fluoride was studied in the following manner. A small copper reaction vessel with a Hoke valve was provided, maintained at constant temperature, and aliquot amounts of the gas phase were pumped off at various intervals, the total pressure of the system and the loss in weight of the reaction vessel being determined. The temperature was kept constant at 15.0°. The over-all results obtained are shown in Fig. 2.

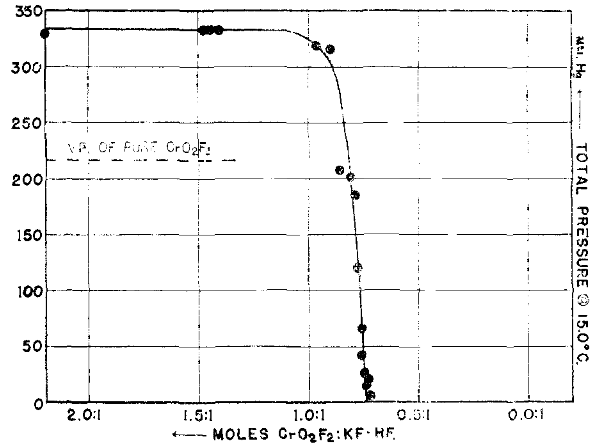

Fig. 2.—System CrO_2F_2 + KF,HF at 15.0°.

The HF content of the potassium bifluoride was determined by alkali titration of a sample; it proved to be 97% KHF_2. Chromyl fluoride was condensed over this pure bifluoride in a molar ratio $2.2CrO_2F_2{:}1KHF_2$. In the initial part of the curve the vapor pressure was appreciably above the vapor pressure of pure chromyl fluoride, indicating that a more volatile constituent was being pumped off simultaneously with the chromyl fluoride. This volatile constituent proved to be hydrogen fluoride. This quantity corresponded to a decrease of about 0.2 to 0.25 mole of hydrogen fluoride per mole of the original KHF_2 as determined by titration. The pressure of the system decreased rapidly at a molar ratio of about 1:1 to about 0.8:1 and reached a value of below 4 mm. at 0.75:1. The composition of the yellow residue was determined by titrating the chromyl fluoride iodometrically and the total acidity by titration with alkali. The ratio CrO_2F_2:HF = 1:0.97. Thus the final mixture contained the compound KF·HF·CrO_2F_2 and about 20 mole % of KF due to loss of HF indicated above.

Analysis of CrO_2F_2.—The following procedure was found convenient. The sample was sublimed into a dry and fresh Kel-F tube, the tube sealed by means of hot tongs (≃ 200°), and weighed. All the chromyl fluoride was then sublimed into one end of the tube by cooling in Dry Ice and the other end cut off with a razor blade and the sample tube quickly inserted into a glass stoppered erlenmeyer flask containing an excess of standard alkali. After complete hydrolysis had taken place, *i.e.*, when all the red crystals had disappeared, forming a pale yellow solution of chromic acid, the Kel-F tube was thoroughly rinsed out with distilled water, all washings added to the hydrolysate, diluted to a desired volume and titrated in the usual manner. The Kel-F tube was dried and weighed with the tip, thus giving the weight of the sample by difference.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY]

A Study of the Solubility Limits at 35° in the System NaBr–NaCl

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RECEIVED JANUARY 17, 1952

A study of the ternary system sodium bromide–sodium chloride–6.6 molal sodium hydroxide at 35° shows that the two salts form a continuous series of solid solutions with no miscibility gap. This experimental result is in disagreement with the calculations of Fineman and Wallace and of Hovi and Hyvönen which indicate limited miscibility below 50° in the binary system sodium bromide–sodium chloride.

Recent thermodynamic and statistical calculations by Fineman and Wallace[2] and by Hovi and Hyvönen[3] have indicated limited miscibility below 50° in the binary system sodium bromide–sodium chloride. The former investigators report an upper consolute point at 341°K. and 0.45 mole fraction of sodium bromide, while the latter estimate a critical solution temperature of 323°K. Both estimates are based upon the nature of the free energy *vs.* composition isotherms for the system. To establish experimentally the existence of any miscibility limits in this system below the reported critical solution temperatures, a study has been made of the ternary system sodium bromide–sodium chloride–6.6 molal sodium hydroxide at 35°. An examination of the phases present at equilibrium in this system showed the absence of any solid phase solubility limits.

Experimental

Choice of Solvent.—Water, the most convenient solvent for a study of this kind, could not be used because below 50.2° sodium bromide crystallizes from water as the dihydrate. Some solubility measurements were carried out in absolute methanol,[4] but the rate of attainment of equilibrium in the solid phase was prohibitively slow. X-Ray examination[5] of the solids present after the pure salts had been agitated for several months in contact with methanol showed, in most cases, the presence of two phases, one a bromide-rich solid solution and the other pure sodium chloride. These results are in qualitative agreement with the observations of Matsen and Beach,[6] who found that at elevated temperatures in the binary system the solution process occurs by the incorporation of chloride ions into the sodium bromide lattice and not *vice versa*.

