La química en la historia, para la enseñanza

His life and work

Kurt Wohl

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Resumen

Kurt Wohl (1896-1962) fue un brillante científico teórico que trabajó en áreas tan diferentes como la fotosíntesis y las llamas. Amargos sucesos antes de la Segunda Guerra Mundial lo obligaron a cambiar de ocupación varias veces, pero a pesar de ello, él contribuyó en forma duradera al tema de termodinámica de soluciones y propiedades de transporte de los gases a altas temperaturas y presiones.

Abstract

Kurt Wohl (1896-1962) was a brilliant theoretician who worked in areas as widely different as photosynthesis and flames. Bitter events before World War II forced him to change activities several times, but in spite of this he made lasting contributions to the thermodynamics of solutions and transport properties of gases at high temperatures and pressures.

Physical chemists and chemical engineers are familiar with Wohl through his model for describing the behavior and phase equilibrium of a real solution. They are generally unaware of his rich contributions in other scientific areas such as the application of thermodynamics and reaction chemistry to photosynthesis and plant respiration, determination of heat capacities and dissociation rates of gases at high temperatures, and the theory of combustion and flames. Here we describe his personal life and career, his scientific achievements, and, in particular, his contributions to thermodynamics and plant physiology.

Life and career (Jost, 1963; von Elbe, 1963)

Kurt Wohl was born in Berlin, on December 3, 1896, the son of Alfred Wohl, a professor of chemistry at the University of Danzig, known for his contributions to the theory of equations of state.

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After participating in the First World War he went to study chemistry at the universities of the Free City of Danzig, Heildelberg, and Berlin. He did his Ph.D. studies at the University of Berlin under the direction of Walther Nernst (1864-1941; 1921 Nobel Prize in Chemistry) and graduated in 1923, summa cum laude, with a thesis related to the specific heat and dissociation of diatomic gases.

After graduation he was appointed assistant in the *Physikalisch-Chemischen Institut* (Physical Chemistry Institute) of Nernst, in Berlin, where he began working with the group of Max Bodenstein (1871-1943). At the Institute he continued his research on the specific heat of gases, their dissociation, explosion methods, and equilibrium states. In addition, he did work on the London theory of the van der Waals forces (Wohl, 1931).

Bodenstein recognized the exceptional characteristics of Wohl and promptly incorporated him to the editorial board of the journal *Zeitschrift für Physikalische Chemie* (*Journal of Physical Chemistry*). Between 1923 and 1933 Wohl had as doctoral students Günther von Elbe, who would become one of the foremost authorities in the area of combustion and flames, and Michel Magat (Wohl and Magat, 1932).

In January 1933 the National Socialist Party assumed the government of Germany and in April 7 of the same year regulations were issued to purge the Civil Service, including the universities, of socialists, democrats, and Jews. The first laws forbade the employment of Jews in government establishments, except in some circumstances like having participating in WWI. Wohl's life suffered a serious change and he could continue working only because he had indeed participated in the First World War. He first accepted a temporary arrangement of semi-retirement from university and between 1936 and 1938 he could perform only work of a technical value, including a position at I. G. Farberindustrie. During this period he developed an interest in the theory of plant assimilation and published several papers dealing with the kinetic and energetic aspects of the subject (Gaffron and Wohl, 1936; Wohl, 1937).

In September 1935 the Nuremberg laws were enacted that prohibited the employment of Jews in almost every activity. In the first supplementary decree of Nov. 14, 1935, these laws were made more specific by defining who was a Jew and by declaring explicitly that "a Jew cannot be a citizen of the Reich, he cannot exercise the right to vote; he cannot occupy public office." Other enactments were designed to complete the process of Jewish segregation.

In the beginning of 1939, as a result of these regulations, Wohl immigrated to England where he stayed a little less than four years. He gave a very successful seminar about photosynthesis at the Balliol College in Oxford; this seminar led to his appointment to the Department of Botany of the university working with William Owen James. While at Balliol he continued the work on the assimilation of CO_2 that he had initiated in Germany with Gaffron (Gaffron and Wohl, 1936).

By the end of 1942 Wohl immigrated to the US where his family had moved before. After some time, and a stay at Princeton University, he accepted a position as professor of chemical engineering at the University of Delaware, Newark. His only son, Hellmut, became a professor of art in the Fine Arts Department at Yale University.

At Delaware he dedicated himself to thermodynamics and combustion processes. He was also interested in gas turbines and jet engines. All these subjects were part of the more general area of transport phenomena, flow processes, and chemical reactions that interested him. Wohl was also interested in the phenomena of diffusion in flames, laminar flames, and turbulent flames, and flame analysis spectroscopy in all wavelengths. His achievements were reflected in the successful conferences he gave during the seven symposia on Combustion and Flame and Explosion Phenomena that took place from 1948 on. The nineth (and last symposium) took place in August 1962 at Cornell University, some time before he died.

Among his achievements we can mention are his serving as a member of the Sub-committee on Combustion of the National Advisory Committee for Aeronautics, charter member of The Combustion Institute, and working as a consultant for the chemical and motor industry. In 1953 he was invited to Göttingen University were he lectured on the thermodynamics and mechanisms of combustion.

