François-Marie Raoult: Past and Modern Look

Jaime Wisniak

Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel 84105,
wisniak@bgumail.bgu.ac.il

Abstract: The academic and research career of Raoult is an example of success against the odds. He was born into a family of modest means and made his academic career far from Paris, the center of scientific power and means. He did his research on the behavior of solutions in general, and electrolytes in particular, before the concepts of molecular association, salt dissociation, and molecular structure had been established. In spite of this, by precise experimental work and brilliant intuition he made fundamental and everlasting contributions to thermodynamics. Raoult's results are discussed against the scientific background of his time and then reanalyzed using current thermodynamic ideas.

Life and Career

Very little is known about Raoult's life and scientific career, and most of it comes from the eulogy read by Jacobus Henricus van't Hoff (1852–1911, 1901 Nobel Prize in Chemistry) at the Chemical Society of London, on March 26, 1902, shortly after Raoult's death [1]. Some additional material is available in a short eulogy by Naumann [2] and a paper by Getman discussing Raoult's achievements in the area of cryoscopy [3].

François-Marie Raoult was born on March 10, 1830, in Fournes, in the north of France. After Raoult finished high school, his father initially got him a position with the tax authorities, planning that his son would eventually transfer to the *Bureaux de l'Enrégistrement*. Although Raoult did so, this type of activity did not satisfy his ambitions, and he persuaded his parents to let him go to Paris to pursue university studies. Without fortune or patronage, young Raoult was a student struggling for a livelihood, unable to finish his studies without himself providing the means [1]. Economic privation forced him to drop out of the university and to look for a job in the provinces. Not withstanding, in 1853, before withdrawing from the university and moving to Reims, he submitted to the *Académie des Sciences* a short communication [4] describing his experimental results on the transport of electrolytes by the action of a galvanic current as well as his findings on electroendosmosis. The closing remark of this communication illustrates the respect that Raoult would show all his life for other scientists: "I leave to others, more fortunate than me, to advance science along the road that I have just opened."

In 1853 Raoult accepted a position as *Aspirant répétiteur* in the Rheims Lycée, and afterwards he moved to the Collège of St. Dié as *Régent de physique*. He returned to Reims as *Professeur adjoint* and was promoted afterwards to *Chargé de cours de physique*. He then moved to the same position at the Collège of Bar-le-Duc. During his wanderings from one institution to another, he continued to study, and eventually, in 1860, he graduated as *Licencié ès-sciences physiques and Agrégé de l'Enseignement secondaire spécial*. In 1862 he left Bar-le-Duc for a corresponding position in Sens. In this small town, in spite of adverse material surroundings and forced to

construct his own equipment [1], he prepared his doctoral thesis, "*Sur les forces electromotrices des éléments voltaiques.*" In 1863 he defended his thesis and was granted the degree of *Docteur ès sciences physiques* from the University of Sorbonne in Paris. The thesis signals the initiation of a brilliant research career that would lead him to scientific leadership in several areas of chemistry and thermodynamics.

In 1867 Raoult accepted a position as *Chargé du cours de chimie* at the *Faculté des Sciences de Grenoble* where he would remain until his death in 1901. His scientific achievements at Grenoble earned him the chair of chemistry, as successor to Leroy.

Raoult was not fond of social life, and the quiet life of a small university town gave him the spiritual tranquility and the environment to work without distraction. In writing about Raoult, van't Hoff has pointed out that he "rarely left France, and for the larger part of his life, lived in that somewhat out-of-way town, Grenoble. Raoult's life thus offers little of attractiveness; it is not romantic; yet after many years of work, the romance was that almost sudden rise to fame, spreading from this nearly unknown corner, first over the frontier of his country, and then back to France, which made him one of the most prominent men of science of his age" [1].

Many honors and prizes were awarded to Raoult in France and abroad as a result of his scientific activities. In 1865 he was appointed *Officier d'Académie*, in 1872 *Officier de l'Instruction Publique*, and in 1872 he received the *Médaille des Societés Savantes*. In 1888 Raoult was awarded the *Prix International de Chimie La Caze* followed by the Davy Medal of the Royal Society (1891). In 1890 he become *Correspondent de l'Institut* and also honorary Fellow of the Society of Rotterdam. Similar honors were bestowed upon him by the Literary and Philosophical Society of Manchester (1892), the Chemical Society of London (1898), and the Academy of St. Petersburg (1899). In 1895 he received the *Prix de l'Institut du France,* and in 1900 he was appointed *Commandeur de la Légion d'Honneur*.

In 1887 van't Hoff asked Raoult to become a member of the editorial board of the journal *Zeitschrift für Physikalische Chemie* that he was publishing together with Wilhelm Ostwald

(1853–1932). Other members of the board were famous scientists such as Marcellin Berthelot (1827–1907), Henri Le Châtelier (1850–1936), Cato Guldberg (1836–1902), Peter Waage (1833–1900), Julius Thomsen (1826–1909), William Ramsay (1852–1916), and Dmitrii Mendelejev (1834–1907).

In 1887 Raoult resigned an additional professorship of chemistry and toxicology at the Grenoble Medical School, which he had held since 1873. In 1900 he reached the retirement age established at the University of Grenoble, but a special decision of the Board of Trustees allowed him to remain in office. Raoult passed away suddenly on April 1, 1901.

