THE COMPUTATION OF THE THERMODYNAMIC PROPERTIES OF REAL GASES AND MIXTURES OF REAL GASES[1]

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I. INTRODUCTION

It is well known that the thermodynamic properties of a pure gas can be computed with reference to a particular standard state from the usual thermodynamic differential equations, and the result expressed in terms of elementary functions or presented in an equivalent tabular or graphical form provided (*1*) the heat capacity at constant pressure [or volume] is known as a function of temperature for some one pressure [or density], and (*2*) there is given an equation of state with determined values of the parameters, or there are available extensive pressure–volume–temperature or equivalent data over the entire range of temperatures and pressures involved.

Moreover, the properties of a gas mixture of invariant composition can be evaluated with reference to a particular standard state of the mixture from the same relations used for pure gases provided thermal and compressibility data on that particular mixture are given. Such a computation is in general pointless.

The problem of importance to be solved in the treatment of the thermodynamic properties of gas mixtures, including mixtures in which chemical reactions may occur, is the computation of the properties of all possible mixtures (with reference to a particular standard state of the constituent gases) from thermal and compressibility data on the pure constituents alone, and a knowledge of certain integration constants of the pure gases. The solution of the problem involves the use of both thermodynamic and statistical methods. Each involves certain assumptions. Since those underlying the thermodynamic discussion can be stated more explicitly and have a more direct physical basis than those on which the statistical treatment rests, it is important to separate the two methods until near the end of the argument when the definite integrals resulting from the thermodynamic discussion are evaluated by use of relations obtained from statistical considerations.

Five methods of attack have been proposed:

1. The ideal gas formulation.
2. The method of van der Waals (92, 100, 181).
3. The Gibbs–Dalton law (61).
4. The Lewis and Randall rule (125).
5. The general limit method (73).

Gillespie (66) suggested that the term "equilibrium pressure" of a gas in a mixture be used to denote the pressure of a pure gas in isothermal equilibrium with a gas mixture through a membrane permeable to that gas alone, and that "partial pressure" of a gas in a mixture be reserved for the product of the mole fraction of the gas in the mixture into the total pressure of the mixture.

In terms of these definitions the ideal gas formulation assumes that (*1*) the equilibrium pressure of a gas in a mixture is equal to its partial pressure, and (*2*) the equation of state of a gas mixture is $pV = \Sigma_i n_i RT$. Instead of (*2*) we may simply assume that the energies of the constituent gases are functions of temperature only (15). The relations for the thermodynamic properties of gas mixtures resulting from this formulation are the familiar ones found in textbooks on thermodynamics, and are the ones approached by the equations given by any of the four other methods as the pressure on the mixture approaches zero or as the equation of state constants are allowed to approach zero.

The four other methods will be considered in detail later.

II. DEFINITIONS AND SYMBOLS

Let p, V, T be the total pressure, total volume, and Kelvin temperature and E, S, H, F_{VT}, F_{pT}, and C_V, and C_p be the total energy, entropy, heat content, T-V thermodynamic potential (work content), T-p thermodynamic potential (free energy), and constant-volume and constant-pressure heat capacities, respectively, of n moles of a pure gas or of $\Sigma_i n_i$ moles of a gas mixture consisting of n_1, n_2, $\cdots$ moles of the gases 1, 2, $\cdots$ Let μ be the chemical potential of a pure gas and μ_i the chemical potential of gas i in a mixture.

Let $C = \Sigma_i n_i/V$ be the concentration of the mixture; and let $C_i = n_i/V$, $x_i = n_i/\Sigma_i n_i$, and f_i be respectively the concentration, mole fraction, and fugacity of gas i in the mixture.

Lower case letters used for an extensive quantity denote the values for 1 mole.

If it is necessary to distinguish between a pure gas and the same gas in a mixture, the subscript k will denote the value of a quantity for the pure gas and i that for the gas in the mixture.

The subscript e denotes the value of a thermodynamic quantity for a pure gas having the same total volume, temperature, and chemical potential as in a gas mixture. Under these conditions the pure gas would evidently be in thermodynamic equilibrium with the mixture through a membrane permeable to that gas alone; and, since the volume is specified, the values of all extensive as well as intensive properties of the gas would be fixed. Such quantities will be called "equilibrium" quantities, e.g., equilibrium pressure, p_e.

The subscript c denotes the value of a thermodynamic quantity for a pure gas having the same total volume, temperature, and number of moles as in a mixture. The concentration (moles per liter) of the pure gas is the same as its concentration in the mixture. Thus p_c is the pressure exerted by a pure gas that has been separated from a mixture and has the total volume and temperature of the mixture.

The subscript P denotes the value of a thermodynamic quantity for a pure gas having the same total pressure, temperature, and number of moles as in a mixture. Thus V_P is the volume of a pure gas that has been separated from a mixture and is at the total pressure and temperature of the mixture.

Thermodynamic relations among certain of the variables are:

$$E = TS - pV + \Sigma_i \mu_i n_i$$

$$
\begin{aligned}
H &= E + pV = TS + \Sigma_i \mu_i n_i \\
F_{VT} &= E - TS = -pV + \Sigma_i \mu_i n_i \\
F_{pT} &= H - TS = \Sigma_i \mu_i n_i \\
C_V &= (\partial E/\partial T)_{Vn} \\
C_p &= (\partial H/\partial T)_{pn}
\end{aligned}
$$

where the subscript n denotes constant composition as well as constant total number of moles if for a gas mixture.

Let ν_i be the stoichiometric coefficient of substance i in the equation representing a chemical reaction, being a negative number for a reactant and positive for a product. The exact mass action law is:

$$\Sigma_i \nu_i \mu_i = 0$$

The mass action constants in terms of partial pressures, K_p, and concentrations, K_C, are defined through the relations:

$$
\begin{aligned}
\ln K_p &= \Sigma_i \nu_i \ln px_i \\
\ln K_C &= \Sigma_i \nu_i \ln \frac{n_i}{V}
\end{aligned}
$$

In the discussion of equilibrium between condensed and gaseous solutions, we shall let y_i be the mole fraction of the i^{th} constituent of the condensed phase, and p_{0i} the vapor pressure of the pure substance at the temperature T.

III. THE METHOD OF VAN DER WAALS

In this method the particular equation of state employed is introduced early in the argument, especially in the calculation of the entropy of a gas mixture.

van der Waals (181) derived a relation for the isothermal variation of the thermodynamic potential F_{VT} for a gas mixture of constant composition by integration of $dF_{VT} = -pdV$ with his equation of state for gas mixtures:

$$p = \frac{RT}{v - b_x} - \frac{A_x}{v^2}$$

where b_x and A_x are functions of the mole fractions and the corresponding equation of state constants of the constituent gases and of certain interaction constants. During the integration the temperature and composition were held constant, so that the integration constant is evidently a function of these variables. The temperature variation was not discussed, although Kuenen (99) determined it, but the variation with composition was evaluated by passing to infinite volume and applying the equations of Gibbs (62) for the energy and entropy of a mixture of ideal gases. Although the method is open to question because of the occurrence of infinite quantities, the resulting expression is in agreement, except for the omission of certain temperature functions, with that derived from the general limit method for a van der Waals gas.

van Laar (100, 101, 102, 103, 104, 105) and van Laar and Lorenz (106, 107, 133) used the general limit method for computing the energy of a gas mixture obeying van der Waals' equation, but because of the difficulty encountered by the occurrence of an improper integral in a similar argument for the entropy they used the equation of Gibbs for the entropy of a mixture of ideal gases, replacing the volume V by $V - b_x$ to correct for the volume effect of the molecules. The term $V - b_x$ is eliminated through the van der Waals equation, so that in the final expressions only the A_x constant appears. From the energy and entropy the other thermodynamic functions of a gas mixture can be derived immediately. Although b_x and A_x are considered independent of pressure and temperature during the integration, van Laar recognized that the A constants for the constituent gases are functions of these variables and in the application of the resulting equations to data he used values appropriate to the experimental range. Application to Bartlett's (3) measurements on the system $H_2O(l)$, $H_2O(g) + N_2(g)$ gave a fair representation for the composition of the gas phase at 50°C. and 1000 atm. total pressure.

Keyes (92) applied the general limit method for the energy of a gas mixture and corrected the Gibbs expression for the entropy for the volume of the molecules, using in both cases his equation of state for gas mixtures:

$$\pi\Omega = \Sigma_i n_i RT$$

$$\pi = p + \frac{(\Sigma_i n_i A_i^{1/2})^2}{(V - \Sigma_i n_i l_i)^2}$$

$$\Omega = V - (\Sigma_i n_i \beta_i) e^{-(\Sigma_i n_i \alpha_i)/V}$$

where β_i, α_i, A_i, and l_i are equation of state constants for the pure gas i. The resulting expression for the variation of the mass action "constant" of the ammonia synthesis equilibrium with pressure gave a satisfactory agreement to 100 atm. and a tolerable agreement to 600 atm. with the empirical smoothing of the measurements of Larson and Dodge (110) and of Larson (108) by Gillespie (64, 65).

IV. THE GIBBS–DALTON LAW

As a starting point in the discussion of the thermodynamic properties of gas mixtures, Gibbs (61) proposed the following law: The pressure of a mixture of different gases is equal to the sum of the pressures of the different gases as existing each by itself at the same temperature and with the same value of its (chemical) potential.

Gillespie (72) called this the Gibbs–Dalton law and pointed out that it contained the essential idea of equilibrium necessary for a general thermodynamic treatment of gas mixtures. It is evident that the different gases "existing each by itself at the same temperature and with the same value of its potential" would each be in equilibrium with the gas mixture through a membrane permeable to that gas alone. The pressure of each pure gas under these conditions is its equilibrium pressure p_e; and the law states that, subject to the conditions:

$$\left.\begin{array}{r}
T \text{ (each pure gas)} = T \text{ (mixture)} \\
V \text{ (each pure gas)} = V \text{ (mixture)} \\
\mu_k = \mu_i \qquad (k \equiv i = 1, 2, \cdots)
\end{array}\right\} \quad \text{(A)}$$

the pressure p of a gas mixture is:

$$p = \Sigma_k p_{ek} \tag{1}$$

The second condition is unnecessary for equation 1 but is required to fix the value of any extensive property of the pure gases.

The results derivable from the Gibbs–Dalton law may be summarized as follows (72):

1. The concentration of a gas is the same at equilibrium on each side of a membrane permeable to it alone; and under conditions A the number of moles of each pure gas is the same as in the mixture:

$$C_i = C_{ek} \qquad (k \equiv i = 1, 2, \cdots) \tag{2}$$

$$n_i = n_{ek} \qquad (k \equiv i = 1, 2, \cdots) \tag{3}$$

2. When conditions A apply the following quantities are additive:

$$S = \Sigma_k S_{ek} \tag{4}$$

$$\left.\begin{array}{lll}
E = \Sigma_k E_{ek} & H = \Sigma_k H_{ek} & F_{VT} = \Sigma_k F_{VT_{ek}} \\
F_{pT} = \Sigma_k F_{pT_{ek}} & C_V = \Sigma_k C_{V_{ek}} & C_p = \Sigma_k C_{p_{ek}}
\end{array}\right\} \quad (5)$$

3. When conditions A apply the following are also true:

$$\left.\begin{array}{r}
T \text{ (each pure gas)} = T \text{ (mixture)} \\
V \text{ (each pure gas)} = V \text{ (mixture)} \\
n_k = n_i, \text{ that is, } C_k = C_i \quad (k \equiv i = 1, 2, \cdots)
\end{array}\right\} \quad \text{(B)}$$

and

$$p = \Sigma_k p_{ck} \tag{6}$$

$$\mu_i = \mu_{ck} \tag{7}$$

$$\left.\begin{array}{lll}
 & S = \Sigma_k S_{ck} & \\
E = \Sigma_k E_{ck} & H = \Sigma_k H_{ck} & F_{VT} = \Sigma_k F_{VT_{ck}} \\
F_{pT} = \Sigma_k F_{pT_{ck}} & C_V = \Sigma_k C_{V_{ck}} & C_p = \Sigma_k C_{p_{ck}}
\end{array}\right\} \quad (8)$$

where the subscript c denotes that conditions B apply. Equation 6 is the usual statement of Dalton's law (47, 48). Although Dalton's law is a consequence of the Gibbs–Dalton law, the converse cannot be proved, since the idea of equilibrium is lacking in Dalton's law.

4. Subject to conditions B:

$$\left(\frac{\partial p}{\partial n_i}\right)_{VT_n} = \left(\frac{\partial p_{ck}}{\partial n_k}\right)_{VT} \qquad (i \equiv k = 1, 2, \cdots) \qquad (9)$$

5. The Gibbs–Dalton law leads to a complete solution of the problem of the determination of the thermodynamic properties of gas mixtures from information on the behavior of pure gases only.

Consider a number of systems, one consisting of a gas mixture and each of the others consisting of one of the pure constituent gases. Let the conditions A apply for all variations. For the gas mixture:

$$\mathrm{d}p = (S/V)\mathrm{d}T + \Sigma_i(n_i/V)\mathrm{d}\mu_i \qquad (10)$$

and for each pure gas:

$$\mathrm{d}p_{ek} = (S_{ek}/V)\mathrm{d}T + (n_{ek}/V)\mathrm{d}\mu_k \quad (k = 1, 2, \cdots) \qquad (11)$$

Thus:

$$\left(\frac{\partial p}{\partial \mu_i}\right)_{T\mu} = \frac{n_i}{V} \equiv C_i \qquad \left(\frac{\partial p}{\partial T}\right)_{\mu} = \frac{S}{V} \qquad (i = 1, 2, \cdots) \qquad (12)$$

$$\left(\frac{\partial p_{ek}}{\partial \mu_k}\right)_{T} = \frac{n_{ek}}{V} \equiv C_{ek} \qquad \left(\frac{\partial p_{ek}}{\partial T}\right)_{\mu_k} = \frac{S_{ek}}{V} \qquad (k = 1, 2, \cdots) \qquad (13)$$

The subscript μ in equation 12 denotes that all of the μ's are constant unless the differentiation is with respect to one of the μ's, in which case all of the other μ's are constant.

Let us *assume* that the total pressure of the mixture is given by the Gibbs–Dalton law. Then from equation 1:

$$\left(\frac{\partial p}{\partial \mu_i}\right)_{T\mu} = \left(\frac{\partial p_{ek}}{\partial \mu_k}\right)_{T} \qquad (i \equiv k = 1, 2, \cdots) \qquad (14)$$

$$\left(\frac{\partial p}{\partial T}\right)_{\mu} = \Sigma_k \left(\frac{\partial p_{ek}}{\partial T}\right)_{\mu_k} \qquad (15)$$

Substitution from equations 12 and 13 into equations 14 and 15 gives:

$$\frac{n_i}{V} = \frac{n_{ek}}{V}$$

$$\frac{S}{V} = \Sigma_k \frac{S_{ek}}{V}$$

Since $n/V = C$, equation 2 is proved; and since V has the same value for the gas mixture and each pure gas, equations 3 and 4 are true. To prove equation 5 we substitute from equations 1, 3, and 4 into the general thermodynamic relations for E, H, etc. given in Section 2 (page 146) and use conditions A.

From equations 2 and 3 and conditions A it is evident that conditions B hold provided the Gibbs–Dalton law is true. Now conditions B and A each define the same state of each pure gas as regards both intensive and extensive thermodynamic properties. Hence when conditions B apply the chemical potential of each pure gas has the same value as in the mixture (equation 7), and equations 1, 4, and 5 become equations 6 and 8. It should be noted that equations 7 and 8 cannot be derived from equation 6 and conditions B alone.

Differentiation of equation 6 with respect to n_i $(= n_k)$, $(i \equiv k = 1, 2, \cdots)$, subject to conditions B gives equation 9.

It is evident that equations 6, 7, and 8 give the properties of a gas mixture in terms of those of the pure constituent gases without requiring any measurements on the mixture.

V. THERMODYNAMIC RELATIONS FOR GAS MIXTURES FROM THE GIBBS–DALTON LAW

Let

$$p_k = \Phi_k(T, n_k/V) \tag{16}$$

be the equation of state for a pure gas. The Gibbs–Dalton law gives for the total pressure p of a gas mixture and for the equilibrium pressure p_{ek} of gas i in the mixture the relations:

$$p = \Sigma_k p_k = \Sigma_k \Phi_k(T, n_k/V) \tag{17}$$

$$p_{ek} = \Phi_k(T, n_k/V) \qquad (k = 1, 2, \cdots) \tag{18}$$

where conditions B apply and the summation of equation 17 extends over all of the gases in the mixture. In this relation as in those immediately following it is not necessary that the form of the function Φ be the same for all of the gases. Thus different equations of state may be used for the different pure gases, and indeed Φ can be evaluated graphically for some or all of the gases involved.

