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$M^{n+} - M(\text{OH})_{n+m}^{m-} - M(\text{OH})_n - \text{H}_2\text{O}$

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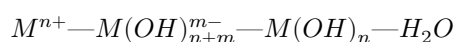
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Abstract

Full Text

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The Rule of Constancy of the Product of the Activities of Simple (Hydrated) Metal Ions and Hydroxo Ions in the Heterogeneous System



(Presented by Academician A. A. Grinberg, February 29, 1960)

Amphoterism is a general property of elements; therefore, in aqueous solutions of ordinary salts, hydroxo ions are present along with simple (hydrated) metal ions. In alkaline solutions, however, besides ions of hydroxo acids there are also simple metal ions. When solutions of metal salts or hydroxides are treated with a solution of caustic soda, hydroxo salts are formed. The solubility of hydroxo salts and the stability of their solutions differ for different metals.

The preparation of hydroxo salts by the interaction of salt solutions with a solution of caustic soda proceeds successively through the stages of formation of hydroxides, hydroxo salts, and their polymeric forms, followed by partial decomposition of the solution with separation of the metal hydroxide ⁽¹⁾. In the solution, after equilibrium has been established, hydroxo salts remain in concentrations determined by the ratio of the concentrations of alkali and metal, which remains constant for each metal under the given conditions ⁽²⁾. By the time the solution decomposes and equilibrium is established, polymeric particles disappear from the solution ⁽³⁾.

The process of decomposition of hydroxo-salt solutions with separation of hydroxide is spontaneous; therefore the hydroxide precipitated from an alkaline solution is more stable and less soluble both in acids and in alkalis. The rate and extent of decomposition are determined chiefly by the chemical properties of the metal and also by the conditions—primarily the temperature and the concentrations of alkali and salt. Thus, for example, it is known that the hydroxides of aluminum, zinc, lead, gallium, and certain other metals are readily soluble in alkalis. However, if the ratio of the concentration of alkali to that of the metal is less than a certain value characteristic of the given metal, these solutions decompose with time, with separation of hydroxide. Other metals, for example indium, also give hydroxo salts (indate), but decomposition begins immediately after preparation.

It is customary to consider that a number of metals do not give hydroxo salts and do not dissolve in alkalis, for example iron. Nevertheless, iron hydroxide, like the hydroxides of other metals, also dissolves in alkalis, but decomposition of

the solution proceeds rapidly and is practically completed within a short period of time. The reason for this may be the far-reaching process of dehydration of the hydroxide and hydroxo salt as a result of polarization. As a rule, the more rapidly hydroxo-salt solutions decompose, the less of them remains in solution after decomposition (^{1,3}).

It is known that in heterogeneous systems the activity of simple metal ions is related to the pH of the solution and to the product of the activities of the hydroxides by the relation (⁵)

$$\text{pH} = \frac{1}{n} \lg \frac{\Pi a}{K_w^n a_M}, \quad (1)$$

and the activity of hydroxo ions by the equation (⁴)

$$\text{pH} = \frac{1}{m} \lg \frac{a_{\text{gh}}}{\Pi a'}, \quad (2)$$

where a_{gh} is the activity of hydroxo ions, and $\Pi a'$ and m are, respectively, the activity product and the basicity of the hydroxo acid.

Since, in heterogeneous equilibrium, pH pertains to two dissociation processes—of the hydroxide and of the hydroxo acid—and since these proceed in the same solution, the right-hand sides of equations (1) and (2) may be equated; after a simple transformation we obtain:

$$\Pi a^{m/n} \Pi a' / K_w^n = a_M^{m/n} a_{\text{gh}} = K. \quad (3)$$

All constant quantities enter the right-hand side of equation (3); therefore the left-hand side is also a constant quantity. Hence it follows that, after decomposition of a solution of a hydroxo salt, i.e., in the established heterogeneous equilibrium, the product of the activities of simple (hydrated) metal ions and hydroxo ions is constant. It should be emphasized that such a change in ion activities—when, with an increase in the activity of hydroxo ions, the activity of simple ions decreases—is observed only for solutions saturated with respect to the hydroxide, in the presence of hydroxide in the solid phase.