We will now analyze the scientific work of Raoult, first on the basis of the ideas prevalent at his time and then with modern thermodynamic concepts.

Raoult's Scientific Work—A General Outline

In his doctoral thesis on electromotive forces, Raoult used different galvanic cells of the Daniell type (John Daniell, 1790–1845) to measure the heat evolved by the chemical reaction and the electrical work produced. Contrary to prevailing opinion, he found that these two values were not necessarily equal. In the ordinary Daniell cell Cu|CuSO$_4$, ZnSO$_4$|Zn both effects amounted to about 23.6 cal/gram equivalent but in the analogous cell Cu|Cu(NO$_3$)$_2$, AgNO$_3$|Ag the reaction heat effect was 16.4 cal/gram equivalent, while the electrical work amounted to 7.8 cal/gram equivalent. He was unable to give a reason for the difference. In another part of his thesis he analyzed the decomposition caused by a galvanic current in a cell. He studied, in particular, the heat effect that accompanied these decompositions and explained them by the excess heat corresponding to the electrical work done by the cell over the heat absorbed by the chemical change. In doing so, he was applying the results found in the first part of his thesis. As a result, he was able to determine directly the heat absorbed by the chemical change that occurs in the cell. Using this procedure he found, for example, that 33.8 cal were required to decompose 9 g of water, a result that compared well with the value 34.5 cal available for formation of the same amount of water from its elements. In the publications that followed his thesis, he claimed that he had developed a reliable experimental method for measuring the heat effect that accompanies chemical reactions that occur under the influence of electric currents [5, 6].

In a subsequent work [7] Raoult summarized his findings by stating that in a galvanic cell, two processes took place. One process was related to changes in the state of aggregation, such as melting and dissolving, and the other process was related to chemical changes and changes in concentration. Only the latter were able to generate electromotive force. He demonstrated these conclusions by changing the state of aggregation of the electrode, for example using copper (or zinc) laminated, polished or unpolished, in powder form, etc. In every case he obtained the same electromotive force. He illustrated this point further by comparing two cells: in one the electrode was solid bismuth at its melting temperature, and in the other the electrode was saturated liquid bismuth.

In 1878 Raoult published his first work on freezing points, where he referred to the proportionality that exists between lowering of the freezing point, lowering of the vapor pressure, and rise of the boiling point in aqueous saline solutions [8].

According to his reasoning these effects must have a common cause because in the three cases the new phase is *pure* water (vapor or solid). He reported measurements for 18 different salts, and concluded that although the increase in boiling point or the depression of the freezing point varied considerably with the nature of the salt, a larger "atomic weight" corresponded to a smaller effect. In the following paper he reported data on the freezing point of aqueous–alcoholic solutions of different concentration (ethanol and various wines) [9]. He found that the lowering of the freezing point was proportional to the concentration of the alcohol, and thus extended to aqueous organic solutions what was known for inorganic solutions. As a practical consequence of his results, he concluded that it should be possible to strengthen a wine by freezing out part of the water. In a following work he reported the lowering of the freezing point of many aqueous organic solutions containing alcohols, sugars, acids, ethers, and other substances such as phenol, chloral, urea, acetamide, and ammonia. He summarized his results by stating that the product of the lowering of the freezing point (caused by one gram of solute in 100 grams of solvent) by the molecular weight of the solute was essentially constant (between 17 and 20) [10]. From this he inferred that the lowering of the freezing point could be used as a measure of the purity of the solvent and to determine the *molecular weight* of the solute, particularly for those solutes where it is not possible to determine the density in the vapor phase. (The reader should remember that determination of molecular weights using Avogadro's hypothesis is based on the density of the vapor.)

The next obvious steps were to show that his conclusion was valid also for solvents different from water [11,12] and to see how it fared with acids, bases, and salts. His preliminary results indicated that strong acids and bases dissolved in water showed a normal decrease in the freezing point, but that for weak acids and bases the decrease was one half of the expected value [13].

By studying families of compounds in the order of the valence of their metals and the basicity of their acids, Raoult reached the unexpected result that the molecular depression of salts, strong acids, and bases could be calculated by the summation of numbers related to their radicals, as follows [14]

Univalent negative radicals	(Cl, Br, OH, NO$_3$)	20
Bivalent negative radicals	(SO$_4$, CrO$_4$, CO$_3$)	11
Univalent positive radicals	(H, K, Na, NH$_4$)	15
Bi- and polyvalent positive radicals	(Ba, Mg, Al$_2$)	8

Applying this method of calculation we get, for example,

HCl: 15 + 20 = 35, instead of 36.7 found
K$_2$SO$_4$: 15 × 2 + 11 = 41, instead of 39 found.

From this result he concluded that the general law of freezing-point depressions was not applicable to salts dissolved in water; it truly applied to the radicals that constitute these salts, as if these radicals were actually mixed in the solution. (See Arrhenius discussion below.) An application of these results was made in deciding whether a double salt existed in solution as such, or split into its components, the former being the case of sodium chloroplatinate, and the latter, the alums [15].

Raoult's work on cryoscopy took place simultaneously with that of Victor Meyer (1848–1897) in Germany, and Emanuele Paternò (1847–1935) in Italy. After that came the theory of solutions developed by Svante Arrhenius (1859–1927, 1903 Nobel Prize in Chemistry) in Sweden and by van't Hoff in The Netherlands.

