Johannes Jacobus Van Laar Unappreciated Scientist

Jaime Wisniak

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

Abstract: Van Laar's academic and research career was adversely affected by psychological traumas he experienced during his youth. Loss of his parents at a young age, submission to a hard discipline, and lack of a formal university education made van Laar emotionally unstable and gave him many enemies, among them van der Waals. Still, Van Laar's scientific achievements have resulted in the transformation of mathematical chemistry into the independent subjects known today as chemical thermodynamics and theory of phase equilibria. Discussed here as well is Van Laar's theory of solutions using the state of thermodynamics at his time and modern thermodynamic concepts.

Life and Career [1, 2]

Johannes Jacobus van Laar (Figure 1) was born in The Hague on July 11, 1860, the son of Johannes Jacobus van Laar, a veterinary surgeon in the Royal Armed Forces, and Johanna Rost van Tonningen. Van Laar lost his parents when he was very young; his mother passed away in 1862 and his father in 1873.

After the death of his mother, the family moved to Haarlem where young van Laar finished elementary school and attended the Hoogere Burgerschool (secondary school). After the death of his father, an uncle, N. A. Rost van Tonningen, ex-Governor of the Dutch caribbean island of St. Eustatius, was appointed van Laar's guardian. Van Tonningen decided that the young man was to become a naval officer, and so, in 1876 after finishing tenth grade, he was sent to the Koninklijk Instituut voor de Marine (Royal Naval Institute) at Willemsoord.

During his stay at the institute, he was promoted first to naval cadet and then to sub-lieutenant. From 1879 to 1881 he served as crew member on several steamships and traveled widely abroad. Before his last trip to the Dutch Indies he visited with Professor Jacobus Henricus van't Hoff (1852–1911, 1901 Nobel Prize in Chemistry) and requested his advise on what subjects he should study to take the kandidaatsexamen (comparable to a B.Sc. examination). Van't Hoff's recommendation was to learn and thoroughly know the classical textbooks Lehrbuch der Experimentalphysik by Adolph Wüllner (1835–1908) and Anorganische Chemie and Organische Chemie by Jeremias Richter (1762–1807). Once van Laar became of age and was no longer under the authority of his guardian, he requested and was granted, an honorable discharge from the Navy.

From the time of his discharge from the Navy until his death, van Laar's life was characterized by a nonfraternizing attitude, defiance of established social and academic codes, and mental breakdowns that eventually would lead to his early retirement from academic life. It is very plausible that these negative characteristics were a result of being orphaned very young and coming under the authority of a rigid guardian, which would force him into the even more rigid discipline of the Navy and a career he disliked. His naval training put him at a distinct disadvantage because it did not allow him to take academic examinations and develop his scientific career in the usual way. Nevertheless, while in the Navy, he acquired solid comprehensive mathematical skills, which would eventually prove advantageous.

In 1891 van Laar enrolled at the Faculty of Mathematics and Natural Science at the University of Amsterdam where he first took courses in physics, chemistry, and mathematics, and he studied under van't Hoff and Johannes van der Waals (1837–1923, 1910 Nobel Prize in Physics). Still, van Laar was not allowed to take any examinations because his secondary education in chemistry and classical languages was insufficient.

Shortly after his enrollment at the university, with the recommendation of van der Waals, van Laar was appointed mathematics teacher at the Rijks Hoogere Burgerschool (secondary school) in Middelburg. This appointment was possible because Dutch law for secondary education allowed those who were not engineers but had served the country in that position to teach technical sciences.

In 1885 van Laar married Woutera Hendrika Timona ten Brink. They had three sons and two daughters. Woutera died of tuberculosis in 1912, and in 1914 van Laar married Maartje Schagen.

