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from 2.3 mm to 15.0 mm. Because of the high absorption at greater pressures, it was impossible to make accurate measurements beyond 15 mm of mercury. Since an increase in pressure increases the number of collisions between molecules, these experiments show that at low pressures an increase in the number of collisions has no effect on the absorption of oxygen in the Schumann region.

The slopes of the lines in Fig. 1 give the absorption coefficient for the nitrogen-oxygen mixture. When expressed in terms of the partial pressure of oxygen, the absorption coefficient for the maximum of the band, 1450A, is 0.55/cm/mm of mercury. Since the measurements were made at a temperature of 25° centigrade, the absorption coefficient reduced to normal temperature and pressure is 460 as compared with the value of 490 per cm at N.T.P. obtained by Ladenburg
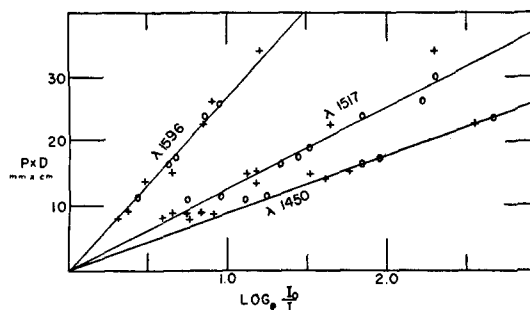

Fig. 1. The logarithm of the opacity of a mixture of 20 percent oxygen and 80 percent nitrogen as a function of the pressure in mm of mercury times the thickness. (0) represents a layer of gas 4.75 cm thick and (+) 2.27 cm.

and Van Voorhis[5] for pure oxygen. The fact that these two values agree to within the experimental error shows that the addition of nitrogen had no influence on the absorption of the oxygen.

[5] Ladenburg and Van Voorhis, Phys. Rev. **43**, 315 (1933).

A Thermodynamic Treatment of Systems, in Particular of Solutions, from the Point of View of Activity and Related Functions

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The purpose of this paper is to present a consistent thermodynamic treatment of solutions based on activity and activity coefficient. On the basis of the argument presented interrelations of these quantities are obtained for dissociated and undissociated components. Expressions are also derived for the fugacity and activity of a component in a gas mixture.

IN 1878 Gibbs deduced an equation for dilute solutions. If this equation were to be redefined in terms of molar units, one of Gibbs' constants identified with the gas constant, and the resulting equation be assumed applicable over the whole range of concentration we would have the ordinary ideal solution definition. In application it was found in general that some solutions approximated very closely to this equation, others only when very dilute, and still others not at all. The latter type, namely solutions of electrolytes, were classified separately and a limiting law obtained by formally patching the existing one.

To extend the usefulness of this type of equation so that it might be applicable to all solutions and reduce to it when "infinitely" dilute and when "ideal," Lewis and Randall replaced the molar concentration factor by a function of the independent variables and named it activity, which was a truly inspired idea. The ratio of the activity to the molar concentration of the species, which they named activity coefficient, thus automatically cataloged all solutions in terms of deviations from the "ideal solution." This general pattern has, however, been partially concealed by their phraseology and some apparent ambiguity in defining their functions; as a result there have appeared in text books a variety of interpretations some of which are justifiable whereas others lead to mutually inconsistent interrelations of the ac-

tivities, in particular for dissociated and undissociated solutes.

In order to make the relations derived herein readily apparent the usual method of partially defining activity, a_i, of a component "i" in a binary system as a function of absolute temperature T, pressure p, and molar concentration X_i (such as mole fraction or molality), by the equation

$$a_i = e^{(F_i - F_i{}^0)/RT} = \phi_i e^{F_i/RT} \qquad (1)$$

will be used. Here R denotes the gas constant, F_i (T, p, X_i) the molar chemical potential ($\mu_i M_i$ of Gibbs) for the state (T, p, X_i) and $F_i{}^0$ a quantity that makes the mole fraction activity equal to the mole fraction of "i" if the solution satisfy the equation of an "ideal" solution. The state for which $F_i = F_i{}^0$, i.e., $a_i = 1$, has been named the "standard state," and so $F_i{}^0$ could be called the molar chemical potential for the standard state. Considered from this point of view $F_i{}^0$ is, by definition, a function of both *temperature* and *pressure* and the "standard state" is free to vary in the (t, p) coordinate plane.