In terms of the expressions for the thermodynamic properties of pure gases given by the general limit method (see Section XII), the Gibbs–Dalton law leads to the conditions B and the following equations for gas mixtures:

$$E = \Sigma_k \left\{ \int_V^\infty \left[p_k - T\left(\frac{\partial p_k}{\partial T}\right)_{V_k} \right] \mathrm{d}V_k + n_k e_k^0 \right\} \tag{19}$$

$$H = \Sigma_k \left\{ \int_V^\infty \left[p_k - T\left(\frac{\partial p_k}{\partial T}\right)_{V_k} \right] \mathrm{d}V_k + p_k V + n_k e_k^0 \right\} \tag{20}$$

$$S = \Sigma_k \left\{ \int_V^\infty \left[\frac{n_k R}{V_k} - \left(\frac{\partial p_k}{\partial T}\right)_{V_k} \right] \mathrm{d}V_k + n_k R \ln \frac{V}{n_k RT} + n_k s_k^0 \right\} \tag{21}$$

$$F_{VT} = \Sigma_k \left\{ \int_V^\infty \left[p_k - \frac{n_k RT}{V_k} \right] \mathrm{d}V_k - n_k RT \ln \frac{V}{n_k RT} + n_k(e_k^0 - Ts_k^0) \right\} \tag{22}$$

$$F_{pT} = \Sigma_k \left\{ \int_V^\infty \left[p_k - \frac{n_k RT}{V_k} \right] \mathrm{d}V_k - n_k RT \ln \frac{V}{n_k RT} + p_k V + n_k(e_k^0 - Ts_k^0) \right\} \tag{23}$$

$$C_V = \Sigma_k \left\{ n_k c_{vk}^{*} - T \int_V^{\infty} \left(\frac{\partial^2 p_k}{\partial T^2} \right)_{V_k} \mathrm{d}V_k \right\} \tag{24}$$

$$C_p = \Sigma_k \left\{ n_k c_{pk}^{*} - n_k R - T \frac{(\partial p_k / \partial T)_{V_k}^2}{(\partial p_k / \partial V_k)_T} - T \int_V^{\infty} \left(\frac{\partial^2 p_k}{\partial T^2} \right)_{V_k} \mathrm{d}V_k \right\} \tag{25}$$

$$\mu_i = \int_V^{\infty} \left[\left(\frac{\partial p_k}{\partial n_k} \right)_{V_k T} - \frac{RT}{V_k} \right] \mathrm{d}V_k - RT \ln \frac{V}{n_k RT} + RT + (e_k^0 - T s_k^0) \tag{26}$$

$$RT \ln f_i = \int_V^{\infty} \left[\left(\frac{\partial p_k}{\partial n_k} \right)_{V_k T} - \frac{RT}{V_k} \right] \mathrm{d}V_k - RT \ln \frac{V}{n_k RT} \tag{27}$$

In these relations the summations extend over all of the gases in the mixture, and:

$$e_k^0 = \int_{T_0}^{T} c_{vk}^{*} \, \mathrm{d}T + e_{0k}^0 \tag{28}$$

$$s_k^0 = \int_{T_0}^{T} \frac{c_{vk}^{*}}{T} \, \mathrm{d}T + R \ln \frac{T}{T_0} + S_{0k}^0 \tag{29}$$

The quantities e_{0k}^0 and s_{0k}^0 are the molal energy and entropy constants for the pure gas k at the temperature T_0, and c_{vk}^{*} the molal constant-volume heat capacity at zero pressure.

In each of the equations 19 through 25 the left-hand side of the equation is the value of a thermodynamic quantity for a gas mixture at V, T, and the mole numbers n_i ($i \equiv k = 1, 2, \cdots$). The terms enclosed in the braces on the right-hand side are to be computed for each pure gas k from equations 16 (or by equivalent graphical methods), 28, and 29 with V, T, and n_k or V, T, n_k/V, having the same values for each pure gas as in the gas mixture, and the sum taken for all of the gases composing the mixture. In equations 26 and 27 the left-hand side is the value of a quantity for gas i in the mixture, and the right-hand side is computed for the pure gas as just described.

The Gibbs–Dalton law leads directly to an expression for the mass action law in terms of concentrations. Let K_C^{*} be the value of K_C at zero pressure. Then from equation 26 and the condition $\Sigma_i \nu_i \mu_i = 0$ for equilibrium in a system in which chemical reaction occurs, we find:

$$\ln \frac{K_C}{K_C^{*}} = -\frac{1}{RT} \Sigma_k \left\{ \nu_k \left[\int_V^{\infty} \left[\left(\frac{\partial p_k}{\partial n_k} \right)_{V_k T} - \frac{RT}{V_k} \right] \mathrm{d}V_k \right] \right\} \tag{30}$$

$$\ln K_C^{*} = -\frac{1}{RT} \Sigma_k \{ \nu_k [e_k^0 + RT - T s_k^0 + RT \ln RT] \} \tag{31}$$

To obtain $\ln K_p$ we add this term to each side of equation 30 and rearrange:

$$\ln \frac{K_p}{K_p^{*}} = -\frac{1}{RT} \Sigma_k \left\{ \nu_k \left[\int_V^{\infty} \left[\left(\frac{\partial p_k}{\partial n_k} \right)_{V_k T} - \frac{RT}{V_k} \right] \mathrm{d}V_k \right] \right\} + (\Sigma_i \nu_i) \ln \frac{pV}{(\Sigma_i n_i) RT} \tag{32}$$

$$\ln K_p^* = -\frac{1}{RT} \Sigma_k\{\nu_k[e_k^0 + RT - Ts_k^0]\} \tag{33}$$

In these equations the terms inclosed in braces are evaluated for each pure gas k from equations 16, 28, and 29 with V, T, n_k/V having the same values for each pure gas as in the mixture. The summations extend over all gases in the mixture, with $\nu_k = 0$ for gases that do not take part in the chemical reaction. The last term of equation 32 is to be computed for the gas mixture, the sum $\Sigma_i n_i$ being taken for all gases in the mixture. It will be noticed that both K_C and K_p are functions of the composition of the equilibrium mixture.

To compute K_C for a given chemical reaction at a given molal volume V and temperature T: (*1*) calculate K_C^* for the given temperature and as a first approximation set $K_C = K_C^*$ (the ideal gas relation), from which a provisional set of equilibrium mole fractions can be obtained; (*2*) these mole fractions are the n_k's which together with V and T permit an approximate evaluation of the right-hand side of equation 30 and hence a second approximation to K_C and the equilibrium mole fractions. The process can be repeated until no further change in composition results. The convergence of the calculation to the final equilibrium composition is rapid.

To compute K_p for a given pressure p and temperature T from equations 32 and 33 the same method is employed. However, the volume of the mixture must be calculated at each stage of the computation from equation 17.

VI. APPLICATION OF THE GIBBS–DALTON LAW TO MIXTURES OF REAL GASES

The Gibbs–Dalton law has never been used for the calculation of the effect of pressure on chemical equilibria. Lurie and Gillespie (134) and Gillespie (72) have pointed out that the law is particularly suited to the computation of the effect of the addition of an inert gas, such as nitrogen, to a univeriant system, as $NH_3(l)$, $NH_3(g)$ or $BaCl_2(s)$, $BaCl_2 \cdot 8NH_3(s)$, $NH_3(g)$. The calculations proceed as follows:

1. Given the total pressure p, temperature T, and composition $x_1, x_2, \cdots$ of the gas phase, to find the equilibrium pressures of the individual gases present. By successive approximations we can compute the molal volume V of the mixture from equation 17, which may be written:

$$p = \Phi_1(T, x_1/V) + \Phi_2(T, x_2/V) + \cdots \tag{34}$$

the desired equilibrium pressures $p_{e1} \equiv \Phi_1(T, x_1/V)$, etc. being evaluated at the same time. The equilibrium pressure of the vapor so determined should agree with the vapor pressure of the univariant system when corrected for the effect of hydrostatic pressure (Poynting relation) and for the solubility (if any) of the inert gas in the condensed complex.

2. Given the total pressure p, the temperature T, and the equilibrium pressures p_{ek} of $m - 1$ of the m substances in the gas phase, to calculate the composition of the gas phase. The equilibrium pressure of the m^{th} substance is computed by difference. From the relations $p_{e1} = \Phi_1(T, n_1/V)$, etc., we can obtain n_1/V, etc., for each gas, whence

$$x_i = \frac{n_i/V}{\Sigma_i(n_i/V)} \tag{35}$$

In some cases the method may require extrapolation of the equation of state or plot of p *vs.* V for the vapor to pressures above the normal vapor pressure of the liquid. Since the effect of hydrostatic pressure on the vapor pressure of a condensed system is small, the extrapolation is in general not severe.

Lurie and Gillespie (134) and Gillespie (72) applied the Gibbs–Dalton law to their measurements on the system $BaCl_2(s)$, $BaCl_2 \cdot 8NH_3(s)$, $NH_3(g) + N_2(g)$ and to those of Larson and Black (109) on $NH_3(l), NH_3(g) + H_2(g) + N_2(g)$. They found that the deviations of the results derived from the Gibbs–Dalton law from the measured values are in the same direction as those derived from the ideal gas law and, up to moderate pressures, roughly one-half as large. At higher pressures there is an indication that Gibbs–Dalton law deviations may pass through zero and change sign. Gerry and Gillespie (60) found that the Gibbs–Dalton law may give results no better than the ideal gas law when the mole fraction of one substance in the gas phase is very small, as in the case of the effect of air, hydrogen, and carbon dioxide on the equilibrium $I_2(s)$, $I_2(g)$ (6, 7, 40).

Cupples (46) applied a method of calculation which is equivalent to the Gibbs–Dalton law to the measurements of Larson and Black mentioned above. Masson and Dolley (138) found that Dalton's law, a consequence of the Gibbs–Dalton law, gave for ethylene–oxygen and ethylene–argon gas mixtures deviations that rose to a maximum of 7 per cent with increasing pressure, then decreased, passed through zero, and became negative. Bartlett, Cupples, and Tremearne (5) found that Amagat's law gave results better than Dalton's law for mixtures of hydrogen and nitrogen.

VII. THE LEWIS AND RANDALL RULE

Lewis and Randall (125) proposed as a basis for the thermodynamic treatment of gas mixtures the rule: The fugacity f_i of a gas in a mixture is equal to the product of its mole fraction x_i into the fugacity f_{Pk} of the pure gas at the total pressure and temperature of the mixture:

$$f_i = f_{Pk}x_i \qquad (i \equiv k = 1, 2, \cdots) \tag{36}$$

The fugacity of a pure gas is defined (123) through the relations:

$$\mu = RT \ln f + \psi(T); \qquad \lim_{p \to 0} \frac{f}{p} = 1 \quad \text{at all temperatures} \tag{37}$$

Consider a pure gas in isothermal equilibrium with a gas mixture through a membrane permeable to that gas alone. The chemical potential of the gas in the mixture is μ_i and that of the pure gas μ_k, where $\mu_i = \mu_k$. According to the Lewis and Randall rule μ_k and hence μ_i can be calculated by substituting into equation 37 the product of the fugacity of the pure gas at the total pressure and temperature of the mixture (in which state it is not in equilibrium with the mixture) times the mole fraction of the gas in the mixture:

$$\mu_i = RT \ln f_{Pk} x_i + \psi_k(T) \qquad (i \equiv k = 1, 2, \cdots) \qquad (38)$$

Thus the Lewis and Randall rule contains the necessary idea of equilibrium for a basis of a thermodynamic treatment of gas mixtures.

The following results may be derived from the rule:

1. Subject to the conditions

$$\left.\begin{aligned} T \text{ (each pure gas)} &= T \text{ (mixture)} \\ p \text{ (each pure gas)} &= p \text{ (mixture)} \\ n_k &= n_i \qquad (i \equiv k = 1, 2, \cdots) \end{aligned}\right\} \quad \text{(C)}$$

the following relations hold:

$$\mu_i = \mu_{Pk} + RT \ln x_i \qquad (i \equiv k = 1, 2, \cdots) \qquad (39)$$

$$V = \Sigma_k V_{Pk} \qquad (40)$$

$$S = \Sigma_k S_{Pk} - \Sigma_i n_i R \ln x_i \qquad (41)$$

$$\left.\begin{aligned} &E = \Sigma_k E_{Pk} \qquad H = \Sigma_k H_{Pk} \qquad F_{VT} = \Sigma_k F_{VT_{Pk}} + \Sigma_i n_i RT \ln x_i \\ &F_{pT} = \Sigma_k F_{pT_{Pk}} + \Sigma_i n_i RT \ln x_i \qquad C_V = \Sigma_k C_{V_{Pk}} \qquad C_p = \Sigma_k C_{p_{Pk}} \end{aligned}\right\} \quad (42)$$

where the subscript P denotes that the conditions C apply. Equation 40 is Amagat's law (1, 2).

2. Subject to conditions C the partial molal volume of a gas in a mixture equals the molal volume of the pure gas:

$$\left(\frac{\partial V}{\partial n_i}\right)_{pTn} = \frac{V_{Pk}}{n_k} \qquad (i \equiv k = 1, 2, \cdots) \qquad (43)$$

3. The Lewis and Randall rule leads to a complete solution of the problem of the determination of the thermodynamic properties of gas mixtures from measurements on pure gases only.

The quantity μ_{Pk} can be computed from equation 37 by substitution of f_{Pk} in the right-hand side. Comparison with equation 38 yields equation 39. Differentiation of equation 39 subject to conditions C gives:

$$\left(\frac{\partial \mu_i}{\partial p}\right)_{Tn} = \left(\frac{\partial \mu_{Pk}}{\partial p}\right)_T \qquad (i \equiv k = 1, 2, \cdots) \qquad (44)$$

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{pn} = \left(\frac{\partial \mu_{Pk}}{\partial T}\right)_p + R \ln x_i \qquad (i \equiv k = 1, 2, \cdots) \qquad (45)$$

where the subscript n denotes constant composition. From general thermodynamic theory the left-hand sides of equations 44 and 45 are equal, respectively, to the partial molal volume and the negative partial molal entropy of the gas *i* in the mixture and the right-hand sides are the corresponding molal quantities for the pure gas. Thus:

$$\left(\frac{\partial V}{\partial n_i}\right)_{pTn} = \frac{V_{Pk}}{n_k} \qquad (i \equiv k = 1, 2, \cdots) \tag{46}$$

$$\left(\frac{\partial S}{\partial n_i}\right)_{pTn} = \frac{S_{Pk}}{n_k} - R \ln x_i \qquad (i \equiv k = 1, 2, \cdots) \tag{47}$$

The first is equation 43. By Euler's theorem:

$$V = \Sigma_i \left[n_i \left(\frac{\partial V}{\partial n_i}\right)_{pTn} \right] = \Sigma_k V_{Pk} \qquad (i \equiv k = 1, 2, \cdots) \tag{48}$$

$$S = \Sigma_i \left[n_i \left(\frac{\partial S}{\partial n_i}\right)_{pTn} \right] = \Sigma_k S_{Pk} - \Sigma_i n_i R \ln x_i \qquad (i \equiv k = 1, 2, \cdots) \tag{49}$$

Thus equations 40 and 41 are proved. Substitution from equations 39, 40, and 41 into the general thermodynamic relations given in Section 2 (page 146) and use of the conditions C give the expressions 42.

Statement 3 follows directly from equations 39 through 42.

VIII. THERMODYNAMIC RELATIONS FOR GAS MIXTURES FROM THE LEWIS AND RANDALL RULE

Let

$$\frac{V}{n_k} = \Phi_k'(p, T) \tag{50}$$

be the equation of state of a pure gas. The Lewis and Randall rule gives the following expression for the volume of a gas mixture:

$$V = \Sigma_k[n_k \Phi_k'(p, T)] \tag{51}$$

where conditions C apply and the summation extends over all of the gases in the mixture. Equation 51 is an equation of state for gas mixtures where the equation for each pure gas is of the form of equation 50. As in the case of the Gibbs–Dalton law, the form of the function Φ_k' may be different for the different gases composing the mixture, and some or all of the functions may be evaluated graphically.