Lowering of the Vapor Pressure—Raoult's Law. In 1892 Raoult began addressing his freezing point investigations to the theory of solutions. At the beginning, he considered the molecular constant 18.5 found for many organic compounds in aqueous solutions to be abnormal, and assumed 37 to be the normal value, thus considering organic compounds to be present in the form of "double molecules." It was natural to determine, from this point of view, whether extreme dilution would not break down those double molecules and consequently double the molecular constants. As had already been proved by Adolph Wüllner (1835–1908), Raoult found that for dilute solutions there was a proportionality between the lowering of the vapor pressure $(P - P^0)$ and the pressure P^0 and that the relative lowering $(P - P^0)/P^0$ was independent of the temperature [16, 17]. In the opening statement of the second paper he claimed that the relative reduction in pressure produced by one *molecule* of a substance dissolved in 100 grams of a volatile liquid could be calculated according to the following expression

$$K = M_1 \frac{P - P_2^0}{w_1 P_2^0}$$

(1)

where P_2^0 is the vapor pressure of the pure solvent, P is the vapor pressure of the solution, M_1 the molecular weight of the solute, and w_1 the weight of solute dissolved in 100 grams of solvent. He then justified this claim by reporting the measurements of K for 12 different liquid solvents—among them water, carbon disulfide, carbon tetrachloride, benzene, acetone, and methanol. For the aqueous solutions he used only organic solutes (sugar, glucose, tartaric acid, citric acid, and urea) because experimental results with inorganic substances had already been reported. Raoult presented his results in a table listing the molecular weight of the solvent (M_2), the reduction of vapor pressure caused by one molecule of solute in 100 molecules of solvent (K), and the value of the ratio K/M_2. He observed that although values of K and M_2 for the solvents used vary almost onefold, the ratio K/M_2 varied very little from the value 0.0105. Using these results, he made the bold generalization that one molecule of a nonsaline substance dissolved in 100 molecules of *any* volatile liquid decreased the vapor pressure of the liquid by the nearly constant fraction of 0.00105, that is

$$\frac{K}{M_2} = 0.0105$$

(2)

An interesting point is that Raoult used the term *molecule* instead of *mole*, a concept that was to become established a long time after Avogadro had proposed in 1811 his hypothesis: equal volumes = equal number of molecules. Actually, the unit *mole* was first introduced into chemistry in 1900 in a book published by Wolfgang Ostwald (1883–1943). In his book

[18] Ostwald defined the mole as the molecular weight of a substance expressed in grams.

An additional important point is that Raoult expressed the concentration of the solution as molecules per 100 grams of solvent, a ratio that, of course, is proportional to the molar ratio n_2/n_1. Raoult also pointed out that the number 0.0105 is approximate. Today we can understand this statement from the fact that $n_2/n_1 = x_2/(1 - x_2)$ so that n_2/n_1 will become equal to the mole fraction x_2 only for very dilute solutions. In this situation, equation (1) will take the form of Raoult's law, as currently stated.

A year later Raoult reported [19] that equation (1) could be applied also to salts such as sodium chlorate, potassium acetate, sodium acetate, lithium chloride, lithium bromide, potassium thiocyanate, calcium nitrate, calcium chloride, and mercuric chloride, at least in alcoholic solution, in which they behave as nonelectrolytes. He remarked that in aqueous solutions these salts "behave as if they are decomposed in their ions." Raoult used the terms *ion* and *electrolyte* that Michael Faraday (1791–1867) [20] had coined and defined in 1834 (see below).

Additional experimental measurements using acids such as acetic and formic acids as solvents lead Raoult to change the value of the ratio K/M_2 from 0.0105 to 0.0161. Raoult attributed this discrepancy to the abnormal vapor density of acetic acid. It was already known that the vapor density of acetic acid exceeded the "normal" value by about 60%, although it was not recognized that this anomaly is caused by dimerization of the acid.

Raoult closed his paper by indicating that the phenomenon of the lowering of the vapor pressure was completely analogous to the lowering of the freezing points of solvents, which he had already described. An example of Raoult's sharp scientific intuition comes from his final statement that most of the anomalies can be explained by admitting that in certain liquids, *the dissolved molecules can be formed from two chemical molecules*.

Additional experimental work with anomalous substances led Raoult to change the expression given by equation (1) to the more general form [21]

$$\frac{P - P_2^0}{P_2^0} \frac{100}{w_1} \frac{M_1}{M_2} = \frac{d'}{d}$$

(3)

or

$$\frac{K}{M_2} = 0.01 \frac{d'}{d}$$

(4)

where d' is now the observed (experimental) density of the saturated vapor and d is that calculated (apparent density) from M_2.

We can summarize Raoult's research results by stating that excellent experimental work coupled with brilliant intuition led him to formulate the following generalizations related to the behavior of dilute solutions:

1. At a given temperature, the vapor pressure of a solution composed of a volatile solvent and a nonvolatile solute is less than the vapor pressure of the pure solvent. The vapor pressure of the solvent is proportional to its mole fraction, but the

decrease in vapor pressure is proportional to the mole fraction of the *solute*.

2. When a small amount of nonvolatile solute is added to a solvent, the boiling point of the solution is higher than that of the pure solvent at the same pressure. The *increase* in boiling point is proportional to the mole fraction of the *solute*.