In 1924 he married the pianist Margarete Wocke. Music accompanied their life and at their home in Zehlendorf (a district of Berlin) their musical evenings were well known. There they would play clarinet, chamber music, and Jewish music, although Hitler had forbid playing the latter. Wohl remained interested all his life in art, literature, painting, and music. After moving to Newark, Wohl's home continued to be a meeting place for musical evenings.

Kurt Wohl died on September 3, 1962, in Newark, Delaware, of complications during a heart operation.

Scientific work
Wohl did research in very different fields that in a way reflect the influence of external events on his life. In Germany he dedicated himself mainly to thermodynamics (equations of state, osmotic pressure, heat effects), in England to heat balance of plant physiological processes, and in the US to thermodynamics of solutions, and phenomena related to combustion. We will now discuss some of Wohl's most important contributions.

1. Energy processes in plants
Wohl worked on the application of thermodynamics concepts to the analysis of energy processes in plants, first in Germany and then in England. He analyzed in particular the processes of energy capture (photosynthesis) and utilization (respiration) (Wohl, 1940; Wohl and James, 1942) and his results will be discussed in what follows.

1.1 Photosynthesis (Wohl, 1937; 1940)
Wohl work in this area is interesting because it reflects what was known (and not known) about photosynthesis sixty years earlier. Photosynthesis in green plants means the transformation of carbon dioxide and water into oxygen and carbohydrate by the action of light. The overall equation for the process is

$$nCO_2 + nH_2O \rightarrow nO_2 + (CH_2O)_n \qquad (1)$$
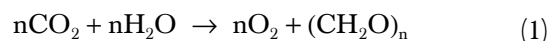
Equation (1) indicates that photosynthesis is a light-energized oxidation-reduction process.

At that time it was not known how the synthesis was achieved, or the chemical intermediates and enzymes involved in the process. The product of the reduction of CO_2 had the empirical formula $(CH_2O)_n$ yet it was not known whether this group left the reaction site as formaldehyde (CH_2O), or in some

more condensed form (Wohl, 1940). The only information available was the amount of incident light absorbed by chlorophyll, as well as the amount of the latter, and the rates of CO_2 consumption and O_2 production.

Wohl first analyzed the energy requirements of the process assuming, as was usual, that formaldehyde was the primary product of photosynthesis. Since eq (1) required 130 kcal/mol of CO_2 or (O_2) and for one photo-act the quantum energy available (red light) was 42.6 kcal, it meant that the reduction of CO_2 required at least three primary photo-acts. Thus it was of interest to learn how the rate of the reaction increased with the increase in light intensity. The available experimental evidence indicated that the curve that described this process started linearly, meaning that the energy of a quantum absorbed by chlorophyll and transmitted to the CO_2 molecule *had to be stored* until the next quantum arrived (Wohl, 1935). Now, according to the second law of thermodynamics, the light energy necessary to implement the process should be larger that the heat of reaction, even if no photo-act was lost. It should be also true because the return to the initial state could only be inhibited by additional amounts of energy (Gaffron and Wohl, 1936).

Hence, four quanta of red light, and not three, as assumed by others, were the theoretical minimum by which photosynthesis could be achieved. Another important consequence was that the fourth photo product was produced in an *irreversible* way.

The next question was how does the CO_2 molecule store up its four quanta? The only possibility was for the CO_2 molecule to be firmly attached to a reducing center, which had to be energetically coupled to the source of quanta, that is, to chlorophyll.

The proposed mechanism was, then

$$X_0 \rightarrow X_1 \rightarrow X_3 \rightarrow X_4 \frac{O_2, (CH_2O)}{H_2O, CO_2} \qquad (2)$$
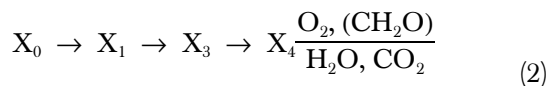
that is, the CO_2 attached to the reducing center X_o, was transformed by four quanta taken from the chlorophyll into three intermediate products, X_1, X_2, and X_3, and finally into the photo-product X_4.

Wohl proceeded then to analyze mathematically the consequences of the kinetics of reaction (2) by comparing the mean time of chemical reaction (τ) with the mean time interval between the arrival of two light quanta at the reducing center (Wohl, 1937, p. 105-121). His conclusions were that nearly all the reducing centers were necessarily occupied by X_4 and that at each reducing center one oxygen molecule would be formed every τ seconds. Wohl conclusions matched the experimental fact that at moderate temperatures and low to medium light intensities, the rate of photosynthesis increased as the intensity increased and was independent of the temperature. At higher light intensity levels the rate became increasingly dependent on temperature and less dependent on intensity, a feature characteristic of chemical reactions.

The next question was related to the structure of the reducing center (photosynthetic unit). It had already been assumed that each reducing center required about 2500 chlorophyll molecules. Gaffron and Wohl (Gaffron and Wohl, 1936) calculated that a single chlorophyll molecule in a dimly illuminated plant would absorb a light quantum only once in several minutes. At this rate the molecule would require nearly an hour to capture the quanta necessary to produce one molecule of O_2. When the plant was fully illuminated the maximum rates of CO_2 uptake and O_2 evolution were fully established. So Gaffron and Wohl postulated that the energy harvest by a large set of chlorophyll molecules was conducted at a single reaction center.

