In order to ascertain whether or not the hydrolysis of a praseodymium solution varied similarly with age, the *p*H values of solutions of various concentrations and various ages were determined. The results are tabulated in Table VII. They indicate that there is no appreciable consistent variation with time in the hydrolysis of a praseodymium solution.

Summary

1. The polarographic behavior, hydrogen ion concentration and hydrolytic properties of praseodymium solutions were studied.
2. In contrast with the observations of Noddack and Brukl and in agreement with Heyrovsky and Kolthoff and Lingane, only a single reduction step was observed in the polarographic reduction of the trivalent praseodymium ion.
3. The corrected half-wave potentials for the praseodymium ion were found to be: (a) with no suppressor or supporting electrolyte: -2.06 for 20 millimolar, -2.04 for 10 millimolar and -1.89 for 2 millimolar: (b) with supporting electrolyte and suppressor: -1.84 for 9 millimolar in 1 *M* lithium chloride, -1.94 for 20 millimolar in 0.1 *M* lithium chloride, -1.96 for 20 millimolar in 0.1 *M* $(CH_3)_4NI$, -1.95 for 20 millimolar and 0.1 *N* lithium chloride at *p*H of 5.88 and -1.96 for 20 millimolar and 0.1 *M* lithium chloride and at a *p*H of 3.08.
4. The half-wave potential varied with the concentration, becoming more electronegative with an increase in concentration.
5. The half-wave potential varied with the *p*H. The lower the *p*H value the more electronegative the half-wave value became.
6. The *p*H of a praseodymium salt solution was found to be independent of age.
7. The degree of hydrolysis of praseodymium salt solutions of various concentrations was determined.
8. It was found that when the praseodymium ion was reduced it underwent a three electron change directly to the metallic state.

IOWA CITY, IOWA RECEIVED NOVEMBER 15, 1948

[CONTRIBUTION FROM THE WILLIAM ALBERT NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

The Ternary System: Hydrazine–Water–Sodium Hydroxide

BY R. A. PENNEMAN[1] AND L. F. AUDRIETH

The hydrazine–water system exhibits a maximum boiling point at 120.1° (760 mm.) corresponding to a composition containing 58.5 mole per cent. hydrazine and 41.5 mole per cent. water[2] (71.5% and 28.5% by weight, respectively). The removal of water by fractional distillation from very dilute hydrazine solutions, such as are obtained in the Raschig synthesis, is effective only until the maximum boiling composition is reached. In practice, however, concentration by this method is continued only until a product containing about 85% hydrazine hydrate (54.4% N_2H_4 by weight) is obtained. To concentrate hydrazine beyond this stage it is customary to distil from such dehydrating agents as barium oxide,[3] sodium hydroxide,[4] or potassium hydroxide.[5]

In the course of experimental work on the preparation of anhydrous hydrazine it was found that certain mixtures of 85% hydrazine hydrate and sodium hydroxide form two liquid phases when heated above approximately 60°. This observation suggested the possibility of concentrating hydrazine by removal of the hydrazine-rich phase. Since this phenomenon had not been reported previously, a quantitative investigation was made of the hydrazine–water–sodium hydroxide system as a function of temperature in the range 50–100°. In addition, hydrazine, water, and (a) potassium hydroxide and (b) potassium carbonate were studied quantitatively at 50°. A qualitative study using still other compounds was carried out in an unsuccessful attempt to find another ternary hydrazine system separating into two liquid phases in the temperature range from 25–100°.

To undertake investigation of the ternary system, hydrazine–water–sodium hydroxide, it was necessary to devise an analytical method for the determination of hydrazine and sodium hydroxide in the presence of each other. Certain precautions, described in the experimental portion of this paper, were necessary to prevent oxidation of hydrazine by atmospheric oxygen during sampling and analysis and to eliminate operational hazards since hydrazine vapor has been found to explode by sparking at 100°.[6]

Experimental

Apparatus.—The equilibrium studies were conducted in a nitrogen atmosphere (to prevent air oxidation) using a closed Pyrex cell (18 × 2.5 cm.) with vigorous internal stirring accomplished by means of a solenoid stirrer similar to one used by Booth and Martin.[7] Stanolind mineral

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(1) Present address: Los Alamos Scientific Laboratory, Los Alamos, N. M.