In terms of the thermodynamic properties of pure gases derived by the general limit method, the Lewis and Randall rule gives the following relations for gas mixtures:

$$E = \Sigma_k \left\{ \int_0^p \left[V_k - T \left(\frac{\partial V_k}{\partial T}\right)_{p_k} \right] dp_k - pV_k + n_k h_k^0 \right\} \tag{52}$$

$$H = \Sigma_k \left\{ \int_0^p \left[V_k - T \left(\frac{\partial V_k}{\partial T}\right)_{p_k} \right] dp_k + n_k h_k^0 \right\} \tag{53}$$

$$S = \Sigma_k \left\{ \int_0^p \left[\frac{n_k R}{p_k} - \left(\frac{\partial V_k}{\partial T}\right)_{p_k} \right] dp_k + n_k S_k^0 \right\} - \Sigma_i n_i R \ln p x_i \tag{54}$$

$$F_{VT} = \Sigma_k \left\{ \int_0^p \left[V_k - \frac{n_k RT}{p_k} \right] \mathrm{d}p_k - pV_k + n_k(h_k^0 - Ts_k^0) \right\} + \Sigma_i n_i RT \ln px_i \tag{55}$$

$$F_{pT} = \Sigma_k \left\{ \int_0^p \left[V_k - \frac{n_k RT}{p_k} \right] \mathrm{d}p_k + n_k(h_k^0 - Ts_k^0) \right\} + \Sigma_i n_i RT \ln px_i \tag{56}$$

$$C_V = \Sigma_k \left\{ n_k c_{vk}^* + n_k R + T \frac{(\partial V_k/\partial T)_{pk}^2}{(\partial V_k/\partial p_k)_T} - T \int_0^p \left(\frac{\partial^2 V_k}{\partial T^2} \right)_{pk} \mathrm{d}p_k \right\} \tag{57}$$

$$C_p = \Sigma_k \left\{ n_k c_{pk}^* - T \int_0^p \left(\frac{\partial^2 V_k}{\partial T^2} \right)_{pk} \mathrm{d}p_k \right\} \tag{58}$$

$$\mu_i = \int_0^p \left[\frac{V_k}{n_k} - \frac{RT}{p_k} \right] \mathrm{d}p_k + RT \ln px_i + h_k^0 - Ts_k^0 \tag{59}$$

$$RT \ln f_i = \int_0^p \left[\frac{V_k}{n_k} - \frac{RT}{p_k} \right] \mathrm{d}p_k + RT \ln px_i \tag{60}$$

In the above relations the summations extend over all gases in the mixture, and:

$$h_k^0 = \int_{T_0}^T c_{pk}^* \, \mathrm{d}T + h_{0k}^0 \tag{61}$$

$$s_k^0 = \int_{T_0}^T \frac{c_{pk}^*}{T} \, \mathrm{d}T + s_{0k}^0 \tag{62}$$

The quantities h_{0k}^0 and s_{0k}^0 are the heat content and entropy constants for the pure gas k at the temperature T_0; c_{pk}^* is the molal constant-pressure heat capacity at zero pressure.

The left-hand sides of equations 52 through 58 refer to the gas mixture at p, T, and the mole numbers n_i ($i \equiv k = 1, 2, \cdots$). The terms enclosed in braces are to be computed for each pure gas k from equations 50, 61, and 62 with p, T, and n_k having the same value for each pure gas as in the mixture, and the sum taken for all gases composing the mixture. The terms not enclosed in braces are to be computed for the gas mixture. In equations 59 and 60 the left-hand side refers to a gas in a mixture, and the right-hand side is to be computed as just described.

The Lewis and Randall rule leads directly to an expression for the mass action constant, K_p. Let K_p^* be the value of K_p at zero pressure. Substitution from equation 59 into the equilibrium expression $\Sigma_i \nu_i \mu_i = 0$ gives:

$$\ln \frac{K_p}{K_p^*} = -\frac{1}{RT} \Sigma_k \left\{ \nu_k \left[\int_0^p \left[\frac{V_k}{n_k} - \frac{RT}{p_k} \right] \mathrm{d}p_k \right] \right\} \tag{63}$$

$$\ln K_p^* = -\frac{1}{RT} \Sigma_k \{ \nu_k [h_k^0 - Ts_k^0] \} \tag{64}$$

Since the integrand of equation 63 is a function of p and T alone, the expression for the mass action function given by the Lewis and Randall rule is independent of the composition of the equilibrium mixture.

IX. APPLICATION OF THE LEWIS AND RANDALL RULE TO MIXTURES OF REAL GASES

A. Compressibility of gas mixtures

In a later section there will be derived a thermodynamic relation for the fugacity f_i of a gas i at a mole fraction x_i in a gas mixture at total pressure p and temperature T:

$$\ln f_i = \frac{1}{RT}\int_0^p \left[\left(\frac{\partial V}{\partial n_i}\right)_{pTn} - \frac{RT}{p}\right] dp + \ln px_i \tag{65}$$

where $(\partial V/\partial n_i)_{pTn}$ is the partial molal volume of the gas in the given mixture. The thermodynamic relation for the fugacity f_k of a pure gas at pressure p and temperature T is:

$$\ln f_k = \frac{1}{RT}\int_0^p \left[\frac{V_k}{n_k} - \frac{RT}{p_k}\right] dp_k + \ln p \tag{66}$$

where V/n_k is the molal volume of the pure gas. The Lewis and Randall rule, $f_i = f_{Pk}x_i$, yields directly equation 60, where f_{Pk} is computed from equation 66 for the total pressure and temperature of the mixture. The error of the Lewis and Randall rule expressed as a ratio is, from equations 60 and 65:

$$\ln \frac{f_i}{f_{Pk}\,x_i} = \frac{1}{RT}\int_0^p \left[\left(\frac{\partial V}{\partial n_i}\right)_{pTn} - \frac{V_k}{n_k}\right] dp \tag{67}$$

The integrand is the increase in volume of a system consisting of a very great quantity of the mixture together with a quantity of the pure gas at the same temperature and pressure when 1 mole of gas is removed from the pure gas and added to the mixture at constant temperature and pressure. It was called the expansion of the gas on mixing by Gillespie (68, 69), who studied this quantity for argon–ethylene (138), hydrogen–nitrogen (4), and methane–nitrogen (95) mixtures. In general the integrand of equation 67 is not zero, as would be required by the Lewis and Randall rule, nor is it zero at zero pressure. The first mixture deviates rather widely from the rule; the other two give much smaller expansions.

Gibson and Sosnick (63), Randall and Sosnick (147), Merz and Whittaker (140), and Krichevsky (97) studied the deviations of the above three mixtures from the Lewis and Randall rule and Sage, Lacey, and their collaborators (151, 152, 154, 157) studied the deviations in mixtures of methane with ethane, *n*-butane, and *n*-pentane. Amagat's law, a consequence of the Lewis and Randall rule, was applied by Masson and Dolley (138) to ethylene–argon, ethylene–oxygen, and argon–oxygen mixtures and by Bartlett, Cupples, and Tremearne (5) to a hydrogen–nitrogen mixture.

The results of these comparisons may be summarized as follows: (*1*) when all gases in the mixture are far above their critical temperatures the Lewis and Randall rule gives good results up to 100 atm. and fair results to several hundred atmospheres; (*2*) when one of the gases in the mixture is close to or below its critical point the rule may fail badly even at 50 atm.; (*3*) for paraffin hydrocarbon mixtures up to 200 atm. the rule gives results to 10 or 15 per cent.

B. Effect of an inert gas on univariant equilibria

Lurie and Gillespie (134) applied the Lewis and Randall rule to their measurements of total pressures and gas compositions in the system $BaCl_2(s)$, $BaCl_2 \cdot 8NH_3(s)$, $NH_3(g) + N_2(g)$ at 45°C. At this temperature the pressure of ammonia above the condensed complex is 7 atm. and that of liquid ammonia is about 17 atm. Strictly, the application of the rule to ammonia is limited to the vapor pressure of the liquid, since in equation 59 the upper limit of the integral is the total pressure in the gas phase. In the region in which the rule could be applied without extrapolation, it gave a fair representation of the observed equilibrium pressures of ammonia.

The calculations were made as follows:

1. Given the total pressure, temperature, and composition of the gas phase, to determine the equilibrium pressures of the constituent gases. We can compute by equation 60 the fugacity of gas i in the mixture. This is the fugacity f_k on the left-hand side of equation 66, so that the corresponding equilibrium pressure p_e of the gas can be calculated from equation 66 by successive approximations.

2. Given the total pressure p, temperature T, and equilibrium pressures $p_{e1}, p_{e2} \cdots$ of $m - 1$ of the m substances present in the gas mixture, to find the composition of the gas phase. We can calculate by equation 66 the corresponding fugacities of the $m - 1$ pure gases at T and p_{e1}, p_{e2}, etc. Substitution of each fugacity into equation 60 gives the corresponding mole fraction of the gas.

Randall and Sosnick (147) extended this calculation to apply to the entire pressure range of Lurie and Gillespie's measurements, to the effects of nitrogen and hydrogen on the equilibrium $CO_2(l) = CO_2(g)$ (145), and to the effects of hydrogen, nitrogen, and their mixtures on the equilibrium $H_2O(l) = H_2O(g)$ (3). This requires an extrapolation of the equation of state to pressure far above the vapor pressure of the liquid, but Randall and Sosnick conclude that such an extrapolation is permissible to the maximum on the James Thomson continuous isotherm. It is difficult to determine from such calculations what part of the disagreement is due to failure of the equation of state extrapolation.

Gerry (quoted in reference 73) found the Lewis and Randall rule "extremely bad for cases of condensible substances at small mole fraction." The system studied was $I_2(s)$, $I_2(g) + X(g)$, where X is air, hydrogen, or carbon dioxide, and the total pressure 1 atm. The errors of the rule greatly exceeded those of the ordinary ideal gas treatment.

C. Chemical equilibria

The Lewis and Randall rule is especially useful in computing the effect of pressure on chemical equilibria in gaseous systems. Given the value of K_p^*, which is a function of the temperature alone, and an equation of state with known values of the constants for each of the pure gases or an equivalent graphical method for evaluating the integrals of equation 63, we can compute the value of K_p at any pressure. From this and the composition of the gas mixture before chemical reaction has occurred we can obtain the composition of the equilibrium mixture. The advantage of this method is that the composition of the equilibrium mixture does not occur on the right-hand side of the equation.

Gillespie (67) first derived equation 63 and applied it to the measurements of the equilibrium $3H_2 + N_2 = 2NH_3$ by Larson and Dodge (108, 110). He evaluated the integrals from the Keyes equation of state (90). The agreement between observed and calculated values of K_p was good up to 300 atm. Von Wettberg and Dodge (182) applied the same method to the equilibrium $CO + 2H_2 = CH_3OH$, evaluating the integrals from the van der Waals equation. The rather wide scattering of some of the points was attributed to lack of equilibrium.

A second method of applying the Lewis and Randall rule to chemical equilibria in gaseous systems differs from the preceding only in the arrangement of the calculations to suit graphical or tabular representation of fugacities. Applying the equilibrium relation $\Sigma_i \nu_i \mu_i = 0$, we obtain from equations 59 and 60 for a chemical reaction at equilibrium:

$$\Sigma_i \nu_i \ln f_i \equiv \ln K_f = -\frac{1}{RT} \Sigma_k \{\nu_k [h_k^0 - Ts_k^0]\} \tag{68}$$

where f_i is the actual fugacity of gas i in the equilibrium mixture. The Lewis and Randall rule gives $f_i = f_{Pk} x_i = (f_{Pk}/p) p x_i$, where p is the pressure of the equilibrium mixture. Thus:

$$\Sigma_i \nu_i \ln f_i = \Sigma_k \nu_k \ln \frac{f_{Pk}}{p} + \Sigma_i \nu_i \ln p x_i \tag{69}$$

or

$$\ln \frac{K_p}{K_f} = \ln \frac{K_p}{K_p^*} = -\Sigma_k \nu_k \ln \frac{f_{Pk}}{p} \tag{70}$$

Values of (f_{Pk}/p) can be computed by use of equation 66 from isothermal compressibility data. Tables of this quantity at various temperatures and pressures have been prepared by Deming and Shupe (49, 51, 52, 53) for a number of permanent gases; by Sage, Lacey, and their collaborators for many hydrocarbons (153, 155, 156, 158, 159); and by other investigators (43, 54, 89). Given K_p^* and values of f_{Pk}/p for the reacting gases we can compute K_p and hence the equilibrium composition of the mixture.

Brown and his collaborators (171) presented on a single plot curves of (f/p) against p_r $(= p/p_{\text{critical}})$ for a number of different values of T_r $(= T/T_{\text{critical}})$ for methane and for pentane. Lewis and his collaborators (126, 127, 128, 129, 130, 131) suggested that for paraffin hydrocarbons of more than two carbon atoms (f/p) can be considered as depending only on p_r and T_r independent of the hydrocarbon (law of corresponding states). They therefore presented a generalized plot of (f_{Pk}/p) *vs.* p_r for various values of T_r good for all such hydrocarbons. Newton (141) presented such a plot not restricted to hydrocarbons, and Newton and Dodge (142, 143) applied equation 70 to the ammonia and methanol synthesis equilibria, evaluating (f_{Pk}/p) from the plot and the critical constants of the gases involved. The agreement between observed and calculated values of K_p was good to 300 atm., fair at 600 atm., but poor at 1000 atm., a result which they attributed to failure of the Lewis and Randall rule.

D. Liquid–vapor equilibria

Consider the equilibrium between the liquid and vapor phases of a binary or multicomponent system at the total pressure p and temperature T. If the liquid is a perfect solution (124) the fugacity of a substance i in the liquid phase is $f_{iL}y_i$, where f_{iL} is the fugacity of the pure liquid of substance i at p and T and y_i its mole fraction in the solution. The Lewis and Randall rule gives for the fugacity of i in the vapor $f_{Pk}x_i$, where f_{Pk} is the fugacity of the pure vapor of i at p and T, and x_i its mole fraction in the vapor. At equilibrium:

$$f_{iL}y_i = f_{Pk}x_i \qquad (i \equiv k = 1, 2, \cdots) \quad (71)$$

Brown and his collaborators (171, 173) discussed the application of this equation to the design of high-pressure hydrocarbon equipment. In general the evaluation of f_{Pk} from equation 66 or from fugacity charts requires extrapolation to pressures above the condensation pressure of the vapor.

Lewis and Luke (130, 131) made the approximation that f_{iL} may be replaced by the fugacity of the pure liquid at its vapor pressure and T. This is equal to the fugacity of the pure vapor at the vapor pressure and T and can be read from the generalized fugacity chart if the vapor pressure at T and the critical constants of the substance are known.

Although the approximations are more severe than those of the Lewis and Randall rule, the results are sufficiently accurate for the design of high-pressure hydrocarbon equipment.

Dodge and Newton (55) derived for liquid–vapor equilibria relations that involve the use of the Lewis and Randall rule for the vapor phase but not the use of generalized fugacity charts.

X. COMPARISON OF THE GIBBS–DALTON LAW AND THE LEWIS AND RANDALL RULE

The Gibbs–Dalton law requires Dalton's law of the additivity of pressure at constant volume and temperature (equation 6) to hold; it leads to the additivity of certain thermodynamic quantities at constant volume and temperature (equation 8); and it requires that $(\partial p/\partial n_i)_{VTn}$ for the mixture equal $(\partial p/\partial n)_{VT}$ for each pure gas.

The Lewis and Randall rule yields Amagat's law of the additivity of volumes at constant total pressure and temperature (equation 40); it gives the result that the difference between certain thermodynamic properties of a gas mixture and the sum of the corresponding properties for the constituents at the total pressure and temperature of the mixture is the same as for ideal gases (equations 39, 41, and 42); and it requires that the partial molal volume $(\partial V/\partial n_i)_{pTn}$ of a gas in a mixture equal its molal volume V/n.

In general, Amagat's law gives results superior to Dalton's law for gas mixtures at temperatures well above the critical temperature of each constituent, while Dalton's law seems to give the better results if one of the constituent gases is below or only slightly above the critical temperature.

The Gibbs–Dalton law is readily applied to the calculation of the composition of the gas phase in equilibrium with a condensed complex yielding one of the constituents. It requires a much shorter extrapolation of the compressibility data on the condensible vapor above the condensation pressure than the Lewis and Randall rule. Gillespie (72) states that at not too high pressures the Gibbs–Dalton law yields too low and the Lewis and Randall rule too high a mole fraction for the vapor that is in equilibrium with the condensed complex.

The Lewis and Randall rule yields a simple expression for the mass action function and the application of the equation to chemical equilibria is facilitated by the use of equation 70 and generalized fugacity charts, although the latter introduces the further approximation of the law of corresponding states. The results are satisfactory to relatively high pressures. The Gibbs–Dalton expression is more involved and has never been applied.

The use of the Lewis and Randall rule together with generalized fugacity charts for the vapor phase of a multicomponent liquid–vapor equilibrium seems to give results sufficiently accurate for engineering calculations. It is possible that the Gibbs–Dalton law would yield more accurate results, but the work would be increased.

XI. THE GENERAL LIMIT METHOD

The procedure called by Gillespie (73) the general limit method assumes that, as the pressure on a real gas or gaseous mixture is reduced at constant temperature and mole numbers, certain thermodynamic properties of a system of real gases approach those of ideal gases in a definite manner. The method was applied by van der Waals (181) to derive an expression for the work content (F_{VT}) of a gas mixture but without elimination of an improper integral introduced through the equation for the entropy. van Laar and Lorenz (106, 107) and Keyes (92) employed the method for the energy of a gas mixture where improper integrals do not appear.

Gillespie (66) was the first to apply the method to the calculation of the fugacity of a gas in a mixture and to derive a general equation for the effect of pressure and composition on chemical equilibrium. He showed how the improper integral that had given difficulty in the past could be transformed by the addition and subtraction of a term. He integrated the relations by means of an equation of state for gas mixtures and made extensive application of the resulting equations to the effect of pressure on chemical equilibrium (67) and the calculation of the equilibrium pressure of a gas in a gaseous mixture (60, 68, 134). The equations gave a good representation of the experimental data.

de Donder (56, 57, 149) used the general limit method to write down directly the work content (F_{VT}) of a gaseous mixture. The method has been applied by van Lerberghe (118, 119, 120, 121), and by Prigogine and Defay (146) to the calculation of the fugacity of a gas in a mixture.

Equations for the fugacity of a gas in a mixture equivalent to that derived by Gillespie were obtained by Gibson and Sosnick (63), Merz and Whittaker (140), van Lerberghe (120), Tunnell (180), Goranson (83), and Sage and Lacey (154).

