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Abstract

Full Text

PHYSICAL CHEMISTRY

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ON THE “DEVIATIONS” FROM RAOULT’ S LAW CAUSED BY CHEMICAL INTERACTION BETWEEN THE COMPONENTS

(Presented by Academician V. A. Kargin, 4 III 1958)

Deviations from Raoult’ s law are usually explained by saying that the forces of cross interaction between molecules of the components differ from the arithmetic mean of the intermolecular interaction forces in each of the components. From this point of view the sign of the deviation is determined by the direction in which the forces of cross interaction differ from the mean value: if they exceed it, then we have a negative deviation, and conversely.

For all its apparent persuasiveness, such an explanation is not only insufficient, but also unsatisfactory. In particular, it excludes sign-changing deviations, which are in fact observed. Moreover, from this point of view chemical interaction between the components of a solution must always lead to negative deviations from Raoult’ s law, which likewise does not correspond to reality.

First, the product of chemical interaction may, although rarely, prove to be a substance more volatile than the components. In this case, despite the chemical interaction, a positive deviation from Raoult’ s law may be observed and even a positive azeotrope may appear.

Second, chemical interaction may lead to positive deviations (of partial vapor pressures) from Raoult’ s law also in those cases when a nonvolatile product is formed.

If in a system of two nonassociated components the reaction

$$mA + nBleftarrowsA_{mB}n, \tag{1}$$

takes place, and $A_{mB}n$ is a nonvolatile substance, then a positive deviation from Raoult’ s law does not occur only when $m = n = 1$. If, however, at least one of the stoichiometric coefficients differs from unity, then a positive deviation of (at least one of) the partial vapor pressures must be observed.

This follows from the following elementary considerations. As a result of reaction (1), the mole fraction of component A becomes equal to $\frac{x - my}{1 - (m + n - 1)y}$, where x is the mole fraction of the same component A in the initial mixture, and y is

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

the mole fraction of the compound $A_{mB}n$ in the equilibrium mixture. According to Raoult’ s law, the partial vapor pressure of component A is

$$p_A = P_A \frac{x - my}{1 - (m + n - 1)y}, \tag{2}$$

and the deviation from Raoult’ s law is

$$\Delta p_A = P_A \frac{y}{1 - (m + n - 1)y} [(m + n - 1)x - m]. \tag{3}$$

Fig. 1

Fig. 2

It follows from (3) that Δp_A changes sign at

$$x = \frac{m}{m + n - 1}. \tag{4}$$

For component B, the change of sign of the deviation from Raoult’ s law will correspondingly occur at

$$1 - x = \frac{n}{m + n - 1}. \tag{4a}$$

We see that, in the present case, a positive deviation of the vapor pressure is caused by chemical interaction, and not by any other process.

Fig. 1

Fig. 2

Of essential importance is the circumstance that the change of sign of the deviation of the partial vapor pressure from the additive value is uniquely determined

Fig. 1 and Fig. 2: schematic diagrams of vapor pressure in a binary system.

Figure 3: Fig. 1 and Fig. 2: schematic diagrams of vapor pressure in a binary system.

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by the stoichiometric coefficients of the reaction equation (1) and does not depend on the equilibrium constant, i.e., on the extent of the chemical interaction.

If a compound A_{mB} is formed (i.e., $n = 1$), then a positive deviation from Raoult' s law is observed only for component B from $x = 0$ to $x = (m-1)/m$. The vapor pressure of component A in this case is below the additive value at all concentrations.

Figure 1 shows a schematic diagram of the vapor pressure of a binary system A—B in which the compound A_2B is formed. The partial vapor pressure of component B is above the additive value for $0 \leq x \leq 0.5$. The straight line AP_B is not tangent to the curve of the partial vapor pressure of B at $x = 1$. The partial vapor pressure of component A is represt—

was presented in two variants (at a constant value of the thermal dissociation constant K of the compound formed): for $P_A = P_B$ and for $P_A = 2P_B$. In the same two variants the curves of the total vapor pressure are shown. As shown in the figure, the straight line P_AP_B is tangent to the curve of the total vapor pressure only at the point P_B, but not at the point P_A. When $P_A = P_B$, the system is necessarily azeotropic; when $P_A \neq P_B$, the appearance of an azeotrope depends on the relationship among P_A, P_B, and K.

The influence of K is shown in Fig. 2, which depicts, along with the limiting case of formation of the undissociated compound A_2B, isotherms of the total vapor pressure corresponding to three successively increasing values of the dissociation constant. Curve II was calculated for the same value of K as the vapor-pressure curves in Fig. 1.

Our calculations were carried out on the basis of the law of mass action, under the assumption that the pseudoternary system A, B, and $A_{mB}n$ obeys Raoult' s law, which in general form may be written as

$$P = \sum p_i = \sum P_i x_i, \tag{5}$$

where P is the total vapor pressure of the system, and x_i is the equilibrium mole fraction of each component. Thus, the schematic diagrams presented in Figs. 1 and 2 depict the vapor pressure of systems in which chemical interaction takes place but which—allowing for this interaction—obey Raoult' s law.

Chemical interaction must be taken into account with obligatory application of the law of mass action. The latter has no other adequate expression, since only in the law of mass action do the stoichiometric coefficients of the reaction equation appear, and these, as we have shown, are of decisive importance for the course of the vapor-pressure curves.

It goes without saying that all our considerations apply only to chemical interactions between the components of a solution and cannot be extended to other processes that cause deviations from Raoult' s law.

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

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