(2) De Bruyn and Dito, *Akad. Amsterdam Versl.*, **11**, 155 (1902/1903); Gmelin-Kraut, "Handbuch der anorganischen Chemie," Vol. 23, Ed. VIII, Verlag Chemie, Berlin, 1936, p. 548.

(3) Hale and Shetterly, THIS JOURNAL, **33**, 1071 (1911); Giguere and Rundle, *ibid.*, **63**, 1135 (1941).

(4) Raschig, *Ber.*, **43**, 1927 (1910).

(5) Wenner and Beckman, THIS JOURNAL, **54**, 2787 (1932).

(6) Bamford, *Trans. Faraday Soc.*, **35**, 1239 (1939).

(7) Booth and Martin, *Ind. Eng. Chem., Anal. Ed.*, **17**, 528 (1945).

oil, U. S. P. heavy grade, was used as the heating bath liquid. The temperature of the bath was controlled to ±0.1° using a continuous heater in conjunction with a relay unit and an auxiliary heater in intermittent operation. The bath temperature was read from a calibrated thermometer graduated in 0.1° divisions.

Analytical Procedure.—Preliminary experimental work had demonstrated that analytical methods involving oxidation of hydrazine to nitrogen using either the direct iodimetric procedure[8] or titration with standard iodate[9] were capable of high accuracy. The iodate method with a few drops of a 0.2% solution of amaranth dye as internal indicator was used for most of the hydrazine analyses.[9,10] Total base (hydrazine and sodium hydroxide) was determined beforehand on the same sample by titration with 0.5 *N* HCl, using either methyl orange or methyl red as an indicator and titrating to the color of a *p*H 4–4.5 buffer.[11]

Since equilibrium studies were carried out at temperatures higher than room temperature, sampling procedures were devised (1) to permit sampling at the bath temperature, (2) to protect the sample from oxygen, moisture, and carbon dioxide, (3) to permit sampling of the lower phase without contamination from the upper phase and (4) to prevent sample loss or change on cooling to room temperature. A nitrogen atmosphere was maintained over the equilibrium mixture. Sampling was accomplished by means of thin glass pipets blown from 3 mm. tubing and drawn out to capillary ends. These pipets had a capacity of about 1 ml. and were accurately weighed before use. They were attached to, and then filled by a 1-ml. hypodermic syringe. The pipet containing the sample was weighed and then crushed beneath the surface of 50 ml. of boiled water in a nitrogen atmosphere and titrated immediately with 0.5 *N* HCl to the methyl orange end-point. Thereafter, an aliquot (in 5 *N* HCl) was titrated with 0.1000 *M* KIO_3. When a sample of the lower phase was taken, the plunger of the syringe was depressed slowly as the end of the pipet was lowered through the upper phase, causing a tiny stream of bubbles to leave the capillary tip, thus preventing any of the upper phase from entering. When the pipet had reached the temperature of the bath, the hypodermic plunger was slowly withdrawn, filling the pipet with liquid. The pipet was then removed, the outside cleaned and allowed to cool to room temperature prior to weighing. Data bracketed in Table I represent examples of analytical results for duplicate samples and for samples taken at one-half to one hour intervals, demonstrating (1) that analytical and sampling methods were of satisfactory reproducibility, and (2) that equilibrium in the liquid system was reached rapidly. Analytical results in duplicate samples show maximum deviations of ±0.1% for hydrazine and ±0.2% for sodium hydroxide. Since values for the percentages of water were determined by difference, they are not included in the following tables.