This, and other concepts about the structure of the photosynthetic unit have been revised and improved many times during the last 50 years. The current explanation is that the photosynthetic unit is composed of three complexes, as explained below.

What do we know today about photosynthesis? First, that the process takes place in the chloroplasts of green plants and that all the light-harvesting chlorophyll and the electron transport pathways are located in the thylakoid membranes of the chloroplast. Second, the actual reactions occur in two stages: the *light stage*, consisting of photochemical reactions, and the *dark stage*, comprising chemical reactions controlled by enzymes. During the first stage the energy of light is absorbed and used to drive a series of electron transfers, resulting in the synthesis of ATP and NADPH. During the dark stage NADPH and the energy-loaded ATP are used to reduce CO_2 to organic compounds.

In the thylakoid membrane there are three complexes named photo system II (PSII), cytochrome *bf* complex (Cyt *bf*), and photo system I (PSI), respectively. PSII and Cyt *bf* are connected by the electron carrier plastoquinone, and Cyt *bf* and PSI are con-

nected by plastocyanin. The whole arrangement is called *Z arrangement*. A photo system is then, a complex of light-absorbing chlorophylls, a reaction-center chlorophyll, and an electron transport system. The chlorophyll molecules feeding excitation energy to the centers are called *antenna chlorophyll*. In the case of PSII the reaction center chlorophyll is called P680 because it absorbs light up to that wavelength. PSI is called P700 for the equivalent reason.

The energy efficiency of photosynthesis is the ratio of energy stored to the energy absorbed. The amount of energy stored can only be estimated because of the myriad of products formed. If eq (1) is used to approximate the actual storage process then the production of one mole of oxygen and 1/6 mole of glucose (formaldehyde) results in the storage of about 117 kcal, at room temperature. Since plants use that part of the solar spectrum that has an estimated mean wave length of 570 nm, then the energy absorbed is about 50 kcal/einstein. To calculate the amount of light energy involved in photosynthesis we need to know the number of einsteins absorbed per mole of oxygen formed. This is called the *quantum requirement*. The minimum quantum requirement is about nine. Therefore, the maximum energy efficiency of photosynthesis is about 117/450, that is, about 26%.

An interesting result is that the actual percentage of solar energy stored by plants is as much as *1%* of the total solar energy received. Also, that respiration by living organisms and combustion of carbon fuels consumes on the average about 10,000 tons of O_2 *every second* on the surface of the earth. At this rate, all the O_2 in the atmosphere would have been used up in about 3000 years (!) (Hall and Rao, 1994). Fortunately, this loss is counterbalanced by the production of carbohydrates and oxygen during photosynthesis. More than that, as stated by Wohl, long ago, the rate of photosynthesis in the green parts of plants is about 30 times as much as the rate of respiration in the same tissues.

1.2 Respiration (Wohl and James, 1942)

In this second project on plant physiology, Wohl analyzed how plants utilized the energy that was captured by photosynthesis, and particularly, the respiration process. His main argument was that respiration in plants and animals was accompanied by transformations of energy. Respiration, like any other process that went on spontaneously, involved a decrease in the Gibbs function (G), and since plant life was always

accompanied by respiration, it was of interest to find how did the plant used the decrease in G.

To keep respiration going there must be a continuous supply of energy, which plants normally obtain from the sun. We have discussed before how plants transform the radiant energy of sunlight into chemical energy by converting carbon dioxide and water into certain activated intermediates that spontaneously continue their chemical way to oxygen and sugars. If we write now

$$\Delta G = \Delta H - T\Delta S \qquad (3)$$

we see that part of the available energy in sunlight utilized by the plant is dissipated as heat (ΔH) and part is absorbed as information ($T\Delta S$) in building complex molecules. The plant uses the heat released to evaporate water (transpiration) from the cell surfaces of the mesophyll. The transpiration process is always accompanied by useful mechanical work (such as lifting the water from the soil to leaf level) because the transpiration stream carries the water and the nutrients needed by the leaves. Anyhow, this mechanical work is very small, for example, raising one kilogram of water to the top of a 60-m high tree requires 0.588 kJ, which is 0.024% of the heat required to evaporate the same amount of water at 25°C (2442 kJ/kg).

Plants utilize energy in two stages: (a) during growth, building up all the necessary organs and structure and (b), on maintenance of the mature plant. During the active growth phase part of the sugar is oxidized to carbon dioxide and part is invested in building permanent plant constituents such as cellulose and proteins, or is stored as starch and fat.

When the plant has achieved his final structure, it may be considered as a thermodynamic system in equilibrium with its environment and suffering inevitably spontaneous changes with a changing environment. The organism maintains itself in a steady state by a continuous supply of energy by photosynthesis and the continuous breakdown of carbohydrate. The important question is determining what fraction of the energy is actually utilized by the organism and what fraction is wasted.

According to Wohl the experimental evidence indicated that all the energy decrease associated with respiration appeared as heat. The decrease in total energy was given by the decrease in the heat combustion of the tissue during the period considered, and this was a measurable quantity.