3. When a small amount of solute is added to a solvent, the freezing point of the solution is lower than that of the pure solvent, as long as the solute does not crystallize. The *decrease* of the freezing point is proportional to the mole fraction of the *solute*.

Scientific Contribution—Modern View

Today, to the student of thermodynamics or physical chemistry, Raoult's results seem obvious but their significance must be judged against the state of science during his lifetime. We will first describe the ideas that were prevalent in the 19th century concerning the structure of matter and the theory of solutions and electrolytes, and then we will show how Raoult's findings can be explained using modern thermodynamic concepts.

A. Atomic Theory. What was the status of the atomic theory by the mid-1800s? The idea that matter is composed of atoms goes back to the Greek philosophers, particularly Democritus (460–370 BCE). By the end of the 18th century, many experimenters were already accepting the idea that every chemical compound contains fixed and constant proportions (by weight) of its constituent elements (the law of definite proportions). John Dalton (1766–1844) converted the atomic Greek philosophy into a scientific theory and applied it for the first time to chemistry. According to Dalton the elements are composed of atoms that are indestructible, atoms of different elements differ in their masses, and a compound is a characteristic grouping of atoms. In his reasoning Dalton made the faulty assumptions that the molecules of an element are always *single atoms* and that hydrogen and oxygen would combine to form HO (instead of H_2O).

By the middle of the 19th century the conflicting opinions on the structure of matter and the indivisibility of molecules had resulted in a chaotic situation regarding chemical notation. For example, Jöns Jacob Berzelius (1779–1848) and his followers used the general formula MO for the chief metallic oxides, while others assigned the formula used today, M_2O. A single formula stood for different substances, depending on the chemist: H_2O_2 was water or hydrogen peroxide; C_2H_4 was marsh gas (methane) or ethylene, and so on.

The First International Congress of Chemists was convened in 1860 in Karlsruhe, Germany to try to solve this and other problems. The first session of the Congress debated the notions of molecule and atom, with Stanislao Cannizzaro (1826–1910) and August Kekulé (1829–1896) as the main speakers. Cannizzaro repeated the arguments he had published two years before [22], offering for the first time in the history of the physical sciences a very clear definition of atoms as distinguished from molecules. To him the atom was the "smallest quantity of each element that enters as a whole into the molecules that contain it," and to determine this quantity one must know the weights of all or most of such molecules and their composition.

The existence of molecules continued to remain in question until 1910 when the results of Jean Perrin (1870–1942; 1926

Nobel Prize in Physics) about Brownian motion were made known [23].

B. Electrochemistry. Alessandro Volta (1745–1827) is generally credited with having developed the first operable battery. Following up on earlier work by Luigi Galvani (1737–1798) on the effects of electricity on animal tissue, Volta performed experiments on electrochemical phenomena that by about 1800 led him to build a simple battery, to be known later as the *voltaic pile*. This device consisted of alternating zinc and silver disks separated by layers of paper or cloth soaked in a solution of either sodium hydroxide or brine. When the silver and the zinc were joined with a wire, electricity flowed continuously through the wire. The term *volt*, a unit of electrical measurement, is named in Volta's honor.

Volta's first experimental results on electrochemical phenomena led to a lively discussion in the scientific community as to whether the electrical current observed was caused by *animal electricity* (as suggested by Galvani) or *chemical electricity* (as claimed by Volta). Galvani's views were supported by Alexander von Humboldt (1769–1859) in Germany, while those of Volta were backed by Charles Coulomb (1736–1806) and other French physicists. Construction of the voltaic pile settled the argument in favor of Volta. Within six weeks of Volta's report, William Nicholson (1753–1815) and Anthony Carlisle (1768–1840) used a chemical battery to discover *electrolysis*. the process in which an electric current produces a chemical reaction, and initiate the science of electrochemistry. In their experiment these two scientists employed a voltaic pile to liberate hydrogen and oxygen from water.

Faraday's experiments performed with the voltaic pile led to his epoch-making paper [20] in which he introduced the terms *electrode*, *anode*, *cathode*, *ion*, *anion* (that which goes up), *cation* (that which goes down), and *electrolyte*, and derived the quantitative laws of electrochemistry. The fundamental relationship of electrochemical cell operation put forth by Faraday is that for every ampere that flows for a period of time, a matching chemical reaction or other change must take place. The extent of these changes is dependent on the molecular and electronic structure of the elements comprising the battery electrodes and electrolyte. When explaining the concepts of anion and cation, Faraday spoke of "bodies" that are evolved at the cathode or the anode.

Today we express Faraday's laws by saying that (a) one chemical *equivalent* of each electrolyte produces one *faraday*, or 96,485 coulombs of charge equal to 26.8 ampere•hours, and (b) the quantities of different elements deposited by a given amount of electricity are in the ratio of their chemical equivalent weights. We also express the electrical work ΔG^0 by the relation $\Delta G^0 = -nF\Delta E^0$, where n is the number of electrons in the balanced chemical equation, F is the Faraday, and ΔE^0 is the standard electromotive force of the cell. Alternatively, we say that one joule of energy is produced when one coulomb of electrical charge is transported across a potential difference of one volt. The sign of ΔG^0 identifies the type of cell: it is negative for a galvanic cell (spontaneous process) and it is positive for an electrolytic cell (nonspontaneous). In addition, we have

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (5)$$

Equation (5) indicates that, in general, the value of ΔG^0 will be different from that of ΔH^0, depending on the value of ΔS^0 for the particular cell reaction (as observed by Raoult, without being able to explain it).

