the final precipitation; and that vanadium would require special treatment. Since this element has not been reported in zirconium ores, and since its presence in significant amounts would be indicated at various stages of the analysis, it would cause no trouble.

The authors desire to express to Dr. W. F. Hillebrand of this Bureau their sincere appreciation of his aid and counsel.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE ROYAL POLYTECHNICAL INSTITUTE OF COPENHAGEN.]

STUDIES ON SOLUBILITY. II. THE SOLUBILITY RATIOS OF SALTS IN STRONG HOMOIONIC SOLVENTS.

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I. Influence of Hydration of the Solute.

In a recent paper[1] a treatment of solubility equilibria in salt solutions was given on the basis of the provisional hypothesis that the stoichiometric activity coefficient in a mixed salt solution is the same for any ion of the same type. It was shown that the general features of the solubility curves in the case of homoionic as well as heteroionic solvents could be accounted for by means of this hypothesis.

The provisional character of the hypothesis was emphasized by pointing out several factors capable of causing deviations from the requirements of the simple assumption. As the principal of these factors we can name the secondary electric effect, which, besides the primary Milner effect, may influence the potential of the ions, and which manifests itself in a way similar to that of incomplete dissociation. Furthermore, there is the hydration of the dissolved ions and finally the electrostriction effect introduced by several authors[2] in order to explain the salting-out effect of salt solutions.

As a start on a general discussion of the influence of these factors we may conveniently put the simpler case of considering not the shape of the solubility curve itself, but the ratio of solubilities or solubility products for salts of varying concentration in the same solvent. If the secondary electric forces exert a similar effect upon the activity coefficients, which presumably is the case when the ions of the solute possess similar molecular structure, deviations from a constant solubility ratio would be due chiefly to changes in the hydration of the dissolved ions. If, on the other hand, constant solubility ratios are actually found, using a solvent of considerably changing vapor pressure, we may be entitled to conclude

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[1] *Kgl. Danske Vidensk. Selsk. Mathemat.-fysiske Medd.*, **2**, 10 (1919); THIS JOURNAL, **42**, 761 (1920).

[2] Euler, *Z. physik. Chem.*, **31**, 360 (1899); Geffeken, *ibid.*, **49**, 257 (1904).

that the solutes concerned are uniformly hydrated as well as also equally acted upon by the secondary electric forces.

The influence of hydration of the solute can readily be accounted for thermodynamically in the following way. If the ions are hydrated in solution and the activity coefficients are, according to our hypothesis, the same for all ions, Equation 23 in the previous paper must be replaced by

$$c'_a \, c''_a f^2 = K \tag{1}$$

where c'_a and c''_a are the concentrations, respectively, of the cation and anion in the anhydrous state, f the activity coefficient and K a constant peculiar to the saturating salt. If this salt be hydrated in the solid state also, we can write

$$c'_a \, c''_a f^2 \xi^{\nu} = K, \tag{2}$$

where ξ indicates the activity of water in the solution and ν the number of molecules of water combined with one molecule of the solid salt.

Assuming the following equilibria to occur between the ions in the hydrated and anhydrous states,

$$K\,n'H_2O^+ \rightleftarrows K^+ + n'H_2O$$
$$A\,n''H_2O^- \rightleftarrows A^- + n''H_2O$$

and assuming the concentration of the anhydrous ions to be negligible when compared with the concentration of the hydrates, the mass action law gives

$$c'_a = \frac{k'}{\xi n'}\,c', \text{ and } c''_a = \frac{k''}{\xi n''}\,c'' \tag{3}$$

where c' and c'' stand for the total (stoichiometric) concentration of the ions.

Introducing these expressions in (2) and putting $n' + n'' = n$ we obtain finally

$$c'c'' = k\,\frac{\xi^{n-\nu}}{f^2}. \tag{4}$$

In this formula $k = K/k'k''$, and $n - \nu$ depends upon the nature of the solute only, while ξ and f are characteristic of the solvent. For the solubility ratio of 2 salts in the same solvent, therefore, we can write

$$\frac{(c'c'')_1}{(c'c'')_2} = \frac{k_1}{k_2}.\ \xi^{(n_1-\nu_1)-(n_2-\nu_2)}, \tag{5}$$

while the ratio of solubilities of the same salt in two solvents is determined by

$$\frac{(c'c'')_{I}}{(c'c'')_{II}} = \frac{f^2_{II}}{f^2_{I}}\left(\frac{\xi_{I}}{\xi_{II}}\right) n - \nu. \tag{6}$$

It is worth noticing that Equation 4 is also arrived at from the assumption of incomplete dissociation, n in that case indicating the total number of water molecules associated with one molecule of partly dissociated salt.