The System: N_2H_4–H_2O–NaOH

The ternary system N_2H_4–H_2O–NaOH was studied at 50, 60, 70, 90 and 100°. Experimental runs were carried out by adding sodium hydroxide, water and hydrazine to the cell and stirring until equilibrium had been achieved. Samples of the two liquid phases were then taken and analyzed using the techniques described above. An additional amount of some one component was then added and a new set of samples taken. Equilibrium in the case of the binary liquids was reached rapidly, as demonstrated by analyses made at hourly intervals. To assure the attainment of equilibrium in case of the triple points, where a solid phase is present, duplicate and triplicate analyses were performed after consecutive additions of either hydrazine or sodium hydroxide in sufficient amount to alter perceptibly the amount of the precipitated phase. This could be done most conveniently by the addition

TABLE I

SYSTEM: HYDRAZINE–WATER–SODIUM HYDROXIDE

Temp., °C.	Lower liquid (L_1), % N_2H_4	Lower liquid (L_1), % NaOH	Upper liquid (L_2), % N_2H_4	Upper liquid (L_2), % NaOH	Phases
100	5.7	70.3	92.7	2.4	$L_1 + L_2$ + NaOH
	6.3	69.7	[c]	[c]	$L_1 + L_2$
	9.2	62.9	87.5	3.0	$L_1 + L_2$
	15.5	54.4	80.6	6.4	$L_1 + L_2$
	23.2	46.1	70.6	11.6	$L_1 + L_2$
	32.9	37.8	59.0	19.1	$L_1 + L_2$
	45.9	27.9	45.9	27.9	Plait point[a]
90			98.1	0.1	Satd. liq. + NaOH
	..	[d]	93.0	1.2	Satd. liq. + NaOH
	..	[d]	92.9	0.9	Satd. liq. + NaOH
	5.9	69.3	92.2	2.0	$L_1 + L_2$ + NaOH
	6.4	68.4	91.6	2.1	$L_1 + L_2$
	..	[c]	90.8	2.3	$L_1 + L_2$
	7.8	65.2	89.5	2.6	$L_1 + L_2$
	9.3	62.8	87.7	3.4	$L_1 + L_2$
	15.9	54.2	..	[c]	$L_1 + L_2$
	16.6	53.4	..	[c]	$L_1 + L_2$
	18.0	51.8	..	[c]	$L_1 + L_2$
	19.9	49.8	75.1	9.2	$L_1 + L_2$
	21.0	48.6	..	[c]	$L_1 + L_2$
	21.9	47.8	72.6	10.8	$L_1 + L_2$
	25.3	44.9	68.9	12.6	$L_1 + L_2$
	35.0	36.9	57.0	20.8	$L_1 + L_2$
	45.6	28.2	45.6	28.2	Plait point[a]
70	6.7	67.6	90.9	3.2	$L_1 + L_2$ + NaOH
	6.8	66.9	..	[c]	$L_1 + L_2$
	{7.8	65.2	{90.0	2.4	$L_1 + L_2$
	{7.8	65.4	{90.0	2.5	$L_1 + L_2$
	9.0	63.0	87.9	3.6	$L_1 + L_2$
	15.2	54.9	..	[c]	$L_1 + L_2$
	17.5	52.0	78.0	8.0	$L_1 + L_2$
	{23.6	45.8	{70.5	12.2	$L_1 + L_2$
	{23.8	45.8	{70.4	12.0	$L_1 + L_2$
	33.6	37.5	57.7	20.1	$L_1 + L_2$
	45.4	28.5	45.4	28.5	Plait point[a]
60	..	[d]	92.6	1.8	Satd. liq. + NaOH
			{91.4	2.0	Satd. liq. + NaOH + NaOH·H_2O
			{91.4	2.3	Satd. liq. + NaOH + NaOH·H_2O
			{91.6	2.3	Satd. liq. + NaOH + NaOH·H_2O
	R(52.0	31.4)[b]	90.0	3.0	L_2 + NaOH·H_2O
	..	[d]	79.6	7.8	L_2 + NaOH·H_2O
	{19.0	51.2	{77.4	8.9	$L_1 + L_2$ + NaOH·H_2O
	{19.0	51.4	{77.5	9.3	$L_1 + L_2$ + NaOH·H_2O
	22.9	47.4	71.7	12.3	$L_1 + L_2$
	{36.7	36.3	55.8	22.7	$L_1 + L_2$
	{36.8	36.2	..	[c]	$L_1 + L_2$
	45.5	29.6	45.5	29.6	Plait point[a]
50	..	[d]	94.0	1.5	Satd. liq. + NaOH·H_2O
	R(46.2	35.9)[b]	93.1	1.7	Satd. liq. + NaOH·H_2O
	..	[d]	87.8	3.7	Satd. liq. + NaOH·H_2O
	R(51.4	30.5)[b]	83.1	7.4	Satd. liq. + NaOH·H_2O
	..	[d]	60.0	17.2	Satd. liq. + NaOH·H_2O
		[d]	45.9	26.2	Satd. liq. + NaOH·H_2O
		[d]	39.3	29.4	Satd. liq. + NaOH·H_2O
		[d]	23.1	40.4	Satd. liq. + NaOH·H_2O