If the components of a solution were miscible in all proportions then a single expression would suffice to evaluate $F_i{}^0$ of each component but because complete miscibility is not in general obtainable in a solution $F_i{}^0$ (or ϕ_i) is evaluated separately for solvent and solute, denoted here by subscripts 1 and 2, respectively. The two equations are, however, limiting values of a single relation, namely the ordinary ideal solution definition.

In order to define ϕ_2 and thus $F_2{}^0$ of a solute the dilute solution law is assumed as a physical hypothesis, namely[1]

$$\frac{x_2}{1 - x_2} e^{-\mu_2/AT} = \phi(T, p), \qquad (2)$$

where x_2 denotes the weight fraction of solute, μ_2 is Gibbs' chemical potential per gram. A, $(= R/M_2)$, is a constant for the particular solute (where M_2 denotes the mole weight of the species), and ϕ (T, p) is a function of T and p

characteristic of the solute. The equation is to be considered as exact for the general case only when treated as a limiting law for $x_2 \to 0$. In terms of molar units Eq. (2), when treated as a limiting law, becomes

$$N_2 e^{-F_2/RT} = \phi_2(T, p), \qquad (3)$$

where ϕ_2 (T, p) is a function of T and p characteristic of the substance. If Eq. (3) be extrapolated over the entire concentration range it becomes the usual definition of an ideal solution. If it be written in the logarithmic form its relation to the definition of activity will be evident. But Eq. (3) presupposes that a molecular weight has been chosen for the component to which it is ascribed, the molar concentration and molar chemical potential being expressed in terms of this mole weight. Therefore since $F_2{}^0$ of the solute activity will be defined in terms of this or a similar equation the solute activity so defined refers to the mole species chosen.

Empirically it is known that for undissociated solutes Eq. (3) expressed as a limiting law for $N_2 \to 0$ exists and here the corresponding mole fraction activity is defined such that

$$RT \ln \phi_2 = - F_2{}^0. \qquad (4)$$

Other molar concentration units could also have been used, for example a common unit is molality, m, the number of solute moles in a kilogram of solvent. The molality activity is defined correspondingly such that

$$RT \ln \eta\phi_2 = - F_2{}^0, \qquad (4a)$$

where η denotes the number of solvent moles per kilogram.

$F_2{}^0$ is therefore a function of T and p and, for different concentration units, will vary in absolute values.[2]

For strong electrolytes it is known that a limit does not exist if the formula weight of the undissociated solute be taken as the effective mole weight of the species. If the electrolyte is assumed, however, to be completely dissociated into its ion parts the mean effective mole weight of the average ion will be not the formula weight

[1] This is equivalent to Gibbs' Eq. (215). Cf. R. W. Goranson, *Thermodynamic Relations in Multicomponent systems*, Carnegie Inst. Washington Publ. No. 408 (1930), pp. 320–322.

[2] Falkenhagen (*Electrolytes*, translated by R. P. Bell, (Oxford, 1934), p. 55) equates the molality, mole fraction, and moles per liter of solution activities; his activities are therefore not equivalent to those of Lewis and Randall.

M_2 of the solute but M_2/ν if ν denotes the number of dissociated parts or ions.

Let a solute RS, if it dissociates, separate into ν parts or ions such that

$$RS \rightleftharpoons \sum_{i=1}^{\nu_+} R_i + \sum_{j=1}^{\nu_-} S_j. \tag{5}$$
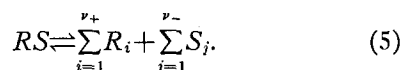
One could then formally generalize the ordinary dilute solution equation and write the expression

$$N_i e^{-F_i/RT} = \frac{\phi_i'(T, p)}{k} = \phi_i(T, p) \tag{6}$$

for the ith species.

Herein $N_2 = (n_1/[n_1+n_2])$ denotes the mole fraction of solute where n_1 and n_2 are the number of moles of solvent and solute, respectively; N_2' denotes the mole fraction of undissociated solute and $N_\pm$ that of a mean species of dissociation, or

$$N_2' = \frac{(1-\alpha)N_2}{1+\alpha(\nu-1)N_2} \quad \text{and} \quad N_\pm = \frac{\alpha k N_2}{1+\alpha(\nu-1)N_2},$$

where α denotes the degree of dissociation and k is in general a constant for the particular solute. The participating or effective parts may be considered as (1) all distinct, $k=1$, (2) two distinct species, $k = [(\nu_+)^{\nu_+}(\nu_-)^{\nu_-}]^{1/\nu}$, or (3) one mean species, $k = \nu$. It is immaterial, however, which viewpoint be taken because Eq. (6) may be divided through by k and thus all three cases become equivalent in treatment so long as the relative proportions of the species remain constant. The relationships are simplified for molality concentrations, namely m, $m' = (1-\alpha)m$, and $m_\pm = \alpha k m$; here too the three cases will be made equivalent by dividing the corresponding equation through by k.

