Reaction Equilibrium of Real Fluid Mixtures

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A theoretical approach to equilibrium calculations for homogeneous real fluid mixtures is presented. The overall approach is developed for, although not theoretically restricted to, a corresponding states equation of state, $z(T_r, p_r)$. The method is applied to the gaseous ammonia synthesis data of Larson and Dodge. Excellent agreement was attained with the data. Quite significant improvement was observed over the ideal gas and ideal solutions approximations.

Given the reaction equation

$$\nu_a a + \nu_b b + \ldots \rightarrow -\nu_\alpha \alpha - \nu_\beta \beta - \ldots \tag{1}$$

the chemical affinity for the reaction is the quantity

$$\lambda \equiv \nu_a \mu_a + \nu_b \mu_b + \ldots + \nu_\alpha \mu_\alpha + \nu_\beta \mu_\beta + \ldots \tag{2}$$

If the value of the chemical affinity is positive, the reaction tends to proceed to the right as long as each of the reactants $a, b, \ldots$ are present. Conversely, if the affinity is negative, the reaction tends to the left as long as each of the species $\alpha, \beta \ldots$ are present. If the chemical affinity is zero then the system is said to be in chemical reaction-equilibrium.

$$[\sum_i \nu_i \mu_i = 0] \Longrightarrow \text{reaction-equilibrium} \tag{3}$$

The accurate calculation of the chemical potential and, in turn, of the chemical affinity is an intermediate objective of this paper. The ultimate goal is to establish the composition at reaction equilibrium. The essence of the procedure is to calculate the affinity when given the composition, and then, by iteration, determine that composition which yields zero affinity.

THEORY

The chemical potential of species a in a single-phase real mixture is readily shown to equal

$$\mu_a(T, p, n_a, n_b, \ldots) = [g_{\mathrm{id}}]_a(T, p^0) + RT \ln(x_a p/p^0) - \int_0^p \left[\frac{RT}{y} - \overline{V}_a(T, y, n_a, \ldots) \right] dy \tag{4}$$

The derivation of this equation assumes the Gibbs-Dalton Law in the zero-pressure limit (2, Appendix D). For ideal gas mixtures, the integrand in Equation (4) is zero; the ideal solution assumption consists of assuming that $\overline{V}_a$ equals the specific volume of pure a at the same temperature and pressure:

$$\overline{V}_a(T, p, n_a, \ldots) = v_a(T, p)]_{\text{ideal solutions}} \tag{5}$$

Although the ideal gas and ideal solution approximations are often useful, they are not always adequate. However, for applications to reaction and/or phase equilibrium, it is rather hopeless to determine the $\overline{V}_i$ from experimental $V(T, p, n_a, \ldots)$. Exhaustive PVT data would be needed at a great number of compositions, most of which would be unstable. In essence, the equilibrium composition itself would be determined via the experiment.

Hence, theoretical means for establishing the $\overline{V}_i$ are desirable. The methods to be presented here are applicable with all PVT functions of state for mixtures. For example, equations of state such as the virial equation and the Benedict-Webb-Rubin equation could be employed, or graphical and tabular generalized functions of state, complemented by mixture rules, could be used. The development to follow is for the Kamerlingh Onnes principle of corresponding states with Kay's mixture rule; it is readily generalized to any other principle and/or mixture rule. Furthermore, the same procedures are applicable with equational functions of state.

Chemical Potential from Principles of Corresponding States

The principles of corresponding states hypothesize that the PVT behavior of all substances (or a class of substances) can be represented by a universal function. For example, the Kamerlingh Onnes principle is

$$\frac{pv}{RT} = z\left(\frac{T}{T_c}, \frac{p}{p_c}\right) = z(T_r, p_r) \tag{6}$$

where T_c is the critical temperature, or the pseudocritical temperature in the case of mixtures, and similarly for p_c.

Other principles have additional independent variables, to distinguish in essence different classes of substances. Examples of additional variables are the critical compressibility factor z_c (*3, 4*) and the acentric factor ω (*5, 6*). Some principles utilize other variables besides T_c and p_c for reduction parameters; for example, intermolecular potential function parameters such as ϵ/k and ϵ/σ^3, respectively (*7, 8*).