We have put forward the supposition that, in aqueous solutions, the product of the activities of simple metal ions and hydroxo ions in an equilibrium heterogeneous system is a constant quantity for all metals (forming hydroxo salts) and is equal to the ionic product of water. Naturally, this conclusion applies only to those metals that form hydroxo salts.

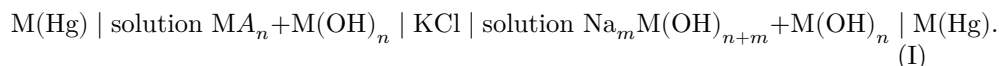
The supposition that the product of the activities of simple and hydroxo ions is equal to the ionic product of water can be tested experimentally. Using equation (3), one may either calculate this product from the activity products of hydroxides and hydroxo acids, or determine this product directly experimentally.

The first way of testing the proposed supposition cannot at present be used because of the absence of reliable values of the activity products of hydroxo acids. We therefore took the second path—that of direct determination of the product of interest to us.

The experiment was carried out as follows. Freshly prepared metal hydroxide was dissolved with solutions of caustic soda of various concentrations. The amount of hydroxide was chosen so that, after dissolution, a portion still remained in the solid phase. The solutions were shaken and kept in a thermostat for one and forty days at 25°. Then the activity of metal ions was measured potentiometrically with the aid of a dropping amalgam electrode. The concentrations of hydroxo ions were taken as equal to the total concentrations of metal in the solution, determined analytically. The amalgam electrodes were calibrated against standard solutions of metal perchlorates, in which the ion activities were calculated by the Debye-Hückel equation. The results of the measurements are given in Table 1.

The obtained activity products were extrapolated to zero concentration of hydroxo ions. The logarithms of the activity products of the ions found in this way are presented in the form of equations of straight lines. As can be seen, these values of the activity products of simple and hydroxo ions are equal to the ionic product of water and differ from it by no more than 0.1.

We also applied a method for determining the activity product of simple and hydroxo ions based on measurement of the e.m.f. of the cell



Without taking the diffusion potential into account, this e.m.f. can be expressed by the formula

$$E = \frac{RT}{nF} \ln \frac{a_M}{a'_M}, \quad (4)$$

where a_M and a'_M are the activities of metal ions in solutions of the simple salt and the hydroxo salt. Substituting the value of a'_M from equation (3) into

equation (4) and solving it with respect to $\lg K$, we obtain:

$$\lg K = -\frac{mF}{2.303RT} E + \lg a_M^{m/n} a_{\text{GI}}. \quad (5)$$

There is no need to determine directly the e.m.f. of this cell. The electrode potentials of the right- and left-hand elements may be determined relative to the calomel reference electrode, with allowance for the diffusion potential. From these data the e.m.f. of cell (1) can be obtained.

