Reports of the Academy of Sciences of the USSR

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1965

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Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1965. Volume 162, No. 4

HEAT ENGINEERING

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STUDY OF THE MECHANISM OF SALT DISTRIBUTION BETWEEN WATER AND STEAM IN EQUILIBRIUM WITH IT BY THE METHOD OF ELECTRICAL-CONDUCTIVITY MEASUREMENT

At the present time, the questions of the equilibrium distribution between water and saturated steam of impurities such as silicic acid, boric acid, or aluminum hydroxide, i.e., compounds belonging to the class of the so-called weak electrolytes, have been studied rather well ([1]). The dissociation of such compounds, not only in steam but also in boiling water at high parameters, is practically completely suppressed even at the minimal concentrations with which one has to deal, and it may be assumed with a sufficient degree of accuracy that the distribution of such substances between water and the steam in equilibrium with it occurs only in the form of molecules. This leads to independence of the distribution coefficient from concentration; this independence, for example, has been traced for silicic acid down to very small concentration values.

Fig. 1. Dependence of the apparent distribution coefficient of NaCl on concentration

The laws governing the equilibrium distribution between water and steam of various nonhydrolyzable (under normal conditions) salts of the type of sodium, potassium, and lithium chlorides, sodium and potassium sulfates, etc.—compounds belonging to the class of the so-called strong electrolytes—have been investigated much less. In particular, the independence of their apparent distribution coefficient from concentration was verified in a comparatively small

range of values of the latter. Such salts constitute complex systems, since in water and in saturated steam at high parameters they will be present in two forms—dissociated and associated (ion pairs, molecules)—each of which must be characterized by its own individual distribution coefficient.

As was shown earlier ([1]), in the distribution of an electrolyte of the type of sodium chloride between water and steam, the established equilibria are described by the scheme

$$\begin{array}{ccccc} \mathrm{NaCl_p} & \underset{K_\mathrm{p}}{\rightleftharpoons} & \mathrm{Na_p^+ + Cl_p^-} & & \text{(steam)} \\ \Big\updownarrow K_\mathrm{m} & & & \Big\updownarrow K_\mathrm{i} & \\ \mathrm{NaCl_v} & \underset{K_\mathrm{dv}}{\rightleftharpoons} & \mathrm{Na_v^+ + Cl_v^-} & & \text{(water)} \end{array}$$

where the subscripts w and p (here and below) denote water and vapor, respectively. Thus, in addition to the interphase equilibria determined by the molecular K_m and ionic K_i equilibrium constants, there are also intraphase equilibria determined by the dissociation constants of the salt in water and vapor:

$$K_\mathrm{m} = a_{\mathrm{NaCl\,p}}/a_{\mathrm{NaCl\,w}} = C_\mathrm{p}(1-\alpha_\mathrm{p})/C_\mathrm{w}(1-\alpha_\mathrm{w}); \tag{1}$$

$$K_\mathrm{i} = a_{\mathrm{Na^+\,p}} \cdot a_{\mathrm{Cl^-\,p}}/a_{\mathrm{Na^+\,w}} \cdot a_{\mathrm{Cl^-\,w}} = C_\mathrm{p}^2\alpha_\mathrm{p}^2 f_\mathrm{p}^2/C_\mathrm{w}^2\alpha_\mathrm{w}^2 f_\mathrm{w}^2; \tag{2}$$

$$K_\mathrm{dw} = a_{\mathrm{Na^+\,w}}a_{\mathrm{Cl^-\,w}}/a_{\mathrm{NaCl\,w}} = C_\mathrm{w}\alpha_\mathrm{w}^2 f_\mathrm{w}^2/(1-\alpha_\mathrm{w}); \tag{3}$$

$$K_\mathrm{dp} = a_{\mathrm{Na^+\,p}}a_{\mathrm{Cl^-\,p}}/a_{\mathrm{NaCl\,p}} = C_\mathrm{p}\alpha_\mathrm{p}^2 f_\mathrm{p}^2/(1-\alpha_\mathrm{p}), \tag{4}$$

where $a_{\mathrm{Na^+}}$, $a_{\mathrm{Cl^-}}$, a_{NaCl} are the active concentrations of sodium and chlorine ions and of sodium chloride molecules; C_p, C_w are the salt concentrations in vapor and water (mol/kg); α_p, α_w are the degrees of dissociation of the salt in vapor and water; f_p, f_w are the mean activity coefficients of the ions in vapor and water. These four equilibrium constants are functions only of temperature and do not depend on the concentration of the dissolved salt.

$$K_\mathrm{app} = C_\mathrm{p}/C_\mathrm{w} \tag{5}$$

is a function of the degree of dissociation α, and therefore of the salt concentration. The dependence of the apparent distribution coefficient on concentration was examined by Class [4]. The formula he proposed for calculating $K_\mathrm{app}^\mathrm{NaCl}$ in the subcritical region (176 bar) could be used only over a narrow range of concentration values, when the dissociation constant of the salt in boiling water

Fig. 2. Solubility of NaCl in saturated vapor. *a*—Moscow Power Engineering Institute; *b*—Straub; *c*—Ulmer

Figure 2: Fig. 2. Solubility of NaCl in saturated vapor. *a*—Moscow Power Engineering Institute; *b*—Straub; *c*—Ulmer

is much greater than its concentration (mol/kg), and the dissociation constant of the salt in vapor is much less than its concentration. However, on the basis of the experimentally obtained values of K_{dw} [3], one may assert that the practically important concentration region extends far beyond these limits, and the use of Class' s formula for processing experimental data led to substantial errors.

