ISOBARIC POTENTIALS OF FORMATION OF DIFFICULTLY-SOLUBLE OXIDE HYDRATES AND BASIC SALTS AND THE pH OF THE SOLUTIONS IN EQUILIBRIUM WITH THE SOLID PHASE

V. L. Kheifets and A. L. Rotinyan

Processes for separating metals, based on differences in the conditions of formation of their difficultly soluble hydrates or basic salts, occupy a greater and greater place both in analytical chemistry, and in the most diverse fields of engineering. A considerable number of reports [1-12, 14, 16] in recent years have been devoted to the present problem, and although they have essentially advanced the status of the problem, it nevertheless is still far from a final solution.

In the present report we thought it expedient to consider the general physico-chemical basis of processes of formation of difficultly soluble metal oxide hydrates and their basic salts.

By hydrolysis reactions, or by the action of alkaline reagents on solutions of the salts of many metals, the formation of difficultly soluble compounds is possible in principle: a) hydrates of the type $Me(OH)_n$, b) basic salts of simple metal salts and their hydrates of the type, $x[Me_bA_d] \cdot y[Me(OH)_n]$, and c) more complex combinations of hydrates and salts of two or more metals.

In each concrete case, that difficultly soluble compound will be formed first, the formation of which is accompanied by maximum decrease in isobaric potential; in other words the compound which has the least solubility.

Relation Between the Isobaric Potential of Formation of the Difficulty Soluble Hydrate of a Metal Oxide and the pH of the Solution

If one considers the system, metal oxide hydrate (solid phase)—solution, as an equilibrium, it is possible to write:

$$Me^{n+} + n\,OH' \rightleftharpoons Me(OH)n. \qquad (1)$$

We employ the following designations:

ΔZ_1^0 — the standard isobaric potential of formation of $Me(OH)_n$ of the elements;

ΔZ_2^0 — the same value for the Me^{n+} ion;

ΔZ_3^0 — the same value for the OH' ion;

$\Delta Z_{hyd.}^0$ — standard isobaric potential for reaction (1).

Proceeding from reaction (1),

$$\Delta Z_2^0 + RT \ln a_{Me^{n+}} + n\Delta Z_3^0 + nRT \ln a_{OH'} = \Delta Z_1^0 + RT \ln a_{Me(OH)_n}. \qquad (2)$$

If the difficultly soluble hydrate occurs in the form of solid phase, i.e., under standard conditions, then $a_{Me(OH)_n} = 1$ and $RT \ln a_{Me(OH)_n} = 0$.

Designating the dissociation constant of water by K_W, equation (2) may be rewritten as:

$$pH = \frac{\Delta Z_1^0 - \Delta Z_2^0 - n\Delta Z_3^0}{2.3nRT} - \log K_W - \frac{1}{n} \log a_{Me^{n+}}. \qquad (3)$$

From equation (3) it is seen that, knowing ΔZ_1^0, ΔZ_2^0 and ΔZ_3^0, it is possible to calculate the pH value corresponding to the equilibrium between hydrate (in the form of solid phase) and solution, for any activities of the metal ions.

On the other hand, since

$$\Delta Z^0_{hyd.} = -RT \ln K = RT \ln a_{Me^{n+}} a^n_{OH'} \quad (4)$$

we may transform equation (2) to

$$\Delta Z^0_1 = \Delta Z^0_2 + n\Delta Z^0_3 + \Delta Z^0_{hyd.} \quad (5)$$

Thus, the values of ΔZ^0_1, ΔZ^0_2 and ΔZ^0_3 or two of these three quantities and the equilibrium value of the pH of formation of the hydrate, enable one to calculate the standard isobaric potential of reaction (1).

Results of some calculations are presented in Table 1. For calculation $\Delta Z^0_3 = 37.58$ [13], is assumed.