During growth, sugars were converted into substances of greater energy content, the additional energy was supplied by the oxidation to CO_2 of part of the available sugar. If we consider the complete oxidation of sugar or starch to CO_2 as the only reaction taking place, then the decrease in the heat of combustion of the plant and its substrate, (*A*), would be equal to the heat of formation of the CO_2 released, (B). In this case, the percentage of the respiratory energy used would be 100 $(A - B)/B$. Unfortunately, to determine the actual efficiency of respiration in maintaining the steady state required knowing the details of many processes like the rate of spontaneous breakdown of all substances other than respiratory substrates, how much sugar was consumed in making a unit replacement, etc. Present knowledge of the metabolic processes was far from enough for making a reasonable estimation.

The most obvious energy wastage was found among primitive and especially among anaerobic saprophytes, For example, yeast under nitrogen would continue to release energy from sugar by vigorous fermentation even when growth was at a standstill and energy utilization was virtually nil. The action seemed to be the result of uncontrolled enzyme activity on susceptible materials, and was not related to the metabolic needs of the organism. Starting from such a condition evolution could be envisaged as a progressive control of expenditure of material and energy.

Metabolic reactions may be spontaneous or non spontaneous. Realization of the latter will require assistance from another reaction or from another source of energy We may then speak of *driving reactions* (spontaneous) and *driven reactions* (non spontaneous).

Wohl stated that respiration processes were an excellent example of this situation. They occurred through numerous chemical steps by which a variety of intermediates and by products was formed. These afforded as many opportunities for the coupling of respiration to synthetic steps. The overall reaction could be considered as a complex package of driving and driven equations. In the particular publication (Wohl and James, 1942) Wohl and James gave several examples of this coupling. One of them was the oxidation of nitrate into ammonia with the help of water only
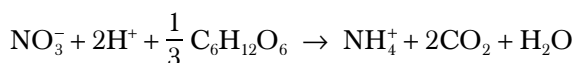
$$NO_3^- + 2H^+ + H_2O \rightarrow NH_4^+ + 2O_2 \quad \Delta G = 64 \text{ kcal} \quad (4)$$
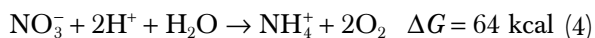
This reaction was not spontaneous, but since the oxygen released could be used to oxidize carbohydrate

$$2O_2 + \frac{1}{3} C_6H_{12}O_6 \rightarrow 2CO_2 + 2H_2O$$
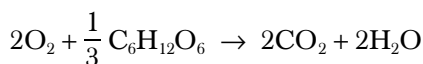
$$\Delta G = -230 \text{ kcal} \tag{5}$$

then, the available energy released by eq (5) was more than enough to drive eq (4). Coupling of both equations allowed realizing the over all reaction

$$NO_3^- + 2H^+ + \frac{1}{3} C_6H_{12}O_6 \rightarrow NH_4^+ + 2CO_2 + H_2O$$

$$\Delta G = -165 \text{ kcal} \tag{6}$$

The energetic linkage of eqs (4) and (5) was $(100)(64/230) = 28\%$ efficient.

It could then be concluded that by breaking the metabolic process into a series of driving and driven chemical reactions the plant was able to utilize the available energy of respiration for all its needs.

According to Wohl, this reasoning could be extended to many other vital processes such as organization, salt accumulation, cell division, and protoplasmic rotation. Only a suitable reaction sequence would allow them to use the decrease in available energy caused by respiration. Wohl illustrated this conclusion pointing out that although plants may exhibit a large energy turnover of anaerobic respiration, the available energy released was essentially lost because the lack of a suitable chemical sequence to utilize it.

Wohl's example of anaerobic respiration is an excellent illustration of the difference between the First law of thermodynamics (quantity of energy) and the Second law (quality of the energy). The fact that a certain amount of energy is released is not a requirement that it must be partly converted into work. In the example in question all the energy released is converted into *lost work*.

At the time of Wohl's review of driving and driven equations it was not known that the normal strategy used by living organisms is to couple a process that releases available energy (downhill) with another that requires energy (uphill). The strategy is very general and includes not only chemical reactions (as illustrated by Wohl), but also simple mass transfer of compounds and ions. For example, in the intestinal lumen, after a meal, there is a high level of Na- and a low level of glucose compared to

the level of the same in the epithelial cells. The glucose-Na symport protein brings the glucose to the lumen using the energy released by the downhill export of Na$^+$. Another example is the cell of the bacteria *Escherichia coli*; here an H-symport protein coupled to a proton pump uses the same principle to export H$^+$ and import lactose.

2. Thermodynamics

2.1 Wohl's equation of state for gases

In 1914 Wohl's father proposed the following equation of state for gases (Wohl, 1916) that did not gain much popularity

$$\left[p + \frac{af_1(T)}{v(v-b)} - \frac{cf_2(T)}{v^3} \right](v-b) = RT \tag{7}$$

In eq (7) a, b, and c are the parameters of the equation, and $f_1(T)$ and $f_2(T)$ functions of the temperature defined as

$$f_1(T) = \frac{T_c}{T} \tag{8}$$

$$f_2(T) = \left(\frac{T_c}{T}\right)^2 \tag{9}$$

This equation presented a series of interesting features, first it transformed the van der Waals parameters a and b, from being constant, into functions of the temperature, and second, it predicted a constant value of 0.267 for the critical compressibility z_c, $z_c = P_c v_c / RT_c$). The equation was not considered very successful because it did not predict the second virial coefficient properly and hence, it was not very accurate for high pressures.

