weight of nitrogen tetroxide introduced into vessel AB was 0.01850 mole, followed by 0.01008 mole of carbon tetrachloride, giving a volume V of 2.11 ml., and containing 8.768 moles per liter of nitrogen tetroxide. The latter is the value for a in the expression $K_b = 4x^2/(a - x^2)$. This expression when solved for $x = 0.008674\sqrt{a}$. In this first experiment x equals 0.02568 mole of nitrogen tetroxide dissociated into nitrogen dioxide per liter of carbon tetrachloride solution.

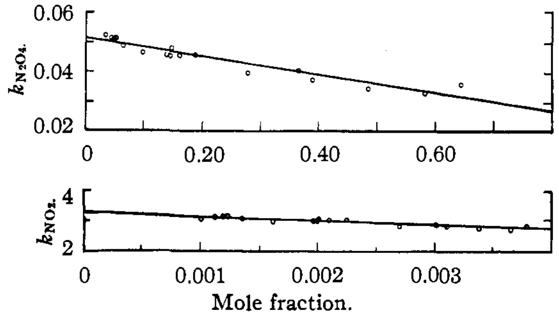

Fig. 3.

Consecutively, values for $(a-x)\ V$, $(a+x)\ V$ and $2xV$ are calculated, which are, respectively, the $N_{N_2O_4}$, $N_{N_2O_4} + N_{NO_2}$ and N_{NO_2} of the following equations. The values for N_{CCl_4} and C_{NO_2} are given in the table. Substituting into the following equations

$$C_{N_2O_4} = k\,\frac{N_{N_2O_4}}{N_{NO_2} + N_{N_2O_4} + N_{CCl_4}}$$

and

$$C_{NO_2} = k'\,\frac{N_{NO_2}}{N_{NO_2} + N_{N_2O_4} + N_{CCl_4}}$$

k is found to be 0.0359 and k' is 2.82.

The two curves, Fig. 3, are reproduced by the following equations obtained by the method of least squares

$$k = 0.05102 - (0.03011 \times N_{N_2O_4})$$
$$k' = 3.271 - (134.25 \times N_{NO_2})$$

The fact that k and k' of the experimental data are so nearly constant indicates that nitrogen tetroxide and nitrogen dioxide form almost ideal solutions in carbon tetrachloride.

Summary

1. The vapor density of nitrogen dioxide over its solutions with carbon tetrachloride at 25° has been measured colorimetrically.

2. A colorimetric method which may be applied to any colored gas or vapor has been described.

3. The constants for solutions of nitrogen tetroxide and nitrogen dioxide with carbon tetrachloride have been calculated and the solutions have been found to be nearly ideal.

UNIVERSITY, N. D. RECEIVED JUNE 21, 1937

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF YALE UNIVERSITY]

Solubility of Sodium and Potassium Chlorides in Corresponding Hydroxide Solutions at 25°

BY GÖSTA ÅKERLÖF AND OLIVER SHORT

Introduction

The solubilities of sodium and potassium hydroxide in water at 25° are about 28.3 and 21.2 molal, respectively. The studies of Freeth, Antropoff, Marcau and Sommer[1] and others have shown that in the presence of the corresponding chlorides the latter form solid phases up to near the hydroxide saturation concentration in pure water. In view of this unusually large concentration range for the existence of the chloride solid phases their solubility curves have been determined in order to study the applicability of the general solubility equation previously suggested by one of us to the data obtained. It appears that within the ordinary experimental errors the solubility curves follow very closely the equation required.

Experimental Procedure

A detailed description may be omitted since previously used methods were followed without any essential variations. The hydroxides employed were analytical reagents that appeared to contain only very faint traces of alkali halides or sulfates. In the case of sodium hydroxide a practically carbonate-free solution was obtained by allowing the saturated liquid to stand undisturbed for several weeks until all suspended matter had settled out. To the stirred, saturated solution of potassium hydroxide were added appropriate

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[1] Freeth, *Phil. Trans. Roy. Soc.*, **A223**, 35 (1932); Antropoff, Marcau and Sommer, *Z. Elektrochem.*, **30**, 457 (1924).