Solubility data of Nikolajew and Rawitch[7] show that sodium bromide crystallizes in the anhydrous condition at room temperature from concentrated sodium hydroxide solutions. These data and those of Schreinemakers for sodium chloride[8] indicate that at 35° the solubilities of

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[1] General Electric Research Laboratory, Schenectady, N. Y.

[2] M. A. Fineman and W. E. Wallace, THIS JOURNAL, **70**, 4165 (1948).

[3] V. Hovi and L. Hyvönen, *Ann. Acad. Sci. Fennica, Math.-Phys., Ser. A*, 106 (1951).

[4] Measurements made by Dr. S. E. Blum, formerly of this Laboratory.

[5] We are indebted to Dr. S. Weissman and the late Dr. A. J. Reis of the Engineering Experiment Station, Rutgers University, for their assistance in the X-ray examination of the solids crystallized from methanol.

[6] F. A. Matsen and J. Y. Beach, THIS JOURNAL, **63**, 3470 (1941).

[7] V. I. Nikolajew and M. I. Rawitch, *Zhur. Obs. Khim.*, **1**, 789 (1931), reported in Seidell, "Solubilities of Inorganic and Metal Organic Compounds," Vol. I, D. Van Nostrand Co., Inc., New York, N. Y., 1940, p. 1156.

[8] F. A. H. Schreinemakers, *Z. physik. Chem.*, **68**, 83 (1910).

these salts in 6–7 molal sodium hydroxide should be about 35 and 12 weight per cent., respectively.

Experimental Procedure.—C.P. NaCl was used without further purification. Baker C.P. analyzed grade NaBr, found to contain 0.08% NaCl, was dried by fusion and then ground and stored at 120°. The solvent, 6.611 molal NaOH, was prepared from C.P. carbonate-free material. Mixtures of the components were brought to equilibrium by rotation at 34.95 ± 0.05° in rubber-stoppered polyethylene bottles containing stainless steel balls to keep the solids well ground. The sampling and analysis of the saturated liquid solutions were carried out as described previously.[9] The solutions were neutralized with nitric acid before analysis.

The compositions of the equilibrium solid phases were obtained by an examination of their X-ray powder diffraction patterns. A slurry of the solid material was removed from a solubility bottle by pipet, filtered rapidly through a small buchner funnel, washed with 10 ml. of petroleum ether and dried in an oven at 120°.[10] The dried, solid agglomerate was broken up in a heated mortar and then added to a warm, thin-walled Pyrex capillary tube which was sealed in the flame of a micro-burner. The filling was carried out in an atmosphere of carbon dioxide.

X-Ray diffraction patterns were made with a Debye–Scherrer camera (360 mm. circumference) using nickel-filtered CuKα radiation. Exposure times of 5–8 hours were used. Calculations of the lattice constants from the resulting photographs were based upon the extrapolation method of Bradley and Jay.[11] Compositions were obtained from lattice constants using the data of Nickels, Fineman and Wallace.[12]

Six weeks of stirring was usually sufficient for the establishment of equilibrium, as indicated by constancy of liquid and, in some cases, solid analyses. As a further check on the attainment of equilibrium, several bottles were prepared by the method of duplicate complexes.[13]

Results.—The data are shown in Table I. When they are plotted on a triangular diagram, the solubility curve runs smoothly between the values for the pure salts, showing no isothermally invariant point. At equilibrium, all solids consisted of a single anhydrous phase. The direction of approach to equilibrium in the solid phase in this system was the same as that observed in the methanol study: the gradual incorporation of chloride ions into the bromide lattice. The distribution of the salts between liquid and solid phases is shown in Fig. 1 in which the mole fraction of sodium bromide in the dissolved salts (y) is plotted against its mole fraction in the solid solution (x). The system represents a markedly non-ideal distribution of the Roozeboom Type I[14] which at lower temperatures will probably display the limited miscibility of Types IV or V.