The integrand of Equation (4) can be determined with the principle represented by Equation (6); the development is readily applicable to the other principles. The point of departure is the integrand of Equation (4):

$$\frac{RT}{p} - \bar{V}_a = \frac{RT}{p} - \left.\frac{\partial[nzRT/p]}{\partial n_a}\right)_{T,p,n_b,\ldots}$$

$$= \frac{RT}{p}[1-z] - \frac{nRT}{p}\left.\frac{\partial z}{\partial n_a}\right)_{T,p,n_b,\ldots} \qquad (7)$$

To evaluate the derivative $\partial z/\partial n_a$ therein, notice that the dependence of z on n_a in Equation (6) is reflected by the pseudocritical constants T_c and p_c, through the selected mixture rule. Hence the chain rule yields

$$\left.\frac{\partial z}{\partial n_a}\right)_{T,p,n_b,\ldots} = \left.\frac{\partial z}{\partial T_r}\right)_{p_r}\left.\frac{\partial T_r}{\partial T_c}\right)_{T}\left.\frac{\partial T_c}{\partial n_a}\right)_{n_b,\ldots}$$

$$+ \left.\frac{\partial z}{\partial p_r}\right)_{T_r}\left.\frac{\partial p_r}{\partial p_c}\right)_{p}\left.\frac{\partial p_c}{\partial n_a}\right)_{n_b,\ldots}$$

$$= -\frac{T}{T_c^2}\frac{\partial T_c}{\partial n_a}\frac{\partial z}{\partial T_r} - \frac{p}{p_c^2}\frac{\partial p_c}{\partial n_a}\frac{\partial z}{\partial p_r} \qquad (8)$$

Given any mixture rule for the pseudocritical constants, the quantities T_c, p_c, $\partial T_c/\partial n_a$, and $\partial p_c/\partial n_a$ can be determined directly, in terms of composition alone. For example, with Kay's rule

$$T_c = \frac{1}{n}\Sigma n_i T_{ci}$$

$$= \frac{1}{n_a + n_b + \ldots}[n_a T_{ca} + n_b T_{cb} + \ldots] \qquad (9)$$

and

$$\left.\frac{\partial T_c}{\partial n_a}\right)_{n_b,\ldots} = \frac{1}{n_a + n_b + \ldots}T_{ca}$$

$$- \frac{1}{[n_a + n_b + \ldots]^2}[n_a T_{ca} + n_b T_{cb} + \ldots]$$

$$= \frac{1}{n}[T_{ca} - T_c] \qquad (10)$$

Similarly

$$p_c = \frac{1}{n_a + n_b + \ldots}[n_a p_{ca} + n_b p_{cb} + \ldots] \qquad (11)$$

$$\left.\frac{\partial p_c}{\partial n_a}\right)_{n_b,} = \frac{1}{n}[p_{ca} - p_c] \qquad (12)$$

Expressions for $\partial T_c/\partial n_a$ and $\partial p_c/\partial n_a$ in terms of the n_i's and the constants (T_{ci}, p_{ci}) of the pure constituents can be obtained by the same procedures for any other mixture rule.

Regardless which mixture rule is employed, substitution of Equation (8) into (7), and in turn into (4), yields

$$\mu_a(T, p, n_a, \ldots) = [g_{\mathrm{id}}]_a(T, p^0)$$

$$+ RT\ln(x_a p/p^0) + RT_c T_r\int_0^{p_r}\frac{z(T_r, p_r) - 1}{p_r}dp_r$$

$$- nR\frac{\partial T_c}{\partial n_a}T_r^2\int_0^{p_r}\frac{1}{p_r}\left[\frac{\partial z}{\partial T_r}\right](T_r, p_r)dp_r$$

$$- \frac{nRT_c}{p_c}\frac{\partial p_c}{\partial n_a}T_r\int_0^{p_r}\left[\frac{\partial z}{\partial p_r}\right](T_r, p_r)dp_r \qquad (13)$$

The first integral on the right-hand side of Equation (13) is readily determined numerically, with a given function $z(T_r, p_r)$. This has been done by several investigators. For, notice that (*9*)

$$\left[\frac{g - g_{\mathrm{id}}}{RT_c}\right](T_r, p_r) \equiv T_r\int_0^{p_r}\frac{z(T_r, p_r) - 1}{p_r}dp_r \qquad (14a)$$

Or, equivalently

$$\gamma(T_r, p_r) \equiv \exp\left(\int_0^{p_r}\frac{z(T_r, p_r) - 1}{p_r}dp_r\right) \qquad (14b)$$

Tables for the fugacity coefficient $\gamma(T_r, p_r)$ have been presented, for example, by Lydersen et al. (*4*) and Pitzer et al. (*6*).