The fact that $z_c = 0.267$ is important for the following reasons: (a) The experimental values of z_c vary between 0.200 and 0.300, with about 60% of the data in the region 0.26 to 0.28, (b) all modern equations of state like Redlich-Kwong, Soave, and Peng-Robinson predict a value of z_c larger than 0.300, way out the experimental range (Walas, 1985).

Kurt Wohl analyzed the reasons for the failure of eq (7) (Wohl, 1928) and concluded that its performance could be improved substantially by simple changing the expression of $f_2(T)$ from than given by eq (9) to

$$f_2(T) = \left(\frac{T_c}{T}\right)^{4/3} \tag{10}$$

First, let us relate the value of the constants a, b, c, to the critical properties, by using eq (7) together with the conditions for an inflection at the critical point, $(\partial P/\partial v)_{T_c} = 0$ and $(\partial^2 P/\partial v^2)_{T_c}$. The result is

$$b = \frac{v_c}{4} \tag{11}$$

$$a = 6v_c^2 P_c \tag{12}$$

$$c = 0.075852 \frac{R^3}{P_c^2} T_c^3 = \frac{8}{3} ab \tag{13}$$

From $z_c = P_c v_c / T_c$ we get $z_c = 0.267$. (14)

In order to study the behavior of the second virial coefficient we transform eq (7) into its virial form, as follows

$$\frac{Pv}{RT} = \frac{v}{v-b} - \frac{\alpha}{RT}\frac{v}{v(v-b)} + \frac{\beta}{RT}\frac{1}{v^2} \tag{15}$$

where $\alpha = af_1(T)$ and $\beta = cf_2(T)$. Equation (15) may be written

$$\frac{Pv}{RT} = \frac{1}{1 - b/v} - \frac{\alpha}{RT}\frac{1}{v(1 - b/v)} + \frac{\beta}{RT}\frac{1}{v^2}$$

Taking advantage that b/v is a very small number we have

$$\frac{Pv}{RT} = \left(1 + \frac{b}{v} + \frac{b^2}{v^2} + \frac{b^3}{v^3} + \ldots\right) - \frac{\alpha}{RT}\frac{1}{v}\left(1 + \frac{b}{v} + \frac{b^2}{v^2} + \ldots\right) + \frac{\beta}{RT}\frac{1}{v^2}$$

and rearranging according to powers of the volume

$$\frac{Pv}{RT} = 1 + \frac{1}{v}\left(b - \frac{\alpha}{RT}\right) + \frac{1}{v^2}\left(b^2 - \frac{\alpha b}{RT} + \frac{\beta}{RT}\right) + \ldots \tag{16}$$

From here we get that the second and third virial coefficients are

$$B = \left[b - \frac{af_1(T)}{RT}\right] \tag{17}$$

$$C = \left[b^2 - \frac{abf_1(T)}{RT} + \frac{cf_2(T)}{RT}\right] \tag{18}$$

Since the second virial coefficient becomes zero at Boyle's temperature (T_B), from eqs (11-13) and (17) we get

$$T_B = \sqrt{\frac{aT_c}{Rb}} \tag{19}$$

Wohl compared the behavior predicted by eq (17)

with the experimental one for a large set of substances that exhibited a quadrupole (such as CO_2) and others having a high dipole moment (such as $CHCl_3$, HCl, N_2O, ethyl ether, and SO_2). The results indicated that the equation held very well for normal substances in the entire gas domain, with an error of 1-2% for the pressure. The second virial coefficient calculated using eq (17) agreed very well with the calculated one in the range $0.8 T_c$ to $2.5 \ T_c$.

2.2 The Wohl model for solution behavior

The estimation of the thermodynamics properties of a real fluid or fluid mixture without experimental data is a very complicated problem involving detailed spectroscopic, structural and interaction potential data, and the use of mechanical statistics. The behavior of liquid solutions cannot be adequately expressed in terms of an equation of state and for this reason it is common practice to describe the deviation from ideal solution behavior by means of excess functions, particularly that of the Gibbs function, G^E. No general theory exists that adequately describes the composition dependence of liquid solution properties; many theoretical approaches have been tried but they have met very little success.

For these reasons, the preferred approach is to develop empirical correlations. In general G^E/RT is a function of T, P, and the composition, but for liquids at low to moderate pressures it is a very weak function of P. Therefore the pressure dependence of activity coefficients is usually neglected.

The many models available today are characterized by expressing the deviation of the liquid phase alone. They contain no information whatsoever about the vapor phase. It is desirable that the G^E/RT model be of sufficient flexibility to represent the various types of behavior of the function G^E (x_1, x_2, x_n, T). Preferable the model should have a sound physicochemical basis so that the numerical values of the parameters in the expression be susceptible to correlation and estimation. No known model for G^E meets all the requirements; the choice of an expression for G^E is usually made on an ad hoc basis.