To show that the 35° miscibility limits calculated from the data of Fineman and Wallace[2] (30.3 and 81.8 weight per cent. sodium bromide) do not represent phases which are stable relative to solid solutions of intermediate compositions, the following experiment was performed. Two homogeneous solid solutions containing 28.2 and 83.7 weight per cent. sodium bromide were prepared by the method of Fineman and Wallace.[2] An intimate mechanical mixture of these two solid solutions was made having the over-all composition of 40.6 weight per cent. sodium bromide, the composition of the equilibrium solid phase in complex number 52. A sample of the wet solid from this complex was removed and replaced by an approximately equal weight of the mechanical mixture. The equilibrium relationships in bottle number 52 were thus disturbed by effectively converting one solid phase into three without appreciably changing the over-all composition ratios. After one month of stirring the solid was removed. X-Ray examination showed the presence of only one phase with a lattice constant of 5.715 Kx. units, compared with a value of 5.726 for the solid originally present in complex number 52. This corresponds to a solid phase composition change from 40.6 to 36.6 weight per cent. sodium bromide.

TABLE I

SYSTEM NaBr–NaCl–6.611 MOLAL NaOH AT 35°

Complex no.	Liquid solution Wt. % NaBr	Liquid solution Wt. % NaCl	Solid solution Lattice constants Kx. units	Solid solution Wt. % NaBr
50	37.03		5.959	100.00
66	35.86	0.70	5.928	93.2
70[a]	34.72	1.16	5.904	88.0
67[b]	34.75	1.23	5.890	84.9
68	34.15	1.46	5.862	78.7
69	33.73	1.61	5.845	74.5
71	33.68	1.68	5.813	66.2
72	33.39	1.60	5.752	48.9
52	32.85	1.75	5.726	40.6
63[a]	30.82	2.06	5.679	22.9
53[b]	30.68	2.13	5.677	22.0
64[a]	29.00	2.46	5.662	15.9
54[b]	29.04	2.41	5.658	13.9
55	27.11	2.86	5.650	10.4
56	25.30	3.23	5.645	8.2
57	21.43	4.27	5.639	3.9
58	18.23	5.11	5.636	3.5
59	13.94	6.49	5.630	0.88
60	8.40	8.58	5.628	.0
61	3.60	10.49	5.628	.0
62		12.07	5.628	.0

[a] NaCl initial solid phase. (In complex 70 the NaBr content exceeded the 25° solubility of this salt so that in preparing the complex at room temperature a small amount of NaBr remained undissolved at the time the NaCl was added.) [b] NaBr initial solid phase.

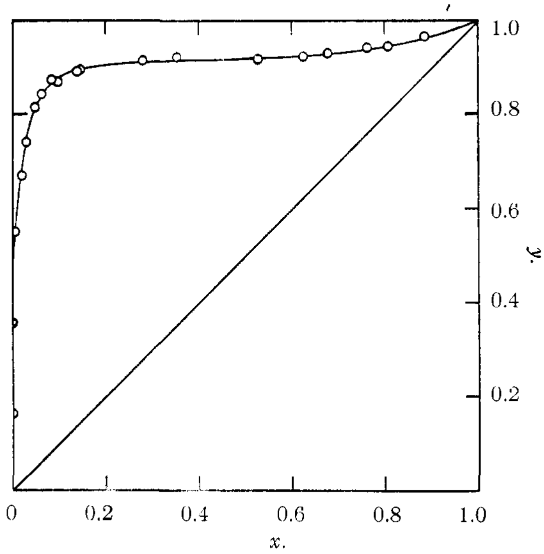

Fig. 1.—Distribution of NaBr and NaCl between liquid and solid solutions at 35°.

Discussion.—Although the results of this investigation, showing complete miscibility at 35° in the system sodium bromide–sodium chloride, are in disagreement with the predictions of Fineman and Wallace[2] and of Hovi and Hyvönen,[3] they do not point explicitly to the errors in the calculations of these workers. They indicate simply that the proposed free energy isotherms at 35° are incor-

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[9] E. L. Simons and S. E. Blum, THIS JOURNAL, **73**, 5717 (1951).

[10] Experiments with one solid solution and one intimate mixture of sodium bromide and sodium chloride showed that 24 hours of heating at 120° produced no change in the X-ray diffraction patterns of the solids.

[11] A. J. Bradley and A. H. Jay, *Proc. Phys. Soc.* (*London*), **44**, 563 (1932).

[12] J. E. Nickels, M. A. Fineman and W. E. Wallace, *J. Phys. Colloid Chem.*, **53**, 625 (1949).

[13] A. E. Hill and N. Kaplan, THIS JOURNAL, **60**, 550 (1938).

[14] B. Roozeboom, *Z. physik. Chem.*, **8**, 521 (1891).

rect, but they do not permit one to assess individually the accuracy of the entropy and enthalpy terms used in obtaining the free energy values.