[a] By interpolation: see "International Critical Tables," Vol. III, Ed. 1, McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p. 398. [b] Data preceded by R represent compositions of wet solids for application of Schreinemakers' method, reference 12. [c] Values not determined. [d] Only one liquid phase present.

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(8) Kolthoff, THIS JOURNAL, **46**, 2650 (1924).

(9) Smith and Wilcox, *Ind. Eng. Chem., Anal. Ed.*, **14**, 49 (1942).

(10) Penneman and Audrieth, *Anal. Chem.*, **20**, 1058 (1948).

(11) Gilbert, THIS JOURNAL, **46**, 2650 (1942).

of anhydrous hydrazine, causing a marked increase in the amount of precipitated solid without changing the analysis of the three components in equilibrium. An alternate procedure was to heat the mixture until all solids had dissolved and then cool it to the operating temperature, whereupon the excess solid would precipitate.

Data for this system at 100° are presented in Table I and are depicted graphically in Fig. 1.

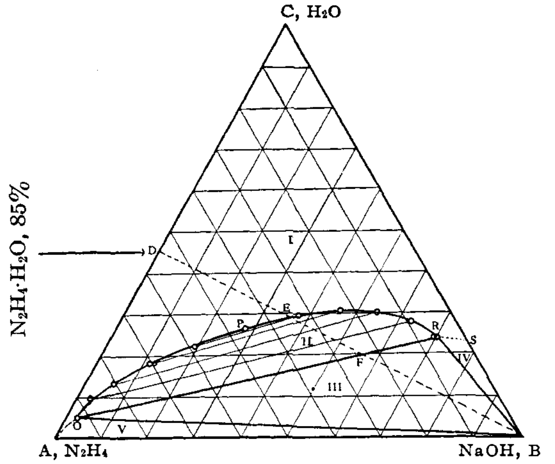

Fig. 1.—System N_2H_4–H_2O–NaOH at 100° (coördinates in wt. per cent. of components): field I, region of complete miscibility; II, region of two liquid phases; III, region of two liquid phases with compositions represented by "O" and "R" in equilibrium with solid NaOH; IV, solid NaOH in equilibrium with liquid RS; V, solid NaOH in equilibrium with liquid OR; "P," plait point.

One important reason for undertaking a study of the ternary system, N_2H_4–H_2O–NaOH, was to determine if concentration of hydrazine could be effected by separation of a hydrazine-rich phase. Since 85% $N_2N_4\cdot H_2O$ is a commercially available material, the effect of adding increasing amounts of sodium hydroxide to it is discussed in terms of the data presented graphically in Fig. 1. The 85% hydrate material is represented by the point "D," and the line DB represents changes which occur as increasing amounts of sodium hydroxide are added to composition "D." Compositions represented by the line DE up to the point where it intersects the binodal curve OPR at "E" consist only of a liquid phase. The interval EF represents compositions which separate into two conjugate liquid phases. Over the interval FB the two conjugate liquid phases "O" and "R" are present together with solid sodium hydroxide. If the addition of sodium hydroxide is stopped at point F, the over-all composition corresponds to 20% H_2O, 24% N_2H_4 and 56% NaOH. According to the lever rule, 100 g. of such a mixture would separate into the two liquid phases, O and R, in the ratio 79 g. of lower phase and 21 g. of upper phase. Since the hydrazine contents of the upper and lower phases are 92.7% N_2H_4, and 5.7% N_2H_4, respectively, 19.5 g. (81.2% of the total hydrazine) is present in the upper phase along with 0.5 g. of NaOH and 1.0 g. of water.

