of…" Nor is it a sophisticated analysis of the scientific discovery of oxygen. Johnson is interested in bigger game: understanding the interconnectedness of knowledge. He uses Joseph Priestley as the lever to explore this theme. As the subtitle suggests, Johnson strives to tell "A Story of Science, Faith, Revolution, and the Birth of America." (Curiously, or perhaps revealingly, Priestley's name does not appear in the book's title or subtitle).

Joseph Priestley was a man of many parts: famed scientist credited with discovering oxygen; controversial theologian who helped found the Unitarian Church; notorious – in some quarters – radical political theorist and supporter of the American and French Revolutions; and political activist who played an underappreciated role in early American politics (Priestley the émigré to the young Republic set a precedent of the scientist-exile repeated frequently in American history). A brilliant polymath, Priestley wrote over 500 books and pamphlets and spoke six languages fluently. He knew all the learned men of the age on both sides of the Atlantic: Boswell, Price, Wedgwood, Bolton, Erasmus Darwin (Charles's grandfather), and others in England; Franklin, Adams, Jefferson, and their cohorts of the Revolutionary generation in America.

Dissecting Priestley the natural philosopher allows Johnson to develop his "overarching moral:" that knowledge should not be compartmentalized nor left to the specialists. A subsidiary theme is that politics must be informed by the insights of science, a point often neglected in our recent history.

Johnson employs what he calls the "long zoom" connecting disciplines and knowledge to argue that Priestley's greatest scientific work was not the oxygen experiment of 1774 on "dephlogisticated air," but earlier experiments in which Priestley – with his good friend Franklin – observed that a flame in a glass cylinder in which a plant was placed continued to burn. The conclusion: plants release oxygen into the air. This process we call photosynthesis, a process in which plants also take in carbon dioxide. From this insight on oxygen and carbon dioxide Johnson is off and running on an "Intermezzo" set in the Carboniferous era 300 million years ago, in which vegetation grew to enormous sizes – club mosses reaching 130 feet in height, conifers sprouting three-foot long leaves – leading to an increase in the proportion of oxygen in the air which didn't last long; but all that vegetation eventually decayed, becoming the energy that fueled the Industrial Revolution (pioneered by some of Priestley's confidants) taking place in the country which sat on top of huge coal fields – "An Island of Coal" Johnson calls it – where Priestley did his initial experiments on oxygen. It *is* all connected, after all.

Johnson is fond of this kind of intellectual flight. Take, for instance, the role of coffee in Priestley's life and work. When the young Priestley first came to London he joined a coterie of natural philosophers who regularly met at the London Coffee House in the shadow of St. Paul's Cathedral (Johnson notes the irony of a group of heretics meeting a stone's throw from the shrine of England's establishment). The coffeehouse – which played a crucial role in 17th- and 18th-century England – provided Priestley with an interdisciplinary culture in which conversations touched on the latest scientific discoveries, the abuses of Parliament, and the fate of nonconformist religion.

This was a remarkably open information network whose members eagerly shared knowledge. (Johnson greatly admires Priestley for his "compulsive" sharing, both from discipline to discipline and among colleagues.) But coffee, Johnson also notes, is a stimulant that affects another kind of network, this one "neurochemical." Coffee became a popular European drink in the mid-16th century, replacing beer and wine as the breakfast beverage. The switch from alcohol to coffee as the daytime drug of choice meant that Europe "emerged from its centuries-long bender" and entered the Age of the Enlightenment.

Caffeine fueled Priestley's extraordinarily productive eight-year period in the 1760s and 1770s. These were the years of his groundbreaking forays in chemistry, including the oxygen experiments and his discovery of soda water; his synthesizing of existing knowledge on electricity; and the writing of numerous books and pamphlets on religion, politics, and education. Such productivity suggests to Johnson a "streak of innovation" similar to Joe DiMaggio's 56-game game hitting streak in 1941.

That was the young Priestley. The elder Priestley lived the last decade of his life in rural Pennsylvania, alone with his books and his experiments. This most convivial of men, this sharer of information and knowledge finally had angered too many in England with his unorthodox religious views and his support of the French Revolution. A Birmingham mob burned his house in 1791, forcing Priestley to seek a haven in a more open-minded country.