TABLE 1

Standard Isobaric Potentials of Formation of Difficultly Soluble Oxide Hydrates (kcal/mole)

Formula of the hydrate	ΔZ^0_1 [13]	ΔZ^0_2 [13]	$\Delta Z^0_{hyd.}$ calculated from equation (5)	pH of formation of the hydrate calculated from equation (3)	pH of formation	
					hydrate according to Fialkov and Akselrud	compounds, according to Britton
$Co(OH)_3$	−142.00	28.90	−58.14	0.9	—	—
$Fe(OH)_3$	−166.30	− 2.53	−51.01	2.6	1.63	2
$Cu(OH)_2$	− 85.50	15.91	−26.24	4.5	4.21	5.3
$Zn(OH)_2$	−132.64	−35.17	−22.29	5.9	5.78	5.2
$Co(OH)_2$	−108.90	−12.80	−20.93	6.4	6.78	6.8
$Fe(OH)_2$	−115.66	−20.31	−20.18	6.7	5.62	5.5
$Cd(OH)_2$	−112.73	−18.55	−19.01	7.0	6.84	6.7
$Ni(OH)_2$	−105.60	−11.53	−18.90	7.1	6.70	6.7

The thermodynamic series of the pH of formation of the hydrates, as is easily observed, is identical with the series proposed by Akselrud and Fialkov [6] but is essentially preferable, because of its specificity, to the Britton [15] series. However, the series of pH of formation of the hydrates in any of its forms has much less value than is usually attributed to it, because in practice the basic salts of the metals, rather than the pure hydrates, usually form.

Relation Between the Isobaric Potential of Formation of Difficultly Soluble Basic Salt and the pH of the Solution

If, instead of a pure hydrate, a basic salt of composition $x[Me_bA_d]y[Me(OH)_n]$, is in equilibrium with the solution, then:

$$(y + bx)\,Me^{n+} + xd\,A^{m'} + ny\,OH' \rightleftharpoons x[Me_bA_d]y[Me(OH)_n], \quad (6)$$

here $m' = \frac{nb}{d}$.

For equation (6), as previously, one may write:

$$(y + bx)\,\Delta Z^0_2 + RT \ln a^{y+bx}_{Me^{n+}} + xd\,\Delta Z^0_4 + RT \ln a^{xd}_{A^{m'}} + ny\,\Delta Z^0_3 + RT \ln a^{ny}_{OH'} =$$

$$= \Delta Z^0_5 + RT \ln a_{bas.} \quad (7)$$

Into equation (7) additional designations are introduced:

ΔZ^0_4 — standard isobaric potential of formation of anion salts of the elements;

ΔZ^0_5 — the same for formation of the basic salt from the elements;

$a_{bas.}$ — activity of the basic salt in the solid state, which at its maximum is assumed to equal unity.

Equation (7) is easily transformed to the following:

$$pH = \frac{\Delta Z_5^0 - (y + bx)\Delta Z_2^0 - xd\,\Delta Z_4^0 - ny\,\Delta Z_3^0}{2.3nyRT} - \frac{y + bx}{ny}\log a_{Me^{n+}} - \frac{xd}{ny}\log a_{A^{m'}} - \log K_W. \quad (8)$$

Since,

$$\Delta Z_{bas.} = RT \ln a_{Me^{n+}}^{(y+bx)}\, a_{A^{m'}}^{xd}\, a_{OH'}^{ny}, \quad (9)$$

where $\Delta Z_{bas.}$ is the standard isobaric potential of reaction (6), equation (7) may be written in the form:

$$(y + bx)\Delta Z_2^0 + xd\,\Delta Z_4^0 + ny\,\Delta Z_3^0 + \Delta Z_{bas.}^0 = \Delta Z_5^0. \quad (10)$$

Depending on whether $RT \ln \underline{a}_{Me^{n+}} \underline{a}_{OH'}^{n} < RT \ln \underline{a}_{Me^{n+}}^{(y+bx)} \underline{a}_{A^{m'}}^{xb} \underline{a}_{OH'}^{ny}$, the basic salt or pure hydrate will separate out in the precipitate.

From equations (9) and (4) it is clear that for an increase of activity of the salt in solution, a transition from formation of the hydrate to formation of basic salt is always inevitable; at the same time, a change of the value of $\underline{x}$ and $\underline{y}$ is possible, i.e., the formation of basic salts of different composition depends on the conditions.

