ALLOWANCE FOR VOLATILITY IN CALCULATION OF EQUILIBRIUM COMPOSITION OF GAS MIXTURE

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Inzhenerno-Fizicheskii Zhurnal, Vol. 12, No. 5, pp. 615–619, 1967

UDC 533.77

This paper gives a method of calculating the equilibrium compositions of gas mixtures which conform to the Amagat law and the Bartlett rule.

A number of industrial processes effected in the gas phase take place at a pressure of several hundred atmospheres. This necessitates consideration of the deviation of the properties of the system from those of an ideal gas.

In using the widely known calculation method we can allow for these deviations by calculating the volatilities of the reagents. However, exact equations for calculating the volatility of components of a solution [1] cannot be used owing to the fact that these equations include the derivative of the volume or pressure of the mixture with respect to the mole fraction of the component, and calculation of the volatility requires an additional equation connecting the parameters of the mixture with the mole fractions of the components contained in this equation as independent variables. No such equation is available at present, and, hence, for practical calculations it is necessary to combine the equations of state of the pure components and introduce several assumptions regarding the nature of the interaction between the molecules of the various components.

The most soundly based of the numerous equations of state describing the P, V, and T properties of pure gases is the equation involving virial coefficients [2, 3]. With increase in the temperature of the process the effect of the virial coefficients on the compressibility factor decreases with increase in the index of the factor and for temperatures at which several large-scale processes are effected in the gas phase, the P, V, and T properties of pure gases are described sufficiently accurately by an equation with second and third virial coefficients:

$$PV = RT\left(1 + \frac{B}{V} + \frac{C}{V^2}\right). \tag{1}$$

In the case of a mixture of real gases the problem of obtaining the equation of state is complicated by the fact that interaction of the molecules of the different components causes deviations of the properties of the mixture from the properties calculated on the assumption of additivity of the respective properties of the pure components. In this case the probability of simultaneous collision of three or more molecules is fairly small and decreases with increase in temperature. Hence, the equation of state which takes dual interactions of the components into account gives an accurate representation of the properties of the mixture in a sufficiently wide range of temperature and pressure. This equation can be written in two ways:

$$V_{\text{m}} = \Sigma N_i V_i^0 + \Sigma N_i N_k \Delta V_{ik}, \tag{2}$$

$$P_{\text{m}} = \Sigma N_i P_i^0 + \Sigma N_i N_k \Delta P_{ik}. \tag{3}$$

Equation (2) can be regarded as Biron's equation [4] extended to a multicomponent system, and Eq. (3) as the generalized Krichevskii-Kazarnovskii equation [5]. However, even in this form the equation of state of the mixture is unsuitable for practical calculations. If dual interactions of the molecules are neglected and ΔV_{ik} is taken as 0, then Eq. (2) is converted to the Amagat law. A mixture with an equation of state

$$V_{\text{m}} = \Sigma N_i V_i^0 \tag{4}$$

is an ideal solution. To calculate the volatility of a component of an ideal solution we have the volatility rule, or the Lewis-Randall rule [6]

$$f_i = f_i^0 N_i, \tag{5}$$

which is suitable for calculations involved in the determination of the composition of a mixture, since f_i^0 is independent of the mole fractions of the components and can be determined if the equation of state of the pure substance is known.

The volatility of the pure substance is expressed by the formula

$$RT\ln f = RT\ln\frac{RT}{V} + PV - RT - \int\limits_{\infty}^{V}(P - P_{\text{id}})\,dV. \tag{6}$$

Using the accepted notation, we rewrite expression (6) for the volatility of the pure component at the pressure and temperature of the mixture:

$$RT_{\text{m}}\ln f_i^0 = RT_{\text{m}}\ln\frac{RT_{\text{m}}}{V_i^0} + P_{\text{m}}V_i^0 - RT_{\text{m}} - \int\limits_{\infty}^{V_i^0}(P_{\text{m}} - P_{\text{id}})\,dV_i^0. \tag{7}$$

Substituting in (7) the value of P_{m} from Eq. (1), we have

$$f_i^0 = \frac{RT_{\text{m}}}{V_i^0}\exp\left[2\frac{B_i}{V_i^0} + \frac{3}{2}\frac{C_i}{(V_i^0)^2}\right]. \tag{8}$$

The equilibrium composition, calculated by using Eqs. (1), (5), and (8), is the composition of a mixture composed of real gases (interaction between molecules of the same component causes a deviation of its properties from those of an ideal gas), and there is no interaction between the molecules of the different components. In other words, the volumes are additive; the mixture conforms to the Amagat law.