The shape of the binodal curve OPR changes only very slightly over the temperature range from 70 to 100°. Data for the isotherms at 70 and 90° are also presented in Table I.

At 60°, the system is more complex because of the appearance of the stable solid phase, $NaOH\cdot H_2O$, m. p., 64.3°. Data for the system at this temperature are also included in Table I and depicted in Fig. 2. It is interesting to note that there is a pronounced decrease in the extent of the binodal curve at 60°. The compositions of the solid phases, NaOH and $NaOH\cdot H_2O$ were determined by applying the "wet residue" method of Schreinemakers.[12]

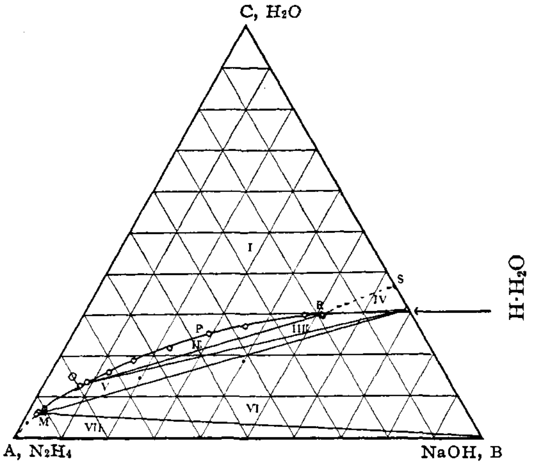

Fig. 2.—System N_2H_4–H_2O–NaOH at 60° (coördinates in weight per cent. of components): field I, region of complete miscibility; II, region of two liquid phases; III, two liquid phases, "O" and "R" in equilibrium with solid $NaOH\cdot H_2O$; IV, solid $NaOH\cdot H_2O$ and liquid RS; V, solid $NaOH\cdot H_2O$ and liquid OM; VI, liquid "M" in equilibrium with solid NaOH and $NaOH\cdot H_2O$; VII, solid NaOH and liquid AM.

Investigation of the ternary system at 50° showed that the two-liquid phase region does not exist at this temperature; relationships are represented by a simple solubility curve. Data are included in Table I. The analysis of samples taken at 50° was complicated by the gelatinous nature of the $NaOH\cdot H_2O$ precipitate. Because of the poor settling properties of the precipitate it was necessary to resort to another means of sampling the liquid phase. A piece of alundum extraction thimble was sealed into the end of a length of 6-mm. glass tubing. This tube was inserted into the slurry and the liquid was allowed to filter through the alundum into the hollow tube. A sample of this liquid was then taken using the pipet technique described previously.

Other Ternary Systems

The system N_2H_4–H_2O–KOH was investi-

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(12) Schreinemakers, *Z. physik. Chem.*, **25**, 305 (1898).

gated qualitatively over the temperature range 25–100°. No indication was found of a two liquid phase region. A quantitative study at 50° revealed the existence of a simple solubility curve with $KOH \cdot H_2O$ as the stable solid phase in equilibrium with the saturated solution. Data are given in Table II.

TABLE II

SYSTEM HYDRAZINE–WATER–POTASSIUM HYDROXIDE AT 50°

Liquid phase, % N_2H_4	KOH	Phases
91.9	1.8	Satd. liq. and $KOH \cdot H_2O$
68.8	12.8	Satd. liq. and $KOH \cdot H_2O$
(23.7	53.8)	Wet residue[12]
59.1	19.1	Satd. liq. and $KOH \cdot H_2O$
42.7	29.3	Satd. liq. and $KOH \cdot H_2O$
38.2	32.2	Satd. liq. and $KOH \cdot H_2O$
19.1	45.6	Satd. liq. and $KOH \cdot H_2O$
13.0	50.2	Satd. liq. and $KOH \cdot H_2O$
4.8	56.0	Satd. liq. and $KOH \cdot H_2O$

The system N_2H_4–H_2O–K_2CO_3 was also investigated qualitatively over the temperature range 25–100° in the search for conjugate liquid phases. Only one liquid phase was found. A quantitative investigation (data for which are given in Table III) was made at 50°. The solid phase in equilibrium with the saturated liquid was found to be $K_2CO_3 \cdot 3/2H_2O$ by Schreinemakers' wet residue method. The solubility of potassium carbonate drops off sharply as the concentration of hydrazine increases.

