Physical Chemistry

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1961

SovietRxiv

Abstract

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On Certain Regularities of Chemical Interaction Expressed by the Law of Mass Action

The dependence of the yield of a reversible chemical reaction of the type $mA + nB \rightleftarrows A_{mB}n$ on the composition of the solution is expressed by the law of mass action in the form of the equation

$$\frac{y}{(C_A - my)^m (C_B - ny)^n} = K, \tag{1}$$

where y is the equilibrium concentration of the compound (the reaction yield); C_A and C_B are the total concentrations of the components; K is the concentration constant.

Formula (1) corresponds to systems which, in addition to the reacting components A and B, contain a solvent present in considerable excess that does not enter into the reaction; it is also assumed that there are no appreciable amounts of intermediate dissociation products of the compound. When the ionic strength of the solution is kept constant, the formula given proves valid over a wide concentration interval.

The isomolar yield diagram of a compound of the type $A_{mB}n$, as applied to purely binary systems, was studied by N. I. Stepanov (^{1}); in doing so, he focused chiefly on the study of singular points located on the diagram outside the region having physical meaning. N. I. Stepanov’ s metric, which constituted an essential part of the theory of physicochemical analysis, did not, however, receive proper development in subsequent years. At the same time, in the practice of physicochemical analysis of complex compounds in solutions, notions became widespread concerning the dependence of the composition-yield of a compound that were based on qualitative reasoning. These notions are reflected in the well-known monograph by A. K. Babko (^{2}) and may be reduced approximately to the following: as the concentration of one of the components is decreased relative to the stoichiometric value, the degree of dissociation of the compound decreases monotonically and, as the concentration of this component tends to 0, i.e., at an infinitely large relative excess of the other component, tends to 0; accordingly, both in the case of isomolar series and in the case of series with a variable concentration of one component, the dependence of the reaction yield on the composition of the solution is expressed by a curve which, at all its points, is convex toward positive ordinates and has at the initial point a maximum slope close to that observed at $K = \infty$.

The statements cited are valid for compounds of the type AB (^{2}) at large values of the formation constant; however, extending them to compounds of the type AB_n (A_{mB}) and $A_{mB}n$, even at large values of K, requires certain limitations, especially if one considers the region of sufficiently small concentrations. Mathematical analysis of equation (1) under the conditions: $C_A = \text{const}$, $C_B = x$; $C_B = \text{const}$, $C_A = x$; $C_A + C_B = C = \text{const}$, $\frac{C_B}{C_A + C_B} = x$, where x is the composition variable, shows that in each of these cases the derivative y'_x, at zero

the concentration of one of the components is equal to 0; thus, the curve at the initial point has not a maximal but a zero slope and, consequently, in some initial segment is turned with its concavity toward the positive ordinates; on this basis one may conclude that, when the concentration of one of the components is decreased in comparison with the stoichiometric value, the change in the degree of dissociation of the compound has a complex character; moreover, as the concentration of the given component tends to 0, the degree of dissociation tends not to 0 but, on the contrary, to 1. These conclusions, as the investigation of the derivative y'_x under the condition $m = 1$ or $n = 1$ shows, do not extend to those cases in which the component whose concentration tends to 0 has, in the formula $A_{mB}n$, an index equal to 1.

Thus, the regularities in the change of the degree of dissociation of a compound as the concentration of one of the components tends to 0 have a qualitatively different character depending on whether the compound contains one or more than one particle of the given component; if more than one, then the degree of dissociation of the compound tends to 1, i.e., the compound decomposes completely; if only one, then the degree of dissociation decreases, but tends not to 0, but to a limit whose magnitude depends on K.

Thus, for example, the curve of the dependence of the yield of a compound of type AB_n on composition in series with variable concentration of component B has, at the initial point ($x = 0$), zero slope, since the tangent of the angle of inclination of the curve at this point, determined by the value of the derivative y'_x, is equal to 0 (and not $1/n$, as followed from the above-mentioned conceptions); whereas in series with variable concentration of component A the tangent of the initial angle of inclination is equal to

$$\frac{C_B^n}{C_B^n + 1/K}$$

(and not 1); in isomolar series, 0 (and not C/n) at the point of component A and

$$\frac{C^{n+1}}{C^n + 1/K}$$

(and not C) at the point of component B. The corresponding values of the degree of dissociation are, as is not difficult to show: 1, $\frac{1}{1 + KC_B^n}$, 1, $\frac{1}{1 + KC^n}$.

Analogous reasoning may also be carried out for compounds of other types ($A_{mB}n$, A_{mB}, AB).

