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ON THE EQUATIONS OF THE LIQUIDUS AND SOLIDUS OF IDEAL SYSTEMS

From the Clapeyron–Clausius equation, written in the form

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Abstract

Full Text

PHYSICAL CHEMISTRY

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ON THE EQUATIONS OF THE LIQUIDUS AND SOLIDUS OF IDEAL SYSTEMS

(Presented by Academician V. A. Kargin, 31 VIII 1956)

From the Clapeyron-Clausius equation, written in the form

$$\ln \frac{P_1}{P_2} = \frac{l\,(T_1 - T_2)}{RT_1T_2},$$

and the equation for the vapor-pressure isotherm of a binary system (Raoult' s law), it follows that

$$\ln \frac{Y_A}{X_A} = \frac{L_A(T_A - T)}{RT_{AT}}; \tag{1}$$

$$\ln \frac{Y_B}{X_B} = \frac{L_B(T_B - T)}{RT_{BT}}, \tag{1a}$$

where Y_A is the mole fraction of component A in the solid phase; X_A is the mole fraction of A in the liquid phase in equilibrium with the solid phase at temperature T; L_A and T_A are, respectively, the heat and temperature of melting of A; R is the universal gas constant; Y_B, X_B, L_B, and T_B are the corresponding quantities for component B.

Equations (1) and (1a) were derived by Van Laar ([1]) for a continuous series of solid solutions. In fact, as we shall see, they are not restricted to the case of a continuous series of solid solutions, but represent, in the most general form, the equation of state of ideal systems, combining the Clapeyron-Clausius equation with Raoult' s law. However, they are not equations of the liquidus $f(x, T) = 0$ or of the solidus $f(y, T) = 0$.

The latter can be derived from (1) and (1a) when additional conditions are varied. In the case when A and B do not form solid solutions, i.e. $Y_A = 1$ and $Y_B = 1$, each of the two equations becomes the well-known Schröder logarithmic equation (the liquidus equation)

$$-\ln X_A = \frac{L_A(T_A - T)}{RT_{AT}}; \tag{2}$$

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$$-\ln X_B = \frac{L_B(T_B - T)}{RT_{BT}}. \tag{2a}$$

Solving (2) and (2a) jointly for the eutectic point ($T = T_E$), at which $X_A + Y_B = 1$, we obtain

$$\exp\left(-\frac{L_A(T_A - T_E)}{RT_{AT}E}\right) + \exp\left(-\frac{L_B(T_B - T_E)}{RT_{BT}E}\right) = 1 \tag{3}$$

From the point of intersection of the curves expressing the dependences

$$1 - \exp\left(-\frac{L_A(T_A - T)}{RT_{AT}}\right) \quad \text{and} \quad \exp\left(-\frac{L_B(T_B - T)}{RT_{BT}}\right)$$

on T, we find T_E. Knowing T_E, we can easily find the composition of the eutectic.

Equation (3) represents the solidus equation of an ideal system with a eutectic.

In the case where A and B form a continuous series of solid solutions without extrema*, $X_A + X_B = 1$ and $Y_A + Y_B = 1$. Combining these conditions with (1) and (1a), we obtain:

$$X = \frac{1 - \exp\frac{L_B(T_B - T)}{RT_BT}}{\exp\frac{L_A(T_A - T)}{RT_AT} - \exp\frac{L_B(T_B - T)}{RT_BT}}. \tag{4}$$

This equation was derived by Seltz[2] by a rather complicated route. It is the liquidus equation for a continuous series of solid solutions obeying Raoult' s law.

The solidus equation, likewise obtained by Seltz, is written in the form:

$$Y_A = \frac{1 - \exp\frac{L_B(T_B - T)}{RT_BT}}{1 - \exp\left(\frac{L_B(T_B - T)}{RT_BT} - \frac{L_A(T_A - T)}{RT_AT}\right)}. \tag{5}$$

Thus, ideal systems (obeying Raoult' s law) correspond to two types of diagrams: the eutectic diagram and the Roseboom type I diagram. They are described by equations (2), (2a), (3), (4), and (5).

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CITED LITERATURE

[1] V. Ya. Anosov, S. A. Pogodin, *Basic Principles of Physicochemical Analysis*, Moscow–Leningrad, 1947, pp. 319-320.
[2] H. Seltz, *J. Am. Chem. Soc.*, **56**, 307 (1934).

* Extrema contradict Raoult' s law.

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

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