He craved a quiet life by then, but his political views soon got him into trouble in his adopted land. It took President Adams's personal intervention to prevent the government from prosecuting Priestley under the Alien and Sedition Laws. Fortunately, all ended well for Priestley, as Johnson notes. His good friend Thomas Jefferson was elected president in 1800, leading Priestley to note that only in old age was he privileged "to find myself in any degree of favour with the governor of the country in which I have lived." Jefferson's administration was "the best on the face of the earth." Jefferson returned the compliment, telling Priestley that "Yours is one of the few lives precious to mankind." *Judah Ginsberg, American Chemical Society, Washington, DC.*

The Language of Mineralogy—John Walker, Chemistry and the Edinburgh Medical School, 1750-1800. M. D. Eddy, Ashgate, Burlington, VT, 2008, xxii + 293 pp, ISBN 0754663329. $114.95.

The Scottish Enlightenment occurred within the context of universities, and yet historians have neglected this institutional framework. Matthew D. Eddy wishes to fill a lacuna in the historiography by stepping inside the Edinburgh classroom, as it were. He discovers that chemistry in the years between Boyle and Lavoisier—figures that dominated the literature—was distinctive and significant. John Walker (1730-1803), minister and professor of natural history, was no revolutionary, but representative of how scholars applied new chemistry in practice and disseminated methods and ideas throughout Europe. Eddy advances a number of important arguments: that the chemistry of fluids (saline) had more practical importance and interest among scholars in Walker's day than pneumatic chemistry of gases of Boyle or Lavoisier; that the language of chemistry and classification based on chemical composition was well underway before Lavoisier; and that early chemistry informed natural history, mineralogy, and geology before the systems of Hutton, Werner, or Linnaeus. 'Systems' were not always grand taxonomies and theories such as theirs, but oftentimes more empirically oriented classifications based on chemical composition, subject to repeated revision, and serving pedagogical and medical ends.

Eddy develops these arguments in five chapters, consulting sources such as lecture notes, syllabi, Walker's personal inventory of texts, his commonplace book, correspondence, and professional writings. The first chapter is a highly selective biography of Eddy's academic career that shows how well connected Walker became and extensive his teaching was. Chapter Two explains how Walker applied his knowledge of principle chemistry (based on the Becher-Stahl tradition), as taught him by William Cullen, to analyze the waters of Hartfell Spa in 1757. Salt production and balneology were two practical arenas in which early chemistry had marked impact. Walker concluded that the waters contained "two forms of iron, salt, sulphur, and a terrestrial principle" (p 75). Chapter Three jumps back to Walker's exposure to Cullen's chemistry and classification and Walker's academic development, professional network, and extensive mineral collecting. Chapter Four then provides a detailed explanation of Walker's mature mineralogical classification based largely on chemical composition (and secondarily on external or natural characteristics such as color and taste). Walker synthesized the work of numerous contemporaries: Joseph Black, Joseph Priestley, Cullen, and especially the Swedes, Johann Gottschalk Wallerius, Axel Frederik Cronstedt, and Torbern Olaf Bergman. Walker's classification system included nineteen classes subdivided into orders.

As an example, the metals: Class 19 were the six 'primary metals,' ordered according to durability, flexibility, and fixidity; Class 18 were 'secondary semimetals' ordered according to whether they were mineralized or 'calciformed'; and Class 17 were 'secondary mundicks' (pyrites) ordered also by mineralization or calciformation. Eddy provides the entire system in an appendix, along with comparisons to other, better known systems, such as those of Bergman, Linnaeus, Wallerius, and Cronstedt. Conspicuously absent is Abraham Werner, who did not use chemical composition as prominently as these other authors did, and who therefore held little interest for Walker.

The final chapter turns to geology, where chemical composition had greater influence than the historiography would suggest. Scholars have concentrated on theoretical controversies (especially the neptunism/vulcanism debate) and discovery of 'deep time,' but again, Eddy discovers more pedagogical concerns among Edinburgh faculty, including a Baconian methodology and aversion to theorization. Walker never discarded a Biblical conception of earth history (of some 5,000-6,000 years' duration), and never allowed for species change. The Creation and the Deluge were periods of intense chemical precipitations (rather than sedimentation or crystallization alone). Shying away from controversies, Walker never specified exact chronologies or developed a cosmology for his chemical conception. He remained committed to the chemistry of the earth and the necessity for classification based on chemical composition, spreading his ideas via scores of influential students. Hutton, one-time student of Walker's, and best known for promoting the vulcanist theory of rock formation, was better grounded in Edinburgh chemistry than we realize: in his important edition of Hutton's *Theory of the Earth* (1805), John Playfair excised many of the chemical descriptions that would expose Walker's influence on Hutton (p 197).