It has been found (15) that the thermodynamic properties of real gases and gas mixtures, expressed in the form of definite integrals, can be derived from two assumptions: one concerning the isothermal variation of the energy of pure gases at low pressure and the other concerning the isothermal variation of the ratio of the equilibrium pressure of a gas in a mixture to its partial pressure at low pressures. The resulting expressions (8, 9, 10) may be considered exact and state the thermodynamic functions of a gas mixture in terms of: *(1)* definite integrals that depend on the properties of the gas mixture for the effect of pressure; *(2)* definite integrals that depend on the heat capacities of the pure constituent gases at zero pressure for the temperature effect; *(3)* certain integration constants for the pure constituent gases; and *(4)* the temperature, pressure (or density), and composition of the mixture. The completion of the solution of the problem is attained on evaluating the integrals of *(1)* above by an equation of state for gas mixtures in which the parameters of the mixture are computed from those of the pure gases and the composition from certain relations usually called combination of constants. The final equations are approximate to the extent that the equation of state for mixtures does not represent the variation of the volumetric behavior of gas mixtures with pressure, temperature, and composition. The resulting equation (75, 76, 77) expressing the mass action constant of a gaseous reaction as a function of pressure, temperature, and composition of the equilibrium mixture contains, in principle, no arbitrary constants, all parameters being evaluated from the volumetric and thermal properties of the pure constituent gases. The equation has been applied to the equilibrium measurements of Larson and Dodge (108, 110) and of Haber (84) for the ammonia synthesis reaction with two of the parameters considered adjustable (those for ΔH and ΔS of the chemical reaction in the standard state). For the first time the three sets of measurements are correlated in a satisfactory method.

Scatchard and Raymond (165) and Scatchard and coworkers (164, 166, 167, 168, 169, 170) have used the relations resulting from the general limit method for the gas phase in the derivation of equations for liquid–vapor equilibria.

Benedict, Webb, and Rubin (38) applied the general limit method to the work content of a gas mixture and employed the results of Mayer (139) to prove that the limit of the quantity they used exists as the pressure approaches zero. The resulting relations were integrated by use of their equation of state (37) together with certain rules for combination of constants. They applied the relations with excellent results to binary (38) and ternary (35, 36) equilibrium mixtures of hydrocarbons in the liquid and gaseous phases.

Although different investigators applied the general limit method to different thermodynamic functions, all arrived at the same equation for the effect of pressure and composition on the fugacity (or, what amounts to the same thing, the chemical potential) of a gas in a mixture—the equation obtained by Gillespie.

The complete solution of the problem of expressing the properties of gas mixtures in terms of those of the pure constituent gases thus involves two steps: (*1*) a general limit method for the exact equations; and (*2*) combination of constants of an equation of state for evaluating certain definite integrals of (*1*).

XII. THE GENERAL LIMIT METHOD FOR PURE GASES

A. The assumptions

Although two assumptions suffice for deriving general relations for the thermodynamic properties of pure gases and gas mixtures, it is desirable to divorce the treatment for gas mixtures from that of pure gases. If this is done we need three assumptions: two for pure gases and of course one additional for gas mixtures.

We shall consider two pressure regions: (*1*) low pressures, at which terms of the order of p^2 are negligible in comparison with terms of the order of p or of unity; and (*2*) very low pressures, at which terms of the order of p are negligible in comparison with unity. Thermodynamic quantities in the region of very low pressure will be denoted by a superscript asterisk.

The two assumptions for pure gases are:

1. At all temperatures[2] the pressure–volume product of a fixed mass of a real gas can be represented at constant temperature and in the region of low pressure by the expression:

$$pV = F(T,m) + A(T,m)p + O(p^2) \qquad (T,m \text{ constant}) \qquad (72)$$

where $F(T,m)$ and $A(T,m)$ depend for a given gas on the temperature T and the mass m, $A(T, m)$ and its temperature derivative are bounded, and $O(p^2)$ represents terms of the order of p^2.

2. At all temperatures[2] the heat content of a fixed mass of a real gas can be represented at constant temperature and in the region of low pressure by the expression:

$$H = f(T,m) + B(T,m)p + O(p^2) \qquad (T,m \text{ constant}) \qquad (73)$$

where $f(T,m)$ and $B(T,m)$ depend for a given gas on T and m, and B and its temperature derivative are bounded.

Substitution from equations 72 and 73 into the general relation:

$$\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p \qquad (74)$$

yields

$$B + O(p) = \frac{1}{p}\left[F - T\left(\frac{\partial F}{\partial T}\right)_m\right] + \left[A - T\left(\frac{\partial A}{\partial T}\right)_m\right] + O(p) \qquad (75)$$

for a fixed mass of a gas in the region of low pressure. Equation 75 can hold only if

$$F - T\left(\frac{\partial F}{\partial T}\right)_m = 0$$

---

[2] The region in the neighborhood of 0°K. is to be excluded.

Integration at constant m gives

$$F = r(m)T \tag{76}$$

where T is thermodynamic temperature and $r(m)$ depends only on m for a given gas. Thus equation 72 becomes:

$$pV = r(m)T + A(T,m)p + O(p^2) \qquad (m \text{ constant}) \tag{77}$$

and in the region of very low pressures:

$$\frac{(pV)^*}{rT} = 1 \tag{78}$$

Since volume is an extensive property of a system, the value of r will be characteristic of each gas if we replace V in equation 78 by V/m, where m is the number of units of mass of the gas in the volume V. Further let m be expressed in terms of moles where 1 mole of a gas is that mass which at a very low pressure and each temperature occupies the same volume as 32 g. of gaseous oxygen measured at the same pressure and temperature. If m is so measured, r is independent of the gas and will be denoted by R. Thus for low pressures we may write:

$$pV = nRT + \frac{n\beta p}{RT} + O(p^2) \tag{79}$$

or:

$$pV = nRT + \frac{n^2\beta}{V} + O\left(\frac{n^2}{V^2}\right) \tag{80}$$

where n is the number of moles in the volume V, β is a pure temperature function ($= ART$ if A is taken for 1 mole of gas) and is so chosen to conform to the usual writing of equations of state.

B. The integration path

We can now proceed to write down all of the thermodynamic functions of a pure gas in terms of the independent variables p and T, or V and T, and transform the improper integrals that occur in the expression for the entropy.

The reference state of a gas is taken at any arbitrarily chosen pressure (p_0) and temperature (T_0), the corresponding volume of n moles being V_0. Since the thermodynamic functions in which we are interested are all state variables we may proceed from the standard state (p_0, T_0) or (V_0, T_0) to any other state (p, T) or (V, T) along any path. We shall use a three-step path involving a state in the region of very low pressure p^* (or V^*). Let the mass of gas remain constant and:

1. Change the pressure from p_0 to p^* (or the volume from the corresponding values V_0 to V^*) at the temperature T_0.
2. Change the temperature from T_0 to T with the pressure held constant at p^* (or the volume at V^*).
3. Change the pressure from p^* to p (or the volume from V^* to V) at the temperature T.

C. Derivations for the independent variables p and T

From the usual thermodynamic relations we find for n moles of a real gas:

$$H(p,T) - H(p_0,T_0) = {}_{T_0}\!\int_{p_0}^{p^*} \left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right] dp + {}_{p^*}\!\int_{T_0}^{T} nc_p^* \, dT + {}_{T}\!\int_{p^*}^{p} \left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right] dp \quad (81)$$

$$S(p,T) - S(p_0,T_0) = -{}_{T_0}\!\int_{p_0}^{p^*} \left(\frac{\partial V}{\partial T}\right)_p dp + {}_{p^*}\!\int_{T_0}^{T} \frac{nc_p^*}{T} dT - {}_{T}\!\int_{p^*}^{p} \left(\frac{\partial V}{\partial T}\right)_p dp \quad (82)$$

$$= {}_{T_0}\!\int_{p_0}^{p^*} \left[\frac{nR}{p} - \left(\frac{\partial V}{\partial T}\right)_p\right] dp + {}_{p^*}\!\int_{T_0}^{T} \frac{nc_p^*}{T} dT + {}_{T}\!\int_{p^*}^{P} \left[\frac{nR}{p} - \left(\frac{\partial V}{\partial T}\right)_p\right] dp - nR \ln \frac{p}{p_0} \quad (83)$$

We can make the following simplifications:

1. Let:

$$h^0 = h_0^0 + \int_{T_0}^{T} c_p^* \, dT; \qquad nh_0^0 = H(p_0,T_0) + {}_{T_0}\!\int_{p_0}^{p^*} \left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right] dp \quad (84)$$

$$s^0 = s_0^0 + \int_{T_0}^{T} \frac{c_p^*}{T} dT; \qquad ns_0^0 = S(p_0, T_0) + {}_{T_0}\!\int_{p_0}^{p^*} \left[\frac{nR}{p} - \left(\frac{\partial V}{\partial T}\right)_p\right] dp + nR \ln p_0 \quad (85)$$

2. From equation 73 and the relation $C_p = (\partial H/\partial T)_p$ we find that

$$C_p^* = \left(\frac{\partial f}{\partial T}\right)_m + O(p) \quad (86)$$

and hence c_p^* is a function of T alone.

3. From equation 79 we find:

$$\lim_{p^* \to 0} \int_{p^*}^{0} \left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right] dp = \lim_{p^* \to 0} \int_{p^*}^{0} \left[\frac{nR}{p} - \left(\frac{\partial V}{\partial T}\right)_p\right] dp = 0 \quad (87)$$

Equations 81 and 83 can now be written:

$$H(p, T) = \int_0^p \left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right] dp + nh^0 \quad (88)$$

$$S(p, T) = \int_0^p \left[\frac{nR}{p} - \left(\frac{\partial V}{\partial T}\right)_p\right] dp - nR \ln p + ns^0 \quad (89)$$

It is understood that the integrals are to be evaluated at the running temperature T. From equations 88 and 89 the other thermodynamic properties of real gases can be written down by use of the relations given in Section II (page 143). These are collected in Section XII E (page 165).

D. *Derivations for the independent variables V and T*

In terms of the independent variables V and T we find for n moles of a real gas:

$$E(V,T) - E(V_0,T_0) = {}_{T_0}\int_{V_0}^{V_*} \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right] \mathrm{d}V + {}_{V_*}\int_{T_0}^{T} nc_v^* \,\mathrm{d}T + {}_{T}\int_{V_*}^{V} \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right] \mathrm{d}V \tag{90}$$

$$S(V,T) - S(V_0,T_0) = {}_{T_0}\int_{V_0}^{V_*} \left(\frac{\partial p}{\partial T}\right)_V \mathrm{d}V + {}_{V_*}\int_{T_0}^{T} \frac{nc_v^*}{T} \,\mathrm{d}T + {}_{T}\int_{V_*}^{V} \left(\frac{\partial p}{\partial T}\right)_V \mathrm{d}V \tag{91}$$

$$= {}_{T_0}\int_{V_0}^{V_*} \left[\left(\frac{\partial p}{\partial T}\right)_V - \frac{nR}{V}\right] \mathrm{d}V + {}_{V_*}\int_{T_0}^{T} \frac{nc_v^*}{T} \,\mathrm{d}T + {}_{T}\int_{V_*}^{V} \left[\left(\frac{\partial p}{\partial T}\right)_V - \frac{nR}{V}\right] \mathrm{d}V + nR \ln \frac{V}{V_0} \tag{92}$$

These equations can also be simplified:
1. Let:

$$e^0 = e_0^0 + \int_{T_0}^{T} c_v^* \,\mathrm{d}T; \qquad ne_0^0 = E(V_0,T_0) + {}_{T_0}\int_{V_0}^{V_*} \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right] \mathrm{d}V \tag{93}$$

Now from equations 84 and 93 we find:

$$nh_0^0 - ne_0^0 = H(p_0,T_0) - E(V_0,T_0) + {}_{T_0}\int_{p_0}^{p_*} \left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right] \mathrm{d}p - {}_{T_0}\int_{V_0}^{V_*} \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right] \mathrm{d}V \tag{94}$$

$$= p_0 V_0 + {}_{T_0}\int_{p_0V_0}^{p_*V_*} \mathrm{d}(pV)$$

$$= nRT_0$$

Since $S(V_0,T_0) = S(p_0,T_0)$ we can replace the former by the expression for the latter obtained from the second of equations 85. This gives on simplification:

$$S(V_0,T_0) + {}_{T_0}\int_{V_0}^{V_*} \left[\left(\frac{\partial p}{\partial T}\right)_V - \frac{nR}{V}\right] \mathrm{d}V - nR \ln V_0$$

$$= -nR \ln p_0 V_0 - nR \,{}_{T_0}\int_{p_0V_0}^{p_*V_*} \mathrm{d} \ln (pV) + ns_0^0$$

$$= -nR \ln nR\, T_0 + ns_0^0 \tag{95}$$

Furthermore, from equation 80 and general thermodynamic relations we find

$$c_p^* - c_v^* = R \tag{96}$$

and from the first of equation 85:

$$s^0 = s_0^0 + \int_{T_0}^{T} \frac{c_v^*}{T}\,\mathrm{d}T + nR \ln \frac{T}{T_0}$$

2. Use of equation 80 for evaluating the volume integrals shows that V^* can be replaced by infinity.

Thus equations 90 and 92 become:

$$E(V,T) = \int_V^\infty \left[p - T\left(\frac{\partial p}{\partial T}\right)_V\right]\mathrm{d}V + ne^0 \tag{97}$$

$$S(V,T) = \int_V^\infty \left[\frac{nR}{V} - \left(\frac{\partial p}{\partial T}\right)_V\right]\mathrm{d}V + nR \ln \frac{V}{nRT} + ns^0 \tag{98}$$

The relations for the other thermodynamic functions are given in Section XII F (page 166).

E. Equations for pure gases in terms of p and T

$$E = \int_0^p \left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right]\mathrm{d}p - pV + nh^0 \tag{99}$$

$$H = \int_0^p \left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right]\mathrm{d}p + nh^0 \tag{88}$$

$$S = \int_0^p \left[\frac{nR}{p} - \left(\frac{\partial V}{\partial T}\right)_p\right]\mathrm{d}p - nR \ln p + ns^0 \tag{89}$$

$$F_{VT} = \int_0^p \left[V - \frac{nRT}{p}\right]\mathrm{d}p + nRT \ln p - pV + n(h^0 - Ts^0) \tag{100}$$

$$F_{pT} = \int_0^p \left[V - \frac{nRT}{p}\right]\mathrm{d}p + nRT \ln p + n(h^0 - Ts^0) \tag{101}$$

$$\mu = \int_0^p \left[\frac{V}{n} - \frac{RT}{p}\right]\mathrm{d}p + RT \ln p + h^0 - Ts^0 \tag{102}$$

$$RT \ln f = \int_0^p \left[\frac{V}{n} - \frac{RT}{p}\right]\mathrm{d}p + RT \ln p \tag{103}$$

In the above equations the definite integrals are to be evaluated at the temperature T. The integration constants are given by the expressions:

$$h^0 = h_0^0 + \int_{T_0}^{T} c_p^*\,\mathrm{d}T \tag{104}$$

$$s^0 = s_0^0 + \int_{T_0}^{T} \frac{c_p^*}{T}\,\mathrm{d}T \tag{105}$$

where the integrals are to be evaluated along the zero pressure curve and h_0^0 and s_0^0 are the molal heat content and entropy constants for the gas at T_0.

F. Equations for pure gases in terms of V and T

$$E = \int_V^\infty \left[p - T\left(\frac{\partial p}{\partial T}\right)_V\right] \mathrm{d}V + ne^0 \tag{97}$$

$$H = \int_V^\infty \left[p - T\left(\frac{\partial p}{\partial T}\right)_V\right] \mathrm{d}V + pV + ne^0 \tag{106}$$

$$S = \int_V^\infty \left[\frac{nR}{V} - \left(\frac{\partial p}{\partial T}\right)_V\right] \mathrm{d}V + nR \ln \frac{V}{nRT} + ns^0 \tag{98}$$

$$F_{VT} = \int_V^\infty \left[p - \frac{nRT}{V}\right] \mathrm{d}V - nRT \ln \frac{V}{nRT} + n(e^0 - Ts^0) \tag{107}$$

$$F_{pT} = \int_V^\infty \left[p - \frac{nRT}{V}\right] \mathrm{d}V - nRT \ln \frac{V}{nRT} + pV + n(e^0 - Ts^0) \tag{108}$$

$$\mu = \int_V^\infty \left[\left(\frac{\partial p}{\partial n}\right)_{VT} - \frac{RT}{V}\right] \mathrm{d}V - RT \ln \frac{V}{nRT} + RT + e^0 - Ts^0 \tag{109}$$

$$RT \ln f = \int_V^\infty \left[\left(\frac{\partial p}{\partial n}\right)_{VT} - \frac{RT}{V}\right] \mathrm{d}V - RT \ln \frac{V}{nRT} \tag{110}$$

In these relations the definite integrals are to be evaluated at the temperature T, and

$$e^0 = e_0^0 + \int_{T_0}^T c_v^* \, \mathrm{d}T; \qquad e_0^0 = h_0^0 - RT_0 \tag{111}$$

$$s^0 = s_0^0 + \int_{T_0}^T \frac{c_v^*}{T} \mathrm{d}T + R \ln \frac{T}{T_0} \tag{112}$$

The temperature integral is to be evaluated along the zero pressure curve.

