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Abstract

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PRECIPITATION ISOTHERM

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In connection with the development of the theory of precipitation chromatography ([1,2]), the need arose to derive, in generalized form, the precipitation isotherm. From the general theory of sorption dynamics and chromatography ([1]) it is known that the sorption isotherm is one of the decisive factors predetermining the nature of the process of dynamic sorption and the success of chromatographic separation of mixtures of substances.

In analytical chemistry, the solubility-product rule is widely used for calculations of precipitation reactions, for determining the solubility of sparingly soluble compounds, etc. ([3,4]). However, for carrying out such calculations there was no need to derive any generalized equation. The practical problems of analytical chemistry were fully satisfied on the basis of simple arithmetical calculations using the solubility-product rule. But in order to clarify the features of the processes of precipitate formation under dynamic conditions in columns of porous media (precipitation chromatography), and to derive the equations of the dynamics of precipitation sorption, it is necessary to have an equation of the precipitation isotherm. This equation must give the functional dependence between the concentration of the ion being precipitated in solution and its concentration in the precipitate (at constant temperature). In the present article, the equation of the precipitation isotherm is derived and this equation is analyzed.

Let us consider the chemical reaction of formation of a sparingly soluble compound:

$$\frac{z_0}{s} A^{z+} + \frac{z}{s} B^{z_0-} \rightleftarrows A_{z_0/s} B_{z/s} \downarrow, \tag{1}$$

where z and z_0 are respectively the valences of ions A and B, and s is the common divisor for the values $|z|$ and $|z_0|$.

Let the following problem be posed. There are solutions of the ions A^{z+} and B^{z_0-}, the initial concentrations of which we shall denote respectively by C_A^0 and C_B^0. After these two solutions are poured together into one vessel, as a result of the precipitation reaction (1) part of ions A and B will pass into the precipitate and part will remain in solution. The process will end with the establishment of equilibrium in the distribution of ions A and B between the solution and the

Fig. 1. Precipitation isotherm at $\lambda = 2$

Figure 1: Fig. 1. Precipitation isotherm at $\lambda = 2$

precipitate. We shall denote the equilibrium concentrations of ions A and B in solution by C_A and C_B, and in the precipitate (calculated per unit volume of solution) by S_A and S_B. To determine the precipitation isotherm of ion A, it is necessary to establish the dependence $S_A = f(C_A)$.

The distribution of ion A between solution and precipitate must obey the law of conservation of matter, the stoichiometric ratio of reaction (1), and the solubility-product rule.

The balance equations of this system are:

$$C_A^0 = C_A + S_A, \tag{2}$$

$$C_B^0 = C_B + S_B. \tag{3}$$

The stoichiometric ratio of the concentrations of ions in the precipitate may be expressed in the form

$$\frac{S_A}{S_B} = \frac{z_0}{z} = \frac{1}{\lambda}, \tag{4}$$

where λ denotes the ratio of the valences z/z_0.

Finally, according to the rule of constancy of the product of activities in an equilibrium solution of a sparingly soluble compound, we have

$$a^{z_0/s} b^{z/s} = L, \tag{5}$$

or

$$a^{z_0} b^{z} = L^s, \tag{6}$$

where a and b are the activities of ions A and B in the equilibrium solution, and L is a constant that has been called the activity product, or solubility product.

Fig. 1. Precipitation isotherm at $\lambda = 2$

Passing from thermodynamic activities to analytical concentrations, equation (6) can be rewritten in the form

$$C_A^{z_0} C_B^{z} = \frac{L^s}{\alpha^{z_0} \beta^{z}}, \tag{7}$$

where α and β are the activity coefficients of the corresponding ions ($a = \alpha C_A;\ b = \beta C_B$).

The system of equations (2), (3), (4), and (7) makes it possible to calculate the equilibrium concentrations C_A, C_B, S_A, and S_B for known initial concentrations C_A^0 and C_B^0. This same system makes it possible to establish the desired precipitation isotherm of ion A.