No indication of two conjugate liquid phases was observed in the temperature interval 25–100° using trisodium phosphate, sodium carbonate, sodium sulfate, potassium carbonate and potassium hydroxide.

TABLE III

SYSTEM HYDRAZINE–WATER–POTASSIUM CARBONATE AT 50°

Liquid phase, % N_2H_4	K_2CO_3	Phases
97.0	0.6	Satd. liq. + $K_2CO_3 \cdot 3/2H_2O$
69.8	2.7	Satd. liq. + $K_2CO_3 \cdot 3/2H_2O$
(27.7	51.7)	Wet residue[12]
53.4	6.0	Satd. liq. + $K_2CO_3 \cdot 3/2H_2O$
40.5	14.3	Satd. liq. + $K_2CO_3 \cdot 3/2H_2O$
28.7	25.0	Satd. liq. + $K_2CO_3 \cdot 3/2H_2O$
16.2	38.5	Satd. liq. + $K_2CO_3 \cdot 3/2H_2O$
7.6	47.9	Satd. liq. + $K_2CO_3 \cdot 3/2H_2O$

Summary

1. Phase relationships in the ternary system hydrazine–water–sodium hydroxide have been studied quantitatively at 50, 60, 70, 90, 100°. At temperatures above approximately 60° this system separates into two liquid phases within certain concentration ranges. A simple solubility curve is observed at 50° with $NaOH \cdot H_2O$ in equilibrium with saturated solutions of hydrazine, water and sodium hydroxide (including the most concentrated hydrazine solution investigated, 93.1% N_2H_4).

2. No evidence for formation of two liquid phases was observed in a study of ternary systems containing hydrazine, water and any one of the following: potassium hydroxide, potassium carbonate, sodium sulfate, sodium carbonate and trisodium phosphate.

URBANA, ILLINOIS RECEIVED AUGUST 26, 1948

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Magnetism and the Third Law of Thermodynamics. Magnetic Properties of Ferrous Sulfate Heptahydrate from 1 to 20°K. Heat Capacity from 1 to 310°K.[1]

BY D. N. LYON AND W. F. GIAUQUE

This paper presents the results of a low temperature magnetic and calorimetric investigation on ferrous sulfate heptahydrate. The work is part of a series of researches on magnetic properties near 1°K. which has been in progress in this Laboratory.

The magnetic susceptibility of ferrous sulfate heptahydrate has been investigated previously by Perrier and Kamerlingh Onnes[1a] at a number of temperatures between 14 and 20°K., and at 64, 77 and 290°K. Their data have been recalculated by Jackson.[2]

Curie's Law, χT = constant, where χ and T represent the magnetic susceptibility and absolute temperature, respectively, is obeyed rather well between 64 and 290°K. However, between 20 and 14°K. the susceptibility is increasing much less rapidly than the high temperature Curie constant would require.

According to Hund's rule the ground configuration of ferrous ion is a $^5D_4$ state. The data of Kamerlingh Onnes and Perrier show that the orbital contribution to the magnetic moment is largely "quenched" in solid ferrous sulfate heptahydrate. Between 64 and 290°K. the Curie constant exceeds the "spin only" value by about 10%. At 14°K. their data are about 2% below the spin only value. This suggested that the heat capacity anomalies arising from depopulation of the upper energy levels might occur at temperatures

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[1] This work was supported in part by the Office of Naval Research, United States Navy.

[1a] Perrier and Kamerlingh Onnes, *Comm. Phys. Lab. Univ. Leiden*, No. 122a (1911).

[2] Jackson, *Comm. Phys. Lab. Univ. Leiden*, No. 163 (1923).