For the basic salt the value of ΔZ_5^0 is unknown, therefore, calculation of $\Delta Z_{bas.}^0$ is possible only from experimental data on the pH of formation of the basic salt. Moreover, for calculation in each individual case it is necessary to know the coefficients $\underline{x}$ and $\underline{y}$.

Mechanism Relating the pH of Formation of a Basic Salt to Its Composition and the Activities of Simple Salts in Solution

Equation (8) may be rewritten in the following form:

$$pH = \frac{\Delta Z_{bas.}^0}{2.3ny\,RT} - \frac{1}{ny}\log m_{Me^{n+}}^{(y+bx)} \gamma_{\pm}^{(y+bx)}\, m_{A^{m'}}^{xd}\, \gamma_{\pm}^{xd} - \log K_W. \quad (11)$$

If there is no other salt having a common anion in the solution,

$$m_{Me^{n+}} = m_s b, \quad m_{A^{m'}} = m_s d \quad (12)$$

($\underline{m}_s$ is the molarity of the salt; $\underline{m}_{Me^{n+}}$, $\underline{m}_{A^{m'}}$ are the molarity of the ions). Then,

$$pH = \frac{\Delta Z_{bas.}^0}{2.3ny\,RT} - \frac{y + bx + dx}{ny}\log \underline{a}_{\pm} - \frac{1}{ny}\log \frac{b^{(y+bx)}\, d^{xd}}{b^{\frac{b}{b+d}}\, d^{\frac{d}{b+d}(y+bx+dx)}} - \log K_W. \quad (13)$$

If we determine the pH of the solution which is in equilibrium with the solid phase at several activities of the salt, and construct a graph of $pH - \log \underline{a}_{\pm}$ we may, by obtaining the angle of inclination of the straight line, easily determine the magnitudes of $\underline{x}$ and $\underline{y}$, as the least integral number values. Thus, it appears feasible to calculate the standard isobaric potential of basic salt by measurements of the pH of the solutions in equilibrium with this salt.

Discussion of the Available Data on the Magnitude of the pH of Hydrate Formation

A large amount of experimental material on the magnitude of the pH of solutions in equilibrium with solid phase was obtained by Gromov, Fialkov and Akselrud, and by Patsenko.

In Fig. 1 are represented data of these authors for a series of zinc salts. Along the ordinate are values of the pH of the solution in equilibrium with solid phase, and along the abscissa axis, the logarithm of the average activity of the salt. The corresponding activity coefficients were taken from Harned and Owen [17]. The angular coefficients, obtained directly, equal 0.48-0.56, 0.84, 1.25 and 1.5. As seen from the figure, for small activities of salt, pure hydrate of $Zn(OH)_2$ forms, and in this case the pH of the hydrate formation actually does not depend on the nature of the anion of the salt.

Formation of pure hydrates in chloride and nitrate solutions occurred up to larger salt activities than in sulfate solutions. At large salt activities the basic salt forms, its composition depending on the nature of the anion. Cal-