A consequence of the zero slope of the composition–yield curve of a compound at the initial point is, as already noted, its concavity in some initial segment. Correspondingly, this concave character of the composition–property curves in the initial segment is also quite regular in the formation in the system of a single compound; numerous experimental curves cited in the literature may serve as an illustration. The notion that the concavity of an experimental composition–property curve indicates the formation of more than one compound is not always correct.

It is necessary further to note that, with a concave character of the initial segment, the curve must possess two special points. We have investigated these points both for series with variable concentration of one of the components and for isomolar series; moreover, both compounds of the type $AB_n(A_{mB})$ and compounds of the type $A_{mB}n$ were considered.

Figure 1* presents a curve showing the yield of a compound of type AB_n as a function of the concentration of component B. The curve has two special points, of which one (P) is a point of inflection, while the other (Q) can be determined by drawing a tangent from the origin coordinates. At point P the first derivative y'_x passes through a maximum ($y''_x = 0$); at point Q the maximum value of the ratio y/x is attained, i.e. $(y/x)'_x = 0$.

The derivative y'_x characterizes the intensity of the chemical interaction, i.e., the amount of compound formed per unit of the added amount of component B at some given composition of the solution; the ratio y/x characterizes the relative yield of the reaction as a whole upon attaining the given composition. Thus, the special points correspond to the maximum intensity of the chemical interaction (P) and to the maximum relative yield of the reaction (Q).

The meaning of these points can be revealed in more detail as a result of determining their coordinates. Mathematical analysis shows:

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* The concentration of component B (x) is shown in Fig. 1 on a reduced scale in comparison with the concentration of the compound (y).

Fig. 1. Dependence of the yield of a compound of type AB_n on the concentration of component B, $C_A = \text{const}$

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$$y^{(P)} = C_A \frac{n-1}{2n}, \qquad x^{(P)} = \frac{C_A}{2}(n-1) + \sqrt[n]{\frac{n-1}{K(n+1)}}; \tag{2}$$

$$y^{(Q)} = C_A \frac{n-1}{n}, \qquad x^{(Q)} = C_A(n-1) + \sqrt[n]{\frac{n-1}{K}}. \tag{3}$$

Fig. 1. Dependence of the yield of a compound of type AB_n on the concentration of component B, $C_A = \text{const}$

It follows from consideration of these expressions that the ordinates of the special points do not depend on the equilibrium constant and are determined exclusively by the given chemical form, whereas their abscissae depend also on the constant. The lower the stability of the compound, the farther these points are displaced along the composition axis, while remaining at one and the same distance from it. Thus, points P and Q correspond to definite, discrete concentrations of the compound. These concentrations are, in a certain sense, critical, since they separate qualitatively different regions of accumulation of the reaction product. As component B is added to component A, accumulation of the compound AB_n at first occurs with increasing intensity of chemical interaction; however, upon reaching $\frac{n-1}{2n}$ of the maximum possible amount of compound ($y = C_A$), the intensity of interaction passes through a maximum and subsequently begins to decrease, although the relative yield of the reaction continues to increase; when the concentration of the compound increases by another factor of two and reaches $\frac{n-1}{n}$ of the maximum value, further accumulation of the reaction product occurs with a decrease in its relative yield. These discrete fractions are equal to 1/4 and 1/2 for compounds of type AB_2; 1/3 and 2/3 for AB_3, etc.

In the case where a compound of type $A_{mB}n$ is formed in the system, the ordinates of points P and Q in a series with variable concentration of component B have the form:

$$y^{(P)} = \frac{C_A}{m} \frac{\sqrt{mn} - \sqrt{m+n-1}}{(m-1)\sqrt{m+n-1}}; \tag{4}$$

$$y^{(Q)} = \frac{C_A}{m} \frac{n-1}{m+n-1}. \tag{5}$$

Under an isomolar change in the composition of the solution, the ordinates of the special points depend on the equilibrium constant K; however, the relation between the ordinates and abscissae is specified by simple ratios into which the value K does not enter.

Thus, for example, for a compound of the type AB_n formed in an isomolar series, we have:

$$ny^{(P)} + Cx^{(P)} = C\frac{n-1}{n+1}; \tag{6}$$

$$y^{(Q)} + Cx^{(Q)} = C\frac{n-1}{n}. \tag{7}$$

In conclusion, it should be noted that the regularities obtained may find practical application in the physicochemical analysis of compounds in solutions; in this regard, the determination of the composition of compounds from the ordinate of point Q in series with a variable concentration of one of the components appears the most promising.

Radium Institute named after V. G. Khlopin
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Received
3 February 1961

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