Table 1
Results of the experimental determination of the ionic product

$-\lg a_M$	$-\lg C_{GI}$	$-\lg K$	Equations of straight lines	$-\lg a_M$	$-\lg C_{GI}$	$-\lg K$	Equations of straight lines
System: NaOH– Zn(OH) ₂ –H ₂ O (24 h)	System: NaOH– Zn(OH) ₂ –H ₂ O (24 h)	System: NaOH– Zn(OH) ₂ –H ₂ O (24 h)	System: NaOH – Zn(OH) ₂ – H ₂ O (24 h)	System: NaOH– Ga(OH) ₃ –H ₂ O	System: NaOH– Ga(OH) ₃ –H ₂ O	System: NaOH– Ga(OH) ₃ –H ₂ O	System: NaOH – Ga(OH) ₃ – H ₂ O
12.20	2.12	14.32	–14.1– 29.13 $C_{GI}^n =$ $m =$ 2	13.50	2.29	15.81	–14.02– 3.42 $C_{GI}^n =$ $m =$ 3
12.47	2.09	14.56	–14.1– 29.13 $C_{GI}^n =$ $m =$ 2	12.75	2.54	15.29	–14.02– 3.42 $C_{GI}^n =$ $m =$ 3
14.22	1.37	15.59	–14.1– 29.13 $C_{GI}^n =$ $m =$ 2	11.96	2.60	14.56	–14.02– 3.42 $C_{GI}^n =$ $m =$ 3
14.94	1.10	16.04	–14.1– 29.13 $C_{GI}^n =$ $m =$ 2	10.38	3.72	14.10	–14.02– 3.42 $C_{GI}^n =$ $m =$ 3
System: NaOH– Zn(OH) ₂ –H ₂ O (40 days)	System: NaOH– Zn(OH) ₂ –H ₂ O (40 days)	System: NaOH– Zn(OH) ₂ –H ₂ O (40 days)	System: NaOH – Zn(OH) ₂ – H ₂ O (40 days)	System: NaOH– Pb(OH) ₂ –H ₂ O	System: NaOH– Pb(OH) ₂ –H ₂ O	System: NaOH– Pb(OH) ₂ –H ₂ O	System: NaOH – Pb(OH) ₂ – H ₂ O
11.96	2.34	14.30	–14.08– 30.2 $C_{GI}^n =$ $m =$ 2	10.37	3.57	13.94	–14.10+ 2.71 $C_{GI}^n =$ $m =$ 2

$-\lg a_M$	$-\lg C_{GI}$	$-\lg K$	Equations of straight lines	$-\lg a_M$	$-\lg C_{GI}$	$-\lg K$	Equations of straight lines
12.01	2.26	14.27	$-14.08 - 30.2 C_{GI}^n =$ $m = 2$	11.17	2.86	14.03	$-14.10 + 2.71 C_{GI}^n =$ $m = 2$
13.61	1.51	15.12	$-14.08 - 30.2 C_{GI}^n =$ $m = 2$	11.31	2.59	13.90	$-14.10 + 2.71 C_{GI}^n =$ $m = 2$
14.39	1.22	15.61	$-14.08 - 30.2 C_{GI}^n =$ $m = 2$	11.61	2.52	14.10	$-14.10 + 2.71 C_{GI}^n =$ $m = 2$
				11.86	2.40	14.26	$-14.10 + 2.71 C_{GI}^n =$ $m = 2$
System: NaOH– In(OH) ₃ –H ₂ O	System: NaOH– In(OH) ₃ –H ₂ O	System: NaOH– In(OH) ₃ –H ₂ O	System: NaOH – In(OH) ₃ – H ₂ O				
30.68	4.61	14.84	$-14.06 - 2 \cdot 10^3 C_{GI}^n =$ $3; m = 1$				
32.74	3.98	14.89	$-14.06 - 2 \cdot 10^3 C_{GI}^n =$ $3; m = 1$				
33.11	4.04	15.08	$-14.06 - 2 \cdot 10^3 C_{GI}^n =$ $3; m = 1$				

If solutions of low concentration are taken, the activity coefficients can be calculated, and consequently so can the activities of the ions; then, by equation (5),

K can be determined (see Table 2).

Table 2

Results for the determination of K from the measured e.m.f. of cell (1)

$-\lg a_{\text{Zn}^{2+}}$	$-\lg a_{\text{GI}}$	e.m.f.	$-\lg K$	$-\lg a_{\text{Pb}^{2+}}$	$-\lg a_{\text{GI}}$	e.m.f.	$-\lg K$
2.0023	2.3042	0.2815	13.83	1.9031	2.6625	0.2802	14.05
2.2043	2.3042	0.2793	13.86	2.3074	2.6625	0.2686	14.06
3.1093	2.3042	0.2532	13.98	2.7618	2.6625	0.2546	14.04
2.0023	3.3468	0.2582	14.09	1.9031	2.8706	0.2735	14.03
2.1043	3.3468	0.2534	14.03	2.3074	2.8706	0.2619	14.04
3.1093	3.3468	0.2239	14.02	2.7618	2.8706	0.2479	14.02
2.0023	3.4216	0.2559	14.08	1.9031	3.9847	0.2395	13.99
2.1043	3.4216	0.2511	14.02	2.3074	3.9847	0.2279	14.00
3.1093	3.4216	0.2226	14.06	2.7618	3.9847	0.2134	13.98
		Average	14.00			Average	14.02
		