Fig. 2. Solubility of NaCl in saturated vapor. *a*—Moscow Power Engineering Institute; *b*—Straub; *c*—Ulmer.

The purpose of the present work is to study the dependence of the apparent distribution coefficient of sodium chloride on concentration over a broad range of variation of the latter, and also to establish the relation of K_{app} to the molecular and ionic equilibrium constants.

Four equilibrium constants determining the distribution of a salt between water and the vapor in equilibrium with it can be related to one another by the simple relation

$$K_{\text{i}}/K_{\text{m}} = K_{\text{dp}}/K_{\text{dv}}. \tag{6}$$

These equilibrium constants also determine the apparent distribution coefficient itself; joint transformation of equations (1), (2), and (5) gives the expression:

$$K_{\text{app}} = K_{\text{m}}(1-\alpha) + \frac{f_{\text{v}}}{f_{\text{p}}}\sqrt{K_{\text{i}}}\alpha_{\text{v}}. \tag{7}$$

And since the activity coefficient is a function of αC, this in principle means that in formula (7) the apparent distribution coefficient is a function of only one variable, α_{v}, or, what is the same, the concentration C_{v}. When $\alpha_{\text{v}} = 1$, then, obviously, $f_{\text{v}} = 1$ and $f_{\text{p}} = 1$, and consequently $K_{\text{app}}\big|_{\alpha_{\text{v}}=1} = \sqrt{K_{\text{i}}}$. When $\alpha_{\text{v}} = 0$, then $K_{\text{app}}\big|_{\alpha_{\text{v}}=0} = K_{\text{m}}$.

Thus, the apparent distribution coefficient reaches its largest value when only molecules are present in the water, and its smallest when only ions are present in the water, varying monotonically between them together with the concentration:

$$\sqrt{K_{\text{i}}} \le K_{\text{v}} \le K_{\text{m}}.$$

Fig. 3. Distribution coefficients of NaCl between vapor and water

Figure 3: Fig. 3. Distribution coefficients of NaCl between vapor and water

Therefore, when plotting the dependence of C_p on C_v in logarithmic coordinates, the curve $C_p = f(C_v)$ will everywhere have a slope greater than unity ($d \lg C_p / d \lg C_v > 1$), with the magnitude of the slope tending asymptotically to unity on approaching an infinitely small concentration (only ions) and an infinitely large concentration (only molecules), $d \lg C_p / d \lg C_v \to 1$ as $C_v \to 0$ and as $C_v \to \infty$.

Fig. 3. Distribution coefficients of NaCl between vapor and water

Obviously, having one experimental solubility point (C_p and C_v) and the values of K_{dv} and K_{dp}, one can calculate all the remaining points. In this way the curves $K_v = f_1(C_v)$ and $C_p = f_2(C_v)$ were constructed for three pressures: 157, 177, and 191 bar (Figs. 1 and 2). As reference points, the experimental values of C_p and C_v were used [5]. Figure 2 shows experimental points of various investigators. As is seen from the figure, the experimental points of MEI and ENIN (a) and of Straub (b) lie close to the theoretical curve, with which Ulmer' s experimental data at low concentrations [5] also agree; all the other Ulmer points lie below the calculated curve.

It should be noted that Ulmer's data, except for the points at low concentrations, are the results of only one very short experiment. Judging by the experimental procedure he describes, it is highly probable that equilibrium between water and vapor was not attained in this experiment, and the value of C_p is therefore somewhat underestimated.

From the values of the constants found, Fig. 3 shows, in logarithmic coordinates, the dependences of K_m and $\sqrt{K_i}$ on γ_v/γ_p. As can be seen, this depend–

the dependence is linear, and the functions K_m and $\sqrt{K_i}$ are rays converging at the critical point $\gamma_v/\gamma_l = 1$. In the present case the value used was not K_i, but $\sqrt{K_i} = \alpha_p C_{pl} f_p / \alpha_v C_v f_v$, since precisely this quantity is the ratio of the ionic concentrations in the vapor and in the water, i.e., the characteristic that is convenient in practice and should be called the ionic distribution coefficient. In general, it should be noted that if in (7) α_v is treated as a parameter, then to each of its values $0 < \alpha_v < 1$ there corresponds its own curve with its own value of the apparent distribution coefficient: $\sqrt{K_i} < K_{app} < K_m$. Figure 3 gives such a family of curves in the parameter α_v (at high pressures they differ little from rays).

An analogous dependence of the dissociation constants K_{dv} and K_{dl} on γ_v/γ_l is obtained in logarithmic coordinates. As is seen from Fig. 4, the values of the experimental K_{dv} (3) lie well on a straight line and, consequently, according to (6), the functions K_{dv} and K_{dl} are a pair of rays converging at the critical point $\gamma_v/\gamma_l = 1$.

Fig. 4. Dissociation constants of NaCl in water and vapor on the saturation line

Figure 4: Fig. 4. Dissociation constants of NaCl in water and vapor on the saturation line

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To construct the ray $K_{\text{dl}} = f(\gamma_{\text{v}}/\gamma_{\text{l}})$, it is thus sufficient to have one experimental point (actual or interpolated); the ray for K_{dl} is obtained with the same degree of reliability as for K_{dv}. In the present calculations, as the reference value of K_{dl} there was adopted a value obtained by extrapolating the values of K_{dl}, obtained in the near-critical region of the vapor solution by the authors Fogo et al. (6), to the saturation curve at 191 bar.

It should be noted that throughout the region covered by graphs 1, 2, and 3, the overwhelming part of NaCl passes into the vapor in undissociated form, and therefore K_{app} is determined mainly by the value of K_{dv}.

Received
17 III 1965

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