Wohl selected to express the excess value of the *molar* Gibbs function, $\Delta g^E/RT$, on similar arguments as those used by Heike Kamerlingh Onnes (1853-1926; 1913 Nobel Prize in Physics) to develop the virial equation of state for gases. The many-body problem was assumed to be the sum of the interactions of clusters of increasing complexity: two body clusters, three-body clusters, and so on. Since the problem consisted now in expressing the deviations caused by *solution*, it was necessary that in each cluster at least one molecule be different from the rest. The resulting expression was (Wohl, 1946)

$$\frac{\Delta g^E}{RT} \frac{1}{\sum q_i x_i} = \sum_{ij} z_i \, z_j \, a_{ij} + \sum_{ijk} z_i \, z_j \, z_k \, a_{ijk+\,\ldots} \qquad (20)$$

where q_i represents the *effective molar volume* of component i and z_i its *volumetric fraction*, given by

$$z_i = \frac{q_i x_i}{\displaystyle\sum_{i=1}^{n} q_i x_i} \qquad (21)$$

The effective volume was considered to be the *volume of influence* of the molecule and hence its actual value would vary from solution to solution, depending on the type of interactions present. Since actual molecules do not touch each other the *minimum* value of the effective volume will clearly be somewhat larger than the *actual molar volume* of the molecule.

Parameter a_{ij} represents the interaction between molecules i and j, parameter a_{ijk} the interaction between molecules i, j, and k, and so on. Clearly then the order of the indexes is not important. The first sum represents the total of interactions in clusters formed by two molecules, the second the total of interactions present in clusters constituted by three molecules and so on (notice here the similarity with the meaning of the virial coefficients). Each additional sum after the first one considers the interactions not taken into account by the previous sum. In addition, each sum is preceded by an appropriate expression of the volumetric fraction to assure that the value of $\Delta G^E/RT$ be zero for $x = 1$ and $x = 0$. Since we are describing the excess property, in every expression at *least one* of the z must carry an index different from the rest.

To illustrate the meaning of the different contributions, let us consider the expansion of the term $\sum_{ij} z_i z_j a_{ij}$ for a binary and ternary solution. For a binary solution we have

$$\sum_{1}^{2} z_i \, z_j \, a_{ij} = z_1 \, z_2 \, a_{12} + z_2 \, z_1 \, a_{21} \ = 2 z_1 \, z_2 \, a_{12} \qquad (22)$$

and for ternary one

$$\sum_{1}^{3} z_i\, z_j\, a_{ij} = z_i\, z_2\, a_{12} + z_1\, z_3\, a_{13} + z_2\, z_1\, a_{21} + z_2\, z_3\, a_{23} +$$

$$z_3\, z_1\, z_{31} + z_3\, z_2\, a_{32}$$

$$\sum_{1}^{3} z_i\, z_j\, a_{ij} = 2z_i\, z_2\, a_{12} + 2z_1\, z_3\, a_{13} + 2z_2\, z_3\, a_{23} \qquad (23)$$

For practical reasons the Wohl expansion is usually *limited to the third or fourth order in z.*

Consider now the expansion of order three for a binary solution. We have

$$\frac{\Delta g^E}{RT} = \left(q_1\, x_1 + q_2\, x_2 \right)\left(2z_1\, z_2\, a_{12} + 3z_1^2\, z_2\, a_{112} + 3z_1\, z_2^2\, a_{122} \right) \qquad (24)$$

Using the fact that for a binary solution $z_1 + z_2 = 1$ and $z_1/z_2 = q_1/q_2$, and defining the two new constants

$$A = q_1\!\left(2a_{12} + 3a_{112} \right) \qquad (25)$$

$$B = q_2\!\left(2a_{12}\, 3a_{122} \right) \qquad (26)$$

we can transform eq (24), after some algebra, to

$$\frac{\Delta g^E}{RT} = A x_1\, z_2^2 + B x_2\, z_1^2 \qquad (27)$$

We now multiply eq (27) by the total number of moles n and then differentiate with respect to n_i, to obtain the activity coefficient of component I (Prigogine and Defay, 1954)

$$\left[\frac{\partial}{\partial n_i}\!\left(\frac{\Delta G^E}{RT} \right) \right]_{n_j, T} = \ln \gamma_i$$

The final result, after some algebra, is

$$\ln \gamma_i = z_2^2\!\left[A + 2z_1\!\left(B\frac{q_2}{q_1} - A \right) \right] \qquad (28)$$

$$\ln \gamma_2 = z_1^2\!\left[B + 2z_2\!\left(A\frac{q_1}{q_2} - B \right) \right] \qquad (29)$$

Equations (28) and (29) represent the *Wohl expressions of the third order* for the activity coefficients in a binary system and they show that these are function of the *three parameters A, B,* and q_1/q_2.