The composition of the gas determined by this method is the second approximation to reality in comparison with the composition of a mixture in which the components, like the mixture as a whole, are ideal gases.

However, additivity of the volumes in a mixture of real gases is not always a sufficiently good approximation to reality. Some authors [7] believe that as the temperature increases the corrections ΔP_{ik} (but not ΔV_{ik}) in Eq. (3) to the law of additivity of pressures become smaller, and, hence, a mixture for which the pressures are additive represents the properties of the real mixture better than a mixture with equation of state (4).

The Lewis-Randall rule is used to determine the volatility of a component of an ideal solution. Hence, expression (5) can be obtained by substitution of Eq. (4) in the formula for the volatility of the component of the gas solution. This can easily be seen by carrying out the appropriate transformations.

We use similar arguments to derive the volatility rule in the case $\Delta P_{ik} = 0$. In this case expression (3) is converted to the Bartlett equation:

$$P_{\mathrm{m}} = \Sigma N_i P_i^0. \tag{9}$$

Using the accepted notation we write the expression for the volatility of the i-th component of the mixture:

$$RT_{\mathrm{m}} \ln f_i = RT_{\mathrm{m}} \ln \frac{N_i RT_{\mathrm{m}}}{V_{\mathrm{m}}} + P_{\mathrm{m}} V_{\mathrm{m}} - RT_{\mathrm{m}} - \int\limits_{\infty}^{V_{\mathrm{m}}} (P_{\mathrm{m}} - P_{\mathrm{id}})\, dV_{\mathrm{m}} - \int\limits_{\infty}^{V_{\mathrm{m}}} \left[\sum_{\substack{k=1\\(k\neq i)}}^{\alpha} N_k \left(\frac{\partial P}{\partial N_i} \right)_{T_{\mathrm{m}} V_{\mathrm{m}} N_{j(j\neq i,\, k)}} \right] dV_{\mathrm{m}}. \tag{10}$$

We replace P_{m} by its value from (9). We note that since the partial derivative $\partial P/\partial N_i$ is taken at constant values of the concentrations of all the components, except the i-th and k-th,

$$N_i + N_k = 1 - \Sigma N_{j(j\neq i,\, k)} = \mathrm{const},$$
$$\frac{\partial N_k}{\partial N_i} = \frac{\partial (c - N_i)}{\partial N_i} = -1.$$

On carrying out the identical transformations we arrive at the expression

$$RT_{\mathrm{m}} \ln f_i = RT_{\mathrm{m}} \ln P_{\mathrm{id}} + P_i^0 V_{\mathrm{m}} - RT_{\mathrm{m}} + \int\limits_{\infty}^{V_{\mathrm{m}}} P_{\mathrm{id}} dV_{\mathrm{m}} - N_i \int\limits_{\infty}^{V_{\mathrm{m}}} P_i^0\, dV_{\mathrm{m}} - \sum_{\substack{k=1\\(k\neq i)}}^{\alpha} N_k \int\limits_{\infty}^{V_{\mathrm{m}}} P_i^0\, dV_{\mathrm{m}} + RT_{\mathrm{m}} \ln N_i + (P_{\mathrm{m}} - P_i^0) V_{\mathrm{m}}. \tag{11}$$

Noting that $N_i + \sum\limits_{\substack{k=1\\(k\neq i)}}^{\alpha} N_k = 1$, and comparing (11) with the formula for the volatility of the pure substance as given, for instance, in [1], we obtain

$$RT_{\mathrm{m}} \ln f_i = RT_{\mathrm{m}} \ln (f_i^0)' + RT_{\mathrm{m}} \ln N_i + (P_{\mathrm{m}} - P_i^0) V_{\mathrm{m}}, \qquad f_i = (f_i^0)' N_i \exp \frac{P_{\mathrm{m}} - P_i^0}{P_{\mathrm{id}}}. \tag{12}$$

Expression (12) provides a volatility rule for solutions which satisfy the Bartlett equation [11].

It should be borne in mind that f_i^0 has a different meaning from $(f_i^0)'$: The latter is the volatility of the pure component i at the temperature and volume of the mixture and is given by an expression similar to (8), but with V_{m} taken instead of V_i^0 for the determination of $(f_i^0)'$.

The equilibrium composition calculated by using Eqs. (1), (8), and (12) is also a second approximation to reality: The pressures are additive, and the mixture satisfies the Bartlett equation.

Let it be required to calculate the equilibrium composition of a mixture of m gases consisting of n elements; the chemical formulas of the components are A, B, X, Y, ... In this case we can make up n independent equations of material balance. These equations do not include the P, V, and T properties, and their form is independent of the equation of state.