In many thermodynamic problems dissociated and undissociated states are not differentiated because to do so would serve no useful purpose. In such cases a quantity can be taken to denote the average molar chemical potential of a dissociated component RS, defined here by $\{F_2\}$, and which is equivalent to the sum of the molar chemical potentials of the parts which make up an average mole weight of solute in the solution.

Thus if α denotes the degree of dissociation

$$\{F_2(T, p, N_2)\} = \sum_{i=1}^{\nu_+} F_i + \sum_{j=1}^{\nu_-} F_j = \nu F_\pm \text{ for } \alpha=1, \tag{7a}$$

$$= (1-\alpha)F_2(T, p, N_2') + \alpha \nu F_\pm$$
$$\text{for } 0 < \alpha < 1, \tag{7b}$$

$$= F_2(T, p, N_2) \quad \text{for } \alpha=0. \tag{7c}$$

The brace is used here to distinguish this quantity from the *chemical potential of the undissociated part* of the solute with which it might otherwise be confused.

Thermodynamically one cannot distinguish between the participating parts but obtains only the mean effect of the composite. Thus, when the variable is the concentration of the solute, a measure will be obtained of $\{F_2\}$ or of some value proportional to $\{F_2\}$ and not of any one constituent species; therefore, if there are ν parts and α remains unity, $\{F_2\}/\nu$ could be and is equivalent to the quantity generally assumed as the molar chemical potential of a mean ion or participating species.

If the condition given by Eq. (5) exists, such that $0 < \alpha < 1$, we have $F_2 = \nu F_\pm$ and if this be combined with Eq. (7b) we have

$$\{F_2(T, p, N_2)\} = F_2(T, p, N_2')$$
$$= \nu F_\pm(T, p, N_\pm). \tag{8}$$

It has just been demonstrated that the molar chemical potential $\{F_2\}$ of the solute in the solution is equivalent to the molar chemical potential F_2 of the undissociated part of the solute and this again equal to the sum of the molar chemical potentials of the species of dissociation or $\nu F_\pm$, assuming coexistence of these species. But unless the degree of dissociation and therefore the number of dissociated and undissociated moles of solute can be determined the concentrations N_2' and $N_\pm$ will not be known. Because ordinarily α is not known it is generally assumed that strong electrolytes are completely dissociated or that

$$N_2' = 0 \quad \text{and} \quad N_\pm = k N_2/[1+(\nu-1)N_2]. \tag{8a}$$

The ideal solution law will accordingly be written as

$$N_\pm e^{-\{F_2(T, p, N_2)\}/\nu RT} = \phi_\pm(T, p) \tag{9}$$

and for solutions sufficiently dilute so that N_2 and m can be considered as proportional to one another, in the form

$$m_{\pm}e^{-\{F_2\}/\nu RT} = \eta\phi_{\pm}(T,\,p) = \phi_{\pm}'(T,\,p), \quad (10)$$

where η denotes the number of solvent moles per kilogram.

If the assumption (8a) be made then changes in chemical potential which are the result of association will be included with other deviations from these solution "laws" and manifested as departures from "ideality."

It is known empirically that, for a solution of a strong electrolyte which is generally assumed to be completely dissociated, Eq. (9) or (10) exists only in the limit as N_2 or $m \to 0$. The mean ionic activity is then given by the expression $a_{\pm}(T,\,p,\,N_{\pm}) = \phi_{\pm}e^{\{F_2\}/\nu RT}$ and the activity of the undissociated solute by the expression $a_2(t,\,p,\,N_2') = \phi_2 e^{\{F_2\}/RT}$ so that

$$\frac{(a_{\pm})^{\nu}}{a_2} = \frac{[\phi_{\pm}(T,\,p)]^{\nu}}{\phi_2(T,\,p)} = K(T,\,p) \quad \text{for } 0 < \alpha < 1, \quad (11)$$

and for an ideal solution defined as one satisfying Eqs. (3) and (9) then

$$\frac{(N_{\pm})^{\nu}}{N_2'} = K(T,\,p), \qquad (11a)$$

which is the equivalent of the law of mass action. If $\alpha = 1$, as is ordinarily assumed for dilute solutions of strong electrolytes, then a_2 is, by definition, zero and Eqs. (5), (7) and therefore (11) do not exist. Thus $(a_{\pm})^{\nu}$ is *not equal* to the activity a_2 of the *undissociated* solute as has sometimes been stated but may be correlated with a quantity defined as the average *activity of the solute* only if the latter be defined by the expression $\{a_2\} = (a_{\pm})^{\nu}$.