Eddy appeals for continued work on how principle chemistry impacted natural history, mineralogy, and geology by the mid 18th century. He is certain that future studies will better determine Walker's legacy among his students, physicians, surgeons, midwives, and other practitioners. I might suggest another avenue for improvement. Eddy should be praised for emphasizing the institutional context of the Scottish Enlightenment, for tying early chemistry firmly to other natural inquiries, and for lucidly explaining an early chemistry and taxonomy; but the reader leaves the book with the impression that Walker's work developed within a political and cultural vacuum. Eddy goes back and forth between his subject's wider context and his intellectual life, but these dual inquiries rarely intersect. Edinburgh University, the Republic of Letters, and Britain function as static units against which Eddy plots the internal dynamics of his main character's professional life. But were Edinburgh professors not politically motivated during these years of the Jacobite Rebellions? Walker was an expert on the Scottish Highlands, and Eddy notes that this interest included the culture and history of the people. Walker worked for the Board of Annexed Estates under King George III on Highland culture and religion (p 33). This suggests a far more complicated personality and career than that presented by Eddy. Numerous historians of natural history and mineralogy since Foucault's *The Order of Things*—Paula Findlan, Alix Cooper, Lisbet Koerner—have argued that power and politics motivated the collection and classification of natural objects, and it would be instructive to apply that sort of analysis for the Edinburgh chemist as he mediated London's control over the Highlands. Another related possibility is that Walker partook in the same early Romantic drive to preserve the dying Celtic culture of the Highlands that had driven the contemporary poet, James Macpherson, to 'discover' the Fingal epic in Gaelic. Walker visited Fingal's Cave on Staffa Island (named after the epic hero) and noted other mythological sites he saw during geological expeditions. Did chemistry, geology, and history all combine into a larger vision for Walker (as for Goethe)?

Aside from Eddy's selective gaze, there is the more technical matter of editorial oversight: the first half of the text suffers from occasional missing articles and prepositions. This being said, any historian interested in broadening his or her knowledge of Enlightenment-era classification and any historian of chemistry convinced that the period between Boyle and Lavoisier—when chemistry of fluids and principles dominated in practice—deserves more focused study will profit from Eddy's text and helpful appendices [On chemistry of fluids, see also A. M. Ross, *The Salt of the Earth: Natural Philosophy, Medicine, and Chymistry in England, 1650-1750*, Brill, Boston, MA, 2007.] *Warren Alexander Dym, Dibner History of Science Fellow [2009-2010] at the Huntington Library in Los Angeles, CA,.*

Making Scientific Instruments in the Industrial Revolution. A. D. Morrison-Low, Ashgate Publishing Ltd., Aldershot, Hampshire, England, 2007, 408 pp, ISBN 978-0-7546-5758-3, $99.95.

The author of this volume, A. D. Morrison-Low, is the Principal Curator of the Science Section of the National Museums of Scotland; and the book itself is in many ways a successor to an earlier volume by John Millburn titled *Adams of Fleet Street, Instrument Maker to King George III*, also published by Ashgate. Whereas Millburn gave a detailed portrait of an important late 18th-century instrument maker based in London, Morrison-Low seeks to extend our knowledge of the trade in Great Britain through the first half of the 19th century and to lesser-known instrument makers based in such cities as Birmingham, Liverpool, Manchester, and Sheffield.

This is primarily an economic study rather than a scientific study and, as such, is concerned largely with the nature, organization, and ownership of the instrument trade rather than with significant advances in instrument design. Drawing on a wide range of data sources made available as a result of the digitalization of governmental and city records, the author has assembled a truly impressive amount of information on a subject which one might have thought was permanently lost to history. She has effectively organized much of it by using tables and graphs, though one should also acknowledge some earlier compilations, such as the impressive *Handlist of Scientific Instrument-Maker's Trade Catalogues, 1600-1914*, assembled in 1990 by R. G. W. Anderson, J. Burnett, and B. Gee, also at the National Museums of Scotland.