For the case of infinite dilution (∞) we obtain

$$A = \ln \gamma_1^\circ \qquad (30)$$

$$B = \ln \gamma_2^\circ \qquad (31)$$

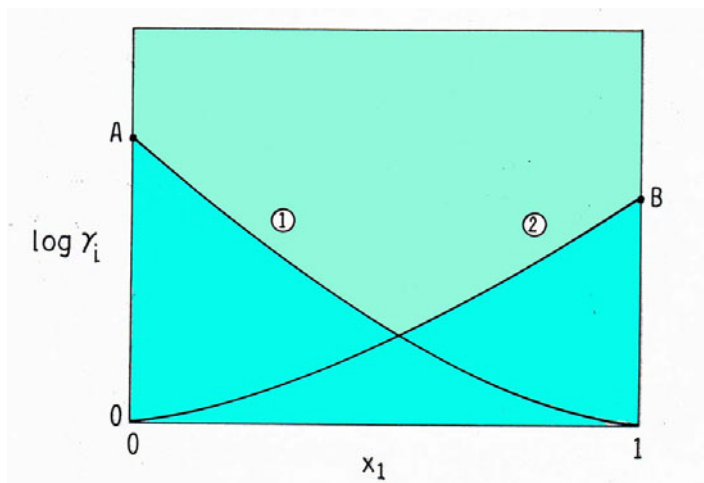which allow us to give a *macroscopic* interpretation to

Figure 1. Activity coefficients as a function of concentration.

the definition of *A* and *B,* stated by eqs (25) and (26). In addition to interaction between molecules (microscopic interpretation) the constants represent the limiting values of the activity coefficients.

To illustrate this point consider the shape of the curves $\gamma_i(x)$ for solutions that have a positive deviation form ideality given in Figure 1 (more than 90% of the known binary systems exhibit this kind of behavior). The shape of these curves will be restricted by the condition that the value of the activity coefficient of a component will change from *A* (or *B*) at infinite dilution, to unity as the component becomes more and more concentrated. In other words, parameter q_1/q_2 represents the "length" of the $\gamma_i(x)$ curves, that is, for the same values of parameters *A* and *B*, we can define a whole family of curves that start from γ_i° and end at $\gamma_i = 1$. Each of these curves will correspond to a different value of q_1/q_2. Parameter q_1/q_2 represents then, the *flexibility* of the model.

Calculation of the Wohl parameters for binary systems

Let us assume now that vapor liquid equilibria data at constant temperature or constant pressure are available for a given system. How can these be used to obtain the pertinent values of the activity coefficient? Unfortunately Wohl left this question unanswered for two very simple reasons: computers were not available at his time and two of the three parameters of his model appear multiplying each other (see eqs 28 and 29).

Today these two facts are not a problem and several procedures are available for answering the question.

Table 1. Wohl parameters for typical systems (Apelblat and Wisniak, 1989).

	A	**B**	$\dfrac{q_1}{q_2}$
benzene + heptane	0.4881	0.6587	1.12
butanol + chlorobenzene	0.6197	0.8260	2.47
1,2-dichloroethane + pentanol	0.6250	1.6003	0.25
diethylamine + methanol	–1.9507	–0.6104	0.89
ethyl acetate + propanol	0.7957	0.5705	0.40
hexane + benzene	0.6946	0.4724	1.00
methyl acetate + 2-propanol	0.8328	0.7627	0.67
methyl ethyl ketone + 2-propanol	0.4474	0.4500	0.29
2,2,4-trimethylpentane + toluene	0.4120	0.0087	0.41

1. Infinite dilution

Equations (28) and (29) can be used to determine parameters A and B by extrapolation of the $\gamma_i(x)$ curves to zero concentration, as illustrated in Figure 1. Although this procedure is in principle correct, in practice it does not work properly because the analytical methods available today are not accurate enough to justify the results of the extrapolation. The analytical methods become less and less accurate as dilution is increased so that the corresponding values of the activity coefficient carry a larger error than the activity coefficients calculated at a higher concentration. Possible future improvement of the analytical techniques may make this procedure viable.

2. Maximum value of g^E

An additional method for calculating the A, B, parameters is to take advantage of the fact that the curve $g^E(x)$ always has an extreme internal value at x^* and that at that particular concentration $\gamma_1 = \gamma_2$. In other words, besides eq (27) we have $\mathrm{d}(g^E/RT)/\mathrm{d}x_1 = 0$. These two conditions lead to the following relations

Table 2. Special cases of the Wohl model.

q_1 / q_2	$z(q_i)$	Model
v_1^l/v_2^l	$z(v_i^l)$	Scatchard-Hamer
1	$z_i = x_i$	Margules
A/B	$z_i = z_i$	Van Laar

$$\frac{A}{RT} = g_{\max} + 2g_{\max}\frac{x_1^*}{x_2^*} - g_{\max}\left(\frac{x_1^*}{x_2^*}\frac{q_1}{q_2}\right)^2 + g_{\max}\frac{q_1}{q_2} \quad (32)$$

$$\frac{B}{RT} = g_{\max} + 2g_{\max}\frac{x_1^*}{x_2^*} - g_{\max}\left(\frac{x_2^*}{x_1^*}\frac{q_2}{q_1}\right)^2 + g_{\max}\frac{q_2}{q_1} \quad (33)$$

where g_{max} is the extreme value of g^E/RT (Wisniak and Segura, 1995).

2. Optimization

The Wohl parameters may be determined using standard optimization techniques such as Simplex, maximum likelihood, etc., together with an objective function. In should be understood that the results produced by this method (mathematical roots) do not necessarily have a valid physical meaning consistent with the theory behind the model. What we are doing is forcing the parameters to comply with a certain mathematical restriction and that is all. In other words, the model may not have "physical roots" but it will be possible to find "mathematical roots" that will give a very good fit of the data. It is then up to the user to decide the kind of solution he desires.

