SOME PROBLEMS CONCERNING THE THERMODYNAMICS
OF PHASE TRANSFORMATION

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The de Londe method is applied to phase transformation processes in multicomponent systems. It is shown that these processes can be described by a single universal coordinate (the transformation level) and one generalized force (the mixing affinity).

In calculations of processes where n-component mixtures are partitioned by a phase transformation method (distillation, rectification, etc.) it is of practical interest to consider the possibility of describing these processes by fewer than n−1 equations. Theoretically, the feasibility of this has been established by the Dewgham theorem [1], according to which the state of a closed system with a known initial state can at any instant of time be described by just two independent variables. The character of these variables is not defined by this theorem, however, but can be defined only following a thermodynamic analysis of the system. Such an analysis in the case of chemical reactions (the de Londe method) [1], using the concept of affinity (generalized potential) yields

$$A = \Sigma v_i \mu_i \tag{1}$$

and the reaction level ξ (universal coordinate) defined by the equation

$$d\zeta = \frac{dn_i}{v_i} . \tag{2}$$

In the case of chemical reactions it is thus possible, on the basis of the initial composition and the stoichiometric equation of a reaction, to calculate the composition at a given reaction level ζ.

Despite the far-reaching analogy between phase and chemical transformation phenomena, it is not possible to make full use of the de Londe method also in the case of phase transformation, because no stoichiometric equations are available for such transformations of an n-component system. Nevertheless, the application of this method would seem desirable here, because the phase transformation level can be easily observed and determined by experiment (unlike the level of a chemical reaction).

During a phase transformation (boiling, for instance) the concentration of a component in the vapor phase depends not only on its concentration in the liquid phase but also on the boiling temperature, which in turn is determined by the concentrations of all other components. The components change phase in definite proportions, therefore, which account for the interaction between all components simultaneously. These proportions may change during the process, but they remain fixed at any instant and we thus may write the stoichiometric equation as

$$v_{1x}N_1 + v_{2x}N_2 + v_{3x}N_3 + \ldots \rightleftharpoons v_{1y}N_1 + v_{2y}N_2 + v_{3y}N_3 + \ldots \tag{3}$$
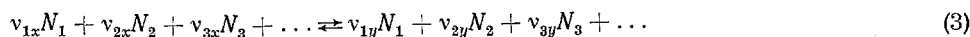
It is characteristic of phase transformation processes that the intramolecular constitution of the components does not change and, therefore, the symbols for the components (N_i) remain the same on both sides of this equation.

In the case of chemical reactions, the stoichiometric ratios are determined by the manner in which the intramolecular constitution of a substance changes; they remain constant during a reaction and do not
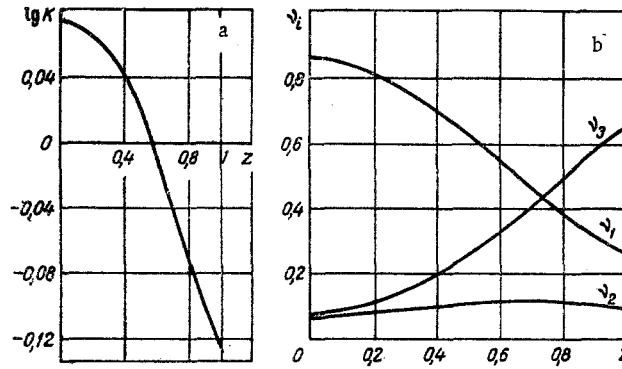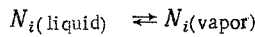
Fig. 1. Curves for verification of Eq. (17) (a) and Eq. (18) (b).

depend on the reaction level. In the case of phase transformations these ratios cannot remain constant, because the proportions vary during the process. Variable stoichiometric ratios are peculiar to Eq. (3) and this method differs thus from the conventional method where an equation of the kind

$$N_{i(\text{liquid})} \rightleftarrows N_{i(\text{vapor})}$$

is written down for each component and the behavior of each component is considered independently of the other components. That method applies to processes where the phases are not undergoing transformation (absorption, extraction, etc.) and the temperature does not depend on the phase composition.

