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Citation: [The Journal of Chemical Physics](#) **2**, 396 (1934); doi: 10.1063/1.1749495

View online: <http://dx.doi.org/10.1063/1.1749495>

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The Theory of Moderate Deviations from van't Hoff's Law

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(March 19, 1934)

A sketch of the application of van der Waals notions to the study of deviations from van't Hoff's law made by A. A. Noyes is given and a modification of the theory is introduced. An osmotic pressure equation is then deduced from a heat of formation equation. The new theory is shown to be, at least formally, in harmony with the old. Both theories result in an equation of the van der Waals type for osmotic pressures. This constitutes an extension of van't Hoff's very useful analogy between dilute solutes and gases.

THE phrase "dilute solutions" has come to refer particularly to solutions for which van't Hoff's theory is valid. Hence throughout this paper we shall use the term "near-dilute" to refer to solutions which although dilute are sufficiently concentrated to show deviations from van't Hoff's law.

I.

The equation

$$\pi(V-\beta)=RT, \quad (1)$$

in which π is the osmotic pressure, V the volume of a solution containing one mol of solute and β is a function of temperature, has been, probably, the most successful, empirically, of all the modified forms of van't Hoff's law. The observation of Morse and Frazer,¹ that better results are obtained in more concentrated solutions with van't Hoff's law if V is replaced by the volume of the solvent used to make up the solution, indicates only one way of using an equation of this type. In this case β is simply taken to be the difference between the volume of the solution and that of the solvent used to make up the solution.

The success of van der Waals in the field of gases under high pressure and of the van't Hoff analogy between dilute solutes and ideal gases made it inevitable that an attempt would be made to treat near-dilute solutions in the van der Waals fashion. This was done independently by Bredig² and Noyes.³ We will give a sketch

(in modern notation) of the theory of Noyes. Noyes was not interested in the variations of osmotic pressure with temperature and called anything that depended upon temperature only a constant. We will introduce temperature explicitly in our sketch.

In van der Waals gas equation we introduce as a correction to p , a term a/V^2 and as a correction to V a constant term b . Now in near-dilute solutions, Noyes assumed, we can neglect the attraction of solute molecules for each other and consider only the attraction between solute molecules and solvent molecules. The correction term to π will then be proportional not to the square of the concentration of the solute but to the product of the concentration of the solute and solvent. But since the concentration of the solvent is nearly constant we can simply take a/V for our correction term. In the correction term to V we shall have to consider both solute and solvent molecules. If we deal with an amount of solution containing one mol of solute and n_1 mols of solvent this term will be $b_2+n_1b_1$ in which the b 's have a significance analogous to the b in van der Waals equation. Since

$$V=n_1\bar{v}_1+\bar{v}_2, \quad n_1=(V-\bar{v}_2)/\bar{v}_1,$$

we have for the osmotic pressure of a near-dilute solution

$$[\pi-a/V][V-\{b_2+(V-\bar{v}_2)b_1/\bar{v}_1\}]=K, \quad (2)$$

in which K depends upon T alone. We can write this as

$$[\pi-a/V][V(1-b_1/\bar{v}_1)-(b_2-\bar{v}_2b_1/\bar{v}_1)]=K, \\ [\pi-a/V][V-\phi]=K', \quad (3)$$

¹ Morse and Frazer, *Am. Chem. J.* **34**, 28 (1905).

² Bredig, *Zeits. f. physik. Chemie* **4**, 444 (1889).

³ A. A. Noyes, *Zeits. f. physik. Chemie* **5**, 53 (1890).

in which K' is a new function of temperature and

$$\phi = (b_2 - \bar{v}_2 b_1 / \bar{v}_1) / (1 - b_1 / \bar{v}_1) \quad (4)$$

is approximately a constant. Noyes simplified Eq. (3) by multiplying out the left-hand side and noting that in the small term $a\phi/V$ we can take $1/V$ proportional to π and he introduced a proportionality "constant" but the proportionality factor is really $1/RT$. Introducing this we get

$$\pi[V - \phi(1 - a/RT)] = K' + a, \quad (5)$$

$$\pi[V - \beta] = RT, \quad (6)$$

which is Eq. (1) with

$$\beta = \phi(1 - a/RT). \quad (7)$$

We have put the right-hand side equal to RT for the equation must reduce to van't Hoff's in the limit as V increases at constant temperature.