In the case of a chemically generated electromotive force, chemical reactions release energy. If these reactions take place with chemicals in proximity to each other (e.g., if they mix), the energy released *heats* the mixture. To produce a voltaic cell, these reactions must occur in separate locations. In the Daniell cell (invented in 1836), a copper wire is placed in a solution of copper sulfate and a zinc wire in a solution of zinc sulfate. Energy is gained when copper ions from the copper sulfate solution are deposited on the copper electrode as neutral copper atoms, thus removing free electrons from the copper wire. At the same time zinc atoms from the zinc wire go into solution as positively charged zinc ions, leaving the zinc wire with excess free electrons. The two reactions are separated physically, with a salt bridge completing the internal circuit:

$$Zn \rightleftharpoons Zn^{2+} + 2e^-$$

$$\frac{Cu^{2+} + 2e^- \rightleftharpoons Cu}{Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu}$$
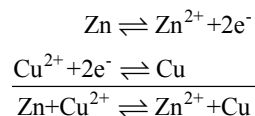
Each of the above reactions is called a half-cell reaction because it represents what happens at the particular electrode. Common practice today is to call *cathode* the electrode where reduction takes place and *anode* that where oxidation takes place. In addition, in the shorthand notation for a cell the cathode is usually written on the left side. Thus a Daniell cell is represented $Cu|CuSO_4, ZnSO_4|Zn$, and the anode corresponds to the reaction $Zn \Leftrightarrow Zn^{2+} + 2e^-$. Extensive data are available today for calculating the different thermodynamic parameters of a particular cell [24, 25].

Let us now analyze Raoult's results on the basis of modern electrochemical ideas.

1. The Daniell Cell. If the two reactions take place at 298.15 K, then for the overall reaction we have $\Delta E^0 = +1.10$ volt, $\Delta G^0 = -106.14$ kJ/gram equivalent (–25.39 kcal/gram equivalent), and $\Delta H^0 = -109.27$ kJ/gram equivalent (–26.10 kcal/gram equivalent) [25]. The first term represents the electromotive force developed by the cell, the second the change in the Gibbs energy caused by the reaction, and the third the heat effect of the same. From these figures we see that for the Daniell cell, the values of ΔG^0 and ΔH^0 are very similar, as claimed by Raoult and others.

2 The Copper–Silver Cell. The cell is $Cu|Cu(NO_3)_2$, $AgNO_3|Ag$. In this case

$$Cu^{2+} + 2e^- \rightleftharpoons Cu$$

$$\frac{2Ag \rightleftharpoons 2Ag^+ + 2e^-}{Cu^{2+} + 2Ag \rightleftharpoons Cu + 2Ag^+}$$
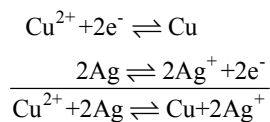
and at 298.15 K, $\Delta E^0 = -0.459$ volt, $\Delta G^0 = 44.33$ kJ/gram equivalent (10.59 kcal/gram equivalent), and $\Delta H^0 = 20.47$ kJ/gram equivalent (4.89 kcal/gram equivalent) [25]. Hence, for the copper–silver cell the values of ΔG^0 and ΔH^0 are very different, as claimed by Raoult against the accepted idea at his time.

3 Electrolysis of Water. The overall nonspontaneous reaction is

$$H_2O \rightleftharpoons H_2 + \tfrac{1}{2}O_2$$
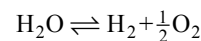
At 298.15 K, $\Delta E^0 = -1.23$ volt, $\Delta G^0 = 118.84$ kJ/gram equivalent (28.36 kcal/gram equivalent), and $\Delta H^0 = 34.15$ kcal/gram equivalent [25]. We can see that the present value for ΔH^0 agrees closely with the value of 33.8 kcal/gram equivalent reported by Raoult.

C. Electrolyte Solutions. It took another 24 years after the Karlsruhe Conference for Svante Arrhenius to complete and defend at the University of Uppsala his doctoral thesis containing, in embryo, the dissociation theory. According to Arrhenius, electrolytes are separated, or dissociated, into electrically charged particles or ions, even when there is no current flowing through the solution. Acids are defined as substances that dissociate in water to yield electrically charged atoms or molecules, called ions, one of which is a hydrogen ion (H^+). Similarly, bases ionize in water to yield hydroxide ions (OH^-). The reaction between an acid and a base leads to the formation of a salt and water; the latter is the result of the combination of a hydrogen ion and a hydroxide ion. Arrhenius' theory received strong support from electrical measurements and from molecular weight studies (freezing point depression, boiling point elevation, and osmotic pressure) carried out by Raoult and others that showed that the number of solute particles was larger than it would be if no dissociation occurred. For example, a 0.001 molal solution of a univalent–univalent electrolyte such as sodium chloride, Na^+Cl^-, exhibits *colligative* properties corresponding to a nonelectrolyte solution whose molality is 0.002; the colligative properties of a 0.001 molal solution of a univalent–divalent electrolyte such as magnesium bromide, $MgBr_2$, correspond to those of a nonelectrolyte solution with a molality of 0.003.