In 1895 van Laar left Middelburg to become a teacher at the Rijks Hoogere Burgerschool in Utrecht. While in Utrecht he applied for a position as an unsalaried lecturer (privaatdocent) of mathematical chemistry at the University of Utrecht, but he was rejected because he did not have a doctor's degree. This rejection resulted in a serious nervous crisis that forced him to retire from his teaching position at the secondary school and support his family from a small pension. After his recovery, he contacted professors Hendrik Willem Bakhuis Roozeboom (1854–1907) and van der Waals and was accepted as an unsalaried lecturer of mathematical chemistry at the University of Amsterdam (1898).

Van der Waals' hostility to van Laar became open in 1902 when he opposed a motion by Bakhuis Roozeboom to appoint van Laar a paid lecturer in mathematical chemistry. As an alternative, van Laar was offered (and accepted) a position as research assistant to Roozeboom. Van Laar served in this position until the death of Roozeboom in 1907. In the

S1430-4171(00)06429-9, Published on Web 11/14/2000, 10.1007/s00897000429a, 560335jw.pdf

Figure 1. Van Laar at age 71.

following years several attempts to appoint van Laar a lecturer in mathematical chemistry were systematically blocked by van der Waals. Finally, in 1907 a compromise was attained, and van Laar was appointed lecturer of mathematics.

In 1910 van Laar approached the City Council of Amsterdam and requested a salary increase and also a promotion to associate professor of Mathematical Chemistry. Both requests were denied, which led to a very serious mental breakdown. Van Laar resigned his academic position and was forced, once again, to support his family with the pension assigned to him. Subsequently, van Laar moved to Switzerland and remained there until his death in December 1938 in Tavel-sur-Clarens. He is buried at the Cimétiere de Clarens.

The social attitude of van Laar and the belligerent position of van der Waals did not prevent his being awarded honors and prestigious prizes: a degree of Doctor Honoris Causa by the University of Groningen (1914), the Bakhuis Roozeboom Medal for his studies on the theory of homogeneous and heterogeneous equilibria (1929), and Correspondent of the Royal Academy of Sciences (1930). In 1930 the journal Chemisch Weekblad published a special issue honoring van Laar. In 1931 he received the Royal Honor of Knight of the Order of the Netherlands Lion, and in 1938 he became an honorary member of the Nederlansche Chemische Vereening.

When analyzing van Laar's personality, van Emmerik [1] expresses his feeling that "van Laar's resignation both in Utrecht and Amsterdam in 1895 and 1912 showed him to have been a nervous man. Sometimes his hand shook with nervous tension. His paranoid concern for mail reaching its destination was excessive. His letters can rarely be called calm or balanced. He was a fighter but his arguments were sometimes very abrasive. Even though he was right, readers cannot help feeling that van Laar was selling himself short. He certainly made many enemies, often unnecessarily. Van Laar was emotionally and socially in bad shape."

The reason for van der Waals' attitude towards van Laar remains unclear. Was the obsessive opposition of van der Waals a reaction to a young man behaving against all the established social and academic canons, or was it fear that a brilliant scientist twenty years his junior would dethrone him from his position at the University of Amsterdam? Van der Waals opposed the appointment of van Laar as his successor. He also opposed the appointment of a German professor, claiming that the German scientific level in thermodynamics was well below that in Holland. Eventually he was able to assure that the vacant position be filled by his son Johannes van der Waals.

Scientific Contribution

Van Laar's scientific achievements have resulted in changing the old subject of mathematical chemistry into the independent subject known today as chemical thermodynamics and theory of phase equilibria. Van Laar wrote twelve books and about 200 papers in the field of mathematical chemistry. Many of his papers were published first in Dutch and later translated and republished in journals like Proceedings of the Section of Sciences of the Koninklijke Akademie van Wetenschappen, Archives Neérlandaises, and Zeitschrift für Anorganische und Allgemeine Chemie [1]. He was a theoretician, not an experimentalist, and in his work he dealt with subjects as varied as electrolyte solutions, osmotic pressure, equilibria in galvanic cells, phase theory, melting point lines, spinodal and plait point lines, the van der Waals equation of state, solid-state reaction rates, and Nernst's heat theorem.