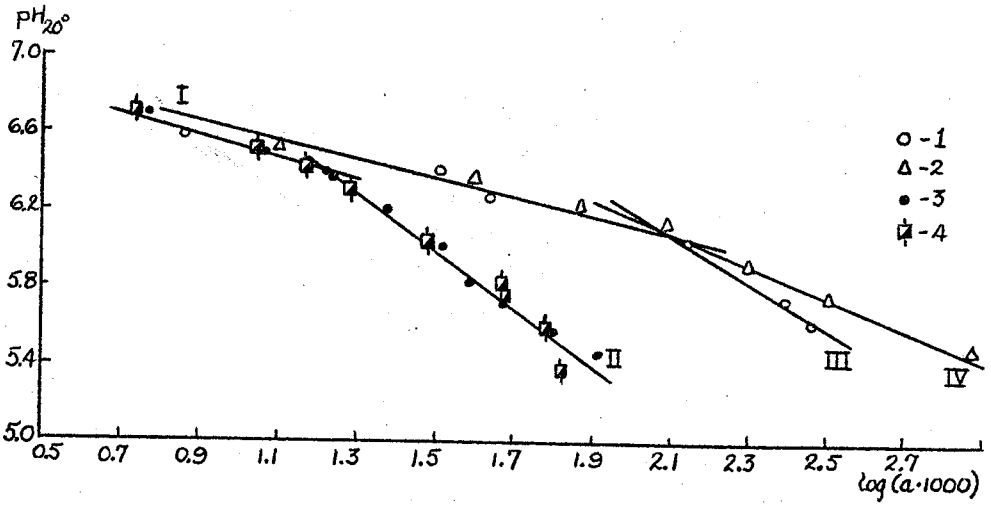

Fig. 1. Relation of pH of formation of hydrate of basic salt to the activity of a metal salt. [$ZnSO_4$, $ZnCl_2$, $Zn(NO_3)_2$]. 1 and 2) According to data [10]; 3) according to data [2]; 4) according to data [6]. I) $Zn(OH)_2$; II) $ZnSO_4 \cdot Zn(OH)_2$; III) $ZnCl_2 \cdot 2Zn(OH)_2$; IV) $Zn(NO_3)_2 \cdot 4Zn(OH)_2$.

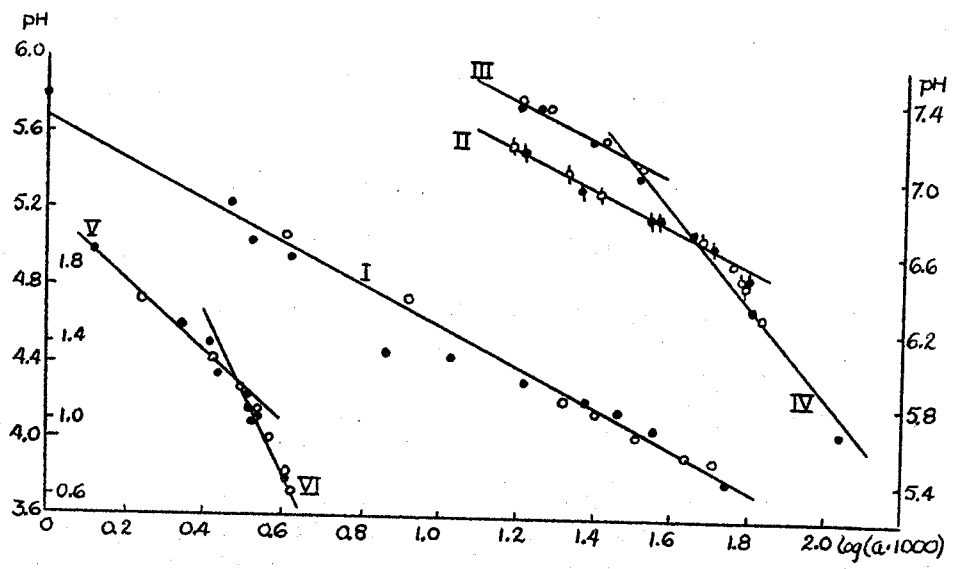

Fig. 2. Relation of pH of formation of the basic salt to the activity of the metal salt. Open circle — according to data [6]; solid circle — according to data [2]. Left external pH scale — for copper sulfate; left internal — for trivalent iron sulfate; right scale — for cadmium sulfate and divalent iron sulfate. I) $CuSO_4 \cdot 2Cu(OH)_2$; II) $FeSO_4 \cdot 2Fe(OH)_2$; III) $CdSO_4 \cdot 2Cd(OH)_2$; IV) $2CdSO_4 \cdot Cd(OH)_2$; V) $Fe_2SO_4)_3 \cdot Fe(OH)_3$; VI) $5Fe_2(SO_4)_3 \cdot 2Fe(OH)_3$.

culation from formula (13) gives the following composition of basic salts: $ZnSO_4 \cdot Zn(OH)_2$, $ZnCl_2 \cdot 2Zn(OH)_2$ and $Zn(NO_3)_2 \cdot 4Zn(OH)_2$. In the region of stable formation of basic salt the nature of the anion and its valence, as would be expected, very strongly influence the magnitude of the pH of formation of the basic salt; therefore, confirmation of the independence from the nature of the anion, of the pH of formation of precipitates [10], as shown by the data of these authors, is justified only for the region of formation of pure hydrate, which is actually encountered very rarely.