Sackur⁴ regarded Eq. (1) as closely analogous to Hirn's gas equation with β dependent only upon the "volume" of the solute and solvent molecules. He explained the absence of any term corresponding to van der Waals a/V^2 somewhat as follows: Since the osmotic pressure is independent of the nature of the semipermeable membrane, we can consider this to be infinitely thin. A solute molecule, then, at the instant it strikes the membrane is attracted by the solvent on one side of the membrane just about as much as by that on the other side. Both Noyes and Sackur gave extensive experimental tests of Eq. (1) using osmotic pressures determined both directly and indirectly. The results were excellent.

Now let us take Sackur's observation that the solvent on both sides of the membrane must be considered and consider anew the correction term to π . It is evident that in determining the effect of the attraction of solvent molecules for solute molecules we need to consider only the *excess* of solvent molecules in a given volume of pure solvent over those in the same volume of solution. If we start with a volume V of solution and remove the one mol of solute the decrease in the volume will be (approximately) \bar{v}_2 . We can restore the volume to its initial value by

adding Δn_1 mols of solvent where

$$\Delta n_1 \bar{v}_1 = \bar{v}_2$$

(approximately). The concentration of the "excess" molecules on the side of the pure solvent is then

$$\Delta n_1 / V = (\bar{v}_2 / \bar{v}_1) / V$$

and the correction factor to π will be (to a sufficient degree of accuracy)

$$-a' / V^2, \quad a' > 0,$$

in which we have absorbed (\bar{v}_2 / \bar{v}_1) into the proportionality constant. The sign will, of course, be the opposite to that of the correction term representing the attraction of the solute molecules for each other, which we shall introduce as (a/V^2) . We have then in place of (3)

$$\begin{aligned} [\pi + a/V^2 - a'/V^2][V - \phi] \\ = [\pi + \alpha/V^2][V - \phi] = RT \end{aligned} \quad (8)$$

with

$$\alpha = a - a'. \quad (9)$$

(We again determine the right-hand side of the equation by considering its limiting form as V increases at constant T .) Multiplying out the left-hand side, neglecting the product of the two correction terms, $(\alpha/V^2)\phi$, and using the approximation $1/V = \pi/RT$ in the small term, $(\alpha/V^2)V$, we get

$$\begin{aligned} \pi[V - \phi + \alpha/RT] &= RT, \\ \pi[V - \beta] &= RT \end{aligned} \quad (10)$$

and we are again led to Eq. (1) with

$$\beta = \phi - \alpha/RT. \quad (11)$$

We shall show in the next section that this theory agrees with modern developments. These early papers present us with a very workmanlike approach to the problem of near-dilute solutions. They have been too long disregarded.⁵

⁵ Van Laar, Kohnstamm, van der Waals and others have worked out a theory of binary solutions based upon van der Waals equation in great detail. (An excellent survey of this work is given in Vol. II of van der Waals-Kohnstamm's *Thermostatik*.) But they have considered van der Waals equation as one applicable to both gases and liquids and have applied it to the solution as a whole. Noyes and Bredig used van der Waals notions in the study of solutes considered as analogous to gases.

⁴ Sackur, Zeits. f. physik. Chemie **70**, 477 (1910).

II.

Today we can approach the theory of near-dilute solutions from an entirely different standpoint. We can base the theory of any solution upon the equation⁶

$$\ln f_1 = \ln N_1 f_1^0 - \int_{(p, N_1)} [(\bar{H}_1 - H_1^0)/RT^2] dT \quad (12)$$

if we can determine $\bar{H}_1 - H_1^0$ as a function of T and N_2 (or N_1). (Throughout this paper we assume that the pressure upon the solution does not vary sufficiently to alter its properties.) If we take component one as the solvent and component two as the solute we shall have in a dilute solution

$$\ln f_1 = \ln N_1 f_1^0$$

and so in a near-dilute solution the correction term in (12) will be small and a rough approximation to the function $\bar{H}_1 - H_1^0$ will be sufficient. A number of different investigations⁷ into the heat of formation, ΔH , of binary solutions, both theoretical and empirical, all agree in giving

$$\Delta H = A(T)N_1N_2 \quad (13)$$

as the limiting form of the function for small values of N_2 . (We can use Biron's relation,⁸ $\Delta V = kN_1N_2$, in which k is a constant, in connection with the equations of van Laar and Lorenz.) We shall consider the function $A(T)$ later.