Because of the book's emphasis, much of it is not of direct interest to the historian of chemistry since most of the output of the instrument makers being studied consisted of the limited production of microscopes, telescopes, surveying instruments, cameras, and other optical devices rather than chemical glassware and hardware. Nevertheless, this book is an important step toward the next logical stage in this process: a study of the rise of large centralized laboratory supply houses in the last half of the 19th century, such as J. W. Griffin & Sons and Townson & Mercer in Great Britain or J. W. Queen & Co. and Eimer & Amend in the United States, as well as the question of how much of the stock which these firms offered for sale was in fact supplied anonymously by the smaller family-owned businesses studied by Morrison-Low. *William B. Jensen, University of Cincinnati, Cincinnati, OH 45221-0172.*

Chronologie Chemie: Entdecker und Entdeckungen. Sieghard Neufeld, Wiley-VCH, Weinheim, 3rd ed., 2003, xi + 441 pp, ISBN 3-527-2424-4; *Från Lavoiser till Strindberg: Kemihistoriska föreläsningar*, Levi Tansjö. Berzelius Sällskapers: Lund, 2008, 293 pp, ISBN 978-91-971637-9-2; *Naissance de la chimie structurale.* Alain Dumon and Robert Luft, EDP Sciences, Les Ulis, 2008, 252 pp, ISBN 978-2-7598-0055-1.

Although it is perhaps too much these days to expect American historians of chemistry to read the monograph literature appearing in various foreign languages, they should at least make an effort to be aware of what titles have been published, as illustrated by the case of the three recent books listed above.

The first of these titles, *The Chronology of Chemistry*, by Siegard Neufeld is a much enlarged 3rd edition of a volume first published in 1976. The first edition chronicled important events in chemistry on a year by year basis from 1800 to 1970; the second edition, published in 1987, extended the chronicle to 1980; and the present edition now takes the survey to the year 2000. For each year the authors of significant papers are listed, followed in each case by a brief paragraph summarizing the importance of the work in question and a list of relevant literature citations. This is a genre of historical reference which has precedents in the German literature (Lippmann, 1921 and Walden, 1950) but no exact parallel in the English literature. In some ways it is a thankless task, as I am sure that many would dispute some of Neufeld's choices, especially for the last few decades. Many of the papers deal with the synthesis of specific compounds at the expense of those dealing with theoretical breakthroughs, and the restriction of the citations to papers in the journal literature overlooks the publication of many important books. Thus no mention is made of Pfaundler's paper (1867) on the application to the kinetic theory of gases to chemical reactions, nor of Horstmann's similar application of the entropy concept (1873), nor of Marcelin's introduction (1910) of the concept of free-energy of activation—all three of which represent key advances in chemical theory. Likewise Gillespie is mentioned for the year 1955 in connection with his later work on superacids, but not for his key review in 1957 with Nyholm which directly led to the formulation of the VSEPR model for predicting molecular geometry—a development which surely had a more significant impact on chemistry than did superacid solvent systems. Nevertheless, anyone who is contemplating the writing of a history of chemistry will want first to review Neufeld's choice of significant contributions.

The second title, *From Lavoisier to Strindberg*, reproduces 15 popular lectures or essays on various themes in the history of chemistry by the late Levi Tansjö (1929-2003). The subjects range from the origins of the law of energy conservation and the second law of thermodynamics to the work of such chemists as Gay-Lussac, Dulong, Ostwald, and Mendeleev. Not unexpectedly, many have a specific Swedish emphasis, including essays dealing with the work of Berzelius, Carl Mosander, Svante Arrhenius, and the alchemical fantasies of the Swedish playwright, August Strindberg. The book is beautifully produced with high quality photographs and paintings but is lacking an index.