The mole fraction and molality[3] "mean ionic" activity coefficients are defined by

$$\gamma_{\pm}(T,\,p,\,N_{\pm}) = \frac{[1+(\nu-1)N_2]a_{\pm}(T,\,p,\,N_{\pm})}{N_2}$$

and $\quad \gamma_{\pm}(T,\,p,\,m_{\pm}) = \dfrac{a_{\pm}(T,\,p,\,m_{\pm})}{m}$,

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[3] This molality coefficient is equivalent to that of Lewis and Randall since here a is equivalent to their "a/k" where $k = [(\nu_+)^{\nu}+(\nu_-)^{\nu}-]^{1/\nu}$. (See reference 7.)

respectively. If the solutions furthermore behave according to the ideal law as defined by Eq. (9)

$$\gamma_{\pm}(T,\,p,\,N_{\pm}) = \alpha\frac{1+(\nu-1)N_2}{1+\alpha(\nu-1)N_2} \quad \text{if } \alpha < 1.$$

Thus for very dilute *ideal* solutions the value of $\gamma_{\pm}(T,\,p,\,N_{\pm})$ may be regarded as equivalent to the degree of dissociation. The corresponding molality activity coefficient is given by

$$\gamma_{\pm}(T,\,p,\,m_{\pm}) = \frac{\alpha(1-N_2)}{1+\alpha(\nu-1)N_2} \quad \text{if } \alpha < 1.$$

It is therefore a linearly decreasing function of the concentration N_2 and unity only in the limit as $m \to 0$.

The activity of the undissociated solute in solution, if *ideal*, would be given by

$$\gamma_2(T,\,p,\,N_2') = \frac{a_2(T,\,p,\,N_2')}{N_2} = \frac{1-\alpha}{1+\alpha(\nu-1)N_2}$$

$$= 1 - \gamma_{\pm}(T,\,p,\,N_{\pm}),$$

which is unity for $\alpha = 0$ and zero for $\alpha = 1$; and by

$$\gamma_2(T,\,p,\,m') = \frac{(1-\alpha)(1-N_2)}{[1+\alpha(\nu-1)N_2]}$$

which, for $\alpha = 0$, is equal to $(1-N_2)$.

It is now a simple matter to evaluate the derivatives of F_2^0, the molar chemical potential of Lewis and Randall's "standard state" which has been defined by Eqs. (1) and (4), (4a), (9), or (10) as a function of T and p—a simple method is as follows. Differentiate Eq. (1) with respect to the independent variables T and p, then let the molar concentration m converge to zero as a limit and we obtain[4]

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[4] Lewis and Randall do not write a pressure derivative of solute activity, in fact their only pressure derivative (reference 7, p. 255) relates to the activity of a simple substance. They do, however, say (reference 7, p. 259) of their standard solute state "the partial molal volume, heat content, and heat capacity are those of the solute at infinite dilution." Their intent seems therefore evident. Some writers (e.g., H. S. Taylor, Ed., *A Treatise on Physical Chemistry*, I (Harned, New York, 1931), p. 761), have assumed that Lewis and Randall's pressure derivative for a simple substance was also applicable for all activities, in which case F_2^0 would not be a function of pressure. Such an activity could readily be written by defining F_2^0 so that

$$\lim_{m \to 0} \frac{a_2(T,\,p,\,m)}{m} = \exp\int_1^p \frac{v_2^*}{RT}\,dp$$

$$\frac{\partial(F_2{}^0/RT)}{\partial T} = \lim_{m\to 0}\left[\frac{-H_2(T,\,p,\,m)}{RT^2}\right]$$

$$= -\frac{H_2{}^*(T,\,p)}{RT^2}, \quad (12a)$$

$$\frac{\partial(F_2{}^0/RT)}{\partial p} = \lim_{m\to 0}\left[\frac{v_2(T,\,p,\,m)}{RT}\right] = \frac{v_2{}^*(T,\,p)}{RT}, \quad (12b)$$

where H_2 denotes the partial molar heat content and v_2 the partial molar volume ($= \partial H/\partial n_2$ and $\partial V/\partial n_2$, respectively, where n_2 denotes the number of solute moles, H the total heat content (Gibbs' x) and V the total volume).