To obtain the calculation system we need to form additional m − n equations which contain the required amounts of components. These equations will be equalities expressing the mass action law in relation to any m − n independent chemical reactions occurring between the considered components. These equalities are expressed in the general case by the volatility of the components of the equilibrium mixture, and, hence, their form depends on the equation of state of the mixture.

We consider this dependence. We write the equation of one of the chemical reactions which may occur between the considered components:

$$aA + bB = xX + yY.$$

The mass action law applied to this reaction is

$$K_{\mathrm{e}} = (f_X)^x (f_Y)^y / (f_A)^a (f_B)^b. \tag{13}$$

We consider the following cases.

1. The components of the equilibrium mixture, like the mixture as a whole, are ideal gases.

In this case Eq. (13) takes the form

$$K_{\mathrm{e}} = \frac{(P_X)^x (P_Y)^y}{(P_A)^a (P_B)^b} = \frac{(P_{\mathrm{m}} N_X)^x (P_{\mathrm{m}} N_Y)^y}{(P_{\mathrm{m}} N_A)^a (P_{\mathrm{m}} N_B)^b} = \frac{(N_X)^x (N_Y)^y}{(N_A)^a (N_B)^b} (P_{\mathrm{m}})^{\Delta},$$

where $\Delta = x + y - a - b$, or

$$K_{\mathrm{e}} (P_{\mathrm{m}})^{-\Delta} = K_1 = (N_X)^x (N_Y)^y / (N_A)^a (N_B)^b. \tag{14}$$

2. The components of the equilibrium mixture satisfy Eq. (1); the mixture conforms to the Amagat law (4).

When rule (5) is applied, Eq. (13) takes the form

$$K_e = (f_X^0 N_X)^x (f_Y^0 N_Y)^y / (f_A^0 N_A)^a (f_B^0 N_B)^b,$$

or

$$K_e / K_f = K_2 = (N_X)^x (N_Y)^y / (N_A)^a (N_B)^b, \tag{14a}$$

where

$$K_f = (f_X^0)^x (f_Y^0)^y / (f_A^0)^a (f_B^0)^b.$$

3. The components of the equilibrium mixture satisfy Eq. (1); the mixture conforms to the Bartlett rule (9).

When rule (12) is used, Eq. (13) takes the form

$$\frac{K_e}{(K_f)' \exp \Delta_1} = K_3 = \frac{(N_X)^x (N_Y)^y}{(N_A)^a (N_B)^b}, \tag{14b}$$

where

$$(K_f)' = [(f_X^0)']^x [(f_Y^0)']^y / [(f_A^0)']^a [(f_B^0)']^b$$

and

$$\Delta_1 = \Big((x + y - a - b) P_{\mathrm{m}} - x P_X^0 - y P_Y^0 +$$
$$+ a P_A^0 + b P_B^0\Big) \times \Big(P_{\mathrm{id}}\Big)^{-1}.$$

Thus, in all the considered cases the theoretical equations expressing the mass action law lead to identical forms; the difference lies in the values of K_1, K_2, and K_3 on the left side of these equations. Since the form of the equations of material balance is the same in all three cases, the theoretical system of equations to determine the equilibrium composition of a mixture of real gases in the cases we have considered will, in general, have the same form as in the case of an ideal gas. Mathematical methods of solving such a system have been dealt with on several occasions [8–10], and, hence, there is no need to dwell on them in this paper.

Strictly speaking, the value of K_3 in Eq. (14b) is not "constant" in the calculation, since its value depends on the composition of the mixture. Hence, the equilibrium composition in this case will be given by the solution of the theoretical system in conjunction with Eq. (9).

Assigning as a first approximation the values of N_i calculated by using equations of the form (14) or (14a), we determine the approximate value of the third parameter of the mixture from the given two, and, then, by solving the theoretical system of equations by the usual methods we determine the composition in the second approximation. The calculation process is then repeated until the results attain the required accuracy.

NOTATION

P is the pressure; V is the volume; T is the temperature; R is the gas constant; B and C are the second and third virial coefficients, respectively; N is the mole fraction; f is the volatility; A, B, X, and Y are the symbols of chemical formulas of substances; a, b, x, and y are the stoichiometric coefficients of corresponding substances in equation of chemical reaction; f_i^0, V_i^0 are the volatility and volume of pure component i at T_m and P_m; $(f_i^0)'$ and P_i^0 are the volatility and pressure of pure component i at T_m and V_m; K_e is the equilibrium constant; P_{id} is the pressure of ideal gas at V_m and T_m. Subscripts i, k, j, X, Y, A, and B are the corresponding values of i-th, k-th, etc., substance; m is the corresponding value of the mixture.

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10 September 1966

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