XIII. THE GENERAL LIMIT METHOD FOR GAS MIXTURES

A. The assumption

The Gibbs–Dalton law and the Lewis and Randall rule each make one assumption as a basis for the thermodynamic treatment of gas mixture. We shall make the following assumption:

At all temperatures the ratio of the equilibrium pressure of each gas in a mixture to the product of the mole fraction of that gas in the mixture into the total pressure of the mixture can be represented in the region of low pressures by the expression:

$$\frac{p_{ek}}{px_i} = 1 + D_i(T, x_1, x_2, \cdots)p + O(p^2) \tag{113}$$

where D_i depends only on the temperature and composition of the mixture, and D_i and its derivatives with respect to T, n_1, n_2, $\cdots$ are bounded.

B. Relations for the region of low pressure

Consider a system of $\Sigma_i n_i$ moles of a gas mixture and k systems each containing n_{ek} moles of one of the constituent gases. In all variations let:

$$\left.\begin{aligned} T \text{ (each pure gas) } &= T \text{ (mixture)} \\ V \text{ (each pure gas) } &= V \text{ (mixture)} \\ \mu_k &= \mu_i \qquad (k \equiv i = 1, 2, \cdots) \end{aligned}\right\} \quad \text{(D)}$$

Each pure gas would be in equilibrium with the mixture if separated from it by a membrane permeable to that gas alone. Hence the properties of the pure gases may be called equilibrium properties of the mixture.

Subject to the condition D the general limit method (equation 113) gives the following results for the region of low pressure:

$$1.\ \Sigma_k p_{ek} = p(1 + D_m p) \tag{114}$$

where D_m is a function of temperature and composition ($= \Sigma_i x_i D_i$).

$$\left.\begin{aligned} 2.\ \frac{n_{ek}}{V} &= \frac{n_i}{V}(1 + 2D_m p) \qquad (k \equiv i = 1, 2, \cdots) \\ C_{ek} &= C_i(1 + 2D_m p) \\ &= Cx_i(1 + 2D_m p) \\ n_{ek} &= n_i(1 + 2D_m p) \end{aligned}\right\} \tag{115}$$

$$3.\ \Sigma_k S_{ek} = S(1 + 2D_m p) \tag{116}$$

$$\left.\begin{aligned} 4.\ pV &= \Sigma_i n_i RT + \frac{(\Sigma_i n_i)\beta_m}{RT} p \\ pV &= \Sigma_i n_i RT + \frac{(\Sigma_i n_i)^2 \beta_m}{V} \end{aligned}\right\} \tag{117}$$

where β_m is a bounded function of temperature and the composition of the gas mixture.

$$\left.\begin{aligned} 5.\ \Sigma_k E_{ek} &= E(1 + 2D_m p) + D_m pV \qquad & \Sigma_k H_{ek} &= H(1 + 2D_m p) \\ \Sigma_k F_{VT_{ek}} &= F_{VT}(1 + 2D_m p) + D_m pV & \Sigma F_{pT_{ek}} &= F_{pT}(1 + 2D_m p) \\ \Sigma_k C_{V_{ek}} &= C_V(1 + D'_m p) & \Sigma C_{p_{ek}} &= C_p(1 + D''_m p) \end{aligned}\right\} \tag{118}$$

where D'_m and D''_m are bounded functions of temperature and the composition of the gas mixture.

To prove (15) these relations we take as independent variables T, μ_1, μ_2, $\cdots$ for the gas mixture and T, μ_k for each pure gas as in equations 10 and 11. Equation 114 follows from equation 113, which may be written for the region of low pressure:

$$p_{ek} = px_i(1 + D_i p) \tag{119}$$

Differentiating equation 114 first with respect to one of the μ's with T and all of the other μ's constant, and then with respect to T with all of the μ's constant, we find for the region of low pressure:

$$\left(\frac{\partial p_{ek}}{\partial \mu_k}\right)_T = \left(\frac{\partial p}{\partial \mu_i}\right)_{T\mu} (1 + 2D_m p) \qquad (k \equiv i = 1, 2, \cdots) \qquad (120)$$

$$\Sigma_k \left(\frac{\partial p_{ek}}{\partial T}\right)_{\mu k} = \left(\frac{\partial p}{\partial T}\right)_\mu (1 + 2D_m p) \qquad (121)$$

Use of equations 12 and 13 gives the first of equations 115 and equation 116. The remainder of the equations 115 follow from the definitions given in Section II (page 143) and the second of the conditions D.

Division of equation 119 by the first of equations 115 gives for the region of low pressure:

$$\frac{p_{ek}V}{n_{ek}} = \frac{pV}{\Sigma_i n_i} [1 + (D_i - 2D_m)p] \qquad (122)$$

Now the left-hand side of this equation refers to the pure gas existing by itself and hence equation 79 applies. This gives the first of equations 117 and the second follows from the first for the region of low pressure where the terms $O(p^2)$ or $O(1/V^2)$ are negligible.

Use of the thermodynamic relations mentioned in Section II and the results already proved together with the conditions D leads to equations 118.

C. Relations for the region of very low pressure

As the pressure becomes very small at constant temperature and composition the relations given in Sections XII and XIII B show that the functions pV, E, H, C_V, and C_p for a gas mixture approach constant values while S, F_{VT}, and F_{pT} decrease or increase without limit in the same manner as $\pm \ln p$. But

$$\lim_{p \to 0} p \ln p = 0$$

Hence the relations for gas mixtures in the region of very low pressures may be summarized from the results obtained in Section XIII B (page 167). Subject to the conditions D, we have the following:

1. Equilibrium relationships:

$$\left.\begin{array}{lll} \left(\dfrac{p_{ek}}{px_i}\right)^* = 1; & \left(\dfrac{C_{ek}}{C_i}\right)^* = 1; & \left(\dfrac{C_{ek}}{Cx_i}\right)^* = 1; \\ \left(\dfrac{n_{ek}}{n_i}\right)^* = 1 & & (k \equiv 1 = 1, 2, \cdots) \end{array}\right\} \qquad (123)$$

2. Additive relationships:

$$\left(\frac{\Sigma_k p_{ek}}{p}\right)^* = 1; \qquad \left(\frac{\Sigma_k C_{ek}}{C}\right)^* = 1 \qquad (124)$$

$$S^* = \Sigma_k S^*_{ek} \tag{125}$$

$$\begin{aligned} E^* &= \Sigma_k E^*_k; \qquad H^* = \Sigma_k H^*_k; \qquad F^*_{VT} = \Sigma_k F^*_{VT_{ek}}; \\ F^*_{pT} &= \Sigma_k F^*_{pT_{ek}}; \qquad C^*_V = \Sigma_k C^*_{V_k}; \qquad C^*_p = \Sigma_k C^*_{pk} \end{aligned} \tag{126}$$

3. The equation of state (independent of the conditions D):

$$(pV)^* = \Sigma_i n_i RT \tag{127}$$

The designation e can be omitted in the relations for E, H, C_V, and C_p, since these quantities are essentially constant in the region of low pressure at constant temperature and mole numbers.

D. General relations

Corresponding to equations 81 and 83 for the heat content and entropy of a pure gas, we have for $\Sigma_i n_i$ moles of a gas mixture of constant composition:

$$\begin{aligned} H(p,T) - H(p_0,T_0) = {} & {}_{T_0}\!\int_{p_0}^{p^*} \left[V - T\left(\frac{\partial V}{\partial T}\right)_{pn} \right] \mathrm{d}p \\ & + {}_{p^*}\!\int_{T_0}^{T} C^*_p \,\mathrm{d}T + {}_{T}\!\int_{p^*}^{p} \left[V - T\left(\frac{\partial V}{\partial T}\right)_{pn} \right] \mathrm{d}p \end{aligned} \tag{128}$$

$$\begin{aligned} S(p,T) - S(p_0,T_0) = {} & {}_{T_0}\!\int_{p_0}^{p^*} \left[\frac{\Sigma_i n_i R}{p} - \left(\frac{\partial V}{\partial T}\right)_{pn} \right] \mathrm{d}p + {}_{p^*}\!\int_{T_0}^{T} \frac{C^*_p}{T} \,\mathrm{d}T \\ & + {}_{T}\!\int_{p^*}^{p} \left[\frac{\Sigma_i n_i R}{p} - \left(\frac{\partial V}{\partial T}\right)_{pn} \right] \mathrm{d}p - (\Sigma_i n_i) R \ln \frac{p}{p_0} \end{aligned} \tag{129}$$

where the subscript n denotes constant mole numbers and C^*_p is the heat capacity of $\Sigma_i n_i$ moles of gas mixture at a very low pressure.

Now from equations 126, 88, and 123:

$$H(p^*,T_0) = \Sigma_k H_k(p^*,T_0) = \Sigma_k n_{ek} h^0_{0k} = \Sigma_i n_i h^0_{0i} \tag{130}$$

where for convenience h^0_{0i} is written for h^0_{0k}, since this will lead to no confusion. And from equations 125, 89, and 123:

$$\begin{aligned} S(p^*,T_0) = \Sigma_k S_{ek}(p^*_{ek},T_0) &= \Sigma_k n_{ek} s^0_{0k} - \Sigma_k n_{ek} R \ln p^*_{ek} \\ &= \Sigma_i n_i s^0_{0i} - \Sigma_i (n_i R \ln p^* x_i) \end{aligned} \tag{131}$$

Also from equation 126 and equation 123:

$$C^*_p = \Sigma_k C^*_{pk} = \Sigma_k n_{ek} c^*_{pk} = \Sigma_i n_i c^*_{pi} \tag{132}$$

Thus from equations 128 and 130:

$$H(p_0,T_0) + {}_{T_0}\!\int_{p_0}^{p^*} \left[V - T\left(\frac{\partial V}{\partial T}\right)_{pn} \right] \mathrm{d}p = H(p^*,T_0) = \Sigma_i n_i h^0_{0i} \tag{133}$$

and from equations 129 and 131:

$$S(p_0,T_0) + {}_{T_0}\int_{p_0}^{p^*}\left[\frac{\Sigma_i n_i R}{p} - \left(\frac{\partial V}{\partial T}\right)_{pn}\right] \mathrm{d}p + (\Sigma_i n_i)R \ln p_0$$

$$= S(p^*,T_0) + (\Sigma_i n_i)R \ln p^*$$

$$= \Sigma_i n_i s^0_{0i} - \Sigma_i(n_i R \ln x_i) \qquad (134)$$

We can now substitute from equations 132, 133, and 134 into equations 128 and 129. Then use of equation 117 shows that we can replace the limit p^* by 0 (compare equation 87), and obtain:

$$H(p,T) = \int_0^p \left[V - T\left(\frac{\partial V}{\partial T}\right)_{pn}\right] \mathrm{d}p + \Sigma_i(n_i h_i^0) \qquad (135)$$

$$S(p,T) = \int_0^p \left[\frac{\Sigma_i n_i R}{p} - \left(\frac{\partial V}{\partial T}\right)_{pn}\right] \mathrm{d}p - \Sigma_i(n_i R \ln p x_i) + \Sigma_i(n_i s_i^0) \qquad (136)$$

where h_i^0 and s_i^0 are given by equations 104 and 105.

The other thermodynamic properties can now be written down as was done for the pure gases. These are collected in Section XIII E below.

We can proceed in a similar fashion to obtain equations for the energy and entropy of a gas mixture in terms of the independent variables V and T, analogous to equations 97 and 98 for a pure gas. These equations are given in Section XIII F.

E. Equations for gas mixtures in terms of p and T

$$E = \int_0^p \left[V - T\left(\frac{\partial V}{\partial T}\right)_{pn}\right] \mathrm{d}p - pV + \Sigma_i n_i h_i^0 \qquad (137)$$

$$H = \int_0^p \left[V - T\left(\frac{\partial V}{\partial T}\right)_{pn}\right] \mathrm{d}p + \Sigma_i n_i h_i^0 \qquad (135)$$

$$S = \int_0^p \left[\frac{\Sigma_i n_i R}{p} - \left(\frac{\partial V}{\partial T}\right)_{pn}\right] \mathrm{d}p - \Sigma_i n_i R \ln p x_i + \Sigma_i n_i s_i^0 \qquad (136)$$

$$F_{VT} = \int_0^p \left[V - \frac{\Sigma_i n_i RT}{p}\right] \mathrm{d}p$$

$$+ \Sigma_i n_i RT \ln p x_i - pV + \Sigma_i n_i(h_i^0 - Ts_i^0) \qquad (138)$$

$$F_{pT} = \int_0^p \left[V - \frac{\Sigma_i n_i RT}{p}\right] \mathrm{d}p + \Sigma_i n_i RT \ln p x_i + \Sigma_i n_i(h_i^0 - Ts_i^0) \qquad (139)$$

$$\mu_i = \int_0^p \left[\left(\frac{\partial V}{\partial n_i}\right)_{pTn} - \frac{RT}{p}\right] \mathrm{d}p + RT \ln p x_i + h_i^0 - Ts_i^0 \qquad (140)$$

$$RT \ln f_i = \int_0^p \left[\left(\frac{\partial V}{\partial n_i}\right)_{pTn} - \frac{RT}{p}\right] \mathrm{d}p + RT \ln p x_i \qquad (141)$$

$$h_i^0 = h_{0i}^0 + \int_{T_0}^T c_{pi}^* \,\mathrm{d}T \qquad s_i^0 = s_{0i}^0 + \int_{T_0}^T \frac{c_{pi}^*}{T} \,\mathrm{d}T \qquad (142)$$

F. Equations for gas mixtures in terms of V and T

$$E = \int_V^\infty \left[p - T\left(\frac{\partial p}{\partial T}\right)_{Vn}\right] \mathrm{d}V + \Sigma_i n_i e_i^0 \tag{143}$$

$$H = \int_V^\infty \left[p - T\left(\frac{\partial p}{\partial T}\right)_{Vn}\right] \mathrm{d}V + pV + \Sigma_i n_i e_i^0 \tag{144}$$

$$S = \int_V^\infty \left[\frac{\Sigma_i n_i R}{V} - \left(\frac{\partial p}{\partial T}\right)_{Vn}\right] \mathrm{d}V + \Sigma_i n_i R \ln \frac{V}{n_i RT} + \Sigma_i n_i s_i^0 \tag{145}$$

$$F_{VT} = \int_V^\infty \left[p - \frac{\Sigma_i n_i RT}{V}\right] \mathrm{d}V - \Sigma_i n_i RT \ln \frac{V}{n_i RT} + \Sigma_i n_i(e_i^0 - Ts_i^0) \tag{146}$$

$$F_{pT} = \int_V^\infty \left[p - \frac{\Sigma_i n_i RT}{V}\right] \mathrm{d}V - \Sigma_i n_i RT \ln \frac{V}{n_i RT} + pV + \Sigma_i n_i(e_i^0 - Ts_i^0) \tag{147}$$

$$\mu_i = \int_V^\infty \left[\left(\frac{\partial p}{\partial n_i}\right)_{VTn} - \frac{RT}{V}\right] \mathrm{d}V - RT \ln \frac{V}{n_i RT} + RT + e_i^0 - Ts_i^0 \tag{148}$$

$$RT \ln f_i = \int_V^\infty \left[\left(\frac{\partial p}{\partial n_i}\right)_{VTn} - \frac{RT}{V}\right] \mathrm{d}V - RT \ln \frac{V}{n_i RT} \tag{149}$$

$$e_i^0 = e_{0i}^0 + \int_{T_0}^T c_{vi}^* \,\mathrm{d}T \qquad s_i^0 = s_{0i}^0 + \int_{T_0}^T \frac{c_{vi}^*}{T} \,\mathrm{d}T + R \ln \frac{T}{T_0} \tag{150}$$

G. General equilibrium relationships

1. *Mass action functions for homogeneous gaseous reactions:* Equations 140 and 148 are relations for the chemical potential of a gas in a mixture. Application of the general condition $\Sigma_i \nu_i \mu_i = 0$ gives equations for the mass functions K_p (in terms of p and T) and K_C (in terms of V and T) for a homogeneous gas reaction. To obtain K_p in terms of V and T we add and subtract the term $RT \ln px_i$ to the right-hand side of equation 148 before applying the general condition of equilibrium. These give:

$$\ln \frac{K_p}{K_p^*} = -\frac{1}{RT} \Sigma_i \left\{\nu_i \left[\int_0^p \left[\left(\frac{\partial V}{\partial n_i}\right)_{pTn} - \frac{RT}{p}\right] \mathrm{d}p\right]\right\} \tag{151}$$

$$= -\frac{1}{RT} \Sigma_i \left\{\nu_i \left[\int_V^\infty \left[\left(\frac{\partial p}{\partial n_i}\right)_{VTn} - \frac{RT}{V}\right] \mathrm{d}V\right]\right\} + (\Sigma_i \nu_i) \ln \frac{pV}{(\Sigma_i n_i)RT} \tag{152}$$

$$\ln K_p^* = -\frac{1}{RT} \Sigma_i \left[\nu_i(h_i^0 - Ts_i^0)\right] \tag{153}$$

$$\ln \frac{K_C}{K_C^*} = -\frac{1}{RT} \Sigma_i \left\{\nu_i \left[\int_V^\infty \left[\left(\frac{\partial p}{\partial n_i}\right)_{VTn} - \frac{RT}{p}\right] \mathrm{d}V\right]\right\} \tag{154}$$

$$\ln K_C^* = -\frac{1}{RT} \Sigma_i[\nu_i(e_i^0 + RT - Ts_i^0 + RT \ln RT)] \tag{155}$$

2. *Equilibrium pressure and equilibrium concentration of a gas in a mixture:* When a pure gas is in isothermal equilibrium through a semipermeable membrane with a mixture containing that gas, the chemical potential of the gas is the same in both phases. Equating the relations for the chemical potential of a pure gas (equations 102 and 109) to those for a gas in a mixture (equations 140 and 148) gives relations for the equilibrium pressure and equilibrium concentration of a gas in a mixture:

$$RT \ln \frac{p_{ek}}{px_i} = \int_0^p \left[\left(\frac{\partial V}{\partial n_i}\right)_{pTn} - \frac{RT}{p}\right] \mathrm{d}p - \int_0^{p_{ek}} \left[\frac{V_k}{n_k} - \frac{RT}{p_k}\right] \mathrm{d}p_k \tag{156}$$

$$RT \ln \frac{C_{ek}}{C_i} = \int_V^\infty \left[\left(\frac{\partial p}{\partial n_i}\right)_{VTn} - \frac{RT}{V}\right] \mathrm{d}V - \int_V^\infty \left[\left(\frac{\partial p_k}{\partial n_k}\right)_{V_kT} - \frac{RT}{V_k}\right] \mathrm{d}V_k \tag{157}$$

The first integral on the right-hand side of these equations applies to the gas mixture; the second to the pure gas.