The third title, *The Birth of Structural Chemistry*, by Alain Dumond and Robert Luft purports to be a history of structural chemistry. However, the term "structural" is a bit vague and appears, by the authors' own reckoning, to include the history of valence, stereochemistry, the periodic table, and the electronic theory of bonding and reactivity. Though the authors have included an impressive bibliography of the primary chemical literature, they appear to be blissfully unaware that a vast secondary literature on the history of all of these subjects already exists. Thus no mention is made of the previous comprehensive histories of valence by Palmer and by Russell, nor of van Spronsen's well-known history of the periodic table, nor of the histories of stereochemistry by Ramsay and by Ramberg. The authors have also substituted newly drawn computer images for all of the original historical versions of the various tables, diagrams and structures which they discuss. Though this makes for a much more attractive book, it leaves the reader wondering just how much the originals have been both misleadingly simplified and subtly modernized. In addition, much that should be included under the rubric of "structural" is missing from this account, such as the packing models of Barlow and Pope, the rise of modern X-ray crystal analysis, and its role in verifying the postulates of classic stereochemistry. As is usual with most French publications, there is also no index. *William B. Jensen, University of Cincinnati.*

Das Dictionnaire de Chymie von Pierre Joseph Macquer (1718-1784). Katja Schmiederer, Wissenschaftliche Verlagsgesellschaft, Stuttgart, 2008, 395 pp, €27.

Probably the best known French chemist of his generation, Pierre Joseph Macquer was the author of a highly regarded textbook (1749-51), which he and other leading chemistry teachers employed in the third quarter of the eighteenth century to help build the reputation of the science as an independent scholarly discipline, and not a mere ancilla to pharmacy, medicine, and assaying. Perhaps even more influential in discipline-building than his textbook, however, was his *Dictionnaire de chymie* (1766), the first such modern dictionary, and a worthy early specialist work inspired by the great general project of Diderot and d'Alembert. Despite the fine contributions of such scholars as Willem Ahlers, William Smeaton, Roy Neville, Wilda Anderson, and Jonathan Simon, Macquer's overall work and influence have not been well studied—until now.

Originating as a revised doctoral dissertation at the University of Marburg (2006) under the direction of Fritz Krafft, Katja Schmiederer presents us a meticulous and finely crafted study that places Macquer's dictionary in the foreground. The author examines a total of fourteen editions of this work, including in this number not only the second French edition of 1778, but also multiple translations into English, German, Italian, and Danish. In this way she creates a chronological framework for her project that extends from 1766 until 1809. But her focus is not exclusively concentrated on the dictionary, nor even narrowly on Macquer's biography, as the subtitle of the book accurately advertises: *Die Originale und Übersetzungen [des Buches] als Spiegelbild der Entwicklung der Chemie und Pharmazie im letzten Drittel des 18. Jahrhunderts.* In particular, a principal theme of the author is the concern that Macquer and his translators had to fulfill the Enlightenment goal of national education (Volksbildung), independent of the influence of church or state, as well as the utilitarian pursuit of useful applications of the science. The latter tendency can be seen ever more prominently as one proceeds chronologically through the various editions and translations.

A lifelong follower of the phlogiston theory, Macquer also taught a modified version of the Aristotelian elements. But he also displayed the sort of critical, flexible, and empirical approach associated with the best Enlightenment scientists: he scorned the pretensions of the alchemists, and he paid careful attention—as can be seen by comparing the first and second French editions—to new evidence that appeared to conflict with phlogistic ideas or Greek element theory. After Macquer's death editors, such as the Englishman James Keir and the Germans J. G. Leonhardi, J. B. Richter, and S. F. Hermbstaedt, added much new material to the dictionary, the last-named adapting the whole work to the antiphlogistic system. Schmiederer argues that although Lavoisier's theory can be viewed as a scientific revolution in the Kuhnian sense, by following the development of Macquer's work through its various incarnations one can nevertheless discern a more gradual and continuous development, the antiphlogistic system thus emerging as "the result of the consistent development of phlogistic chemistry" (p 339).

The book is completed by excellent primary and secondary bibliographies and a usable name index. *Alan Rocke*, *Case Western Reserve University.*

What a Time I am Having. Vivien Perutz, Ed., Cold Spring Harbor Laboratory Press, Cold Spring Harbor, NY, 2009, xxix + 506 pp, ISBN 9780-0-87969-864-5, $39.

This extensive collection of Max Perutz's letters, amplified by brief biographical sketches and explanatory introductions to each chapter, serves as a highly informative complement to the Perutz biography by Georgina Ferry, *Max Perutz and the Secret of Life,* also published by Cold Spring Harbor Laboratory Press (2008). That book was reviewed in the previous issue of THIS JOURNAL (*Bull. Hist. Chem.,* **2009**, *34*, 69-71).