If $\nu > n$, *i. e.*, if the salt is more hydrated in the solid than in the dissolved state, increasing concentration of the solvent will tend to increase the solubility. This effect for the case $n = 0$ has been studied by H. Goldschmidt.[1] If $n > \nu$, the effect will be the opposite; increasing concentration will tend to diminish the solubility corresponding to the well known salting-out effect of salt solutions. This effect necessitates an increase in the activity of the less hydrated or anhydrous substance at constant stoichiometric concentration, a fact that has been recently pointed out by Bjerrum,[2] and used by him to explain the behavior of the hydrogen electrode according to this view.

We shall in the following, apply Equation 5 to the solubilities of salts in strong homoionic solvents. Consideration of this formula shows that—granting the validity of our hypothesis—2 salts will exhibit a constant solubility ratio either when dissolved in solvents having the same ξ, *i. e.*, the same vapor pressure, or when $n_1 - \nu_1 = n_2 - \nu_2$, *i. e.*, the difference in hydration of the two salts in the dissolved and solid states is the same. Materially differing values of the solubility product ratios as produced by different hydrations are to be expected only when dealing with solvents of very high concentration.

II. Experiments with Potassium Hydroxide as Solvent.

As already indicated in the previous article, potassium hydroxide possesses a marked power of reducing the solubility of other substances, a fact which is probably connected with a high degree of hydration of the hydroxyl ion. When using this solvent we are able to employ, therefore, salts as soluble as potassium chloride, bromide, and iodide as saturating salts, the solubility in strong solutions of potassium hydroxides being sufficiently diminished for the treatment of the solution in accordance with the above considerations.

Furthermore, on account of the great solubility of potassium hydroxide, very great alterations in the water activity can be obtained with this solvent, which, therefore, according to Equation 5, is especially fitted for an examination of degrees of hydration.

The results of a series of measurements on univalent potassium salts at 20° are given in Table I.

The figures in this table denote number of mols in one liter of solution. We see the solubilities of the 3 halides and of potassium chlorate steadily decreasing with rising concentration of potassium hydroxide. The solubility of potassium nitrate seems to keep constant in the most concentrated solutions, and with the iodate a slight increase is noted.

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[1] *Z. physik. Chem.*, 17, 145 (1895).

[2] *Medd. K. Vetenskapsakad. Nobelinst.*, 5, No. 16 (1919).

TABLE I.

Solubility of Salts in Potassium Hydroxide Solutions at $t = 20°$.

C_{KOH}.	KCl.	KBr.	KI.	KNO_3.	$KClO_3$.	KIO_3.
4.71	1.605	...	...	0.847	0.0924	0.0390
5.06	...	...	...	...	0.0882	0.0362
6.35	...	...	...	...	0.0609	0.0256
7.90	0.712	1.012	...	0.455	....	....
7.95	...	...	...	0.450	0.0445	0.0179
8.60	...	...	...	...	0.0410	....
9.41	0.405	0.693	1.72	0.364	0.0351	0.0144
10.95	0.273	0.515	1.23	0.298	0.0287	0.0130
11.10	0.253	0.451	1.176	...	....	0.0128
12.19	0.191	0.348	0.933	0.271	0.0254	0.0131
12.92	0.168	0.306	0.824	...	....	0.0135
13.84	0.138	0.247	...	...	....	....
14.02	0.136	0.246	0.672	0.241	0.0215	0.0154
14.85	0.121	0.214	...	0.232	0.0195	0.0194
15.02	0.118	0.210	0.558	0.233	0.0191	....

The solubility products P are calculated from these data, for instance for potassium chloride as $P = C_{KCl}(C_{KOH} + C_{KCl})$. The ratios of the products appear in the next table.

TABLE II.

Ratios of the Solubility Products of Salts in Potassium Hydroxide Solutions at $t = 20°$.

