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DEPENDENCE BETWEEN THE COEFFICIENT OF DIFFUSION AND THE CONCENTRATION OF NONAZEOTROPIC BINARY MIXTURES

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An empirical relation is obtained between the coefficient of diffusion and the difference in equilibrium molar fractions of the low-boiling-point component in the vapor and liquid phases of six nonideal binary systems.

Because of the complexity and inadequate study of the process of diffusion in liquid mixtures, the dependence of the coefficient of molecular interdiffusion of the components on the composition cannot yet be expressed strictly analytically. Various approximate equations allowing for one or another factors, which are not always known in practice, have been proposed for calculating the coefficients of diffusion of binary mixtures [1-3]. For example, the Wilke equation includes the dependence of the activity and viscosity of the components on the composition, while the Darken equation includes the dependence of the coefficient of activity of the components on the concentration. In the majority of cases, however, neither the activities nor their coefficients are known, nor the equilibrium concentrations of the components in the liquid and vapor phases of the mixture.

The forces of interaction of the molecules of the components have the determining influence on the intensity of interdiffusion of the components and the phase equilibrium of nonideal mixtures. These forces are very small in mixtures which are ideal or close to it. For such mixtures the total and partial pressures and the coefficient of diffusion can be calculated sufficiently reliably by the additivity rule with allowance for their linear dependence on the concentrations of the components. The composition of the vapor phase of an ideal solution of a mixture is also easy to calculate, knowing the composition of the equilibrium liquid phase. For nonideal mixtures a departure from the ideal (linear) dependence occurs because of the influence of the forces of molecular interaction. The value of the excess concentration of one of the components in the vapor phase relative to the concentration of the same component in the liquid phase evidently can characterize to a greater or lesser degree the nonideal nature of the processes of vaporization and diffusion. The excess concentration ΔX in the vapor phase is a function of the thermodynamic parameters (temperature, pressure, and concentration of the mixture) and of the processes taking place in the liquid layer at the boundary between the vapor phase and the main mass of liquid far from the phase interface. Therefore, greater correspondence should be observed between the coefficient of diffusion D_l in the boundary layer and the value of the excess concentration ΔX than between ΔX and the coefficient of diffusion D for the main mass of liquid.

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In this connection it seems desirable to analyze the dependence of the quantities D_l and ΔX on the composition for a number of nonideal binary systems. Such an analysis was carried out for six nonazeotropic systems having components which are fully miscible in the entire range of concentrations. The experimental values of the coefficients of diffusion were borrowed from the following reports: [4] for methanol – water; [5] for acetone – water, acetone – carbon tetrachloride, and acetone – benzene; [6] for carbon tetrachloride – acetic acid; [7] for hexane – toluene. The data on the equilibrium between liquid and vapor were taken from [8]. The presence of these and other experimental data served as the basis for the analysis of these binary systems.

For the carbon tetrachloride – acetic acid system the vapor composition was determined roughly from the analogous data for the carbon tetrachloride – benzene and acetic acid – benzene systems.

The boiling temperatures of the pure components of each mixture at atmospheric pressure differ by no more than 50°C.

For some of the systems under consideration the temperature at which the coefficient of diffusion was determined does not coincide with the temperature of equilibrium of liquid and vapor, for which there are experimental data. However, this mismatch lies in the range of 15-20°. If one considers that the composition of the vapor phase is a function mainly of the concentration and depends relatively little on the temperature, then this temperature mismatch should not have an important effect on the results of the analysis.

In order to establish the dependence between the coefficient of diffusion and the excess concentration ΔX, which is essentially a relative quantity, it proved convenient to introduce into the analysis the diffusional simplex $R = D/D_0$, showing the ratio between the actual coefficient of diffusion D of the mixture and the ideal coefficient D_0, equal to the coefficient of diffusion of the same mixture if it were an ideal solution. Thus, the diffusional simplex R characterizes the degree of ideality of a given mixture. For the concentration of the boundary layer such a simplex will have the form $R_l = D_l/D_{0l}$. For pure components and ideal mixtures the simplices R and R_l equal one.