3. *Effect of an inert gas on a univariant equilibrium:* In a univariant equilibrium between a pure substance S_1 in a gas phase and one or more condensed phases:

$$NH_3(l) = NH_3(g) \qquad (p_{01}, T)$$

$$I_2(s) = I_2(g) \qquad (p_{01}, T)$$

$$\frac{1}{8}\,BaCl_2\cdot 8NH_3(s) = \frac{1}{8}\,BaCl_2(s) + NH_3(g) \qquad (p_{01}, T)$$

the pressure p_{01} is a function of temperature alone. The chemical potential μ_{c1} and molal volume $\bar{v}_{c1}$ of S_1 in the condensed phases are:

$$\mu_{c1} = -(\Sigma_j \nu_j \mu_j)/\nu_1; \qquad \bar{v}_{c1} = -(\Sigma_j \nu_j v_j)/\nu_1 \tag{158}$$

where v_j is the molal volume of the condensed phase j, the algebraic sign of ν_j is negative for a reactant and positive for a product, and the sum extends over all of the condensed phases. In the first two of the above changes in state $\bar{v}_{c1}$ is simply the molal volume of the condensed phase; for the last, Gillespie (71) called $\bar{v}_{c1}$ the partial molal volume of S_1 in the condensed complex.

Let the condensed phases be separated from the gas phase by a semipermeable membrane and subjected to the hydrostatic pressure p whereby the equilibrium pressure of S_1 increases from p_{01} to p_{e1}. Then:

$$\mu_{c1}(p,T) = \mu_{c1}(p_{01},T) + \int_{p_{01}}^{p} \bar{v}_{c1}\, \mathrm{d}p \tag{159}$$

Now the chemical potentials $\mu_{c1}(p,T)$ and $\mu_{c1}(p_{01},T)$ of S_1 in the condensed complex must equal those of S_1 in the pure gas phase at (p_{e1},T) and (p_{01},T), respectively. These are given by equation 102. Making these substitutions, we obtain:

$$RT \ln \frac{p_{e1}}{p_{01}} = -\int_{p_{01}}^{p_{e1}} \left[\frac{V}{n} - \frac{RT}{p}\right] \mathrm{d}p + \int_{p_{01}}^{p} \bar{v}_{c1}\, \mathrm{d}p \tag{160}$$

This is the exact Poynting relation.

Now let the univariant system be at equilibrium under its vapor pressure p_{01} and let an inert gas that does not react chemically with S_1 and is insoluble in the condensed complex be introduced into the system until the total pressure becomes p. The equilibrium pressure p_{e1} of S_1 in the system can be computed from equation 156 or from equation 160. These computations will be considered later. If we substitute the value of p_{e1} from equation 160 into equation 156 we obtain:

$$RT \ln \frac{px_1}{p_{01}} = -\int_0^p \left[\left(\frac{\partial V}{\partial n_1}\right)_{pTn} - \frac{RT}{p}\right] \mathrm{d}p + \int_0^{p_{01}} \left[\frac{V_k}{n_k} - \frac{RT}{p_k}\right] \mathrm{d}p_k + \int_{p_{01}}^{p} \bar{v}_{c1}\, \mathrm{d}p \qquad (161)$$

The first integral refers to the gas mixture, the second to the pure substance S_1, and the third to the condensed complex.

4. *Equilibrium between gaseous mixtures and condensed solutions:* The chemical potential $\mu_{ci}(p, T, y_i)$ of a volatile component i of a liquid (or solid) solution at p, T, and mole fraction y_i is:

$$\mu_{ci}(p,T, y_i) = \mu_{ci}(p_{0i},T) + RT \ln y_i + RT \ln \gamma_i + \int_{p_{0i}}^{p} \bar{v}_{ci}\, \mathrm{d}p \qquad (162)$$

where $\mu_{ci}\ (p_{01},T)$ is the chemical potential of the component under its own vapor pressure p_{0i} and is given by equation 102, $\bar{v}_{ci}$ is the partial molal volume of the substance S_i in the condensed solution, and γ_i is its activity coefficient in this phase. The latter has been discussed by Scatchard (162, 163), Scatchard and coworkers (164, 165, 166, 167, 168, 169, 170), and Hildebrand (85), who give references to the earlier work. The chemical potential of S_i in the gas phase is given by equation 140. Equating these two expressions we obtain for isothermal equilibrium at T:

$$RT \ln \frac{px_i}{p_{0i}y_i} = -\int_0^p \left[\left(\frac{\partial V}{\partial n_i}\right)_{pTn} - \frac{RT}{p}\right] \mathrm{d}p + \int_0^{p_{0i}} \left[\frac{V_k}{n_k} - \frac{RT}{p_k}\right] \mathrm{d}p_k + \int_{p_{0i}}^{p} \bar{v}_{ci}\, \mathrm{d}p + RT \ln \gamma_i \qquad (i = k) \qquad (163)$$

The first integral is to be evaluated for the gas mixture, the second for the pure gas k, and the third for the condensed phase.

Equation 163 applies directly to each component whose critical temperature is above T. Hildebrand (85) has suggested a method of determining a fictitious value of p_{0i} for a component above its critical temperature.

XIV. INTEGRATION OF THE EQUATIONS

A. The equation of state for pure gases

Aside from graphical methods we can evaluate the definite integrals with respect to pressure or volume occurring in the thermodynamic properties of pure gases from an equation of state of the type $(V/n) = F(p, T)$ or $p = f(V/n, T)$. All of the useful equations of state that have been applied to a number of substances are of the latter type. The Keyes equation (90) has four adjustable constants and gives a fair representation of the volumetric behavior of gases, being especially satisfactory for gases whose isometrics are nearly linear. The equation of Benedict, Webb, and Rubin (37) contains eight adjustable constants and gives an excellent representation of the compressibility data to about twice the critical density. Below the critical temperature this equation gives satisfactory results into the liquid region and permits calculation of the vapor pressure to about 1 per cent. Results of intermediate accuracy are given by the Beattie–Bridgeman equation of state (17, 18, 19, 21) with five adjustable contants. This equation is:

$$p = \frac{nRT}{V} + \frac{n^2\beta}{V^2} + \frac{n^3\gamma}{V^3} + \frac{n^4\delta}{V^4} \tag{164}$$

$$\beta = RTB_0 - A_0 - Rc/T^2$$

$$\gamma = -RTB_0b + A_0a - RB_0c/T^2$$

$$\delta = RB_0bc/T^2$$

The equation has been applied to the compressibility measurements of a number of substances and the values of the constants A_0, a, B_0, b, and c are listed in table 1. The equation gives satisfactory representation of the volumetric behavior of gases to about the critical density and has been used to compute the limiting densities (20), the Joule–Thompson coefficient and pressure variation of the constant pressure heat capacity (12, 13, 14, 41), the heat content and entropy (78, 81, 82, 148), the chemical potential (79), and the fugacities (113, 135, 137) of gases. In general the calculated values agree well with experimental results.

Equation 164 has two main defects. The first is that the second virial coefficient divided by RT, β/RT, approaches the limit B_0 at high temperatures instead of passing through a maximum and then decreasing with increasing temperature. This is more a theoretical than a practical defect: helium is the only gas exhibiting such a maximum below room temperature (at about −75°C.); neon and hydrogen have maxima at about 400°C., and other gases probably well above 1000°C. The second defect has more practical importance. The constant c, which was introduced to account for the curvature of the isometrics, should be a function of density and is so expressed in the equation of Benedict, Webb, and Rubin, who use three adjustable constants to represent the density variation of c.

To express V/n as a function of p and T we may solve equation 164 for V/n to any number of terms desired (16, 161). For the purpose of determining the variation of many of the thermodynamic properties of pure gases with pressure it is sufficient to use the expression:

$$\frac{V}{n} = \frac{RT}{p} + \frac{\beta}{RT} \tag{165}$$

$$\frac{\beta}{RT} = B_0 - \frac{A_0}{RT} - \frac{c}{T^3}$$

TABLE 1

Values of the constants of the Beattie–Bridgeman equation of state for several gases

$$p = [RT(1 - \epsilon)/V^2][V + B] - A/V^2$$

$$A = A_0(1 - a/V) \qquad B = B_0(1 - b/V) \qquad \epsilon = c/VT^3$$

Units: normal atmospheres; liters per mole; °K. (T°K. = t°C. + 273.13); R = 0.08206

GAS	A_0	a	B_0	b	$10^{-4} \times c$	MOLECULAR WEIGHT	REFERENCES
He	0.0216	0.05984	0.01400	0.0	0.0040	4.00	(19, 21)
Ne	0.2125	0.02196	0.02060	0.0	0.101	20.2	(19, 21)
A	1.2907	0.02328	0.03931	0.0	5.99	39.91	(19, 21)
H_2	0.1975	−0.00506	0.02096	−0.04359	0.0504	2.0154	(19, 21)
N_2	1.3445	+0.02617	0.05046	−0.00691	4.20	28.016	(19, 21)
O_2	1.4911	0.02562	0.04624	+0.004208	4.80	32	(19, 21)
Air	1.3012	0.01931	0.04611	−0.01101	4.34	28.964	(19, 21)
I_2	17.0		0.325		4000	253.864	(60)
CO_2	5.0065	0.07132	0.10476	+0.07235	66.00	44.000	(19, 21)
NH_3	2.3930	0.17031	0.03415	+0.19112	476.87	17.0311	(21, 27)
CH_4	2.2769	0.01855	0.05587	−0.01587	12.83	16.0308	(19, 21)
C_2H_4	6.1520	0.04964	0.12156	+0.03597	22.68	28.0308	(70, 21)
C_2H_6	5.8800	0.05861	0.09400	+0.01915	90.00	30.0462	(23)
C_3H_8	11.9200	0.07321	0.18100	+0.04293	120.00	44.0616	(26)
1-C_4H_8	16.6979	0.11988	0.24046	+0.10690	300.00	56.0616	(29)
iso-C_4H_8	16.9600	0.10860	0.24200	+0.08750	250.00	56.0616	(25)
n-C_4H_{10}	17.7940	0.12161	0.24620	+0.09423	350.00	58.077	(31)
iso-C_4H_{10}	16.6037	0.11171	0.23540	+0.07697	300.00	58.077	(30)
n-C_5H_{12}	28.2600	0.15099	0.39400	+0.13960	400.00	72.0924	(28)
neo-C_5H_{12}	23.3300	0.15174	0.33560	+0.13358	400.00	72.0924	(22)
n-C_7H_{16}	54.520	0.20066	0.70816	+0.19179	400.00	100.1232	(172)
CH_3OH	33.309	0.09246	0.60362	+0.09929	32.03	32.0308	(111, 114)
$(C_2H_5)_2O$	31.278	0.12426	0.45446	+0.11954	33.33	74.077	(19, 21)

GAS	$A_0^{1/2}$	$B_0^{1/3}$	$10^{-2} \times c^{1/2}$	GAS	$A_0^{1/2}$	$B_0^{1/3}$	$10^{-2} \times c^{1/2}$
He	0.14697	0.241014	0.0632	C_2H_4	2.48032	0.495371	4.7624
Ne	0.46098	0.274129	0.3178	C_2H_6	2.42487	0.454684	9.4868
A	1.13609	0.340017	2.4474	C_3H_8	3.45254	0.565665	10.9545
H_2	0.44441	0.275717	0.2245	1-C_4H_8	4.08631	0.621843	17.3205
N_2	1.15953	0.369529	2.0494	iso-C_4H_8	4.11825	0.623168	15.8114
O_2	1.22111	0.358927	2.1909	n-C_4H_{10}	4.21829	0.626752	18.7083
Air	1.14070	0.358590	2.0833	iso-C_4H_{10}	4.07476	0.617451	17.3205
I_2	4.12311	0.687534	63.2456	n-C_5H_{12}	5.31601	0.733104	20.0000
CO_2	2.23752	0.471410	8.1240	neo-C_5H_{12}	4.83011	0.694929	20.0000
NH_3	1.54693	0.324437	21.8374	n-C_7H_{16}	7.38377	0.891341	20.0000
CH_4	1.50894	0.382290	3.5819	CH_3OH	5.77139	0.845126	5.6595
				$(C_2H_5)_2O$	5.59267	0.768833	5.7732

Sartori (160) reports constants for water vapor for the temperature range 400–480° C.

This gives satisfactory results, except for calculation of the density itself, to moderate pressures (12, 13, 14, 60, 75, 76, 77, 79).

In order to compute values of the thermodynamic properties of a pure gas at various pressures we can proceed as follows:

1. For the most accurate values use equation 164 to evaluate the integrals of equations 97, 98, 106 through 110 and compute the pressure from equation 164. Note that equation 164 gives the value of pV which occurs in equations 106 and 108.
2. For more approximate results use equation 165 to evaluate the integrals of equations 88, 89, and 99 through 103. Now pV can be expressed by equation 165.

B. Relations among the equation of state constants and evaluation of the constants from critical data

From a study of the equation of state constants and critical constants of gases Keyes (93) found that the relation:

$$c = 0.023 \frac{A_0^3}{R^3 B_0^2}$$

held fairly well for non-polar gases. Hirschfelder and Roseveare (86) have interpreted the constants A_0, B_0, and c of equation 164 in terms of the energy of interaction and collision diameters of molecules by comparison of the second virial coefficient β/RT with that given by the 6–12 potential of the Lennard-Jones (115, 116) theory. They find 0.024 for the theoretical value of the coefficient. Corner (44) used a 6–9 potential and found the value 0.013. He extended the method to the third virial coefficient γ/RT which gave the theoretical relations:

$$a = 0.45B_0; \qquad b = -0.1B_0$$

The equation of state constants of a good many of the non-polar gases are in fair agreement with these relations. Stockmayer (174, 175) used an exponential in place of an algebraic temperature function in β/RT for polar gases and found a similar relation among B_0, A_0, and D (the constant replacing c).

The law of corresponding states originally arose through the prediction of a critical point by van der Waals' equation and the possibility of writing a reduced equation of state containing only universal constants. It fell into disrepute but recently interest has revived in both the practical and the theoretical aspects of the law (32). From equation 164 we note that the following are dimensionless ratios:

$$A_{0r} = \frac{A_0}{R^2 T_c^2/p_c}, \qquad B_{0r} = \frac{B_0}{RT_c/p_c}, \qquad c_r = \frac{c}{RT_c^4/p_c} \tag{166}$$

$$a_r = \frac{a}{RT_c/p_c}, \qquad b_r = \frac{b}{RT_c/p_c}$$

In these p_c and T_c are the critical pressure and temperature of the substance to which the constants apply. The relations are written in this form since the value of the critical volume, v_c, is never known so exactly as those of p_c and T_c, and the critical ratio $p_c v_c/RT_c$ is known to be approximately constant.

Keyes (93) found that the first three of these ratios for the substances whose equation of state constants were known fell into two groups, each surprisingly constant: one group of the non-polar gases and the other of the polar gases. Maron and Turnbull (136) and Brown (42) proposed to determine the equation of state constants of gases whose critical pressure and temperature are known but compressibility unknown by determining the values of A_{0r}, B_{0r}, c_r, a_r, b_r, for nitrogen and then use these to compute the parameters for other gases by equation 166. Although they obtained good results it might be preferable to consider the ratios somewhat variable and to evaluate them for a gas as nearly similar as possible to the gas for which the parameters are desired.