Thus, the proposition may be regarded as proved that

$$a_{\text{M}}^{m/n} a_{\text{GI}} = K_w. \quad (6)$$

The product of the activities of simple (hydrated) metal ions and hydroxo ions in the heterogeneous equilibrium system $M^{n+} - M(\text{OH})_{n+m}^{m-}$

$-M(\text{OH})_2 - \text{H}_2\text{O}$ is a constant quantity and is equal to the ionic product of water at the given temperature.

On the basis of this rule one can calculate the activity products of hydroxo acids, the instability constants of hydroxo ions, the number of coordinated hydroxyl ions around the central metal ion and, consequently, the basicity of hydroxo acids, the isobaric-isothermal potentials of hydroxo-ion formation, the pH of the isoelectric points of hydroxides, and a number of other quantities.

To determine the activity product of hydroxo acids, it is necessary to solve the equation $\Pi a^{m/n} \Pi a' / K_w' = K_w$ with respect to $\Pi a'$:

$$\Pi a' = K_w^{m+1} / \Pi a^{m/n}. \quad (7)$$

The instability constant is expressed by the equation

$$K = \Pi a K_w^m / \Pi a'. \quad (8)$$

Substituting into this equation, in place of a' , its expression from equation (7), we obtain

$$K = \Pi a^{\frac{n+m}{n}} / K_w. \quad (9)$$

Thus, by equation (9) one can calculate the instability constants of hydroxo ions. Similarly, the pH values of the isoelectric points of hydroxides can be calculated. The isobaric potentials of hydroxo-ion formation can be calculated from equation (6)

$$\Delta Z^0 = \Delta Z_{M(OH)_n}^0 + m\Delta Z_{OH'}^0 - 2.3RT \lg \Pi a' + 2.3mRT \lg K_w. \quad (10)$$

Substituting into it the value of $\Pi a'$ from equation (7), we obtain

$$\Delta Z^0 = \Delta Z_{M(OH)_n}^0 + m\Delta Z_{OH'}^0 + 2.3\frac{m}{n}RT \lg \Pi a - 2.3RT \lg K_w. \quad (11)$$

As can be seen, to calculate the quantities indicated above it is necessary to know only the activity products of hydroxides, which are known for most metals. By way of example, Table 3 gives calculated values for several hydroxo acids and hydroxo ions.

Table 3

Calculated values of $\Pi a'$, K , and ΔZ^0 for several hydroxo acids and hydroxo ions

Hydroxo ion	$\lg \Pi a$	$\Pi a'$	K	ΔZ^0 , kcal/mol
$Zn(OH)_4^{2-}$	-17.4 (7)	$2.51 \cdot 10^{-25}$	$6.31 \cdot 10^{-21}$	-216.40
$Pb(OH)_4^{2-}$	-15.35 (8)	$2.24 \cdot 10^{-27}$	$5.01 \cdot 10^{-17}$	-178.91
$Al(OH)_4$	-31.70 (9)	$3.72 \cdot 10^{-18}$	$5.01 \cdot 10^{-29}$	-303.89
$In(OH)_4$	-36.92 (10)	$2.04 \cdot 10^{-16}$	$5.89 \cdot 10^{-36}$	-222.10
$Ga(OH)_6^{3-}$	-36.29	$1.95 \cdot 10^{-20}$	$2.63 \cdot 10^{-59}$	-342.02

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