Van Konynenburg and Scott [3] have made the interesting observation that although the mathematics of van Laar is impeccable, the difficulties of numerical calculations in pre-computer days made it impossible to calculate accurately more than a few points. Consequently, the curves drawn in van Laar's papers are sometimes quantitatively wrong, sometimes even qualitatively wrong. Moreover, although many errors in figures in earlier papers are corrected in later papers, no mention is ever made of the fact that the earlier figures were wrong.

The contributions of van Laar to the theory of solutions are very important, even today. We will now discuss them in detail, first using the original ideas of van Laar, and then using more recent concepts.

Van Laar's Theory of Solutions

Historical View. In 1910 van Laar deduced the following expression for the molar heat of mixing, ΔH of a binary solution [4]:

$$\Delta H = \frac{n_1 n_2 b_1 b_2}{n_1 b_1 + n_2 b_2}\left(\frac{a_1^{0.5}}{b_1} - \frac{a_2^{0.5}}{b_2}\right)^2 \qquad (1)$$

where n_i is the number of moles, and a_i, b_i are the van der Waals constants for the particular component. Equation 1 was derived for the case where (a) there is no volume change on mixing at constant temperature and pressure ($\Delta V = 0$, unexpanded liquids), (b) the entropy of mixing is given by that corresponding to an ideal solution

$$\Delta S = -R[X_1 \ln X_1 + X_2 \ln X_2] \tag{2}$$

and (c) the van der Waals constants of the mixture are represented by the following mixing rules:

$$\sqrt{a_{mixt}} = X_1\sqrt{a_1} + X_2\sqrt{a_2} \tag{3}$$

$$b_{mixt} = X_1 b_1 + X_2 b_2 \tag{4}$$

as suggested by van der Waals when postulating that the molar volume of a pure liquid well below its critical temperature can be replaced approximately by the value of its *b* constant [5]. Van Laar also calculated the partial heat of mixing of each component $\left(\Delta\bar{H}_i\right)$ by differentiating eq 1 according to the number of moles of each component. The pertinent expressions are (using van Laar's nomenclature)

$$\Delta\bar{H}_1 = \frac{\partial\Delta H}{\partial n_1} = \frac{\alpha X_1^2}{(1+rX_1)^2} = \frac{x_2^2 b_1 b_2^2}{(X_1 b_1 + X_2 b_2)^2}\left(\frac{a_1^{0.5}}{b_1} - \frac{a_2^{0.5}}{b_2}\right)^2 \tag{5}$$

$$\begin{aligned}\Delta\bar{H}_2 &= \frac{\partial\Delta H}{\partial n_2} = \frac{\alpha X_2^2}{(1+r)(1+rX_1)^2} \\ &= \frac{X_1^2 b_1^2 b_2}{(X_1 b_1 + X_2 b_2)^2}\left(\frac{a_1^{0.5}}{b_1} - \frac{a_2^{0.5}}{b_2}\right)^2\end{aligned} \tag{6}$$

where

$$\alpha = \frac{(b_2\sqrt{a_1} - b_1\sqrt{a_2})^2}{b_1^3}$$

$$r = (b_2 - b_1)/b_1 \tag{7}$$

In a later paper, van Laar and Richard Lorenz (1863–1929) improved the model used for developing eq 1 by assuming that b_i can be replaced by the molar liquid volume of the pure component, V_i^L, yielding

$$\Delta H = \frac{X_1 X_2 V_1^L V_2^L}{X_1 V_1^L + X_2 V_2^L}\left(\frac{a_1^{0.5}}{V_1^L} - \frac{a_2^{0.5}}{V_2^L}\right)^2 \tag{8}$$