C_{KOH}.	$\frac{KBr}{KCl}$.	$\frac{KI}{KCl}$.	$\frac{KNO_3}{KCl}$.	$\frac{KNO_3}{KClO_3}$.	$\frac{KIO_3}{KClO_3}$.
4.71	....	....	0.457	10.6	2.39
5.06	....	....	....	....	2.42
6.35	....	....	....	....	2.40
7.90	1.67	....	0.622	....	....
7.95	....	....	....	10.6	2.49
9.41	1.76	4.76	0.898	10.8	2.44
10.95	1.77	4.92	1.100	10.6	2.22
11.10	1.82	4.96	....	....	....
12.19	1.83	5.15	1.42	10.9	1.94
12.92	1.84	5.14	....	....	....
13.84	1.80	....	....	....	....
14.02	1.83	5.15	1.81	11.5	1.40
14.85	1.80	....	1.93	12.1	1.02
15.02	1.80	4.89	2.00	12.4	....

Inspection of these figures shows that 4 of the 5 ratios actually do exhibit constant values over considerable ranges of concentrations.

Since all of the saturating salts are anhydrous in the solid state, Equation 5 can be written for this case

$$\frac{P_1}{P_2} = \frac{k_1}{k_2} \cdot \xi^{n_1 - n_2}. \qquad (7)$$

For the most dilute solutions of the solvent this ratio cannot be expected to give constant values in the case of the more soluble salts. As soon as the solubility is sufficiently diminished the ratio is found to be quite constant for the halides. Since the water activity ξ changes largely in this region of concentrations this result requires $n_1 = n_2$. All of the halides, therefore, are hydrated to the same extent in solution. As a consequence of Equation 7 and 8 a slight difference in the degree of hydration has a very marked influence upon the solubility ratio, and the test furnished by these experiments for equal hydration of the ions Cl^-, Br^- and I^- must be considered, therefore, as a rather rigid one. From the constancy of P_1/P_2 in the case of the halides we are furthermore justified in concluding that our hypothesis concerning the equality of the activity coefficient holds good for these systems, because it may be considered as highly improbable that this simple result could be given by a compensation of independent effects.

The figures given in the last 2 columns furnish the expected constant values only in the more dilute solutions, and for KNO_3/KCl the values change throughout the whole range of concentrations. According to the ideas stated above, we are led to attempt an explanation of these deviations by the assumption of differently hydrated ions. For these calculations the water activity ξ occurring in Equation 7 must be known.

The water activity is closely connected with the vapor pressure and can with sufficient exactness be put equal to this. From Dieterici's[1] measurements of the vapor pressure of potassium hydroxide solutions at 0°, the following expression can be derived,

$$p = 1.18 - 0.059\,M - \frac{0.2}{M} \qquad (8)$$

where M is the molal concentration ($= C_{KOH}$ in Table II) and p is its vapor pressure. The expression holds good between $M = 5$ and $M = 15$, as shown by the figures in Table III.

TABLE III.

Activity of Water in KOH Solutions, Observed and Calculated by Means of Equation 8.

M.	Obs.	Cal.
4.52	0.85	0.85
6.55	0.75	0.75
10.2	0.56	0.55
14.0	0.336	0.334

We shall first consider the values of P_{KNO_3}/P_{KCl} exhibiting the greatest changes. If the increasing values of this ratio are to be interpreted as due to hydration, the chlorine ion must evidently contain more water combined with it than the nitrate ion. Calculation according to Equation 7 gives the following result:

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[1] *Wied. Ann. Physik*, 50, 47 (1893).

TABLE IV.

Ratio P_{KNO_3}/P_{KCl} = P_1/P_2, Water activity, and ξ, $n_1 - n_2$ in KOH Solutions of the Molal Concentration M.

M.	ξ.	P_1/P_2.	$n_2 - n_1$.
10.95	0.516	1.10	1.7
12.19	0.444	1.42	1.2
14.02	0.339	1.81	1.0
14.85	0.291	1.93	
15.02	0.282	2.00	1.0

In this table are considered only the stronger solutions of potassium hydroxide in which the solubility is sufficiently small. We see from these figures that the changes in P_1/P_2 are accounted for by assuming the chlorine ion to have combined with it one of two molecules of water more than the nitrate ion. That the number is not quite constant may be explained by the dehydrating power of the solvent, the measure of which is given by $1/\xi$. When this is the case, the assumption that the number of anhydrous ions is negligible in comparison with the number of hydrated ones of course does not hold true any longer and thus the calculation of $n_1 - n_2$ is uncertain. As the data do not, however, admit of more detailed calculations, we shall confine ourselves to emphasizing that only a small difference of one or two water molecules in the hydration of the two ions may suffice to explain the large change in the solubility ratios of the corresponding salts.