From equations (4), (3), and (7) we have:

$$S_A = \left[\frac{1}{\lambda}S_B = \frac{1}{\lambda}(C_B^0 - C_B) = \frac{1}{\lambda}\left(C_B^0 - \frac{L^{s/z}}{\beta\alpha^{1/\lambda}C_A^{1/\lambda}}\right)\right] = \frac{C_B^0}{\lambda} - \frac{L^{s/z}}{\lambda\beta\alpha^{1/\lambda}C_A^{1/\lambda}}. \tag{8}$$

After introducing the additional notation

$$G = \frac{C_B^0}{\lambda}, \qquad H = \frac{L^{s/z}}{\lambda\beta\alpha^{1/\lambda}}, \tag{9}$$

the equation of the precipitation isotherm (8) takes the form

$$S_A = G - \frac{H}{C_A^{1/\lambda}}. \tag{10}$$

Let us analyze the precipitation-isotherm equation obtained.

1) The graph of such an equation is a hyperbola (see Fig. 1), beginning at the point $C_{A,\min}$ (at $S_A = 0$):

$$C_{A,\min} = \left(\frac{H}{G}\right)^{\lambda} = \frac{L^{s/z_0}}{\alpha\beta^{\lambda}(C_B^0)^{\lambda}}. \tag{11}$$

The curve approaches asymptotically the value $S_A = S_{A,\max}$, at which $H/C_A^{1/\lambda} \to 0$ and, consequently:

$$S_{A,\max} = G = \frac{C_B^0}{\lambda}. \tag{12}$$

Thus, the graph of the precipitation isotherm belongs to the type of convex isotherms. Correspondingly, the dynamics of precipitation sorption will occur—

···in the regime of sorption dynamics with a convex isotherm ([1]). In the case, for example, of frontal sorption dynamics, the formation of a stationary front is predicted.

Fig. 2. Precipitation isotherms: $1 - C_B^0 = 1 \cdot 10^{-2}$; $2 - C_B^0 = 1 \cdot 10^{-3}$; ($L = 1 \cdot 10^{-10};\ z = z_0 = 1;\ \alpha \approx \beta \approx 1$).

Figure 2: Fig. 2. Precipitation isotherms: $1 - C_B^0 = 1 \cdot 10^{-2}$; $2 - C_B^0 = 1 \cdot 10^{-3}$; ($L = 1 \cdot 10^{-10};\ z = z_0 = 1;\ \alpha \approx \beta \approx 1$).

2) The degree of convexity of the precipitation-isotherm plot can be characterized by the slope of the tangent at the initial point of the isotherm, i.e., at $C_A = C_{A,\min}$. To this end, let us take the derivative of the isotherm (8)

$$\frac{dS_A}{dC_A} = \frac{1}{\lambda^2 \beta \alpha^{1/\lambda}} \left(\frac{L^s}{C_A^{z+z_0}} \right)^{1/2}. \tag{13}$$

The tangent of the angle of inclination of the tangent to the isotherm at the point $C_{A,\min}$ will be:

$$\left(\frac{dS_A}{dC_A} \right)_{C_A = C_{A,\min}} = \frac{\alpha \beta^\lambda (C_B^0)^{\lambda+1}}{\lambda^2 L^{s/z_0}}. \tag{14}$$

For sparingly soluble compounds having a very small solubility product L, the derivative at the initial point acquires a very large value and, consequently, the initial angle of inclination of the precipitation-isotherm plot is close to 90°.

Thus, precipitation isotherms in the case of formation of sparingly soluble precipitates have a sharply convex form. For the dynamics of precipitation sorption and precipitation chromatography this conclusion is of great importance. The degree of blurring of the boundaries of sorption zones in a chromatographic column depends, among other factors, also on the degree of convexity of the sorption isotherm ([1]). In the literature on precipitation chromatography it is noted ([2], [5]) that precipitate zones on chromatograms have, as a rule, exceptionally sharp and even boundaries. This experimental fact is partly explained by the nearly limiting convex form of the precipitation isotherms for sparingly soluble precipitates.

