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Abstract

Full Text

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GAS-GAS PHASE EQUILIBRIUM AND MOLECULAR INTERACTION

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At the present time about twenty binary systems are already known that give gas-gas stratification. At the same time, a great diversity is revealed in their properties, which naturally causes serious difficulties in the theoretical explanation of the observed effects. Here it is sufficient to refer to the role of the polarity of one of the components, to which initially decisive importance was attributed in the occurrence or absence of the indicated type of phase equilibrium. An important stage for experiment and theory was the study of helium solutions, which revealed new characteristic features. The past year has been marked by new experimental and theoretical achievements. In particular, it has turned out that other systems also possess the properties of helium solutions.

Thanks to the development of statistical methods, it is possible not only to explain the observed phenomena, but also a possibility is opened up—one that is already being justified by experience—of predicting the behavior of a new system from the properties of the individual components. In papers ([1], [2]) a statistical method was developed for studying binary condensed systems, based on the introduction of partial two-index functions of conditional distributions F_s. As was shown, for condensed systems, including compressed gas, the principal contribution to the configurational integral is made by states to which the distribution functions $F_\parallel$ correspond. Therefore in what follows we shall assume here that for $s, k > 1$, $F_{sk} = 0$.

The explicit expression for the distribution function $F_\parallel^a(q)$ (the index a indicates that in the chosen molecular volume v_1 around the coordinate q there is a molecule of species a, while in the remaining cells, equal to the molecular volumes, there will be one particle of either species in each) has the form:

$$F_\parallel^a(q) = C\,\frac{1+\dfrac{N_b}{\theta v}(K_{bb}-K_{ab})}{\left[1+\dfrac{N_a}{\theta v}K_{aa}\right]\left[1+\dfrac{N_b}{\theta v}K_{bb}\right]-\dfrac{N_{aN}b}{\theta^2 v^2}K_{ab}^2}, \tag{1}$$

where N_a and N_b are the mole fractions of the components; $\theta = kT$; T is the temperature, k is Boltzmann' s constant;

$$K = \int_{v-v_1} \left\{ \int \frac{\partial \Phi(r)}{\partial q_0} \varphi(r)\, dq_0 \right\} dq', \qquad r = |q_0 - q'|;$$

Φ is the molecular potential; q_0 are the coordinates of the center of the sphere of volume v_1; φ is a positive function, on which we shall dwell below.

The expression for the function $F_{\parallel}^{b}(q)$ is obtained in an analogous way (the only difference is in the expression for the numerator).

In the theory developed earlier an approximate condition for the phase transformation was established, corresponding to the vanishing of the denominator in expression (1). This means that, for values of T and v satisfying the latter condition, equilibrium states of the system are not realized. Indeed, if the denominator tends to zero, then expression (1) can make sense only if the constant C is equal to zero, i.e., to a phase tran-

corresponds to the presence of a singularity in the configurational integral Q_N, since $C = Q_N^{-1}$.

At first glance it seems strange that the condition for a phase transition, which contains thermodynamic quantities, should also include the microscopic quantity q. But, first of all, the possibility is not excluded (and it is realized for condensed systems) that for a given value of v the functionals K are identical for all points q or for an entire region of the molecular volume, and then the microscopic quantity is not singled out.

A more rigorous condition for a phase transition, not containing a microscopic quantity, is connected with integrating expression (1) over the molecular volume (this makes it possible to calculate the configurational integral ([1])).

Even if the denominator in expression (1) vanishes for some fixed position of an arbitrary particle in the volume v_1, and for other positions is not equal to zero, it does not follow from this that "C" can be different from zero (from the fact that the integrand goes to infinity it would still seem not to follow that the configurational integral will be divergent). But it is difficult to agree with this. If this were so, the system could exist even though the most probable configurations should be forbidden, which seems completely improbable.

After these remarks let us return to the functions φ entering into the functionals K. Earlier, for a pure substance, the possibility was shown of representing the function φ in the form of a linear dependence, namely:

$$\varphi(r) = \begin{cases} 0, & r \leqslant a, \\ \dfrac{r-a}{b-a}, & a \leqslant r \leqslant b, \\ 1, & r > b. \end{cases}$$

Since in what follows only molecular systems are considered, for them we use the Lennard-Jones potential. In this case

$$a = \frac{\sigma}{\sqrt[6]{3}}$$

(σ is the potential parameter); the constant b will be expressed through the molecular volume v, i.e. $b = \beta r_0$, where

$$\frac{4}{3}\pi r_0^3 = v.$$

The studies carried out have shown that the change of the parameter β as a function of temperature and density retains the same character for all the substances considered. Thus, for example, at the critical point $\beta \sim 4$, at the triple point for the liquid phase $\beta \sim 28$, and for the solid phase $\beta \sim 34$.