amounts of warm, concentrated barium hydroxide solution and the precipitate was allowed to settle for a week. The hydroxide concentration of the initial solution before the chlorides had been introduced was determined by neutralizing with an excess of hydrochloric acid and evaporating to dryness followed by a light ignition over a flame. The chloride concentration was determined likewise in the case of the more dilute hydroxide solutions by neutralizing the sample and weighing the dry residue. Assume that x, y and z are the weights of hydroxide, chloride and water, respectively, in the sample. Known quantities are the sample weight a, the total weight of chloride and hydroxide as chloride b, the ratio of the weights of hydroxide and water c. Solving for y and z we obtain

$$y = \frac{Rac - b(c + 1)}{c(R - 1) - 1}$$
$$z = \frac{b - a}{c(R - 1) - 1}$$

where R is 1.4620 and 1.3288 for sodium and potassium hydroxide solutions, respectively. The sum of y and z subtracted from a gives the amount of hydroxide present. At higher ionic strengths the chloride concentration was determined directly by precipitation as silver chloride. All solubility determinations were carried out in duplicate and the average accuracy of the results seems to be about 0.5%. The experimental data are summarized in Tables I and II, where all concentrations are expressed in moles per 1000 grams of water. Among the older data in the literature only those of Freeth for sodium hydroxide–chloride solutions approach ours closely but unfortunately the number of data given at 25° is very small. Particularly at higher hydroxide concentrations the data of Antropoff, Marcau and Sommer do not agree with ours even though they were obtained by smoothing a large number of measurements over a considerable temperature range.

TABLE I

EXPERIMENTAL DATA FOR THE SYSTEM SODIUM CHLORIDE–SODIUM HYDROXIDE–WATER AT 25° WITH THE CHLORIDE PRESENT AS SOLID PHASE

NaOH, *m*	NaCl, *m*	NaOH, *m*	NaCl, *m*
0.920	5.613	12.35	1.074
1.858	5.048	13.27	0.940
2.714	4.672	14.38	.781
3.070	4.486	15.20	.714
3.812	4.048	16.25	.580
4.798	3.610	17.32	.533
5.721	3.206	17.83	.492
6.688	2.635	19.30	.451
7.141	2.442	20.30	.421
8.031	2.173	21.05	.396
8.876	1.956	21.94	.371
9.824	1.588	22.82	.356
11.437	1.280	23.68	.350
11.582	1.253	23.56	.346

TABLE II

EXPERIMENTAL DATA FOR THE SYSTEM POTASSIUM CHLORIDE–POTASSIUM HYDROXIDE–WATER AT 25° WITH THE CHLORIDE PRESENT AS SOLID PHASE

KOH, *m*	KCl, *m*	KOH, *m*	KCl, *m*
1.023	4.079	8.37	0.894
1.053	4.056	9.43	.750
2.033	3.397	10.54	.638
2.126	3.365	11.28	.529
2.897	2.889	12.53	.433
3.150	2.778	13.42	.370
3.998	2.473	14.44	.311
4.102	2.265	15.53	.281
5.187	1.847	16.59	.247
5.273	1.839	18.42	.210
6.108	1.444	19.32	.198
6.203	1.576	20.64	.183
7.210	1.246	20.55	.184
7.211	1.175		

Equations for the Solubility Curves

In the deduction of the general solubility equation referred to above two assumptions were made that are not strictly valid although in the case of more concentrated solutions they appear to represent close approximations to the true conditions: first, that for strong electrolytes of the same valence type the ratios of the logarithms of their activity coefficients vary linearly with the concentration (k_1 value), second, that for two electrolytes present in mixed solutions of constant total ionic strength the logarithm of the activity coefficient of either one of them varies linearly with its concentration (k_2 value). Harned and Harris[2] have shown that for sodium and potassium hydroxide–chloride solutions the second assumption is not applicable. The curve for the logarithm of the activity coefficient of the hydroxides is not linear but has a decided curvature. Since in the case of the chlorides the same probably is true, it is necessary to apply a correction to the term in the original equation representing the second assumption. Introducing a linear correction term, we thus obtain the following general equation

$$\log \gamma_{R(\mu_T)} + k_1\mu_T + (k_2 + k_3(\mu_T - \mu_x))(\mu_T - \mu_x) + {}^1/_2 \log \mu_T + {}^1/_2 \log \mu_x = \log a \quad (1)$$

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(2) Harned and Harris, THIS JOURNAL, **50**, 2633 (1928).