Using the equation (No. (3) reference 6)

$$\bar{H}_1 - H_1^0 = (1 - N_1)[\partial \Delta H / \partial N_1]_{T, p} + \Delta H$$

we can obtain from (13) the equations

$$\left. \begin{aligned} \bar{H}_1 - H_1^0 &= A(T)N_2^2 \\ \bar{H}_2 - H_2^0 &= A(T)N_1^2 \end{aligned} \right\} \quad (14)$$

In order to compare our results with the earlier theory as outlined and supplemented

above, we shall deduce the dependence of the osmotic pressure of the solute upon the composition of the solution expressed in terms of V . The osmotic pressure will be given (with a sufficient degree of accuracy) by the equation⁹

$$\pi \bar{v}_1 = -RT \ln (f_1/f_1^0)$$

and using (12) and the first of Eqs. (14) we get

$$\begin{aligned} \pi \bar{v}_1 &= -RT \ln N_1 + N_2^2 T \int (A/T^2) dT \\ &= -RT \ln N_1 + BN_2^2 \end{aligned} \quad (15)$$

with

$$B = T \int (A/T^2) dT. \quad (16)$$

Or $\pi \bar{v}_1 = -RT \ln (1 - N_2) + BN_2^2$

$$= RT(N_2 + \frac{1}{2}N_2^2 + \dots) + BN_2^2$$

$$= N_2RT + (RT/2 + B)N_2^2$$

approximately, since N_2 is small. Now

$$\begin{aligned} V &= \frac{N_1 \bar{v}_1 + N_2 \bar{v}_2}{N_2} = \frac{\bar{v}_1 + (\bar{v}_2 - \bar{v}_1)N_2}{N_2} = \frac{\bar{v}_1}{N_2} + \bar{v}_2 - \bar{v}_1 \\ N_2 &= \frac{\bar{v}_1}{V + \bar{v}_1 - \bar{v}_2} = \frac{\bar{v}_1}{V} \frac{1}{1 + (\bar{v}_1 - \bar{v}_2)/V} \\ &= \frac{\bar{v}_1}{V} (1 - (\bar{v}_1 - \bar{v}_2)/V) \quad (17) \end{aligned}$$

approximately, since as long as N_2 is small, V will be very large compared to $\bar{v}_1 - \bar{v}_2$. This gives, neglecting powers of $1/V$ higher than the second,

$$\begin{aligned} \pi \bar{v}_1 &= \frac{RT \bar{v}_1}{V} (1 - (\bar{v}_1 - \bar{v}_2)/V) + (RT/2 + B)(\bar{v}_1/V)^2, \\ \pi &= \frac{RT}{V} [1 - (\bar{v}_1 - \bar{v}_2)/V + (\frac{1}{2}RT + B)\bar{v}_1/RTV] \\ &= \frac{RT}{V} [1 + \beta/V], \end{aligned}$$

where

$$\beta = B\bar{v}_1/RT + \bar{v}_2 - \bar{v}_1/2. \quad (18)$$

The term β/V appears as a correction to van't Hoff's law and hence will be small; we can use

⁶ Coleman and Germann, *J. Chem. Phys.* **1**, 847 (1933).
⁷ Baud, *Bull. Soc. Chim.* (4) **17**, 329 (1915); Van Laar and Lorenz, *Zeits. f. anorg. Chemie* **146**, 42 (1925); Heitler, *Ann. d. Physik* (4) **80**, 630 (1926); Hildebrand and Wood, *J. Chem. Phys.* **1**, 817 (1933); Coleman and Germann, reference 6.

⁸ Biron, *J. Russ. Phys.-Chem. Soc.* **41**, 569 (1909).