The physical meaning of the stoichiometric ratios in Eq. (3) becomes clear, if one considers that (as can be easily demonstrated) in a closed system containing $G_0 = 1$ mole

$$\nu_{ix} = \nu_{iy} = \nu_i, \qquad \Sigma \nu_i = 1, \tag{4}$$

and that from Eq. (2) with the phase transformation level

$$dz = \frac{dM}{G_0},$$

we have

$$\nu_i = \frac{dn_i}{dM}. \tag{5}$$

Evidently, in phase transformations the stoichiometric ratio represents the concentration of a respective component in the transported mass (undergoing transformation). In other words, the difference between two consecutive states consists in that a quantity dM of a substance with concentrations $\nu_1, \nu_2, \ldots,$ has been transformed from one phase to another, irrespective of any particular transfer mechanism. A similar conclusion was reached by D. B. Spaulding [2] on the basis of a Reynolds flow model.

A stoichiometric ratio is related to the phase concentrations according to the expression

$$\nu_i = -\frac{x_i y_i}{x_{i0}} \left[1 + \frac{\Delta H_i}{R} B \right], \tag{6}$$

which follows from Eq. (5) with these relations:

$$-dn_{ix} = dn_{iy} = -d\left[x_i(1-z)\right] = d\left[y_i z\right];$$

$$x_{i0} = x_i(1-z) + y_i z; \quad k_i = \frac{y_i}{x_i}; \quad \frac{d \ln k_i}{d\left(\frac{1}{T}\right)} = -\frac{\Delta H_i}{R}. \tag{7}$$

The quantity B can be determined from condition (4) as follows:

$$\frac{d\left(\frac{1}{T}\right)}{d \ln\left(\frac{z}{1-z}\right)} = \frac{1 - \Sigma \dfrac{x_i y_i}{x_{i0}}}{\Sigma \dfrac{\Delta H_i}{R} \cdot \dfrac{x_i y_i}{x_{i0}}}. \tag{8}$$

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TABLE 1. Constants of the Phase Transformation, Calculated for the Evaporation of a Hexane–Heptane–Octane Mixture: $\Delta H_1 = 6950$ cal/mole, $\Delta H_2 = 7430$ cal/mole, $\Delta H_3 = 8880$ cal/mole, $P = 760$ mm Hg

z	x_1	x_2	x_3	y_1	y_2	y_3	v_1	v_2	v_3	$\lg K$
0	0,600	0,100	0,300	0,864	0,062	0,074	0,864	0,062	0,074	0,076
0,130	0,563	0,105	0,332	0,845	0,068	0,087	0,825	0,075	0,100	0,072
0,330	0,497	0,111	0,392	0,811	0,078	0,111	0,742	0,096	0,162	0,048
0,440	0,457	0,112	0,431	0,784	0,084	0,132	0,667	0,099	0,224	0,033
0,670	0,367	0,111	0,522	0,715	0,096	0,189	0,495	0,121	0,384	—0,035
0,805	0,316	0,105	0,579	0,665	0,099	0,236	0,383	0,114	0,503	—0,074
0,895	0,285	0,101	0,614	0,637	0,099	0,262	0,320	0,105	0,575	—0,102
1,000	0,256	0,096	0,658	0,600	0,100	0,300	0,256	0,096	0,658	—0,125

The validity of the proposed method must be ascertained thermodynamically and, since the nature of a mixture does not affect the general law of the thermodynamics, it will suffice to verify this method on ideal mixtures.

An increment of the Gibbs function for a system described by a single stoichiometric equation is

$$dG = -SdT + VdP + Ad\zeta. \tag{9}$$

During equilibrium

$$dG = 0, \quad dT = 0, \quad dP = 0$$

and simultaneously

$$A = 0. \tag{10}$$

The affinity is, by definition,

$$A = \left(\frac{\partial G}{\partial \zeta} \right)_{P,T} = \left(\frac{\partial H}{\partial \zeta} \right)_{P,T} - T \left(\frac{\partial S}{\partial \zeta} \right)_{P,T}. \tag{11}$$

The thermodynamic function can be broken down arbitrarily into the normal function (θ) and the mixing function (M):

$$A = A^\theta + A^M. \tag{12}$$

From the equilibrium condition (10) we have $-A^\theta = A^M$ and this allows us to deal further with mixing functions only, which depend on the composition only.