In eq 8, X_i is the mole fraction of component *i*. This equation can also be written

$$\Delta H = \frac{X_1 X_2 V_1^L V_2^L}{X_1 V_1^L + X_2 V_2^L} Q \tag{9}$$

where

$$Q = \left(\frac{a_1^{0.5}}{V_1^L} - \frac{a_2^{0.5}}{V_2^L}\right)^2 \tag{10}$$

It would appear that eq 9 contains three unknown parameters (V_1^L, V_2^L, and *Q*) but van Laar and Lorentz recognized that by defining two auxiliary parameters *A* and *B* where

$$A = \frac{Q}{RT}V_1^L$$

$$B = \frac{Q}{RT}V_2^L \tag{11}$$

the equation could be arranged so that only two parameters need to be determined,

$$\Delta H = \frac{ABX_1X_2}{AX_1 + BX_2} \tag{12}$$

In eq 12, *A* and *B* must have the same sign, otherwise, at some value of *X* there will be an infinite value for Δ*H*. Inspection of eqs 1, 8, and 12 indicates that the van Laar model predicts that heats of mixing will always be positive, that is, isothermal mixing of two components is always accompanied by an absorption of heat (endothermic process). In addition, the heat of mixing will be zero for the case where

$$\frac{a_1^{0.5}}{V_1^L} = \frac{a_2^{0.5}}{V_2^L} \tag{13}$$

Because according to the van der Waals equation the critical pressure of a pure gas is related to the constants *a* and *b* by $P_c = a/27b^2$ [7], eq 13 will be true if the two components have approximately equal critical pressures. This situation will correspond to the solution behaving ideally. Consequently, van Laar's theory predicts that the nonideality of a solution increases with increasing difference in the critical pressures of the components. These predictions, unfortunately, are contrary to experimental facts. We can illustrate these statements by comparing the behavior of solutions of chlorine (P_c = 7.71 MPa) and carbon tetrachloride (P_c = 4.56 MPa), with that of solutions of carbon disulfide (P_c = 7.90 MPa) and methanol (P_c = 8.10 MPa). The first solution behaves ideally while the second is so nonideal that it splits into two liquid phases. The corresponding expressions for the activity coefficients are

$$\ln\gamma_1 = \frac{A'}{\left(1 + \frac{A'}{B'}\frac{X_1}{X_2}\right)^2} \tag{14}$$

$$\ln\gamma_2 = \frac{B'}{\left(1 + \frac{B'}{A'}\frac{X_2}{X_1}\right)^2} \tag{15}$$

where $A' = b_1Q/RT$ and $B' = b_2Q/RT$.

Modern View. Van Laar's solution theory can be expressed in modern terms using the concepts of excess property and activity coefficients. An excess property, M_E, of a solution is defined as the difference between the actual value of the property and the property's value if the solution were ideal [7]

$$M_{\mathrm{E}} = M - M_{\mathrm{ideal}} \tag{16}$$

Let us apply this definition to the entropy and the change in the Gibbs function

$$\Delta S_{\mathrm{E}} = \Delta S - \Delta S_{\mathrm{ideal}} = 0 \tag{17}$$

$$\Delta G_{\mathrm{E}} = \Delta G - \Delta G_{\mathrm{ideal}} \tag{18}$$

At constant pressure, according to the definition of *G*, we have

$$\begin{aligned} \Delta G_E &= \Delta H_E - T\Delta S_E = \Delta H_E - T\Delta S_E \\ &= \Delta U_E + P\Delta V_E - T\Delta S_E \end{aligned} \tag{19}$$

It follows then, that for van Laar's simplifying assumptions

$$\Delta G_E = \Delta H_E = \Delta U_E \tag{20}$$

Thus, eqs 1, 8 and 12 are also expressions for ΔG_{E}, and eqs 5 and 6 represent the values of $\Delta \bar{G}_{E_i}$. Moreover, using the relation $\Delta \bar{G}_{E_i} = RT\ln\gamma_i$ [7] we see that eqs 5 and 6 also represent the activity coefficients according to van Laar's theory. Two important features of eqs 5 and 6 should be noted:

(1) The logarithms of the activity coefficients are inversely proportional to the absolute temperature. This result follows directly from the assumption that ΔS_{E} equals 0 as we will now show. Let us write the Maxwell relation for ΔG_{E} as follows [7]

$$d\Delta G_{\mathrm{E}} = -\Delta S_{\mathrm{E}} dT + \Delta V_{\mathrm{E}} dP \tag{21}$$

hence

$$\left(\frac{\partial \Delta G_{\mathrm{E}}}{\partial T}\right)_{P,X} = -\Delta S_E \tag{22}$$

Using van Laar's assumption

$$\left(\frac{\partial \Delta G_{\mathrm{E}}}{\partial T}\right)_{P,x} = -\Delta S_{\mathrm{E}} = 0 \tag{23}$$

Because [7]

$$\Delta G_{\mathrm{E}} = \sum x_i \Delta \bar{G}_{E_i} = RT\sum x_i \ln\gamma_i \tag{24}$$

it follows that

$$\left(\frac{\check{Z}T\ln\gamma_i}{\check{Z}T}\right)_{P,x} = 0 \tag{25}$$

Equation 25 can only be true if the product $T\ln\gamma_i$ is constant, or

$$\ln\gamma_i \propto \frac{1}{T} \tag{26}$$

Solutions for which the product $T\ln\gamma_i$ is constant are called regular solutions.

(2) The second important feature of eqs 5 and 6 is that van Laar's theory predicts that the activity coefficients of both components are larger than one; hence, his theory always predicts positive deviations form Raoult's law. This result follows from eq 3, which says that $a_{\mathrm{mixt}} < X_1 a_1 + X_2 a_2$ whenever $a_1 \neq a_2$.

In 1946 Wohl [8] developed a more general model for ΔG_{E} and showed that van Laar's model is a special case of it. Wohl selected to express ΔG_E along similar lines to those used to develop the virial equation of state for gases, that is, by adding the total interactions present in clusters of molecules of increasing complexity (clusters formed by two molecules, three molecules, and so on). On each cluster, at least one molecule must be different from the rest. For one mole of mixture of a binary solution the resulting expression is

$$\frac{\Delta G_{\mathrm{E}}}{RT} = AX_1 z_2^2 + BX_2 z_1^2 \tag{27}$$

where *A* and *B* are constants defined as

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

$$B = q_2\left(2a_{12} + 3a_{122}\right) \tag{28}$$

and q_i represents the *effective molar volume* of component *i* and z_i, its *volumetric fraction* (or *q* fraction)

$$z_i = \frac{q_i X_i}{\sum_{i=1}^{2} q_i X_i} \tag{29}$$

Parameter a_{12} represents the interaction between molecules 1 and 2.

As shown previously, $\frac{\Delta \bar{g}_i^{E}}{RT} = \ln\gamma_i$, hence

$$\ln\gamma_1 = z_2^2\left[A + 2z_1\left(B\frac{q_1}{q_2}\right) - A\right] \tag{30}$$

$$\ln\gamma_2 = z_1^2\left[B + 2z_2\left(A\frac{q_2}{q_1}\right) - B\right] \tag{31}$$

Equations 30 and 31 are 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.

In his paper Wohl showed that if the ratio q_1/q_2 is assumed to be equal to A/B, then his expression for $\Delta G_E/RT$ becomes identical to that of van Laar's. For this situation eqs 27, 30, and 31 become

$$\frac{\Delta G_E}{RT} = \frac{2a_{12}X_1X_2q_1q_2}{X_1q_1 + X_2q_2} \tag{32}$$

$$\ln\gamma_1 = \frac{A'}{\left(1 + \dfrac{A'}{B'}\dfrac{X_1}{X_2}\right)^2} \tag{33}$$

$$\ln\gamma_2 = \frac{B'}{\left(1 + \dfrac{B'}{A'}\dfrac{X_2}{X_1}\right)^2} \tag{34}$$

where now $A' = 2q_1a_{12}$ and $B' = 2q_12a_{12}$.