The integrand $[1/p_r][\partial z/\partial T_r](T_r, p_r)$ can be determined from the given function $z(T_r, p_r)$, and then integrated. Tables for this integral are also available in the latter references (*4, 6*):

$$\left[\frac{h - h_{\mathrm{id}}}{RT_c}\right](T_r, p_r) \equiv$$

$$- T_r^2\int_0^{p_r}\frac{1}{p_r}\left[\frac{\partial z}{\partial T_r}\right](T_r, p_r)\,dp_r \qquad (15)$$

Also, the third integral is readily seen to equal $z(T_r, p_r) - 1$. Collecting these expressions for the integrals and substituting into Equation (13), one gets

$$\mu_a(T, p, n_a, \ldots) = [g_{\mathrm{id}}]_a(T, p^0)$$

$$+ RT\ln(x_a p/p^0) + RT\ln\gamma\left(\frac{T}{T_c}, \frac{p}{p_c}\right)$$

$$+ nR\frac{\partial T_c}{\partial n_a}\left[\frac{h - h_{\mathrm{id}}}{RT_c}\right]\left(\frac{T}{T_c}, \frac{p}{p_c}\right)$$

$$- \frac{nRT}{p_c}\frac{\partial p_c}{\partial n_a}\left[z\left(\frac{T}{T_c}, \frac{p}{p_c}\right) - 1\right] \qquad (16)$$

wherein the quantities T_c, p_c, $\partial T_c/\partial n_a$, and $\partial p_c/\partial n_a$ are given by the selected mixture rule, as functions of composition alone. Thus, given the T, p, and composition, μ_a can be evaluated, via the latter equation, with tabulations which are available for each of the bracketed quantities on the right-hand side (*4, 6*). The above derivation of Equation (16) is analogous to developments given by Gamson and Watson (*10*) and Joffe (*11*), who derived expressions for the fugacity coefficient. Therewith, Joffe calculated the fugacity coefficients for equilibrium mixtures of NH_3-H_2-N_2-A; Pitzer and Hultgren (*12*) correlated well the fugacities of an inert solution, propane-isopentane.

For ideal gas mixtures

$$\mu_a(T, p, n_a, \ldots) = [g_{\mathrm{id}}]_a(T, p^0) + RT\ln(x_a p/p^0) \qquad (17)$$

And for ideal solutions

$$\mu_a(T, p, n_a, \ldots) = [g_{\mathrm{id}}]_a(T, p^0)$$

$$+ RT\ln(x_a p/p^0) + RT\ln\gamma_a(T, p) \qquad (18)$$

where $\gamma_a(T, p)$ is the fugacity coefficient of pure a at the temperature T and pressure p of the mixture.

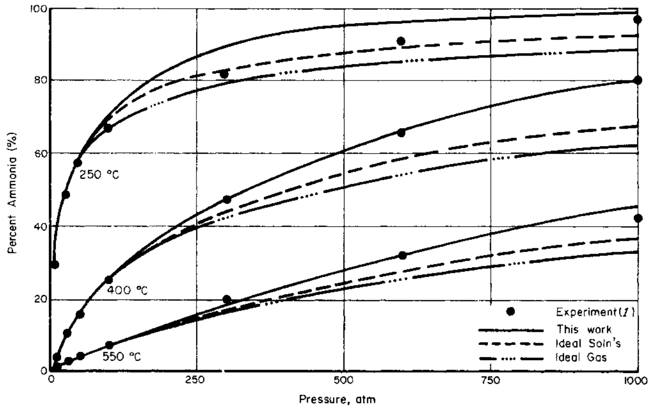

Fig. 1. Equilibrium percentage of NH_3 (from 0.5 mole N_2, 1.6213 moles H_2, and 0.00638 moles A as components) versus pressure. (*a*) t = 250°C., (*b*) t = 400°C., (*c*) t = 550°C.