Let us apply these ideas to Raoult's findings. According to Raoult the three properties of a solution, lowering of the vapor pressure, elevation of the boiling point, and lowering of the freezing point, depend on the nature of the solvent and the mole fraction of the solution, but not on the identity of the solute. Today, we use the term *colligative property* to describe a property of a substance that depends on the number of particles present, but not on their nature. Colligative properties provide a powerful tool for determining the molecular weight of the solute. When applied to solutions of electrolytes, they provide a mean for determining the number of solute particles (ions) and thus serve to validate and illustrate Arrhenius' theory of electrolytic dissociation.

Osmotic pressure is also a colligative property, and although Raoult performed some osmotic pressure measurements [26], it was van't Hoff who suggested the equation that described the phenomenon.

Let us now use all the above information to discuss Raoult's findings.

1. Raoult's Law. First, let us describe qualitatively what happens at the surface of a pure solvent and at the surface of a solution composed of the solvent and a nonvolatile substance like sodium chloride. Consider the situation illustrated in Figure 1. Two closed vessels A and B are located inside a constant temperature bath. Vessel A contains pure solvent *1* and vessel B a solution of *1* and a nonvolatile salt *2*. The
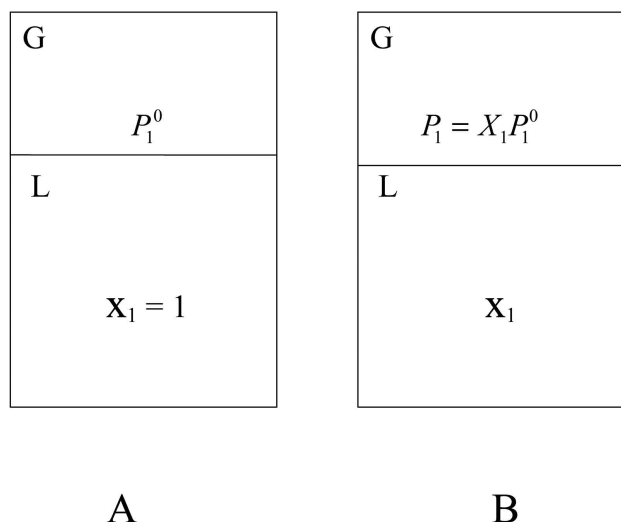
Figure 1. Two vessels used to illustrate Raoult's Law.

conditions are such that a liquid (L) and vapor phase (G) are present. For both vessels to be in thermal equilibrium, it is necessary that their internal pressures be different. According to the kinetic theory of gases, pressure is interpreted as the number of collisions occurring per unit surface and unit time. Consider a molecule moving from the bulk of the liquid in the direction of the surface. What happens to the molecule when it reaches the surface will depend on its angle of approach and kinetic energy. Molecules having the proper value of both parameters will be able to leave the liquid and become part of the vapor space. The situation in the vapor phase is similar. Every so often molecules in the vapor phase will collide with the surface of the liquid and again, if they have the proper kinetic energy and angle of impact, they will return to the liquid. In the case of a pure liquid, the surface available for leaving the liquid is exactly the same as the surface available for returning to it, hence the equilibrium pressure at a given temperature will be exactly equal to the vapor pressure $\left(P_1^0\right)$. This is not the situation for the surface of a liquid solution. Since it is composed of solvent *and* solute molecules, the former are able to escape only from the part of the surface where they are present. If the solution is ideal (no interaction between the solvent and the solute), the fraction of surface available for evaporation will be proportional to the mole fraction of the solvent (x_1). On the other hand, the molecules of the solvent present in the vapor phase having a partial pressure P_1 can return to the liquid through the entire exposed surface. At equilibrium the escape tendency and the tendency to return are equal, thus

$$P_1 = x_1 P_1^0 \tag{6}$$

which is Raoult's law.

The concept of chemical potential can be used to develop Raoult's law in a more fundamental way. Consider again Figure 1: for each vessel the condition for thermodynamic equilibrium is that the chemical potential of the solvent be the same in each of the phases present in the vessel

$$\mu_{1,A}^{L,0} = \mu_{1,A}^{G,0} \quad \left(T, P_1^0\right) \tag{7}$$

$$\mu_{1,B}^{L} = \mu_{1,B}^{G} \quad (T,P) \tag{8}$$

where the superscript *0* indicates pure material. For vessel B we can write [27]

$$\mu_{1,B}^{L} = \mu_{1,B}^{G} = \mu_{1,B}^{L,0}(T,P) + RT\ln \hat{a}_{1,B} \tag{9}$$

where $\hat{a}_1$ is the activity of component *1* in solution. By definition $\hat{a}_1 = \hat{f}_1/f_1^0$ where $\hat{f}_1$ is the fugacity of component *1* in the solution and f_1^0 is the fugacity of the pure component in the standard state. Now, let us calculate the difference between the chemical potentials of component *1* in the vapor phase of both vessels, that is, $\left(\mu_{1,B}^{G} - \mu_{1,A}^{G,0}\right)$. From Maxwell's relations we have, for ideal gas behavior [27],

$$d\mu_1^G = RTd\ln P \tag{10}$$

Integration of equation (10) for an isothermal process yields

$$\mu_{1,B}^{G}(T,P) - \mu_{1,A}^{G,0}\left(T,P_1^0\right) = RT\ln\frac{P}{P_1^0} \tag{11}$$