The editor (often times herself recipient of letters), daughter of Max Perutz, has been fortunate in having access to hundreds of letters Max penned to his wife and children, his sister, parents, personal friends, and many scientists over a period of about 70 years. While most are original in the form of collections of the recipients, sources also include copies found in his office files, his personal diaries, and numerous archives. Some of these memorabilia still in private hands will be deposited in the archive at Churchill College, Cambridge.

In her preface, Vivien describes her ambitious project, the myriad sources, and her decisions about what to include and to edit. An opening memoir of Max Perutz by the late David Blow provides a concise account of Perutz's life and accomplishments, all of which has been described in more detail in Ferry's biography. It is nevertheless helpful as an opening section and prepares the reader to proceed in "getting to know Max" the person. The editor has provided several features of great help in following Perutz/s story: a timeline of major events in Max's life; a list of the 80 correspondents, with brief biographical sketches; a list of the 100 illustrations; and archival repositories of the letters.

The book title is taken from the opening line of a letter Max wrote to his wife Gisela from the US in 1950. It conveys his enthusiasm for life in many forms, which is amply confirmed in his highly articulate writing, first in German (translated into English for this collection) and then gradually in English, as he lived out the major part of his life in England. The eight chapters are grouped by the decades of Max's life, from the 1930s to the 2000s. Each is prefaced with explanatory information about the highlights of that decade, and the editor has also provided useful and sometimes lengthy footnotes to amplify an issue or event.

Correspondence from the 1930s is comprised mostly of letters to a young woman Max admired very much: Evelyn Baxter (later Evelyn Baxter Machin). Having saved all his letters, she returned them to Max when he was in his eighties. They provide personal accounts of his years as a chemistry student first in Vienna and then at Cambridge, the beginning of his life-long investigations on hemoglobin, and his adventures as an ardent skier and rock climber. Of Jewish origin but baptized as a Roman Catholic, Max deplored the political turmoil of the late 1930s, commenting on the *Anschluß* and concentration camps with utter disdain. In 1940, having completed his doctorate under W. L. Bragg, he was interned as an alien, as was his father. Letters to his parents and sister, first from England and then Canada, describe his frustration and anxiety about his future: when would he be released? Should he consider a position at Cal Tech in the US? With the intercession of Bragg, Max was released and able to return to Cambridge University in 1941, where he remained for the rest of his life; a loyal Anglophile, he never had to settle for a position in America, much to his relief. After he was married in 1942, the volume of his correspondence was magnified with often daily letters to Gisela, as well as frequent letters to her parents in Berlin. Because Gisela's "Berlin German" and his Austrian language were incompatible, they settled on English as their 'native tongue!" It was in this decade that Max initiated an association with the Rockefeller Foundation, which supported his research continously from that time on. With the founding of the Medical Research Council in 1947 his program was not only financed but recognized as a valid investigation into molecular structure of biological systems. It is remarkable how detailed descriptions of his slow but positive research results on hemoglobin were conveyed to his reading audience—wife, relatives, as well as to fellow scientists. How much the nonscientists comprehended the reports is problematic. His readers might have understood somewhat more clearly his account of war effort investigation of ice and later his project on glaciology, sponsored by the Royal Society. The love of the Alps must have been a compelling inspiration for these diversions from chemistry. His travels to the US and Canada are recorded for posterity in his personal diary, which the editor has reproduced.