Determination of the Chemical Affinity

The chemical affinity for a homogeneous reaction may be obtained by combining Equations (2) and (16):

$$\lambda = RT \Big[\ln K_p(T) + \Sigma\nu_i \ln(x_i p/p^0) + \Big\{ \ln \gamma \left(\frac{T}{T_c}, \frac{p}{p_c}\right) \Big\} \Sigma\nu_i \Big] + n\Sigma\nu_i \Big\{ \frac{\partial T_c}{\partial n_i}(n_a, n_b, \ldots) \left[\frac{h - h_{id}}{T_c}\right]\left(\frac{T}{T_c}, \frac{p}{p_c}\right) - \frac{RT}{p_c}\frac{\partial p_c}{\partial n_i}(n_a, \ldots)\left[z\left(\frac{T}{T_c}, \frac{p}{p_c}\right) - 1\right]\Big\} \tag{19}$$

where the definition

$$\ln K_p(T) \equiv \frac{1}{RT} \Sigma\nu_i [g_i]_{id} (T, p^0) \tag{20}$$

has been utilized. Thus for a given reaction, the chemical affinity at a given temperature, pressure, and composition can be calculated using Equation (19) with (1) a mixture rule for $T_c(n_a, n_b, \ldots)$, $p_c(n_a, \ldots)$, $[\partial T_c/\partial n_i](n_a, \ldots)$, $[\partial p_c/\partial n_i](n_a, \ldots)$; and (2) tabulations or graphs such as those in reference *4* or *6* for the functions $z(T_r, p_r)$, $\gamma(T_r, p_r)$, $[(h - h_{id})/T_c](T_r, p_r)$; and (3) a tabulation or graph such as the JANAF tables (*13*) for the equilibrium constant $K_p(T)$. Conversely, if the composition is unknown, Equation (19) can be solved by iteration for the equilibrium composition, when $\lambda = 0$. Thus when the initial amounts of each species are given, then the amount of each species n_i can be expressed in terms of one independent variable, say the extent of reaction, via the reaction equation (1). Then, with these expressions Equation (19) can be solved iteratively for the equilibrium composition. In cases with more than one reaction, Equation (19) is used once for each independent reaction. Comings (*14*) outlines a method for determining equilibrium composition, which is theoretically equivalent to the foregoing, and which is based on Joffe's (*11*) earlier fugacity coefficient version of Equation (16). However, the use of the method was not illustrated with an application.

COMPARISON WITH EXPERIMENT

Larson and Dodge (*1*) studied experimentally the reaction

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftarrows NH_3 \tag{21}$$

A slight excess of hydrogen was present in the initial mixture as was a small amount of argon. Joffe (*11*) had used his analog to Equation (16) to calculate the equilibrium constant from the given experimental composition, and compared his calculated value to $K_p(T)$ between 450° and 500°C. Practically, though, it is the converse which is desired: find the equilibrium composition, given $K_p(T)$. This task, which is more formidable, is the one addressed in the present paper. Figure 1 compares the results at various temperatures of calculated equilibrium composition and the experimentally determined composition. The figure also includes the calculated compositions obtained with the ideal solutions and ideal gas approximations. To evaluate the quantities in Equation (19), the JANAF tables (*13*), the Lydersen-Greenkorn-Hougen tables (*4*), and Kay's mixture rule (*15*) were employed. [It should be mentioned that the results of Equation (19) differed little when the Joffe (*16*) or Stewart-Burkhardt-Voo (*17*) mixture rules were used; at most temperatures the agreement with the data was slightly worse and at some slightly better.] Due to the nonlinear implicit character of Equation (19), the iterative calculation was, of necessity, relegated to a computer program; see Nierode (*2*) for the details of this program.

Tables 1, 2, 3, and 4 summarize the comparisons between calculated and experimental compositions for seven temperatures. From the figures and tables it is apparent that the present method is superior to the ideal gas and ideal solutions results, especially for temperatures 350°C. and above. The comparison is less favorable at 250° and

TABLE 1. AVERAGE ABSOLUTE DEVIATION FROM NH_3 DATA (%)

Method	250°	300°	350°	400°	450°	500°	550°
This work	4.95	5.00	3.60	2.10	3.76	4.60	3.74
Ideal solution	3.72	3.64	5.40	6.09	7.70	8.51	7.40
Ideal gas	3.84	5.50	7.15	8.35	10.40	11.30	10.90

TABLE 2. OVERALL AVERAGE DEVIATION (%)

Method	Average deviation
This work	3.99
Ideal solution	6.07
Ideal gas	8.26

TABLE 3. OVERALL AVERAGE DEVIATION (%)
(EXCLUDING 250° AND 300°C.)