Su and Chang (176) made use of the relations of equation 166 and equation 164 to write the reduced equation:

$$p_r = \frac{T_r}{v_r} + \frac{\beta_r}{v_r^2} + \frac{\gamma_r}{v_r^3} + \frac{\delta_r}{v_r^4} \tag{167}$$

$$\beta_r = T_r B_{0r} - A_{0r} - c_r/T_r^2$$

$$\gamma_r = -\,T_r B_{0r} b_r + A_{0r} a_r - B_{0r} c_r/T_r^2$$

$$\delta_r = B_{0r} b_r c_r/T_r^2$$

$$p_r = p/p_c, \qquad v_r = vp_c/RT_c, \qquad T_r = T/T_c$$

They re-smoothed the compressibility data on seven hydrocarbons (methane, ethane, ethylene, propane, *n*-butane, isopentane, and *n*-heptane) to give p_r in terms of v_r and T_r, averaged p_r for the seven gases, and determined the values of A_{0r}, B_{0r}, c_r, a_r, and b_r in the usual manner. The average deviation of the calculated from the observed value of p_r was 0.7 per cent; and of the computed pressures from the observed pressures for the seven gases, 1 per cent. Application of this equation with the same value of the reduced constants to nine other gases (argon, helium, neon, hydrogen, oxygen, nitrogen, carbon dioxide, air, and ethyl ether) gave a representation of the pressures to 0.63 per cent.

In general, when the equation of state constants of a gas are not known but the critical pressure and temperature are known, we can use equation 167; or it is perhaps better to employ equation 164 or 165 with the values of the constants determined from equations 166 and the following values of Su and Chang:

$$A_{0r} = 0.4758 \qquad a_r = 0.1127 \tag{168}$$

$$B_{0r} = 0.18764 \qquad b_r = 0.03833$$

$$c_r = 0.05$$

Thus in equations 164 and 165:

$$A_0 = 0.4758 \left(\frac{RT_c}{p_c}\right)^2 p_c \qquad a = 0.1127 \left(\frac{RT^c}{p_c}\right) \tag{169}$$

$$B_0 = 0.18764 \left(\frac{RT_c}{p_c}\right) \qquad b = 0.03833 \left(\frac{RT_c}{p_c}\right)$$

$$c = 0.05 \left(\frac{RT_c}{p_c}\right) T_c^3$$

C. The equation of state for gas mixtures

An equation of state for gas mixtures is an equation expressing the pressure of the mixture in terms of the volume, temperature, and the mole numbers and equation of state constants of the pure constituent gases. The earlier investigators felt that the equation of state of a gas mixture of constant composition had the same form as that of a pure gas and that each parameter of the mixture, say B_m, was related to the corresponding parameters of the pure gases by the relation:

$$B_m = \Sigma_i \Sigma_j x_i x_j B_{ij} \tag{170}$$

where x_i, x_j are mole fractions and the sums go over all of the species present in the mixture. The method of computing the interaction parameter B_{ij} for the interaction of unlike molecules from B_{ii} and B_{jj} has been the subject of a number of theoretical investigations (39, 59, 132, 181). The early workers in this field proposed the relations:

$$B_{ij} = \tfrac{1}{2}(B_i + B_j) \qquad \text{(linear combination)} \tag{171}$$

$$B_{ij} = B_i^{1/2} B_j^{1/2} \qquad \text{(square-root combination)} \tag{172}$$

$$B_{ij} = \tfrac{1}{8}(B_i^{1/3} + B_j^{1/3})^3 \qquad \text{(Lorentz combination)} \tag{173}$$

where B_i and B_j are written for B_{ii} and B_{jj}, respectively. The first relation gives the largest value of B_{ij} and the second, the smallest. Equation 172 was used for the a constant of van der Waals' equation of state and theory indicates that equation 173, averaging of molecular diameters, applies to the b constant, although equation 171, which gives nearly the same value when B_i and B_j do not differ greatly, has been frequently used for b.

The use of these combination rules in the van der Waals equation gave a moderately successful representation of the properties of gas mixtures (58, 101, 102, 103, 104, 105, 106, 107, 178, 179). The Keyes equation for gas mixtures gave better results (91, 92, 94, 95, 134), and that of Benedict, Webb, and Rubin, excellent results (35, 36, 38).

The use of combination of constants in equations 164 and 165 gives a good representation of the compressibilities of gas mixtures (11, 24, 34, 88), the expansion of gases on mixing (68, 69), and equilibria in gaseous phases (60, 73, 74, 75, 76, 77, 112, 113, 114).

Attempts have been made to write an equation of state for gas mixtures by finding combination rules for the virial coefficients (45, 50, 81, 82, 96, 144) or other properties of the mixture not involving the individual equation of state constants (5, 80, 98, 122). Su, Huang, and Chang (177) used the reduced equation 167 with the constants given in equations 168 and the pseudo-critical pressure and temperature of the mixture introduced by Kay (87) to calculate the pressures of gaseous mixtures.

The use of linear and quadratic combination rules for certain of the parameters of the Lennard-Jones (115, 116) expression for the second virial coefficient was found to give good representation of the properties of gas mixtures by Lennard-Jones and Cook (117), Hirschfelder and Roseveare (86), and Beattie and Stockmayer (33). The success of these investigations suggests that the second virial interaction coefficient β_{12}/RT be written in terms of B_{012}, A_{012}, and c_{12} of equation 164 as:

$$\frac{\beta_{12}}{RT} = B_{012}\left[1 - \frac{A_{012}}{B_{012}RT} - \frac{c_{12}}{B_{012}T^3}\right] \tag{174}$$

and that the B_{012} outside the brackets be obtained by Lorentz combination, and (A_{012}/B_{012}) and (c_{12}/B_{012}) by square-root combination.

Stockmayer (175) showed that A_0 should be split into two terms for a polar gas: one corresponding to the attractive constant A_0 for a non-polar gas and the other depending on the dipole moment. Each is to be combined separately by square-root combination for a gas mixture containing polar gases.

Practical considerations require that an equation of state for gas mixtures involve fairly simple combination rules for the constants. A study (34) of various methods of combining the constants A_0, B_0, and c of equation 164 for the system methane–n-butane indicated that the best representation of the compressibilities of the mixtures are obtained by square-root combination for A_{012} and c_{12}, and Lorentz combination for B_{012}. The average percentage deviation of the computed from the observed pressures was 0.74 per cent, about half of which is caused by the failure of equation 164 to represent the pressures of the pure gases. The simpler rules, square-root for A_{012} and linear for B_{012} and c_{12}, represented the measurements with about twice as large an average percentage deviation. In this study linear combination was used for a_{12} and b_{12}.

Using square-root combination (equation 172) for A_{012} and c_{12}, Lorentz combination (equation 173) for B_{012}, and linear combination (equation 171) for a_{12} and b_{12} in equation 170 to obtain the parameters for a gas mixture, we find from equation 164 the following equations of state for $\Sigma_i n_i$ moles of a gas mixture:

$$p = \frac{\Sigma_i n_i RT}{V} + \frac{(\Sigma_i n_i)^2 \beta_m}{V^2} + \frac{(\Sigma_i n_i)^3 \gamma_m}{V^3} + \frac{(\Sigma_i n_i)^4 \delta_m}{V^4} \tag{175}$$

where

$$\left.\begin{aligned}
\beta_m &= RTB_{0m} - A_{0m} - \frac{Rc_m}{T^2} \\
\gamma_m &= -RTB_{0m}\,b_m + A_{0m}\,a_m - \frac{RB_{0m}\,c_m}{T^2} \\
\delta_m &= \frac{RB_{0m}\,b_m\,c_m}{T^2}
\end{aligned}\right\} \tag{176}$$

and

$$\left.\begin{aligned}
A_{0m} &= (\Sigma_i x_i A_{0i}^{1/2})^2 \\
B_{0m} &= \tfrac{1}{8}\,\Sigma_i\Sigma_j x_i x_j (B_{0i}^{1/3} + B_{0j}^{1/3})^3 = \tfrac{1}{4}(\Sigma_i x_i B_{0i}) + \tfrac{3}{4}(\Sigma_i x_i B_{0i}^{1/3})(\Sigma_i x_i B_{0i}^{2/3}) \\
c_m &= (\Sigma_i x_i c_i^{1/2})^2 \\
a_m &= \Sigma_i x_i a_i \\
b_m &= \Sigma_i x_i b_i
\end{aligned}\right\} \tag{177}$$

The approximate equation 165 becomes for a gas mixture:

$$V = \frac{\Sigma_i n_i RT}{p} + \frac{(\Sigma_i n_i)\beta_m}{RT} \tag{178}$$

where β_m is given by equations 176 and 177.

Equations 175 and 178 in conjunction with equations 176 and 177 purport to represent the pressure [or volume] of a gas mixture as a function of V, T, n_1, n_2, $\cdots$ [or p, T, n_1, n_2, $\cdots$] containing parameters of the pure gases 1, 2, $\cdots$ only. No measurements on mixtures are necessary. These relations can be used to evaluate the integrals of Section XIII, paragraphs E, F, and G.

The general limit method gives a partial though exact solution of the problem of expressing the thermodynamic properties of real gases and gas mixtures in terms of those of pure gases. The general limit method and combination of constants in an equation of state give a complete though approximate solution to the problem. The approximation is introduced through the equation of state and the combination rules.

D. Integrated approximate equations for pure gases

The definite integrals of the general relations of Section XII F (page 166) can be expressed in terms of the equation of state constants of a gas by evaluation of the integrands from equation 164. The resulting equations state the thermodynamic properties of gases in terms of the independent variables V and T. Less exact but simpler expressions in terms of p and T may be derived from the use of equation 165 in the relations of Section XII E (page 165). These are sufficient for many purposes and are given below.

$$E = -\left[\frac{A_0}{RT} + \frac{3c}{T^3}\right] np - nRT + nh^0 \tag{179}$$

$$H = \left[B_0 - \frac{2A_0}{RT} - \frac{4c}{T^3}\right] np + nh^0 \tag{180}$$

$$S = -nR \ln p - \left[\frac{A_0}{RT^2} + \frac{3c}{T^4}\right] np + ns^0 \tag{181}$$

$$F_{VT} = nRT \ln p - nRT + nh^0 - nTs^0 \tag{182}$$

$$F_{pT} = nRT \ln p + \left[B_0 - \frac{A_0}{RT} - \frac{c}{T^3}\right] np + nh^0 - nTs^0 \tag{183}$$

$$\mu = RT \ln p + \left[B_0 - \frac{A_0}{RT} - \frac{c}{T^3}\right] p + h^0 - Ts^0 \tag{184}$$

$$RT \ln f = RT \ln p + \left[B_0 - \frac{A_0}{RT} - \frac{c}{T^3}\right] p \tag{185}$$

From the usual thermodynamic relations and equation 165 we find for the heat capacities and the Joule and Joule–Thompson coefficient the following relations:

$$C_V = nc_V^* + \frac{6c}{T^4}\,np \tag{186}$$

$$C_p = nc_p^* + \left[\frac{2A_0}{RT^2} + \frac{12c}{T^4}\right] np \tag{187}$$

$$C_p - C_V = nR + \left[\frac{2A_0}{RT^2} + \frac{6c}{T^4}\right] np \tag{188}$$

$$C_V\left(\frac{\partial T}{\partial V}\right)_E = -\left(\frac{\partial E}{\partial V}\right)_T = \left[\frac{\partial(p/T)}{\partial(1/T)}\right]_V \tag{189}$$

$$= -\left[\frac{A_0}{R^2\,T^2} + \frac{3c}{RT^4}\right] p^2 \tag{190}$$

$$C_p\left(\frac{\partial T}{\partial p}\right)_H = -\left(\frac{\partial H}{\partial p}\right)_T = -\left[\frac{\partial(V/T)}{\partial(1/T)}\right]_p \tag{191}$$

$$= n\left[-B_0 + \frac{2A_0}{RT} + \frac{4c}{T^3}\right] \tag{192}$$

In the absence of compressibility data from which A_0, B_0, and c can be determined, we can estimate the values of these constants for use in the above equations from the critical pressure and temperature by means of equations 169.

The above relations do not include any of the terms involving the third or higher virial coefficients. The expansion of equation 164 ending at the term in p^2:

$$\frac{V}{n} = \frac{RT}{p} + \frac{\beta}{RT} + \left[\frac{\gamma}{(RT)^2} - \frac{\beta^2}{(RT)^3}\right] p + \left[\frac{\delta}{(RT)^3} - \frac{3\beta\gamma}{(RT)^4} + \frac{2\beta^3}{(RT)^5}\right] p^2 \tag{193}$$

proposed by Scatchard (161) reproduces the density to moderately high pressure and may be employed to extend equations 179–192 to higher pressures.

E. Integrated approximate equations for gas mixtures

The most accurate results are obtained from the general relations of Section XIII F (page 171) and the complete equation of state for gas mixtures, equation 175. These express the properties of gas mixtures in terms of the independent variables V, T, and the mole numbers. The equations given below come from the approximate equation (equation 178) and the general relations of Section XIII E; they express the properties of gas mixtures in terms of p, T, and the mole numbers.

If we write the second virial coefficient β_m of a gas mixture in the form of equation 170, β_{ii} and β_{jj} are the virial coefficients of the pure gases i and j, and the interaction coefficient β_{ij} is by equations 176 and 177:

$$\beta_{ij} = \frac{RT}{8}(B_{0i}^{1/3} + B_{0j}^{1/3})^3 - A_{0i}^{1/2}A_{0j}^{1/2} - \frac{Rc_i^{1/2}c_j^{1/2}}{T^2} \qquad (194)$$

Let

$$D_{ij} = 2\beta_{ij} - \beta_{ii} - \beta_{jj} \qquad (195)$$

then

$$\frac{D_{ij}}{RT} = -\left[\frac{3}{4}(B_{0i}^{1/3} - B_{0j}^{1/3})(B_{0i}^{2/3} - B_{0j}^{2/3}) - \frac{(A_{0i}^{1/2} - A_{0j}^{1/2})^2}{RT} - \frac{(c_i^{1/2} - c_j^{1/2})^2}{T^3}\right] \qquad (196)$$

where

$$D_{ii} = D_{jj} = 0, \qquad D_{ij} = D_{ji} \qquad (197)$$

For each pair of gases D_{ij} is an algebraic function of temperature and the coefficients are computed from the A_0, B_0, and c constants for the two gases. At constant temperature D_{ij} is simply a number for a given pair of gases.

The expression:

$$\left(\frac{\partial V}{\partial n_i}\right)_{pTn} - \frac{RT}{p} = \frac{1}{RT}\left[\frac{\partial(\Sigma_i n_i)\beta_m}{\partial n_i}\right]_{Tn}$$

$$= \frac{1}{RT}[2\Sigma_j x_j\beta_{ij} - \Sigma_i\Sigma_j x_i x_j \beta_{ij}] \qquad (198)$$

$$= \frac{1}{RT}[\beta_{ii} + \Sigma_j x_j D_{ij} - \tfrac{1}{2}\Sigma_i\Sigma_j x_i x_j D_{ij}] \qquad (199)$$

$$= \frac{1}{RT}(\beta_i + D_i) \qquad (200)$$

where the summations extend over all species present in the gas mixture, β_i has been written for the second virial coefficient β_{ii} of the pure gas i, and D_i/RT is the difference between the partial molal volume of gas i in the mixture and its molal volume at the same pressure and temperature as computed by equation 165:

$$\frac{D_i}{RT} = \left(\frac{\partial V}{\partial n_i}\right)_{pTn} - \left(\frac{RT}{p} + \frac{\beta_i}{RT}\right) \qquad (201)$$

In general D_i is much smaller than β_i, and it depends on the temperature, composition, and equation of state constants of all gases present in the mixture. We may write D_i in the following forms:

$$\frac{D_i}{RT} = \frac{1}{RT}(\Sigma_j x_j D_{ij} - \tfrac{1}{2}\Sigma_i\Sigma_j x_i x_j D_{ij}) \qquad (202)$$

$$= -\left[\frac{3}{4}(B_{0i}^{1/3} - \Sigma_i x_i B_{03}^{1/3})(B_{0i}^{2/3} - \Sigma_i x_i B_{0i}^{2/3}) - \frac{(A_{0i}^{1/2} - \Sigma_i x_i A_{0i}^{1/2})^2}{RT} - \frac{(c_i^{1/2} - \Sigma_i x_i c_i^{1/2})^2}{T^3}\right] \qquad (203)$$

where the summations extend over all gases present.