Let us now consider possible applications of the phase-transition condition for a binary mixture, which we rewrite here in the form:

$$1 + \frac{N_a}{\theta v} K_{aa} + \frac{N_b}{\theta v} K_{bb} + \frac{N_{aN} b}{\theta^2 v^2} \left(K_{aa} K_{bb} - K_{ab}^2\right) = 0. \tag{2}$$

In the experimental study of gas-gas phase equilibrium, Ciklis found that the equilibrium curves of coexisting phases for systems containing helium, in the pressure—mole-fraction plane, have a characteristic horn ([3]). The latter adjoins the pure, least volatile component. As the temperature is raised, the curves become more symmetrical, as is the case for other investigated binary systems.

In works ([1,2]) it was shown that, when there is weak interaction of molecules of the a- and b-kinds, i.e. when

$$|K_{bb}| \ll |K_{aa}|, \tag{3}$$

the system separates in the vicinity of the critical point of the less volatile component (let us say the a-component) and at a temperature $T > T_{\text{cr}}^a$, which also determines the gas-gas type equilibrium. This is also confirmed experimentally by the examples of helium solutions. The above-mentioned horn precisely

and is formed at temperatures close to the critical temperature of the pure solvent. In this connection it should be borne in mind that in the vicinity of the critical point of the a-component $K_{ab} \simeq K_{aa}$ (2) and, for $T > T_{\text{cr}}^a$,

$$1 + \frac{K_{aa}}{\theta v} > 0.$$

At the same time, the properties of helium solutions may also be exhibited by other mixtures that do not possess a pronounced energetic difference between the components (in the accepted terminology, this is gas–gas separation of the first type). This follows from the fact that the general equation (2) also has a solution in the vicinity of the critical point of the a-component at $T > T_{\text{cr}}^a$, if the condition

$$K_{bb} \simeq K_{aa}. \tag{4}$$

is satisfied. In the case of a mixture, for the function φ we shall adopt, as for pure substances, the linear representation indicated above. Let T and r_0 be the corresponding parameters of the critical point of the pure a-component. Then, taking into account that for a one-component system the temperature of the phase transition (including the critical temperature) is equal to

$$T = -\frac{K_{aa}}{kv}, \tag{5}$$

one can calculate what the parameter β in the integral K_{bb} must be in order for the above equality (4) to hold. The final result of the calculations has the form:

$$\beta \simeq \frac{3.31\,\frac{\varepsilon}{k}\,\sigma^4}{Tr_0^4}, \tag{6}$$

where ε and σ are the parameters of the Lennard-Jones potential for particles of species b.

The equality of interest to us will certainly not take place if the calculated value of the parameter β is in contradiction with the established general character of its variation. Let us explain this using the system water–carbon dioxide as an example.

For the critical state of water $T = 647^\circ\text{K}$, $r_0 = 2.8$ Å. For the separation condition to be fulfilled, β, according to (6), should be approximately equal to four. But for the given molecular volume v, i.e., for the given r_0, β cannot assume the indicated value. The value $\beta \sim 4$ is realized in the critical state of CO_2, i.e., when $r_0 = 3.34$ Å. For r_0 substantially smaller than the latter, the value of β must be much greater than four. Thus, in the vicinity of the critical point of pure water $K_{bb} \neq K_{aa}$, and separation of the first type does not occur. This is also confirmed in a recent work (4).

Conversely, for the system water–normal butane $\beta \sim 21$, which is characteristic for the given r_0 (in the critical state of C_4H_{10}, $r_0 = 4.64$ Å). For this system, separation of the first type is possible in the vicinity of the critical point of water, which again is confirmed experimentally (5).

For such systems as N_2—H_2O, CO_2—H_2O, and C_2H_4—H_2O, both conditions (3) and (4) are certainly not fulfilled in the vicinity of the critical point of water, and gas-gas separation of the first type does not occur.* On the contrary, separation of the first type should certainly occur, in particular, for the systems C_6H_{10}—H_2O, C_6H_{14}—H_2O, and C_8H_{18}—H_2O.

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* In such systems, separation far from the critical point of the less volatile component (of the second type) is possible, as is evident from the literature (4), and also from the results of the work of D. S. Tsiklis and V. Ya. Maslennikova (5).

Note: Figure translations are in progress. See original paper for figures.