Replacing equations (9) and (11) in equation (8), we get

$$\mu_{1,B}^{L,0}(T,P_1^0) + RT\ln \hat{a}_1 = \mu_{1,B}^{G,0}(T,P_1^0) + RT\ln\frac{P}{P_1^0} \tag{12}$$

or

$$\mu_{1,A}^{G,0}(T,P_1^0) - \mu_{1,B}^{L,0}(T,P) = RT\ln \hat{a}_1 - RT\ln\frac{P}{P_1^0} \tag{13}$$

Using equation (7)

$$\mu_{1,B}^{L,0}(T,P_1^0) - \mu_{1,B}^{L,0}(T,P) = RT\ln \hat{a}_1 - RT\ln\frac{P}{P_1^0} \tag{14}$$

The left hand side of equation (14) represents the change in the chemical potential of pure liquid component 1 between the states (T, P_1^0) and (T,P). This change is given by

$$\mu_{1,B}^{L,0}(T,P) - \mu_{1,A}^{L,0}(T,P_1^0) = RT\ln\frac{f_1(T,P_1^0)}{f_1(T,P)} \tag{15}$$

Since the liquid may be considered incompressible, the difference given by the right hand side of equation (15) is extremely small or nil. Hence equation (14) leads to

$$P = \hat{a}_1 P_1^0 \qquad (16)$$

Equation (16) represents Raoult's law *in terms of activities* (real solution). If the liquid phase behaves ideally then $\gamma_1 = 1$ and $\hat{a}_1 = x_1$, so that

$$P = x_1 P_1^0 \qquad (17)$$

which is Raoult's law for ideal solutions.

B. Molecular Weight of Compounds that Associate in the Gas Phase. Many years ago it was suggested that nonideal behavior of gases may be attributed to the formation of different chemical species. For example, in a pure gas consisting of component A, various equilibria may be postulated:

$$2A \leftrightarrow A_2 \quad \text{(dimerization)} \qquad (18)$$

$$3A \leftrightarrow A_3 \quad \text{(trimerization)} \qquad (19)$$
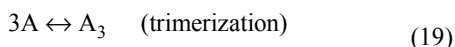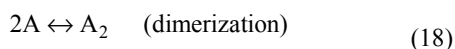
The equilibrium constant for dimerization reflects the interaction of two molecules at a time, and therefore a relationship can be established between this constant and the second virial coefficient. Similarly, the trimerization equilibrium constant is related to the third virial coefficient, and so on. Regardless of the degree of association, this chemical viewpoint considers the forces between molecules to be chemical rather than physical (van der Waals forces). The chemical viewpoint is particularly appropriate to describe those systems in which strong forces of attraction exist between molecules, such as hydrogen bond formation. To illustrate the argument, let us consider the dimerization of acetic acid, as given by equation (18). Assuming that α is the fraction of molecules that dimerize, the thermodynamic equilibrium constant is

$$K = \frac{(\alpha/2)(1-\alpha/2)}{(1-\alpha)^2 P} \qquad (20)$$

Many authors have analyzed the state of association of acetic acid in the vapor phase [28–31]. Although there is general agreement that the dimer is the predominant species, it is still not clear whether the next-most-prevalent species is a trimer [28] or a tetramer [29]. Nevertheless, there is substantive experimental evidence that the molecular weight of acetic acid varies from about 67 at high temperatures and pressures (477 K, 108.4 kPa) to about 105.7 at low temperatures and pressures (324 K, 6 kPa) [29]. The dimerization constant of carboxylic acids in the gaseous phase has been measured experimentally by Taylor [30]. For acetic acid the values of the constant indicate that dimerization is very strong, even at low pressures. For example, at 313.15 K and 1.6 kPa, acetic acid is 80% dimerized, while at the normal boiling point (391.1 K, 101.325 kPa) it is 84.2% dimerized. We see then that Raoult was correct in attributing the discrepancy of his results for the lowering of the vapor pressure of acids like acetic and formic, to their abnormal vapor density.

3. Elevation of the Boiling Point by a Nonvolatile Solute. Consider again the situation that is described in Figure 1. For vessel *B*, the condition of equilibrium is given by equation (8). If the solvent behaves according to Raoult's law, then its activity coefficient is 1, and its chemical potential is given by

$$\mu_{I,B}^L = \mu_{I,B}^{L,0}(P,T) + RT\ln\hat{a}_{1,B} = \mu_{I,B}^{L,0}(P,T) + RT\ln x_1 \qquad (21)$$

Using the result of equation (8) and rearranging yields

$$\frac{\mu_{1,B}^G}{T} - \frac{\mu_{1,B}^{L,0}}{T} = R\ln x_1 \qquad (22)$$

Differentiating with respect to the temperature, at constant pressure gives

$$\left[\frac{\partial \mu_{1,B}^G}{\partial T} - \frac{\partial \mu_{1,B}^{L,0}}{\partial T}\right]_P = R\left[\frac{\partial \ln x_1}{\partial T}\right]_P \qquad (23)$$