If we start from the assumption that the excess concentration characterizes the departure of the vaporization of the mixture from ideality, then the difference $P = (1 - \Delta X)$ can be considered as a kind of criterion – a simplex characterizing the ideality of the mixture. For pure components the simplex P equals one; for ideal mixtures P will have a larger numerical value than for the corresponding nonideal mixture, since ΔX for a nonideal mixture is larger than ΔX for an ideal one.

Since the excess vapor concentration depends on the diffusion in the boundary layer, the simplex R_l must also be taken at the concentration X_l of the boundary layer. To make it possible to clearly compare the quantities P and R_l, the points of the R curves corresponding to the vapor concentration X_l must be normalized to the concentration X of the main mass of liquid as to a parameter.

In a first approximation the numerical value of the concentration of the boundary layer can be represented as the arithmetic mean of the equilibrium concentrations of the vapor and liquid,

$$X_l = 0.5(X + Y) = X + 0.5\Delta X. \tag{1}$$

All the binary mixtures under consideration are distinguished by a positive departure from the ideal (linear) dependence of the pressure on the composition, expressed by the Raoult law. At the same time, they have a negative departure of the coefficient of diffusion from the corresponding values for the ideal case, which is well seen from Fig. 1.

For each of the six binary systems the variation of the simplices P(X) and R_l(X) has the same character for the most part. The curves of P and R_l correspond to each other (for a given mixture) to a considerable degree. The approximate dependence between the simplices P and R_l can be represented in the form of the following empirical generalizing equation:

$$P = R_l. \tag{2a}$$

With allowance for the physical meaning of the simplices, we obtain

$$D_l = D_{0l}(1 - \Delta X). \tag{2b}$$

Curves of the coefficients of diffusion D_c calculated from Eq. (2b) are presented in Fig. 1 for all the systems considered here.

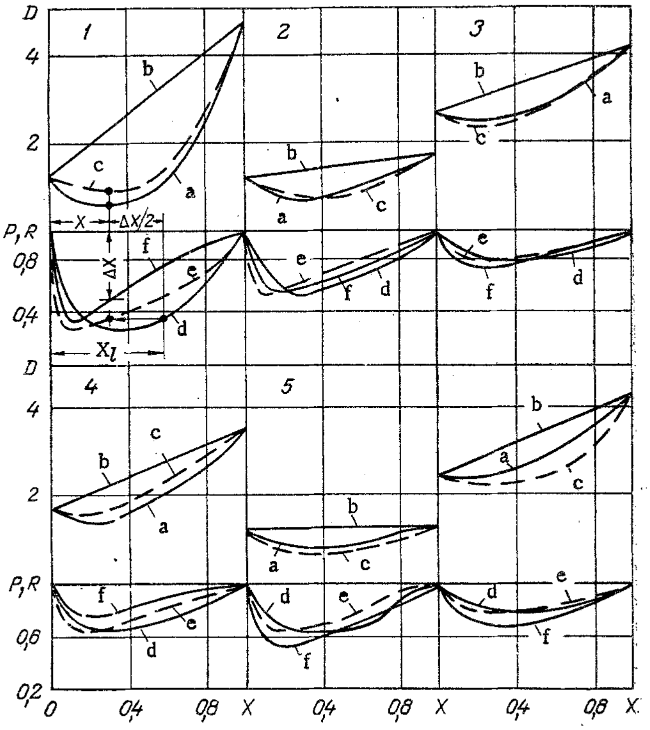

Fig. 1. Dependence of the quantities D, D_0, D_c, R, R_l, and P on the concentration X of binary systems: 1) acetone – water (D at 25°C, ΔX at 25°C); 2) methanol – water (15, 25); 3) acetone – benzene (25, 25); 4) acetone – carbon tetrachloride (25, 40); 5) carbon tetrachloride – acetic acid (25, 40); 6) hexane – toluene (25, 69-110). a) $D \cdot 10^5$, cm^2/sec; b) D_0; c) D_c; d) R; e) R_l; f) P.