Fineman and Wallace[2] assumed that the entropy of formation of the solid solution between 0 and 350°K. is the entropy of random mixing, while Hovi and Hyvönen[3] based their entropy calculations upon a postulated local order for the solid solution lattice. The enthalpy values used by the latter investigators were also calculated on the basis of their postulated lattice structure, while those used by Fineman and Wallace were determined experimentally on solids prepared by fusion of mixtures of the pure salts. Such experimental enthalpies may not be characteristic of the solid solutions in their equilibrium state at room temperature. In the potassium bromide–potassium chloride system Fontell and co-workers[15] have shown that the enthalpy determined calorimetrically at 25° for a 50 mole per cent. solid solution prepared by fusion is 10 cal. per mole higher than the value determined in the same manner for a preparation obtained by isothermal, isobaric crystallization from water (and therefore more nearly in a state of thermodynamic equilibrium at room temperature[16]). The sensitivity of the free energy isotherms to small changes in the enthalpy values is illustrated by Wallace and Fineman's recalculation[17] of the phase diagram for the potassium bromide–potassium chloride system originally proposed by Fontell[18] on the basis of his measurements of the heats of formation in this system. By choosing an analytical expression for the data which was statistically more satisfactory than the one used by Fontell (thus effectively altering Fontell's enthalpy values by amounts ranging up to 25 cal.) they obtained a critical solution temperature at 240°K. compared to Fontell's calculation of 398°K.

The calculations of both pairs of investigators are probably correct in predicting incomplete miscibility below about 250°K., but the uncertainties in the free energy values (arising from the enthalpy and entropy assumptions) make it difficult to establish with confidence a critical solution temperature. The results of this investigation indicate that, while partial miscibility is to be expected in this system, the critical solution temperature must lie below 308°K.

Acknowledgment.—The authors acknowledge with appreciation the support given to this investigation by the Rutgers University Research Council.

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[15] N. Fontell, V. Hovi and A. Mikkola, *Ann. Acad. Sci. Fennica, Math.-Phys.*, **Ser. A**, 54 (1949).

[16] J. A. Wasastjerna, *Soc. Sci. Fennica Commentationes Phys.-Math.*, **15**, No. 3 (1949).

[17] W. E. Wallace and M. A. Fineman, *ibid.*, **14**, No. 6 (1948).

[18] N. Fontell, *ibid.*, **10**, No. 12 (1939).

SCHENECTADY, NEW YORK

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE GEORGIA INSTITUTE OF TECHNOLOGY]

The Relative Acidity of Water, Methanol and Other Weak Acids in Isopropyl Alcohol Solution[1]

BY JACK HINE AND MILDRED HINE

RECEIVED APRIL 30, 1952

The relative acidity of five indicators is determined in isopropyl alcohol solution. By use of one, 4-nitrodiphenylamine, the acidity of about thirty-five alcohols and amides is determined. Methanol is found to be more acidic than water. This, and the decrease in basicity resulting from the successive substitution of alkyl groups for the hydrogen atoms of water is explained in terms of "B-strain" and electronic effects. The relative effect of various R groups on the acidity of several functional groups and the effect of solvent changes on the relative strength of acids are also discussed.

Introduction

In relation to an investigation of the mechanism of the basic hydrolysis of chloroform,[2] it was found that the reaction proceeded much more slowly in methanolic solution than in water or aqueous dioxane. There are several other reactions proceeding by the mechanism

$$\mathrm{HA} + \mathrm{B}^- \overset{\text{fast}}{\rightleftarrows} \mathrm{A}^- + \mathrm{HB}$$

$$\mathrm{A}^- \xrightarrow{\text{slow}} \text{products}$$

(where B^- is the conjugate base of the solvent) described in the literature which are also slowed by the addition of methanol to an aqueous reaction mixture. These include the formation of ethylene oxide from ethylene halohydrins[3] and the dealdolization of diacetone alcohol.[4] In none of the three cases mentioned is the effect due to the change in dielectric constant, since it is not shared by other low dielectric solvents such as dioxane, *t*-butyl alcohol and isopropyl alcohol. On the other hand, compounds such as ethylene glycol and glycerol, known to be somewhat more acidic than water,[5] have an effect similar to but somewhat larger than that of methanol. Stephens, McCabe and Warner[3] have suggested that their data may be explained by the postulate that methanol is a stronger acid than water.

By comparing the effect of 1 *M* methanol on the solubility of calcium hydroxide with its effect on

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[1] Presented, in a preliminary form, before the Section on Physical and Inorganic Chemistry of the XIIth International Congress of Pure and Applied Chemistry, New York, N. Y., Sept. 10–13, 1951.

[2] J. Hine, THIS JOURNAL, **72**, 2438 (1950).

[3] J. E. Stevens, C. L. McCabe and J. C. Warner, *ibid.*, **70**, 2449 (1948).

[4] G. Åkerlöf, *ibid.*, **50**, 1272 (1928).

[5] L. Michaelis, *Ber.*, **46**, 3683 (1913); L. Michaelis and P. Rona, *Biochem. Z.*, **49**, 232 (1913).