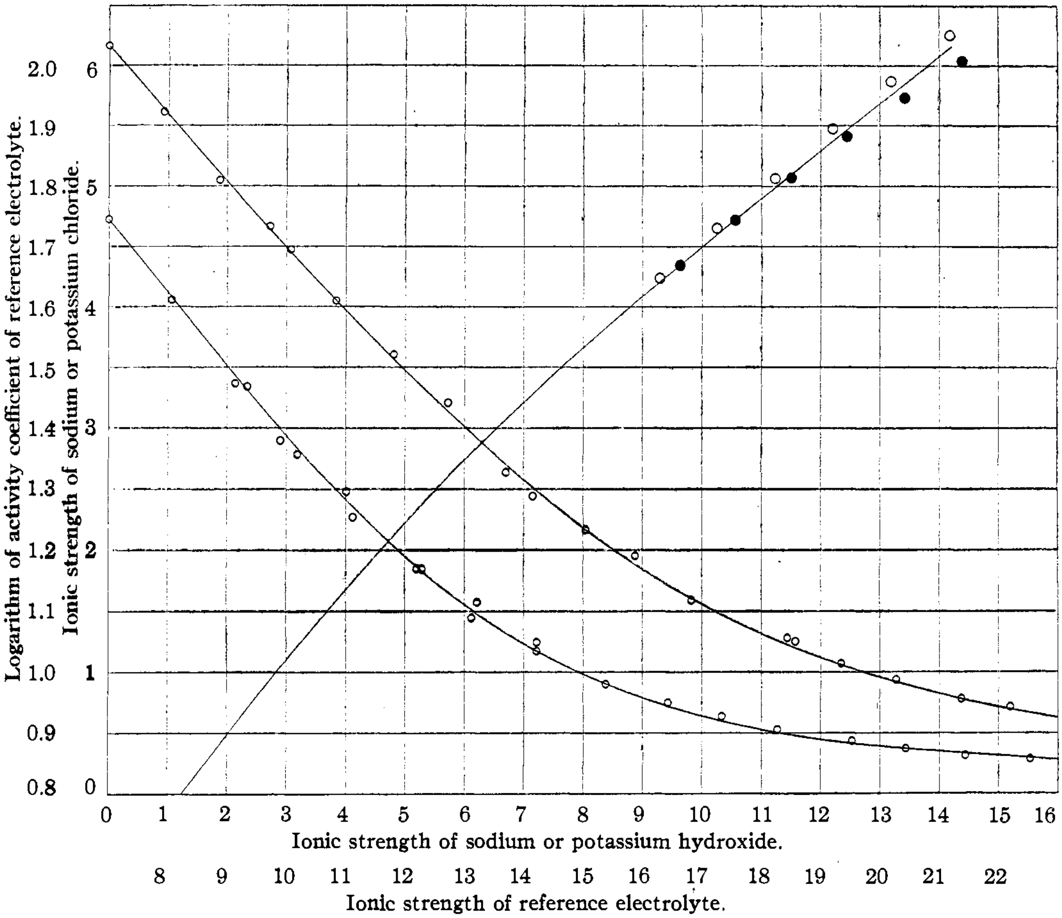

Fig. 1.—Calculated curves for the solubility of sodium and potassium chlorides in the corresponding hydroxide solutions at 25°.

where γ_R is the activity coefficient of the reference electrolyte, k_1, k_2 and k_3 empirical constants, μ_T the total ionic strength of the solution, μ_x the concentration of the electrolyte forming the solid phase and a the activity of the latter. Using hydrochloric acid as reference electrolyte and employing the data of Åkerlöf and Teare[3] we obtain from the known thermodynamic behavior of the chlorides and the experimental results given in Tables I and II the following equations.