While the conclusion drawn from the constant solubility ratios must be considered as a rigorous one, as referred to above, other sources of deviations than diversities in the degrees of hydration may possibly be responsible for the deviations when dealing with systems furnishing varying solubility ratios as in the case of potassium chloride-potassium nitrate. As long as we are unacquainted with the true degrees of hydration of the ions it is difficult to decide whether or not secondary electric forces, etc., play a part in the phenomena observed.

From the constant values of the solubility ratio given in the last 2 columns of Table II we may argue, in analogy in the case of the halides, that the corresponding ions, NO_3^-, ClO_3^- and IO_3^- are equally hydrated and equally influenced electrically by the solvent at concentrations less than 10 M. The deviations appearing at higher concentrations may be explained by the dehydrating action of the solvent but are here looked upon as more likely due to the secondary electric influence which increases strongly in this region of concentrations. The action upon the three ions increases in the sequence ClO_3^-, NO_3^-, IO_3^-.

As a result of this investigation, we can affirm the necessity of dividing the series of salts here dealt with in 2 separate groups, namely, KCl, KBr, KI; and KNO_3, $KClO_3$, KIO_3—each comprehending salts of similar molecular structure. The salts in either of these groups exhibit similar behavior as solutes when compared together, thus permitting the inference that the salts belonging to the same group are hydrated to the same extent and equally acted upon by electric forces in the solvent within a very considerable domain of concentrations.

It may be added that the occurrence of constant solubility ratios in the case of easily soluble salts must be looked upon as an essential requirement for the carrying out of the thermodynamic calculations of affinities referred to in a previous paper.[1]

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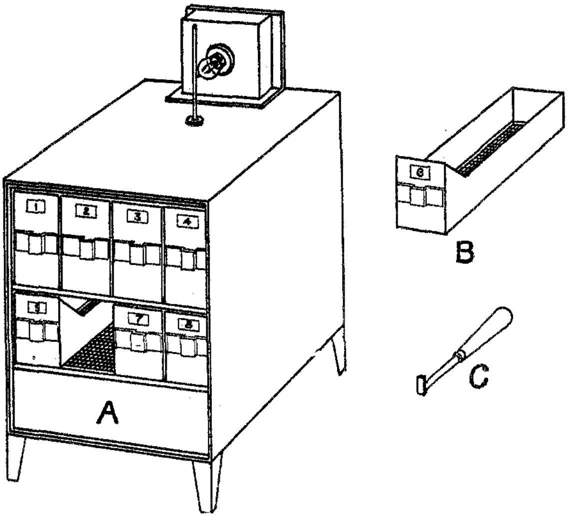
NOTES.

An Equipment for Drying Ovens.—The effective capacity of the ordinary drying oven can be increased from 5- to 10-fold by equipping it with metal drawers or trays as shown in the accompanying sketch. Each tray can hold a number of crucibles, small dishes or drying bottles, and because it is so easy to insert or withdraw one of the trays with its load without disturbing the others, the back part of the oven space is as available as the front. The supports of the trays are the wire mesh shelves of the oven; and to provide for the insertion of the thermometer in the usual way one tray should be made shorter than the others.

With the design as shown, the whole front of the oven is closed when all of the trays are in position. This is a decided advantage because with such an arrangement, opening the oven doors has little effect in decreasing the temperature, and since the withdrawal of one tray does not leave a large opening, and also because of the mass of hot metal of the remaining trays, the cooling is slight when objects are put into or taken out of the oven. The idea of keeping the front closed is carried still further by inserting a metal sheet at A to close the space below the first shelf.



The detail of a tray is shown at B. The bottoms are made of 12 mm. wire mesh to permit a free circulation of air throughout the interior of

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[1] *Medd. K. Vetenskapsakad. Nobelinst.*, 5, No. 25, 18 (1919).