Specifically, let us consider the integral

$$\int_0^1 dS^M = S_1^M - S_0^M = \int_0^1 \frac{A^M + \left(\frac{\partial H^M}{\partial \zeta} \right)}{T} d\zeta, \tag{13}$$

representing the total change of entropy of a mixture during a process from $\zeta = 0$ to $\zeta = 1$. During a phase transformation from an ideal mixture with the composition x_{i0} there is produced a vapor with the composition y_{i1}, while in a complete transformation within a closed system

$$y_{i1} = x_{i0}; \quad n_{i1} = n_{i0},$$

i.e., the compositions and the quantities of the initial and the final phases are the same in a complete transformation. Therefore, the mixing entropies of these phases are also the same:

$$S_1^M = -R\Sigma n_{i1} \ln \frac{y_{i1}}{y_{i,\text{norm}}} = S_0^M = -R\Sigma n_{i0} \ln \frac{x_{i0}}{x_{i,\text{norm}}},$$

if in the normal state we let $y_{i,\text{norm}} = x_{i,\text{norm}}$. Since the heat of mixing in ideal mixtures is zero, Eq. (13) becomes

$$\int_0^1 dS^M = \int_0^1 \frac{A^M}{T}\,d\zeta = 0. \tag{14}$$

According to Eq. (1), with the volatility equation and the activity equation, the mixing affinity can be expressed as

$$A^M = \Sigma v_i RT \ln \frac{f_i}{a_i} = RT \ln K, \tag{15}$$

where

$$\ln K = \Sigma v_i \ln \frac{f_i}{a_i} = \Sigma v_i \ln k_i. \tag{16}$$

A substitution into (14) will yield:

$$\int_0^1 \ln K\,d\zeta = 0. \tag{17}$$

Equation (17) represents the formal thermodynamic relation between the variables determining the phase transformation of an ideal n-component mixture. It expresses the fact that ideal mixtures of the same composition have the same mixing entropy regardless of their aggregate state.

All concentrations during a phase transformation must satisfy Eq. (17), as long as the phase transformation level z is equivalent to the reaction level ζ and the stoichiometric ratios have been defined correctly.

Another formal relation between phase transformation variables follows directly from Eq. (5):

$$\int_0^1 v_i\,dz = x_{i0}. \tag{18}$$

This equation reflects the fact that the quantity of a component transformed from one phase to another in a complete process within a closed system is equal to the initial quantity of this component.

It follows from (17) and (18) that the average value K = 1 is reached when

$$v_i = x_{i0}. \tag{19}$$

As an example, we will consider the evaporation of a ternary mixture: hexane–heptane–octane at P = 760 mm Hg. For each specific evaporation level z (within the range from 0 to 1) the temperature as well as the corresponding values of k_i and x_i were determined from the condition

$$\Sigma x_i = \Sigma \frac{x_{i0}}{(1-z) + k_i z} = 1$$

by the matching method. Then, the stoichiometric ratios v_i were determined from Eq. (6) and the values of ln K were determined from Eq. (16).

The results of one such calculation are shown in Table 1. The graph of log K = f(z) is shown in Fig. 1a, indicating that the net area between the log K curve and the z-axis is zero in accordance with Eq. (17). The graphs of v_i = f(z) are shown in Fig. 1b; evidently, condition (18) is satisfied here. The value K = 1 occurs at z $\simeq$ 0.53 and, according to Fig. 1b, condition (19) is almost exactly satisfied at this value of z.

Consequently, the proposed method of describing phase transformations by means of stoichiometric equations (3), while allowing the de Londe method to be used to the full extent, yields also physically valid results. At the same time, there appears the possibility of applying these results to nonequilibrium phase transformation processes on the basis of their analogy to chemical reactions [3], with the problem having been pretty well solved for the latter case.

NOTATION

A   is the affinity;
v_i is the stoichiometric ratio;
μ_i is the chemical potential of a component;
ζ is the degree of reaction process;

n_i is the number of moles of a component;

z is the phase transformation level;

M is the number of moles of the mixture;

x_i, y_i is the mole fractions of component i in phase x and in phase y respectively;

ΔH_i is the heat of phase transformation;

R is the gas constant;

k_i is the phase distribution factor

G is the Gibbs function;

S is the entropy;

V is the volume;

T is the temperature;

H is the enthalpy.

Subscripts:

x, y refer to phase x and to phase y respectively;

0 denotes initial state;

1 denotes final state;

i refers to component i;

M denotes mixing functions;

θ denotes normal functions.

LITERATURE CITED

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