Method	Average deviation
This work	3.56
Ideal solution	7.02
Ideal gas	9.62

TABLE 4. HIGH-PRESSURE DEVIATIONS (%)

Method	600 atm. ($7 \lesssim p_r \lesssim 14$)	1,000 atm. ($12.5 \lesssim p_r \lesssim 20$)
This work	4.37	3.35
Ideal solution	9.10	12.37
Ideal gas	15.34	18.94

300°C., when pressures are intermediate. At these conditions the percentage of $NH_3 \simeq 80\%$, while $T_r \simeq 1.7$ and $p_r \simeq 3$ for the mixture. [Note that at fixed T and/or p, T_r and p_r will vary with composition as T_c and p_c change; for example, see Equations (10) and (12).] Thus the discrepancy may be due to the inability to correlate NH_3 (and H_2, *18*) well with the Kamerlingh Onnes principle when the reduced temperature is significantly below 2 (reduced Boyle temperature ≈ 2.4), especially for p_r from 1.5 to 3.5 (that is, for pressures in the neighborhood of the minima on the z versus p_r isotherms). In any case, because most substances are correlated much better than NH_3 and H_2 by the Kamerlingh Onnes principle, the reaction being considered provides a severe test for the algorithm employed here. Even so, the new method shows a significant improvement over ideal solutions and ideal gas approximations.

CONCLUSION

The present theoretical scheme for establishing equilibrium composition excels the ideal gas and ideal solutions methods for the ammonia synthesis data of Larson and Dodge (*1*). Thus it can be surmised that the new scheme is in general superior. Also, it should be mentioned that the present approach refers only to the concept of chemical potential, without relying on the concepts of fugacity, fugacity coefficient, activity coefficient, etc. Inasmuch as these latter concepts tend to perplex students, this is a significant pedagogical benefit, if not a theoretical one.

The present method is not restricted to usage with the Kamerlingh Onnes principle of corresponding states and/or the Lydersen-Greenkorn-Hougen tables; other additional and/or alternative parameters are readily included. Equational functions of state for mixtures could also be used. Comings (*14*) outlines a method which employs the Redlich-Kwong equation, using Joffe's (*11*) fugacity coefficient version of Equation (16). Prausnitz (*19*) presents a fugacity coefficient counterpart of Equation (16) for the virial equation of state; the corresponding expression for the chemical potential is

$$\mu_a(T, p, n_a, \ldots) = [g_{id}]_a\,(T, p^0) + RT \ln\,(x_a p/p^0) - p \sum_i \sum_j x_i x_j\,[B_{ij}(T) - 2B_{ia}(T)] + \ldots \quad (22)$$

Thus, as statistical-mechanical means for establishing PVT behavior become more practical, the present scheme may be employed therewith.

It should also be mentioned that the approach given here is readily adapted to situations where the temperature and/or pressure are not known. Thus for, say, adiabatic constant-pressure reaction, Equation (19) would be complemented by an energy balance, $\Delta H = 0$, to give two equations in two unknowns (the temperature and extent of reaction). Like the equilibrium equation—Equation (19) with $\lambda \equiv 0$—the energy equation can be represented in a form such that the various terms could be evaluated with the Lydersen-Greenkorn-Hougen and JANAF tables. In addition to the tabulations used for Equation (19), the standard enthalpies of formation and ideal gas model c_p for each species from JANAF would be used, plus $[\{c_p - c_{p,\,id}\}/R](T_r, p_r)$ and $[\mu c_p](T_r, p_r)$ from, say, Lydersen-Greenkorn-Hougen.

NOTATION

B, C = virial coefficients
c_p = specific heat, $\partial h/\partial T)_{p, n_a, n_b, \ldots}$
G = Gibbs free energy
g = specific Gibbs free energy
g_{id} = g of ideal gas model
H = enthalpy
h = specific enthalpy
h_{id} = specific enthalpy of ideal gas model
K_p = equilibrium constant for ideal gas model
N_0 = Avogardo's number
n = total number of moles
n_i = moles of constituent i
p = pressure
p^0 = pressure at the standard state
R = universal gas constant
S = entropy
T = temperature
T_c, p_c = mixture pseudocritical temperature and pressure
T_{ci}, p_{ci} = critical temperature and pressure of pure species i
T_r, p_r = T/T_c and p/p_c
V = volume
$\overline{V}_i$ = partial molal volume of component i
v = specific volume
x_i = mole fraction of species i
y = dummy variable
z = compressibility factor

Greek Letters

γ = fugacity coefficient
ϵ = intermolecular potential energy parameter
ν_i = stoichiometric reaction coefficient
λ = chemical affinity
μ = Joule-Thomson coefficient, $\partial T/\partial p)_h$
μ_i = chemical potential of species i
σ = intermolecular potential distance parameter

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