For the ideal case the coefficient of diffusion of a mixture is easily calculated on the basis of its linear dependence on concentration, knowing the coefficient of diffusion for an infinite dilution of one component in the other at the given temperature:

$$D_{0l} = D_1(1-X_l) + D_2X_l. \tag{3}$$

The maximum departure of the coefficients of diffusion calculated from Eq. (2b) from the corresponding experimental values for organic binary mixtures lie in the range of 10-20%. For water – organic systems it reaches 25% (methanol – water) and 45% (acetone – water). The relatively large departure for the acetone – water mixture may be explained, in addition to other reasons, by the fact that acetone and water differ very considerably in permittivity, dipole moments, and the ratio of their components from the other mixtures considered here. This undoubtedly shows up in the influence of the forces of the electrostatic interaction of the molecules on the diffusion and vaporization and, as a consequence, on the unequal accuracies of Eqs. (2) when they are applied to different binary systems.

NOTATION

X, Y, equilibrium molar concentrations of first (low-boiling-point) component in the liquid and vapor phases of the mixture, respectively; ΔX, difference between equilibrium and molar concentrations of vapor and liquid (excess concentration); X_l, concentration of interphase boundary layer; D, coefficient of molecular interdiffusion of mixture components in the liquid phase at the concentration X; D_0, coefficient of diffusion of mixture for the ideal case at a concentration X; D_c, coefficient of diffusion calculated from Eq. (2b); D_1, coefficient of diffusion of first component at its infinite dilution in the second component; D_2, coefficient of diffusion of second component at its infinite dilution in the first component; $P = (1 - \Delta X)$, concentration simplex; $R = D/D_0$, diffusional simplex; $R_l = D_l/D_{0l}$, diffusional simplex at the concentration X_l of the interphase boundary layer.

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EFFECT OF PHYSICOCHEMICAL PROCESSES ON GAS GENERATION IN HEAT PIPES

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This paper examines the results of tests on heat pipes of various modifications. The results obtained on gas generation are compared with theory.

In the operation of heat pipes there are a number of complex physicochemical processes occurring in the working liquid, the capillary structure, and on the internal surface, and these processes result in the formation of a solid deposit and noncondensible gas (hydrogen). These products of electrochemical corrosion can appreciably alter the initial heat-pipe parameters, and in the course of time can put it out of commission. The rate of these processes varies and is determined by the nature of interaction of the heat-transfer agent with the porous wick structure and the type of wall material, and also by the thermodynamic characteristics of each of the heat-pipe elements. An increase in temperature intensifies these processes without changing their nature.

The authors have conducted comprehensive tests on heat pipes to determine the rate of formation of noncondensible gas and deposit as a function of temperature and time. The tests were conducted at elevated temperature.

The authors of [2-4] attempted to find an empirical correlation between the release of hydrogen and time and temperature, and compare it with the experimental data obtained. The objective of the present comprehensive tests is the inverse problem: to compare the experimentally obtained amount of hydrogen with the theoretical prediction [1]. The combination of heat-pipe wall material and heat-transfer agent may be varied, since the method of calculation accounts for the chemical and thermodynamic properties of both these agents.

To conduct qualitative comprehensive tests all the requirements of technical and vacuum cleanliness were observed (degreasing of the heat-pipe surface, use of chemically pure and degassed heat-transfer agents, etc.). Chromel – Copel thermocouples were used to measure the temperature drop along the entire length of the heat pipes. Only pipes for which the temperature drop $\Delta t \leq 1°C$ were used for the tests. A special vacuum fan was used to sample the noncondensible gas.

For the tests the heat pipes were mounted vertically in a special thermoelectric heater, and heat was removed from the condensation zone by natural air convection. The volume of the gas plug was determined by means of thermocouples located in the condensation zone. A qualitative analysis of the gas plug was carried

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