Fig. 2. Precipitation isotherms:
$1 - C_B^0 = 1 \cdot 10^{-2}$; $2 - C_B^0 = 1 \cdot 10^{-3}$;
($L = 1 \cdot 10^{-10};\ z = z_0 = 1;\ \alpha \approx \beta \approx 1$).

Replacing in equation (13) the equilibrium concentration of the precipitated ion C_A by the equilibrium concentration of the precipitating ion C_B (according to equation (7)), we obtain:

$$\frac{dS_A}{dC_A} = \frac{\alpha \beta^\lambda C_B^{\lambda+1}}{\lambda^2 L^{s/z_0}}. \tag{15}$$

It is evident from this equation that, in general, the steepness of the precipitation-isotherm plot of ion A depends on the solubility product L, the valence ratio λ, the activity coefficients (the ionic strength of the solution), and the equilibrium concentration of the counterion B; moreover, the latter, in turn, depends on its initial concentration C_B^0 (see equation (3)).

3) In the isotherm equation (10) there are two constants: G and H. One of them, the constant G, according to (9), depends on the initial concentration of the precipitating ion C_B^0 and on the ratio of the ion valences λ, and gives the equation of the asymptote (12). The other constant, H, according to (9), does not depend on the concentration of ion B, but depends only on the constant of the solubility product of the given precipitate, the activity coefficients* and the ratio of the ion valences.

* The activity coefficients of the ions are conventionally taken as constants on the assumption that the ionic strength of the solution changes during the reaction within limited bounds, since if initially there are solutions of substances AM and NB, then after mixing the solutions, even in the case of practically complete transfer of ions A and B into the precipitate according to reaction (1), ions M and N still remain in the solution at the initial concentrations (provided that these ions are not OH^- and H^+).

Thus, for the given precipitation reaction (1), the only "controllable" constant in the isotherm equation (10) is the constant G. The influence of the initial concentration of the precipitating ion C_B^0 through the constant G on the course of the precipitation isotherm is manifested in the fact that, as the concentration C_B^0 increases, the quantity $C_{A,\min}$ (11) decreases—the isotherm shifts to the left —while the quantity $S_{A,\max}$ (12) increases, i.e., the capacity of precipitation, so to speak, increases. Figure 2 gives precipitation isotherms for ion A in two analogous systems differing by a factor of 10 in the initial concentration of the precipitating ion C_B^0. As can be seen, the isotherm with the larger C_B^0 lies above the isotherm with the smaller C_B^0.

Thus, with an increase in the concentration of the precipitating ion B, the precipitatability of ion A improves, which can be characterized by two indicators: first, by lower values of the initial concentration of ion A at which the precipitation process begins:

$$C_{A,\min}^0 = C_{A,\min} = \frac{L^{s/z_0}}{\alpha\beta^\lambda (C_B^0)^\lambda}, \tag{16}$$

as follows from equations (2) and (11), and, second, by a larger "capacity of precipitate absorption" $S_{A,\max}$ (12).

4) The precipitation isotherm (10) takes on a fairly simple form if it is expressed in dimensionless concentrations. Thus, if the concentration of ion A in the precipitate is measured in fractions of $S_{A,\max}$, and in solution—

in fractions of $C_{A,\min}$, then we obtain the precipitation isotherm equation in the following form:

$$\theta = 1 - \eta^{-1/\lambda}, \tag{17}$$

where $\theta = S_A/S_{A,\max}$, $\eta = C_A/C_{A,\min}$.

Equation (17) may be called the reduced form of the precipitation isotherm. Its distinctive feature is that it contains only one independent parameter—the valence ratio λ.

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