(A) Sodium chloride–sodium hydroxide solutions

$$\log \gamma_{HCl(\mu_T)} - 0.0875\,\mu_T - (0.0135 - 0.00105\,(\mu_T - \mu_x))(\mu_T - \mu_x) + {}^1/_2\,(\log \mu_T + \log \mu_x) = 0.7782 \quad (2)$$

(B) Potassium chloride–potassium hydroxide solutions

$$\log \gamma_{HCl(\mu_T)} - 0.1180\,\mu_T + (0.0128 + 0.00080\,(\mu_T - \mu_x))(\mu_T - \mu_x) + {}^1/_2\,(\log \mu_T + \log \mu_x) = 0.4621 \quad (3)$$

The activities of the solid phases were calculated using as values for their solubility in pure water at 25° 6.162 and 4.826 molal for sodium and potassium chloride, respectively.

Discussion of the Results

Plotting the values calculated for μ_x from equations (2) and (3) at various values of μ_T up to 16, the highest ionic strength at which directly measured values of the activity coefficient of the reference electrolyte are available, the curves shown in Fig. 1 are obtained. As clearly indicated by this figure the experimental data fit the calculated curves very closely. Therefore it may appear that it should be possible to turn the problem around and use the solubility data for solutions of ionic strengths higher than 16 to calculate the activity coefficient of the reference electrolyte. After proper interpolation to round concentrations, we obtain from the data in Tables I and II the following table for calculated values of the logarithm of the activity coefficient of hydrochloric acid. The agreement of the solu-

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(3) Åkerlöf and Teare, This Journal, 59, 1855 (1937).

μ_T	(1) NaCl-NaOH solutions	(2) KCl-KOH solutions	(3) Average of (1) and (2)	(4) E. m. f. data extrapolated
16	1.618	1.624	1.621	1.618
17	1.700	1.712	1.706	1.700
18	1.778	1.796	1.787	1.778
19	1.854	1.878	1.866	1.856
20	1.926	1.958	1.942	1.935
21	1.987	2.035	2.011	2.019

bility values with those obtained by extrapolation of the e. m. f. values of Åkerlöf and Teare is quite striking. Whether the differences between the values calculated from the solubility data are within the experimental errors is not entirely certain but we do believe it to be highly probable since any inaccuracy in the constants employed for their computation magnifies the error in direct ratio to the increase in ionic strength. It may therefore appear to be justifiable to draw the conclusion that the equation given by Åkerlöf and Teare for the calculation of the logarithm of the activity coefficient of hydrochloric acid may be relied upon to produce values of fairly high accuracy for solutions up to 20 molal.

Equations identical in form with those employed for the chloride–hydroxide solutions apparently may be used in a large number of similar cases. Table III gives a summary of the constants obtained from a large number of our own solubility determinations and data in Volume IV of "Int. Crit. Tables" for some of the systems studied. The variation of the k_2 values relative to the k_1 constants follows in general the simple relationships previously found.[4] However, in several cases the deviations are too large to be explained by experimental errors although they also may be caused by the k_3 term.

TABLE III

SUMMARY OF SOLUBILITY CONSTANTS OF VARIOUS SYSTEMS CALCULATED ACCORDING TO EQUATION (1)

System	Solid phase	log a	k_1	k_2	k_3
$NaCl$–$NaNO_3$–H_2O	$NaCl$	0.7782	−0.0875	−0.0466	0.0022
	$NaNO_3$	.4830	− .154	.0189	.0013
KCl–KNO_3–H_2O	KCl	.4621	− .118	− .0600	.0054
	KNO_3	− .0365	− .220	.0570	− .00104
$NaNO_3$–$NaOH$–H_2O	$NaNO_3$	.4830	− .154	.0174	.0018
KNO_3–KOH–H_2O	KNO_3	− .0365	− .220	.0217	.0090
$NaCl$–$NaOH$–H_2O	$NaCl$	.7782	− .0875	− .0135	.00105
KCl–KOH–H_2O	KCl	.4621	− .118	.0128	.00080

Summary

The 25° isotherms for the systems $NaCl$–$NaOH$–H_2O and KCl–KOH–H_2O have been determined with the chlorides present as solid phases. The solubility curves may be calculated accurately using formulas derived from a general solubility equation. The constants needed to calculate the solubility curves at 25° for sodium and potassium nitrate in solutions of the corresponding hydroxides and chlorides and for the chlorides in solutions of the nitrates have also been evaluated.

NEW HAVEN, CONN. RECEIVED JULY 14, 1937

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[4] Åkerlöf, THIS JOURNAL, **56**, 1439 (1934).