The activity and activity coefficient can now be written as the line integral[5]

$$\gamma_\pm(T,\,p,\,N_\pm) = \frac{a_\pm(T,\,p,\,N_\pm)}{N_\pm}$$

$$= \exp\int_{T_0,\,p_0,\,N_\pm=0}^{T,\,p,\,N_\pm}\frac{H_2{}^*-H_2}{\nu RT^2}dT + \frac{v_2-v_2{}^*}{\nu RT}dp$$

$$+\left[\frac{N_\pm}{\nu RT}\frac{\partial\{F_2\}}{\partial N_\pm}-1\right]d\ln N_\pm, \quad (13)$$

where $N_\pm = N_2/[1+(\nu-1)N_2]$ and $\exp A$ denotes e^A. This and the following line integrals represent the most general expressions and may be integrated over any path between the two limits. It can be broken up into three parts and because the limit of $\gamma_\pm$ as $N_2\to 0$ is, by definition, unity for all temperatures and pressures, it is possible to proceed from $(T_0,\,p_0,\,N_{\pm 0})$ to $(T,\,p,\,N_\pm)$ along constant T and p paths in which case the first two terms under the integral sign vanish; for example, in order to evaluate $\gamma_\pm(T,\,p,\,N_\pm)-\gamma_\pm(T_0,\,p_0,\,N_{\pm 0})$ one may integrate from $(T_0,\,p_0,\,N_{\pm 0})$ to $(T_0,\,p_0,\,N_\pm=0)$ and then from $(T,\,p,\,N_\pm=0)$ to $(T,\,p,\,N_\pm)$. If the temperature and pressure derivatives of $\gamma_\pm$ can be expressed as known functions of $(T,\,p,\,N_\pm)$

over the region considered then the difference $\gamma_\pm(T,\,p,\,N_\pm)-\gamma_\pm(T_0,\,p_0,\,N_{\pm 0})$ may be obtained by integrating Eq. (13) from $(T_0,\,p_0,\,N_{\pm 0})$ to $(T,\,p,\,N_\pm)$ without the necessity of evaluating either $\gamma_\pm(T_0,\,p_0,\,N_{\pm 0})$ or $\gamma_\pm(T,\,p,\,N_\pm)$.

The molality activity coefficient may be obtained by replacing $N_\pm$ by $m_\pm$ in Eq. (13) or by multiplying the right hand side of this equation by $(1-N_2)/[1+(\nu-1)N_2]$.

If the solute is not dissociated then ν is replaced by unity, $N_\pm$ by N_2, $a_\pm(T,\,p,\,N_\pm)$ by $a_2(T,\,p,\,N_2)$ and $\gamma_\pm(T,\,p,\,N_\pm)$ by $\gamma_2(T,\,p,\,N_2)$. The equation then conforms with Lewis and Randall's definition of the activity of an undissociated solute.

SOLVENT

The solvent activity is defined so that $F_i{}^0 = F(T,\,p)$ where $F(T,\,p)$ denotes the molar free energy of the pure solvent substance.[6]

The mole fraction activity and activity coefficient can thus be evaluated as the line integral

$$\gamma_1(T,\,p,\,N_1) = \frac{a(T,\,p,\,N_1)}{N_1}$$

$$= \exp\int_{T_0,\,p_0,\,N_1=1}^{T,\,p,\,N_1}\frac{H-H_1}{RT^2}dT + \frac{v_1-v}{RT}dp$$

$$+\left[\frac{N_1}{RT}\frac{\partial F_1}{\partial N_1}-1\right]d\ln N_1. \quad (14)$$

This integral may be subdivided as was Eq. (13) and the same reasoning applied to it since, by definition, γ_1 has the same limit unity as $N_1\to 1$ for all values of T and p.

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if the "standard state" were assumed to be at the fixed pressure $p=1$. L. H. Adams (Chem. Rev. 19, 1 (1936)) has interpreted their definition of activity as the latter alternative. (See reference 6.)

[5] If the differential form be preferred it can be obtained as follows: (a) for "$d\ln\gamma_\pm$" delete the "exp" and integral sign. (b) for "$d\ln a$" delete the "exp" and integral sign and cancel out "$d\ln N$" or "$d\ln m$," as the case may be, from each side of the equation. This method can be used for all the line integrals expressed in this paper but is not, however, applicable to line integrals in general.