The present value of van Laar's equation is evidenced by the fact that the largest bank of vapor–liquid equilibrium data [9] uses it as one of the models to correlate the data.

Liquid–Liquid Equilibrium. An important feature of van Laar's equation is that it is able to predict if a given solution will split into two liquid phases (liquid–liquid equilibrium). The conditions for existence of a critical solution point (consolute point) are [5]

$$\left(\frac{\partial^2\Delta G}{\partial X_1^2} = \frac{\partial^2\Delta G^E}{\partial X_1^2} + \frac{RT_c}{X_1X_2} = 0\right)_{P,T} \tag{35}$$

$$\left(\frac{\partial^3\Delta G}{\partial X_1^3} = \frac{\partial^3\Delta G^E}{\partial X_1^3} + RT_c\frac{X_1 - X_2}{X_1^2X_2^2} = 0\right)_{P,T} \tag{36}$$

$$\left(\frac{\partial^4\Delta G}{\partial X_1^4} = \frac{\partial^4\Delta G^E}{\partial X_1^4} + 2RT_c\frac{1 - 3X_1X_2}{X_1^3X_2^3} > 0\right)_{P,T} \tag{37}$$

where T_c is the critical solution temperature. Application of eq 32 indicates that it satisfies the conditions for stability with the following coordinates for the consolute point (T_c, X_{1c}) composition

$$T_c = \frac{2X_1X_2A'^2B'^2}{R[A'X_1 + B'X_2]^3} \tag{38}$$

$$X_{1c} = \frac{[(A/B)^2 + 1 - (A/B)]^{0.5} - (A/B)}{1 - (A/B)} \tag{39}$$

In equation (38) $A' = ART_c$ *and* $B' = BRT_c$.

From eqs 38 and 39, it is possible to express the values of A' and B' as a function of the critical solution

$$A' = \frac{13.5(1 - X_{1c})}{2(1 + X_{1c})(2 - X_{1c})^2} \tag{40}$$

$$B' = \frac{13.5X_{1c}}{2(1 + X_{1c})^2(2 - X_{1c})^2} \tag{41}$$

Acknowledgment. Special thanks are given to Dr. van Emmerik for letting me have a copy of his thesis, reference 2, and some pictures of van Laar.

References and Notes

1. van Emmerik, E. P. J. J. Van Laar (1860–1938). A Mathematical Chemist. Ph.D. Thesis, Delft Technological University, Delft, 1991.
2. van Emmerik, E. P. Some Milestones in the Life and Work of the Mathematical Chemist J. J. Van Laar. paper presented at the *CALPHAD X1X Conference*, Noordwijkerhout, Holland, June 18–22, 1990.
3. van Konynenburg, P. H.; Scott, R. L. *Phil. Trans. Royal Soc.* **1980,** *298A,* 495–539.
4. van Laar, J. J. *Z. Phys. Chem.* **1910,** *72,* 723–751.
5. Prigogine, I.; Defay, R. *Chemical Thermodynamics;* Longmans, Green: London, 1954.
6. van Laar, J. J.; Lorenz, R. *Z. Anorg. Allgem. Chem.* **1925,** *146,* 42–44.
7. Levine, I. N. *Physical Chemistry*, 4th ed.; McGraw-Hill: New York, 1997.
8. Wohl, K. *Trans. AIChE* **1946,** *42,* 215–249. Corrections: *Chem. Eng. Progr.* **1953,** *49,* 218–219.
9. *Chemical Data Series, Vol I: Vapor-Equilibrium Data Collection*, DECHEMA e.V.: Frankfurt am Main, Germany, 1999.