But [27]

$$\left(\frac{\partial \mu_1/T}{\partial T}\right)_P = -\frac{\overline{H}_1}{T^2} \qquad (24)$$

where $\overline{H}_1$ is the partial molar enthalpy of component *I* in the solution. In other words, equation (23) becomes

$$-\frac{\overline{H}_{1,B}^G - \overline{H}_{1,B}^L}{T^2} = R\ln x_1 \qquad (25)$$

The numerator of the left hand side represents the partial molar heat of vaporization of the solvent, $(\Delta\overline{H}_{\text{vap}})_1$, so that

$$\left(\frac{\partial \ln x_1}{\partial T}\right)_P = -\frac{(\Delta\overline{H}_{\text{vap}})_1}{RT^2} \qquad (26)$$

In a small range of temperatures (for example, for dilute solutions), the value of $\Delta\overline{H}_{1,\text{vap}}$ may be considered independent of temperature and equation (26) can be integrated from the boiling point of the solvent, T_1^0, to the boiling point of the solution with concentration x_1, to get

$$-\ln x_1 = \frac{(\Delta\overline{H}_{\text{vap}})_1 \Delta T_b}{RTT_1^0} \qquad (27)$$

For a dilute solution the difference between T and T_1^0 is small and TT_1^0 can be replaced by $\left(T_1^0\right)^2$ to give finally,

$$-\ln x_1 \cong \frac{\left(\Delta\overline{H}_{vap}\right)_1 \Delta T_b}{R\left(T_1^0\right)^2} \tag{28}$$

or

$$-\ln\left(1-x_2\right) \cong \frac{\left(\Delta\overline{H}_{vap}\right)_1 \Delta T_b}{R\left(T_1^0\right)^2} \tag{29}$$

where ΔT_b represents the elevation of the boiling point caused by a nonvolatile solute present at concentration x_1.

Equation (29) can be easily extended to *real* solutions if we consider that as the concentration of the solvent increases, the behavior of the solution concerning it becomes more and more ideal. If the concentration of the *solute* is low enough, we can expand the logarithm term on a Taylor series to get

$$\ln\left(1-x_2\right) = -x_2 - \frac{x_2^2}{2} - \frac{x_2^3}{3} - \ \ldots\ldots$$

so that equation (28) becomes, finally

$$\Delta T_b = \frac{R\left(T_1^0\right)^2}{\left(\Delta\overline{H}_{vap}\right)_1} \tag{30}$$

All the terms on the right hand side of equation (30) are positive, hence addition of a nonvolatile solute will increase the boiling point of the pure solvent. If the solution is dilute enough, the increase will be proportional to the mole fraction of the *solute*.

Although equation (30) can be used as such, it is more common to express the concentration as moles of solute per 1000 grams of solvent (m)

$$x_2 = \frac{m}{1000/M_1 + m} \tag{31}$$

where M_1 is the molecular weight of the solvent. Hence

$$\Delta T_b = \left[\frac{R\left(T_1^0\right)^2 M_1}{1000\Delta\overline{H}_{vap,1}}\right]m = K_b m \tag{32}$$

$$K_b = \frac{R\left(T_1^0\right)^2}{n_1\left(\Delta\overline{H}_{vap}\right)_1} \tag{33}$$

In equation (33) K_b is the *molal boiling point* (or *ebullioscopic constant)* of the solvent, and n_1 is the number of moles of solvent in 1000 grams of solvent.

4. Lowering of the freezing point. Just as a solution has a higher boiling point than the pure solvent, so it has a lower freezing point, provided that no solute separates in the solid phase. Clearly then, the above thermodynamic analysis can be applied to the case of the lowering of the freezing point of a pure solvent caused by the addition of a small amount of a solute. The only thing to do is replace the heat of vaporization of the solvent by its heat of fusion, and the boiling temperatures by the pertinent fusion temperatures. Equations (32) and (33) become

$$\Delta T_f = \left[\frac{R\left(T_1^0\right)^2 M_1}{1000\Delta\overline{H}_{f,1}}\right]m = K_f m \tag{34}$$

$$K_f = \frac{R\left(T_1^0\right)^2}{n_1\Delta\overline{H}_{f,1}} \tag{35}$$

where subscript f represents fusion. In equation (35) K_f is the *freezing-point-depression (cryoscopic) constant* of the solvent and n_1 the number of moles of solvent in 1000 grams of solvent. It should be clear that equation (34) describes only the lowering of the freezing point of a very dilute solution in equilibrium with *pure, solid solvent*. Also, it describes the variation with composition of the freezing point of a dilute solution, whether it behaves ideally or not at higher concentrations. In addition, the freezing point depression constant K_f is clearly a function only of the solvent.

Although equations (33) and (35) have the same structure, for a given solvent the cryoscopic constant is usually much larger than the ebullioscopic one. Both constants carry the change of entropy ($\Delta H/T_1^0$) of the phase transformation. The increase in disorder when going from the liquid state to the vapor state is much larger than the one that occurs on going from the liquid state to the solid one. For this reason the cryoscopic method for determining molecular weight is more precise than the ebullioscopic one.

Conclusion

Like Avogadro and Duhem, Raoult made his academic career far from Paris, the center of scientific power and means. His research on the behavior of solutions in general, and electrolytes in particular, was performed before the concepts of molecular association, salt dissociation, and molecular structure had been established. In spite of this, precise experimental work and brilliant intuition, without the help of mathematical tools, led to fundamental and everlasting contributions to thermodynamics.

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