In Fig. 2 data for some other metals are provided. As seen from the figure, copper at all concentration intervals studied gives only one compound – the basic salt $CuSO_4 \cdot 2Cu(OH)_2$ ($3CuO \cdot SO_3 \cdot 2H_2O$). At small salt activites cadmium also forms a similar compound. At large salt activities the less basic cadmium salt, $2CdSO_4 \cdot Cd(OH)_2$ ($3CdO \cdot 2SO_3 \cdot H_2O$), forms. The compounds formed from di- and tri-valent iron are of great interest. Unfortunately, we did not find in the literature any data on the activity coefficients for ferrous and ferric sulfates. We record below the results of all calculations carried out on the assumption that the activity coefficients of $FeSO_4$ solutions, at identical molarity, are equal to those for sulfates of other divalent metals, for instance, copper, zinc and cadmium. For $Fe_2(SO_4)_3$ we assumed that the activity of the salt was equal to the corresponding activity of the sulfates of trivalent metals, such as aluminum and indium [17]. With these assumptions it seems that divalent iron, within the concentration limits studied, should form only one compound, $FeSO_4 \cdot 2Fe(OH)_2$ ($3FeO \cdot SO_3 \cdot 2H_2O$).

Trivalent iron gives two compounds, $Fe_2(SO_4)_3 \cdot Fe(OH)_3$ and $5Fe_2(SO_4)_3 \cdot 2Fe(OH)_3$ ($Fe_2O_3 \cdot 2SO_3 \cdot H_2O$ and $2Fe_2O_3 \cdot 5SO_3 \cdot H_2O$). The first of these compounds agrees with the compound observed by Posnjak and Merwin [18]. However, the anhydrous basic salt, $Fe_2(SO_4)_3 \cdot Fe(OH)_3$, is stable only at temperatures above 75°.

At lower temperatures the salts of the same composition with 4, 5, 6, 7 and 9 molecules of water of crystallization appear to be stable. The second compound of trivalent iron indicated above agrees with the basic salt $2Fe_2O_3 \cdot 5SO_3 \cdot 17H_2O$ (copiapite), if it is considered that at room temperature the basic salt $5Fe_2(SO_4)_3 \cdot 2Fe(OH)_3$ crystallizes with 16 molecules of water. Posnjak and Merwin point out that copiapite in contact with saturated solution is stable at temperatures below ~90°.

It should be pointed out that the composition of the solid phase, cited by Gromov, does not agree with the data presented above. Gromov gives one composition of the basic salt, $3Fe_2O_3 \cdot 2SO_3 \cdot H_2O$, for all concentration intervals of the salt.

A similar situation occurs also for the composition of basic salts of other metals, cited by Gromov.

Determining the compositions of some basic salts, we calculated the values of the standard isobaric potentials of their formation. Results of the calculations are given in Table 2. For the calculations we assumed the values $\Delta Z^0_{SO_4''} = -176.10$, $\Delta Z^0_{Cl'} = -31.33$, $\Delta Z^0_{NO_3'} = -26.25$. From data in the Table it is seen that the standard isobaric potentials of formation of the basic salts $\Delta Z^0_{bas.}$ are greater than $\Delta Z^0_{hyd.}$ for the pure hydrates. From values of $\Delta Z^0_{bas.}$ and the standard isobaric potential of formation of pure hydrate, $\Delta Z^0_{hyd.}$, one can determine the standard isobaric potentials of formation of the basic salt from the hydrate and simple salt $-\Delta Z^0_{simple}$. These values are recorded in the fourth column of Table 2.

TABLE 2

Standard Isobaric Potentials of Formation of Difficultly Soluble Basic Salts (kcal/mole).