⁹ Lewis and Randall, *Thermodynamics*, p. 214.

here the approximation $1/V = \pi/RT$ and this gives upon rearranging

$$\pi(V - \beta) = RT.$$

We obtain Eq. (1) once again.

In order to determine the dependence of β upon T we will go back to the function $A(T)$. The theoretical investigations⁷ indicate that A will be very nearly constant over moderate temperature ranges. Hildebrand¹⁰ believes that whenever there are no orientations between the molecules of two substances when they are mixed to form the solution, then A will be a constant. We do not believe that $\bar{H}_1 - H_1^0$, can ever be *strictly* independent of temperature, except in the trivial case of ideal solutions. We believe that when we pass by a series of continuous states from a liquid solution to a gaseous solution (which is ideal or can be made so by an increase in its temperature), $\bar{H}_1 - H_1^0$ should ultimately approach zero. This is not possible if A is strictly independent of temperature. (See reference 6). It seems therefore that although we can ordinarily assume A to be *approximately* constant, we must proceed with caution especially in cases where we suspect large orienting effects.

If A is a constant then from (16) we have

$$B = -A$$

and from (18)

$$\beta = -A\bar{v}_1/RT + \bar{v}_2 - \bar{v}_1/2. \quad (19)$$

We see that as far as the form of this equation is concerned it is in harmony with the older theory in both its original form (Eq. (7)) and its modified form (Eq. (11)). Comparing Eqs. (11) and (19) we get the relations¹¹

¹⁰ Hildebrand, J. Am. Chem. Soc. **51**, 66 (1929).

¹¹ It will be of interest to consider the second of these equations in connection with the treatment of this problem given by Bancroft and Davis (J. Phys. Chem. **32**, 1 (1928)). They calculate the osmotic pressures of benzene and toluene in solutions composed of these two substances, *assuming them to be ideal*. They then show that these calculated pressures can be fitted by an equation of the van der Waals type over a *surprisingly large* range of compo-

$$\phi = \bar{v}_2 - \bar{v}_1/2, \quad (20)$$

$$A\bar{v}_1 = \alpha. \quad (21)$$

In order to get Eq. (1) from (8) we dropped a small term $(\alpha/V^2)\phi$. We can proceed backwards and derive (8) from (1) by adding this same small term. Thus from Eq. (13), with A taken as constant over the temperature range considered, we can derive an osmotic pressure equation *having the same form as van der Waals gas equation*. However, such formal considerations can not, of course, give support to the interpretation of the constants concerned which is involved in Eqs. (20) and (21). Using Noyes' original treatment we get instead of (21) $A\bar{v}_1 = \phi a$ and hence A must always be positive. This is not true.

It has not been the purpose of this paper to develop new equations but rather to give new meanings to old ones which already have received ample experimental confirmation; namely Eqs. (1) and (13).¹² We have tried to show that the van't Hoff analogy can be extended in the way originated by Noyes and Bredig, and that this extension agrees with modern developments.

sitions. But for the osmotic pressure of the benzene they used

$$\alpha = 0.79198 \text{ atmos.} - (\text{liters})^2$$

and for the osmotic pressure of the toluene

$$\alpha = 0.8338 \text{ atmos.} - (\text{liters})^2.$$

(We are using our own notation.) These values give (assuming $\bar{v}_1 = v_1^0$)

$$A = 7.3 \text{ liter-atmos.} = 0.74 \text{ kilojoules}$$

and

$$A = 9.3 \text{ liter-atmos.} = 0.94 \text{ kilojoules.}$$

But in an *ideal* solution A must vanish and a comparison with the table given in reference 6 shows that these values are much too large to be negligible. These values are, as a matter of fact, much larger than the actual value of A which is (reference 6) 0.298 kilojoules. (A is identical with the α_2 given in the table in this case.) The ideal solution is, according to our treatment, the only case in which the complete van der Waals equation is not necessary—in this case alone does the equation degenerate into one exactly analogous to Hirn's gas equation, $p(V-b) = RT$.

¹² Besides the references cited, see Hildebrand (reference 10) for indirect confirmation of this equation with A considered as a constant.