[6] Lewis and Randall state "$a/N = 1$ when $N = 1$" and since a is in general a function of $(T,\,p,\,N_1)$ this would restrict $F_i{}^0$ to be a function of T and p only. However, they also state "if a pure liquid or a pure solid X at atmospheric pressure be chosen as the standard state of unit activity we may change the activity" by a change of concentration. This is presumably a slip but if not they should have said

$$\lim_{N_1\to 1}\frac{a_1(T,\,p,\,N_1)}{N_1} = \exp\int_1^p\frac{v}{RT}dp,$$

where v denotes the molar volume of the pure substance. It would be inconvenient for correlation purposes to have the solute and solvent defined unsymmetrically in this way and it is assumed here that the first quotation represents the intent of Lewis and Randall. This agrees with the pressure derivative as written by Schottky (W. Schottky, Thermodynamik (Berlin, 1929), p. 284). L. H. Adams has interpreted the definition of solvent activity as the second alternative which is symmetrical with his definition of solute activity.

If we wished to treat the solvent as a dissociated substance and consider the activity and activity coefficient of a mean resulting contributory part of the dissociated solvent, we could proceed as for a solute or by purely formal means substitute the symbol $\pm$ for the subscript "1" in Eq. (14) where $\pm$ denotes a mean solvent ion, and divide the right hand side of the equation through by ν with the exception of unity in the bracket.

We note then that, for systems miscible in all proportions, it is immaterial which of the two definitions we assign to the components because it is evident that the two definitions will express the same relation; here, however, the mole fraction will be the preferred unit of concentration because as N_2 approaches unity m becomes infinite.

GAS MIXTURES

Gaseous constituents are miscible in all proportions and therefore a single expression will suffice to evaluate the activities of these components. An activity and activity coefficient of a gas component could then be defined by Eq. (13) or (14). It has been customary, however, to define for gases a quantity called fugacity.

An ideal binary gas mixture, by definition, satisfies the relations $p_i = N_i p$ and $F_i(T, p, N_i) = F(T, p_i)$, where p denotes the total pressure and p_i the pressure constituent i would have if it existed by itself at the same temperature and with the same value of its chemical potential. $F(T, p_i)$ denotes the free energy per mole of i at T and p_i. These relations, however, become applicable in general to real gas mixtures only for small values of p. The physical hypothesis will, accordingly, be written as

$$\lim_{p \to 0} p N_i e^{-F_i/RT} = \phi_i(T). \tag{15}$$

The fugacity, f_i, of component i will be defined by Eq. (1), in which f_i replaces a_i, and the relation $RT \ln \phi_i(T) = -F_i^0$, and may be written as

$$\frac{f_i(T, p, N_i)}{p N_i} = \exp \int_{T_0, \, p=0}^{T, \, p, \, N_i} \frac{H^* - H_i}{RT^2} dT$$
$$+ \left[\frac{p v_i}{RT} - 1 \right] d \ln p + \left[\frac{N_i}{RT} \frac{\partial F_i}{\partial N_i} - 1 \right] d \ln N_i, \tag{16}$$

where H^0 is a function of T only.

When $N_i = 1$ then p denotes the pressure of the pure constituent i and the equation reduces to Lewis and Randall's[7] definition of fugacity for a simple gas; H_i and v_i become H and v, the heat content and volume per mole, respectively, and the last term vanishes.

If the activity, a_i, of a gas component i be defined by

$$a_i(T, p, N_i) = f_i(T, p, N_i)/f_i(T, p),$$

$f_i(T, p)$ denoting the fugacity of the pure constituent, it will be evident that this activity may be expressed by Eq. (14). When Eq. (3) is satisfied over the entire concentration range then $a_i/N_i \equiv 1$ and $f_i(T, p, N_i) \equiv N_i f_i(T, p)$. When Eq. (15) is satisfied over the entire pressure range then

$$f_i(T, p, N_i) \equiv N_i p.$$

In conclusion the writer wishes to acknowledge the helpful criticism received from L. H. Adams.

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[7] G. N. Lewis and M. Randall, (*Thermodynamics and the Free Energy of Chemical Substances* (New York, 1923), p. 192), for their definition of F^0 "complete the definition by making the fugacity of a perfect gas equal to the pressure." For the argument it is not necessary to assume $|v - RT/p|$ converges to zero but merely that it remains finite as p converges to zero because we are concerned here with ratios, not differences.