Formula of basic salt	$\Delta Z^0_{bas.}$	$\Delta Z^0_{hyd.}$	ΔZ^0_{simple}
$ZnSO_4 \cdot Zn(OH)_2$	−27.95	−349.57	−5.66
$ZnCl_2 \cdot 2Zn(OH)_2$	−49.30	−367.82	−4.72
$Zn(NO_3)_2 \cdot 4Zn(OH)_2$	−94.70	−623.75	−5.54
$CuSO_4 \cdot 2Cu(OH)_2$	−60.50	−339.21	−8.02
$FeSO_4 \cdot 2Fe(OH)_2$	−47.20	−434.57	−6.84
$CdSO_4 \cdot 2Cd(OH)_2$	−45.60	−427.69	−7.58
$2CdSO_4 \cdot Cd(OH)_2$	−29.05	−512.07	−10.04
$Fe_2(SO_4)_3 \cdot Fe(OH)_3$	−73.00	−722.64	−21.98
$5Fe_2(SO_4)_3 \cdot 2Fe(OH)_3$	−196.00	−3093.37	−94.00

SUMMARY

1. We showed the feasibility of calculation of the standard isobaric potentials of formation of basic salts and pure hydrates from measurements of the pH of solutions in equilibrium with the solid phase of the basic salt or pure hydrate.

2. We worked with the experimental data available in the literature. It showed that in practically all cases at large concentrations the basic salts form. The compositions of these salts were determined. Pure hydrates form only in the case of zinc at small initial ionic concentrations.

3. For a series of metals, we calculated the standard isobaric potentials of the reaction of formation of basic salts from ions, elements, and also from the pure hydrates and simple salts.

LITERATURE CITED

[1] A. F. Kapustinsky, J. Appl. Chem., 16, 50 (1943).

[2] B. V. Gromov, J. Appl. Chem., 21, 260 (1948); Non-Ferrous Metals, No. 3 (1948).

[3] Ya. A. Fialkov and N. V. Akselrud, Ukrain. Chem. J., 16, 75 (1950).

[4] A. L. Rotinyan and V. Ya. Zeldes, J. Appl. Chem., 23, 717 (1950).*

[5] A. L. Rotinyan and V. Ya. Zeldes, J. Appl. Chem., 23, 936 (1950). **

[6] N. V. Akselrud and Ya. A. Fialkov, Ukrain. Chem. J., 16, 283 (1950).

[7] N. V. Akselrud and Ya. A. Fialkov, Ukrain. Chem. J., 16, 296 (1950).

[8] A. L. Rotinyan and V. Ya. Zeldes, J. Appl. Chem., 24, 604 (1951).***

[9] N. V. Akselrud and L. I. Kaganova, Ukrain. Chem. J., 17, 837 (1951).

[10] N. V. Akselrud and V. G. Patsenko, Ukrain. Chem. J., 17, 835 (1951).

[11] I. E. Apeltsin, J. Appl. Chem., 23, 51 (1950).****

[12] I. L. Korenman, J. Gen. Chem., 21, 10 (1951).*****

[13] W. Latimer. The Oxidation States of the Elements and Their Potentials. N. Y. (1938).

[14] P. N. Kovalenko and V. N. Nesterovich, Ukrain. Chem. J., 18, 635 (1952).

[15] Kh. T. S. Britton. Hydrogen Ions. United Sci.-Tech. Press (1936).

[16] P. N. Kovalenko, J. Appl. Chem., 26, 814 (1953).******

[17] Harned and Owen. Physical Chemistry of Solutions of Electrolytes, Foreign Lit. Press (1952).

[18] E. Posnjak and G. Merwin, J. Am. Chem. Soc., 44, 1965 (1922).

Received December 24, 1953

Lensoviet Leningrad Institute of Technology

---

* See Consultants Bureau Translation, page 757.
** See Consultants Bureau Translation, page 991.
*** See Consultants Bureau Translation, page 675.
**** See Consultants Bureau Translation, page 47.
***** See Consultants Bureau Translation, page 9.
****** See Consultants Bureau Translation, page 741.