For a gas 1 in a binary mixture:

$$D_1 = D_{12}x_2^2 \tag{204}$$

and for a gas 1 in a ternary mixture:

$$D_1 = D_{12}x_2^2 + D_{13}x_3^2 + (D_{12} + D_{13} - D_{23})x_2x_3 \tag{205}$$

The thermodynamic properties of gas mixtures follow.

$$E = -\left[\frac{A_{0m}}{RT} + \frac{3c_m}{T^3}\right](\Sigma_i n_i)p - (\Sigma_i n_i)RT + (\Sigma_i n_i h_i^0) \tag{206}$$

$$H = \left[B_{0m} - \frac{2A_{0m}}{RT} - \frac{4c_m}{T^3}\right](\Sigma_i n_i)p + (\Sigma_i n_i h_i^0) \tag{207}$$

$$S = -(\Sigma_i n_i R \ln px_i) - \left[\frac{A_{0m}}{RT^2} + \frac{3c_m}{T^4}\right](\Sigma_i n_i)p + (\Sigma_i n_i s_i^0) \tag{208}$$

$$F_{VT} = (\Sigma_i n_i RT \ln px_i) - (\Sigma_i n_i)RT + (\Sigma_i n_i h_i^0) - T(\Sigma_i n_i s_i^0) \tag{209}$$

$$F_{pT} = (\Sigma_i n_i RT \ln px_i) + \left[B_{0m} - \frac{A_{0m}}{RT} - \frac{c_m}{T^3}\right](\Sigma_i n_i)p + (\Sigma_i n_i h_i^0) - T(\Sigma_i n_i s_i^0) \tag{210}$$

$$\mu_i = RT \ln px_i + \left(\frac{\beta_i}{RT} + \frac{D_i}{RT}\right)p + h_i^0 - Ts_i^0 \tag{211}$$

$$RT \ln f_i = RT \ln px_i + \left(\frac{\beta_i}{RT} + \frac{D_i}{RT}\right)p \tag{212}$$

$$C_V = (\Sigma_i n_i c_{vi}^*) + \frac{6c_m}{T^4}(\Sigma_i n_i)p \tag{213}$$

$$C_p = (\Sigma_i n_i c_{pi}^*) + \left[\frac{2A_{0m}}{RT^2} + \frac{6c_m}{T^4}\right](\Sigma_i n_i)p \tag{214}$$

$$C_p - C_V = (\Sigma n_i)R + \left[\frac{2A_{0m}}{RT^2} + \frac{6c_m}{T^4}\right](\Sigma_i n_i)p \tag{215}$$

For the Joule and Joule–Thompson coefficients we obtain the same relations as equations 190 and 192 with the constants of the pure gases replaced by those of the mixture and n replaced by $\Sigma_i n_i$.

F. Integrated approximate equilibrium relationships

From the general equilibrium relations of Section XIII G (page 171) we find the following equations:

1. *Mass action functions for homogeneous gaseous reactions:* Equations 151 and 153 become:

$$\ln \frac{K_p}{K_p^*} = -\left[\frac{\Sigma_i \nu_i \beta_i}{RT} + \frac{\Sigma_i \nu_i D_i}{RT}\right]\frac{p}{RT} \tag{216}$$

$$= -\left\{\Sigma_i\nu_i B_{0i} - \frac{\Sigma_i\nu_i A_{0i}}{RT} - \frac{\Sigma_i\nu_i c_i}{T^3}\right\}\frac{p}{RT}$$

$$+ \left\{\tfrac{3}{4}[\Sigma_i\nu_i(B_{0i}^{1/3} - \Sigma_i x_i B_{0i}^{1/3})(B_{0i}^{2/3} - \Sigma_i x_i B_{0i}^{2/3})]\right.$$

$$\left. - \frac{[\Sigma_i\nu_i(A_{0i}^{1/2} - \Sigma_i x_i A_{0i}^{1/2})^2]}{RT} - \frac{[\Sigma_i\nu_i(c_i^{1/2} - \Sigma_i x_i c_i^{1/2})^2]}{T^3}\right\}\frac{p}{RT} \tag{217}$$

$$\ln K_p^* = \frac{1}{R}\left[\int_{T_0}^{T}\frac{(\Sigma_i\nu_i c_{pi}^*)}{T}\,\mathrm{d}T\right] - \frac{1}{RT}\left[\int_{T_0}^{T}(\Sigma_i\nu_i c_{pi}^*)\,\mathrm{d}T\right]$$

$$- \frac{1}{RT}(\Sigma_i\nu_i h_{0i}^0) + \frac{1}{R}(\Sigma_i\nu_i s_{0i}^0) \tag{218}$$

$$= \int_{T_0}^{T}\left[\int_{T_0}^{T}(\Sigma_i\nu_i c_{pi}^*)\,\mathrm{d}T\right]\frac{\mathrm{d}T}{T^2} - \frac{1}{RT}(\Sigma_i\nu_i h_{0i}^0) + \frac{1}{R}(\Sigma_i\nu_i s_{0i}^0) \tag{219}$$

All summations extend over all species in the mixture, the stoichiometric coefficient ν being zero for a gas that does not enter into the chemical reaction.

Equations 217 and 219 express K_p in terms of the temperature, pressure, composition of the equilibrium mixture, the equation of state constants for all gases present, the heat capacities of the gases entering into the reaction, and the heat content and entropy constants of the gases entering into the reaction. The last two sums of equation 219 may be considered adjustable in the absence of heat content and entropy data on the gases. Although equation 217 was derived for moderate pressures, it applies through a compensation of errors to gaseous equilibria at high pressure. Gillespie and Beattie (75, 76, 77) found it possible to correlate the measurements of the ammonia synthesis equilibrium to 1000 atm. including equilibrium mixtures containing argon and those containing no argon. They used linear combination for B_{012} and c_{12}.

To compute the composition of the equilibrium mixture given the initial compositions, the pressure, the temperature, and the necessary constants for the pure gases we first calculate K_p^*. From K_p^* (the ideal gas value of K_p) compute the composition of the equilibrium mixture. Use these values of the mole fractions in the right-hand side of equation 217 to calculate a provisional value of K_p from which provisional values of the compositions can be obtained. Repeat until no change in the calculated compositions results. In general two approximations are sufficient even at high pressures.

2. *Equilibrium pressure of a gas in a mixture:* Equation 156 gives:

$$\ln\frac{p_{ek}}{px_i} = \frac{\beta_i}{RT}\left(\frac{p - p_{ek}}{RT}\right) + \frac{D_i}{RT}\frac{p}{RT} \qquad i \equiv k = 1, 2, \cdots \tag{220}$$

If we express D_i in terms of D_{ij}, we find for a gas 1 in a ternary mixture:

$$\ln\frac{p_{e1}}{px_1} = \frac{\beta_1}{RT}\left(\frac{p - p_{e1}}{RT}\right)$$

$$+ \frac{1}{RT}[D_{12}x_2^2 + D_{13}x_3^2 + (D_{12} + D_{13} - D_{23})x_1x_2]\frac{p}{RT} \tag{221}$$

For a binary mixture all terms in the bracket except the first disappear. The general equation 156 was derived (10) a number of years ago, and the approximate equation 220 was obtained by Gillespie (69).

To compute the equilibrium pressure of a gas given the total pressure and composition of the mixture, place p_{ek} on the right-hand side of the equation equal to its ideal gas value px_i for the first approximation. Then repeat the calculation with the provisional value of p_{ek} resulting from the first approximation.

To compute the composition of a mixture of n gases given the total pressure and $n - 1$ values of p_{ek}, use the ideal gas values $x_i = p_{ek}/p$ for the compositions occurring on the right-hand side of the equation. Repeat if necessary.

3. *Effect of an inert gas on a univariant equilibrium:* Let

$$\bar{v}_{c1}(p,T) = \bar{v}^*_{c1}(0,T)(1 - \kappa_1 p) \tag{222}$$

where $\bar{v}^*_{c1}$ is the (extrapolated) value of $\bar{v}_{c1}$ at zero pressure and κ_1 is the compressibility of this quantity.

The Poynting equation (equation 160) gives:

$$\ln \frac{p_{e1}}{p_{01}} = -\frac{\beta_1}{RT}\left(\frac{p_{e1} - p_{01}}{RT}\right) + \bar{v}^*_{c1}\left(\frac{p - p_{01}}{RT}\right) - \frac{\kappa_1}{2}\left(\frac{p^2 - p^2_{0i}}{RT}\right) \tag{223}$$

where p_{01} is the equilibrium pressure of the condensed complex under its own vapor pressure and p_{e1} is the equilibrium pressure under the pressure p. When the pressure p is obtained by forcing an inert gas insoluble in the condensed complex into the system, we find from equation 161:

$$\ln \frac{px_1}{p_{01}} = \left(\bar{v}^*_{c1} - \frac{\beta_1}{RT}\right)\left(\frac{p - p_{01}}{RT}\right) - \frac{D_1}{RT}\frac{p}{RT} - \frac{\kappa_1}{2}\left(\frac{p^2 - p^2_{01}}{RT}\right) \tag{224}$$

$$= \left(\bar{v}^*_{c1} - \frac{\beta_1}{RT}\right)\left(\frac{p - p_{01}}{RT}\right) - \frac{D_{12}x_2^2}{RT}\frac{p}{RT} - \frac{\kappa_1}{2}\left(\frac{p^2 - p^2_{01}}{RT}\right) \tag{225}$$

In equation 225 x_2 is the mole fraction of the inert gas in the gas phase. If the inert gas is soluble in the condensed complex, equations 226 and 227 should be used.

Equation 224 combines equation 220 for the equilibrium pressure of a gas in a mixture and equation 223 for the Poynting effect. It was derived by Gerry and Gillespie (60).

Equation 225 is used to compute p_{01} given p and x_1, or to compute x_1 given p and p_{01} in the manner described under equation 221.

4. *Equilibrium between gaseous mixtures and condensed solutions:* Equation 163 gives:

$$\ln \frac{px_i}{p_{0i}\,y_i} = \left(\bar{v}^*_{ci} - \frac{\beta_i}{RT}\right)\left(\frac{p - p_{0i}}{RT}\right) - \frac{D_i}{RT}\frac{p}{RT} - \frac{\kappa_i}{2}\left(\frac{p^2 - p^2_{0i}}{RT}\right) + \ln \gamma_i \tag{226}$$

For component 1 of a binary system:

$$\ln \frac{px_1}{p_{01}\,y_1} = \left(\bar{v}^*_{c1} - \frac{\beta_1}{RT}\right)\left(\frac{p - p_{01}}{RT}\right) - \frac{D_{12}x_2^2}{RT}\frac{p}{RT} - \frac{\kappa_1}{RT}\left(\frac{p^2 - p^2_{01}}{RT}\right) + \ln \gamma_1 \tag{227}$$

This equation was derived by Scatchard and Raymond (165). For the use of equation 227 see under equation 225.

The relations given in the last three paragraphs have been applied to numerous equilibria. Lurie and Gillespie (134) used an equation similar to equation 224 to correlate their measurements on the equilibrium $BaCl_2 \cdot 8NH_3(s)$, $BaCl_2(s)$, $NH_3(g) + N_2(g)$ and applied it to the data of Pollitzer and Strebel (145) on the system $CO_2(l)$, $CO_2(g) + N_2(g)$; they used combination of constants in the Keyes equation of state. Gerry and Gillespie (60) applied the relation to the correlation of the data on the vapor pressure of iodine determined by the gas stream method. Apparent discrepancies caused by the use of different inert gases were resolved. Scatchard and coworkers (164–170) and Benedict and coworkers (35) applied equation 227 to liquid–vapor equilibria at about 1 atm. pressure. Here the pressures were low and the parameters D_{12} and κ_1 could be placed equal to zero; the main effect was that introduced by γ_1. Goff and coworkers (81, 82) applied an equation similar to equation 225 to moist air; they used a combination of second virial coefficients. Stockmayer (175) applied equation 226 to the data of Saddington and Krase (150) and Bartlett (3) on the system $H_2O(l)$, $H_2O(g) + N_2(g)$ and to unpublished data on the system $H_2O(l)$, $H_2O(g) + CO_2(g)$; he used a special method for combining A and D (corresponding to A_0 and roughly to Rc/A_0) for the polar gases.

The effects predicted by the ideal gas law may be obtained by placing the parameters β and D equal to zero in equations 220, 223, 224, and 226. In general the mole fraction of a vapor in a gas mixture is greater than that computed by Dalton's law (sometimes as much as 100 times), but it may be less if the inert gas is above its Boyle temperature.

G. The energy and entropy constants

From equations 88 and 104 we find that the heat content constant h_0^0 is the molal heat content of a gas at T_0 and a very low pressure p^*; from equations 97 and 111, e_0^0 is the molal energy at T_0 and p^*; and from equations 89 and 105 $s_0^0 - R \ln p^*$ is the molal entropy at T_0 and p^*. The parameters h^0, e^0, and $s^0 - R \ln p^*$ are the corresponding molal quantities at T and p^*. If we choose a standard state of 1 atm. and T_0, we note that h_0^0, e_0^0, and s_0^0 are approximately equal to the molal heat content, energy, and entropy of the gas in the standard state (see equations 179, 180, and 181).

The evaluation of h_0^0 and s_0^0 ($e_0^0 = h_0^0 - RT_0$) depends on what changes in state of the gas mixture are to be studied, and may be made on the basis of the following considerations:

1. *Chemical reactions may occur among the constituent gases:* Arbitrary values, say zero, may be assigned to the molal heat content and entropy of all elementary substances in the standard state p_0, T_0. The constants h_0^0 and s_0^0 for such elements as are gases under these conditions can be computed from equations 180 and 181, and for elements that are not gases and gases that are not elements can be calculated from these equations and other thermodynamic data. Thus from the usual relations we can compute the heat content and entropy of an

element in the condensed state at its vapor pressure and T_0, add the heat content and entropy of vaporization to give these quantities for the vapor at the vapor pressure and T_0, and apply equations 180 and 181 to determine h_0^0 and s_0^0. For a gaseous compound we can compute $\Sigma_i \nu_i h_{0i}^0$ and $\Sigma_i \nu_i s_{0i}^0$ from equations 217 and 219 from equilibrium measurements of a reaction in which the compound is formed from its elements or of some reaction involving the compound with other substances whose constants are known. This has been done for the ammonia synthesis reaction (75, 76).

When interested only in the effect of pressure on chemical equilibrium at constant temperature, we can use equation 217 with K_p^* considered to be an adjustable parameter.

2. *No chemical reaction occurs:* We can assign arbitrary values to the molal heat content and entropy of each individual substance or indeed to the mixture if the composition is constant. If the temperature is to vary the values are assigned only at p_0, T_0, but if the temperature is to be constant for all variations we can assign arbitrary values at p_0 and any temperature.

XV. COMPARISON OF THE GENERAL LIMIT METHOD WITH THE LEWIS AND RANDALL RULE AND THE GIBBS–DALTON LAW

The Lewis and Randall rule requires additivity of volumes at constant total pressure and temperature (equation 40). The Gibbs–Dalton law requires the additivity of pressures at constant total volume and temperature (equation 6). The general limit method places no such severe restrictions on the equation of state for gas mixtures; it does require that the pV product for a gas mixture approach $\Sigma_i n_i RT$ in a certain manner as the pressure approaches zero (equations 117).

The Lewis and Randall rule, the Gibbs–Dalton law, and the general limit method together with combination of constants in an equation of state each give a complete solution to the problem of computing the general thermodynamic properties of gas mixtures from data on the pure constituent gases alone. The latter gives the most accurate representation of the properties of gas mixtures; the Lewis and Randall rule and the Gibbs–Dalton law frequently give calculated values that bracket the measured value, one giving a high and the other a low value.

The Lewis and Randall rule requires that the partial molal volume of a gas in a mixture equal the molal volume of the pure gas measured at the temperature and total pressure of the mixture. It gives in place of equation 200 the relation:

$$\left(\frac{\partial V}{\partial n_i}\right)_{pTn} - \frac{RT}{p} = \frac{\beta_i}{RT} \tag{228}$$

that is, it requires that $D_i = 0$. If we delete all terms containing any mole fractions on the right-hand side of the equations of Section XIV F (page 183) we obtain the approximate equilibrium relationships given by the Lewis and Randall rule, the approximation being that of equation 165 for pure gases. Thus the rule predicts that K_p, p_{ei}/px_i, etc. do not depend on the composition of the gas mixture but only on the properties of pure gases.

The requirement of the Gibbs–Dalton law is given in equation 9. From equation 175 we find, on dropping terms after the second:

$$\left(\frac{\partial p}{\partial n_i}\right)_{VTn} - \frac{RT}{V} = (\beta_i + \beta_m + D_i)\frac{\Sigma_i n_i}{V^2} \qquad (i \equiv k = 1, 2, \cdots) \tag{229}$$

To the same number of terms the Gibbs–Dalton law predicts:

$$\left(\frac{\partial p}{\partial n_i}\right)_{VTn} - \frac{RT}{p} = 2\beta_i \frac{n_{ck}}{V^2} \tag{230}$$

where V and T have the same values in equations 229 and 230, and $n_{ck} = n_i$, the number of moles of gas i in $\Sigma_i n_i$ moles of the mixture.

Equation 229 used in equation 157 gives for the equilibrium concentration C_{ek} of a gas in a mixture:

$$\ln\frac{C_{ek}}{C_i} = (\beta_i + \beta_m + D_i)\frac{C}{RT} - 2\beta_i \frac{C_{ek}}{RT} \qquad (i \equiv k = 1, 2, \cdots) \tag{231}$$

where C is the concentration of the mixture and C_i the concentration of gas i in the mixture. The Gibbs–Dalton law requires that the right-hand side of equation 231 be zero.

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