The highlight of the 1950s was the substantial progress in working out the hemoglobin structure through the use of heavy atom markers and the first three-dimensional X-ray structure. He was named a fellow of the Royal Society in 1954. With growing recognition and respect for the structure work being carried out in Perutz's group, he received numerous invitations to lecture. A noteworthy trip was that in 1961 to give the Weizmann lectures in Israel, and he took the opportunity to plan an extensive trip to the Near East with his wife, children, and mother, well documented in a diary, portions of which are reproduced in the book. He is forthright in his observations, such as that about the contrasting impressions in Jerusalem. He found the Church of the Holy Sepulcher a "..shapeless and labyrinthine conglomerate of shabby chapels belonging to a multiplicity of different Christian sects..", while the Dome of the Rock "…was built in the 7th century on a magnificent open site…and shows the great flowering of Islamic art at a time when Europe went through the Dark Ages." The awarding of the Nobel Prize in Chemistry to Perutz and John Kendrew, his former student and colleague, certainly constituted the apex of the 1960s. Once again he recorded the Stockholm ceremony and accompanying events with articulate candor, such that the reader has the sensation of experiencing the events first hand, rubbing shoulders with other Nobel laureates as well: Watson, Crick, and John Steinbeck. After years of managing in inadequate quarters, Perutz and his group were finally able to occupy the newly built MRC Laboratory, officially opened by Queen Elizabeth, in 1962. Refinements in the structure of hemoglobin continued steadily, and before the decade had ended, attention was being directed toward the mechanism of oxygen uptake and release, as well as the possible role of hemoglobin in diseases. Max, serving as the first chairman of the European Molecular Biological Organization (EMBO) beginning in 1963, was compelled to travel extensively in this capacity; and he provided details of these experiences as well.

In the 1970s Perutz traveled extensively on lecture tours, which are documented through his vivid descriptions. Much of his research progress—further refinements in the structure of hemoglobin and its role in oxygen transport—is outlined, sometimes with hand drawn sketches, primarily to his son Robin.

Upon his retirement as chairman of the Laboratory of Molecular Biology and with permission by the Medical Research Council, Max Perutz continued working in the laboratory as a research scientist. This had been his practice from the outset—to work with his own hands alongside his collaborators, and he maintained this routine until very shortly before his death in 2002. In the last two decades of his life, Max sustained his commitment to molecular biology, which was recognized in the form of several awards; but he branched out into studying the causes of afflictions such as Huntington's disease and AIDS. These new areas of interest are documented in great detail in the correspondence. He also became actively concerned with politics and wrote essays directed to a wider public than just scientists.

To be sure, this assemblage of personal letters serves as documentation of the scientific accomplishments of Perutz, a Nobel Prize winner who is less familiar to the general public than, say, Linus Pauling. But beyond this accomplishment, the editor has collected insight into Perutz the man—far more than scientist alone. He had deep interest in not only science but religion, history, and politics. Social issues such as contraception, genetic engineering, and human and religious rights are recurring themes in his correspondence. A voracious reader, he would often report in his letters whatever he was reading for pleasure at the time; books would span the horizon from early classics to *Catcher in the Rye*. Max was fluent in French and Italian and his (nearly) native language English, as well as his own native German. He was a sincere patron of art. architecture, the theater, and music: on one occasion, when snowbound in

Canada, he expressed his main concern—that he would fail to make it to Washington, DC the next day in time for the 'Philadelphia Philharmonic' concert. He provided clear descriptions of the design and architecture of sites he visited, such as the Washington capitol ("dignified but hideous"). As might be expected of a scientist with meticulous skills, he respected order and cleanliness, often giving a report on the condition of a hotel room or lobby. These traits could only be honed in a person with extremely keen powers of observation, so richly gifted was this man.

Qualities evident in this Renaissance man are: skill for organization, imagination, honesty, and a strong ethical sense. During the war he expressed shock at what he considered moral decline in the behavior of British citizens through public love making, rudeness, and drunkenness. Perutz had very high standards with regard to communication through lectures, scientific publications, not to mention correspondence. He is quoted as saying, "Presentation of a scientific discovery is, or at least should be, a work of art" (p 228). He was his own worst critic in evaluating his public lectures, sometimes reporting that one had gone badly—but also freely inclined to identify those that had gone well.

Perutz had keen insight in evaluating individuals; he selected his coworkers with great care and success. In dealing with scientists and pubic figures at all levels, he managed to maintain an objective perspective but was always sensitive to their feelings. Through it all, he maintained a sense of humor. While visiting Cambridge, MA in the US, where he lectured at both institutions, he reported to his wife that one of his functions "..was to tell people at Harvard what goes on at MIT and vice versa."

The editor and all the staff at Cold Harbor Spring Laboratory Press are to be commended for their remarkable success in bringing Max Perutz to life for those of us who did not have the good fortune to know him personally. *Paul R. Jones, University of Michigan*.

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1. O. T. Benfey, "Dimensional Analysis of Chemical Laws and Theories," *J. Chem. Educ.*, **1957**, *34*, 286-288.
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