Table 1 gives values of the Wohl parameters for some representative systems, which were obtained using the method proposed by Wisniak and Apelblat (1989).

We have indicated before that parameter represents the flexibility of the Wohl model. By making certain assumptions regarding its value the Wohl model may be transformed into other known models, as indicated in Table 2. With this assumption the number of parameters is reduced to two, namely A and B.

In table 2 v_i^l represents the molar liquid volume.

2.3 Liquid-liquid equilibrium and the Wohl model

How general is Wohl's equation for representing phase equilibrium? Wisniak and Segura have shown (Wisniak and Segura, 1995) that eq (27) is also capable of representing liquid-liquid equilibrium and have determined the range of values of the parameters for this situation. Their results have indicated that systems that are highly immiscible correspond to small values of the ratio q_1/q_2. In other words, we see that the latter ratio should be considered a highly flexible parameter that allows representation of many cases of vapor-liquid equilibrium and many immiscible systems.

2.4 Flames and combustion processes
(von Elbe, 1963)

The present state of knowledge about combustion processes makes it difficult to recall the rudimentary state of combustion science in the early 1920's when Wohl entered this field of research as a Ph.D. candidate. Some basic phenomena such as detonation waves and combustion waves had already been described but little was known about its possible impact on the growing technology of fuel utilization. Not only that, there was a widespread disbelief that it might be practically impossible to use thermodynamics and thermochemical methods to determine combustion gas parameters. Nernst, then director of the Physics Institute of the University of Berlin, had initiated an experimental study of the subject of determining explosion pressures under optimized conditions, i.e., a spherical vessel with central ignition. The basic equipment had been built by Mathias Pier (1882-1965). Wohl choose hydrogen and chlorine as his test mixture and after some brilliant theoretical and experimental work he was able to demonstrate an excellent correlation between theory and experiment, based on the calculation of dissociation equilibria (Wohl, 1924). The dissociation energy of chlorine at 0 K, then unknown, was found to be 57 ± 2 kcal·mol^{-1}, as compared to the now accepted value of 57.22 kcal·mol^{-1}; for hydrogen the dissociation energy was found to be about 100 kcal·mol^{-1}, as compared to the modern value of 103.2 kcal·mol^{-1}. The heat of dissociation of chlorine as a function of the temperature, at constant pressure, was given by Q (kcal·mol^{-1}) $= 57 + 2.978 \times 10^{-3} T - E_T$ where E_T is the energy of atomic vibration in the chlorine molecule, calculated as an Einstein function with 2.2 degrees of freedom and $\beta_v = 902$. The degree of dissociation of chlorine varied from 0.051% at 800 K to 86% at 2300 K, and for hydrogen from 0.16% at 1700 K to 3% at 2300 K.

Wohl also measured the mean value of the specific heat at constant volume of chlorine, hydrogen, and HCl and found that for chlorine it was 6.83 cal·mol^{-1} ($\pm 1.3\%$) between 291 and 1335 K, and that up to 2000 K it was given by $4.963 + (E_T - E_{291})/(T - 291)$ cal·mol^{-1}, where again E_T was the energy of atomic vibration in the chlorine molecule, calculated as an Einstein function with 2.2 degrees of freedom and $\beta_v = 902$. For hydrogen the specific heat at constant volume was $4.963 + (E_T - E_{291})/(T - 291)$ cal·mol^{-1}, calculated as an Einstein function with 2 degrees of freedom and $\beta_v = 3420$.

In a following work (Wohl and Kadow, 1925) reported that improved methods of calculation yielded that the specific heats at constant volume, of chlorine and HCl, were better represented by the equations $4.963 + (E_{Cl} - 93)/(T - 291)$ for chlorine ($\beta_v = 902$), and $4.963 + E_{HCl}/(T - 291)$ for HCl ($\beta_v = 3420$).

Wohl's results were a breakthrough in the knowledge of explosions and removed existing doubts and misconceptions of the thermochemical approach to the determination of flame gas parameters. His research in the field gave impetus to the accumulation of the large body of data and computational procedures, which eventually would make engine and rocket technology possible.

After moving to the University of Delaware Wohl renewed his interest in combustion phenomena and studied a wide range of flame stability conditions; the combined flow and mixing problems in laminar and turbulent jets of burning fuel gas; and the gradient structure of combustion waves. At Delaware, he determined a vast amount of experimental data on the transport properties of gases at temperatures in the range 1000 to 2000 K, which were important for testing the rigorous kinetic theory of dilute gases, without the occurrence of disturbing effects such as dissociation, excitation, or ionization. They also became important for the analysis of problems in gaseous reactions.

As stated by von Elbe, his former Ph.D. student, Wohl's contributions to the science of combustion are lasting and destined to enter into textbooks and handbooks for generations of scientists and engineers (von Elbe, 1963).

Conclusions

Wohl was a pioneer not only in combustion chemistry but also in many other fields. His broad interest, coupled to political events that took place in pre-war Germany led him to other areas such as thermodynamic of solutions and applications of thermodynamics to processes taking place in green plants. Many of his results continue to be actual and useful and have set the way to the development of important areas fuel for rockets and combustion engines.

Acknowledgment

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