[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF CORNELL UNIVERSITY.]

ANHYDROUS HYDRAZINE. III. ANHYDROUS HYDRAZINE AS A SOLVENT.[1]

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In 1873, Gore[2] determined the approximate solubilities of a large number of substances in liquid ammonia. That liquid ammonia is an ionizing solvent has been shown by Cady.[3] Franklin and Kraus[4] studied the solubility in liquid ammonia of a large number of elements, and of various organic and inorganic compounds.

Other inorganic substances[5] which act as ionizing solvents include such compounds as water, liquid hydrogen cyanide, liquid sulfur dioxide, concentrated nitric acid, arsenic trichloride, arsenic tribromide, phosphorus oxychloride, antimony trichloride, thionyl chloride, sulfuryl chloride, dimethyl sulfate, chlorosulfonic acid, concentrated sulfuric acid, and sulfur dichloride.

Nonaqueous ionizing solvents have also been investigated by McIntosh,[6] Archibald,[7] Calvert,[8] Walden,[9] Garner,[10] and Schlesinger.[11]

That anhydrous hydrazine is a poor conductor of the electric current has been shown by Cohen and Lobry de Bruyn.[12] The solubilities of sodium chloride, sodium nitrate, potassium chloride, potassium bromide, potassium iodide, potassium nitrate, and barium nitrate in anhydrous hydrazine have been determined by de Bruyn.[13] Welsh[14] has shown that sodium hydrazide is soluble in anhydrous hydrazine. In the present paper, the solubilities of a large number of substances in anhydrous hydrazine have been approximately determined as a preliminary investigation to the study of chemical reactions in this solvent. The results of the present investigation are described under the following headings: (1) Materials

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[1] For the previous articles of this series, see Hale and Shetterly, THIS JOURNAL, **33**, 1071–6 (1911); Welsh, *Ibid.*, **37**, 497–508 (1915). The experimental work of this article was completed in June, 1913.

[2] *Proc. Roy. Soc.*, **21**, 140 (1873).

[3] *J. Phys. Chem.*, **1**, 707–13 (1897).

[4] *Am. Chem. J.*, **20**, 820–36 (1898).

[5] For a complete summary of the literature related to ionizing solvents up to 1902, see Walden, *Z. anorg. Chem.*, **29**, 371 (1902).

[6] *Trans. Am. Electrochem. Soc.*, **21**, 121 (1912).

[7] THIS JOURNAL, **29**, 665, 1416 (1907).

[8] Drude's *Ann. Physik.*, **1**, 483 (1900).

[9] *Ber.*, **32**, 2862 (1899); *Bull. Acad. St. Petersburg*, 1055–82 (1911).

[10] *Am. Chem. J.*, **46**, 236–40 (1911).

[11] THIS JOURNAL, **33**, 1924–33 (1912).

[12] *Proc. Acad. Wettenschappen*, **5**, 551–6 (1903); *J. Chem. Soc.*, **84**, II, 405 (1903).

[13] *Rec. trav. chim.*, **15**, 174–84 (1896).

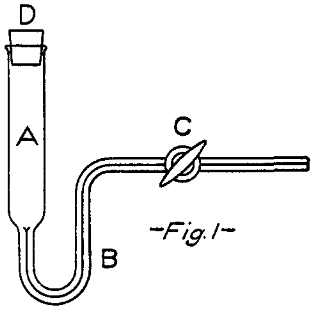
[14] THIS JOURNAL, **37**, 497–508 (1915).

Used; (2) Apparatus Employed; (3) General Procedure; (4) Table of Results; (5) Summary.

Materials Used.

The anhydrous hydrazine employed as solvent in the experimental work described in the following pages was prepared by first partially dehydrating commercial hydrazine hydrate with sodium hydroxide according to the method of Raschig.[1] Further removal of water was effected by treatment with barium oxide after the method of de Bruyn.[2] The form of distillation apparatus employed and the procedure followed in the respective distillations were those described by Welsh.[3] The product was found on analysis to contain 99.7% hydrazine. The hydrazine was stored in 50 cc. sealed tubes. That no decomposition of hydrazine preserved in this way had taken place after a period of two years was shown by the fact that no appreciable increase in pressure could be noted when the containers were opened.

The solutes employed, with the exception of those noted below, were the ordinary pure chemicals of standard manufacture. Water of crystallization was removed wherever it was possible to accomplish this without decomposition. The salts of lanthanum, samarium, praseo- and neodymium which were employed were such as had been prepared during the course of certain investigations in this laboratory.



-Fig. 1-

Apparatus Employed.

The solubility determinations were made in the form of apparatus shown in Fig. 1. The glass tube *A*, approximately 7 cm. in length and 1 cm. in diameter, was connected to a supply of pure, dry nitrogen through the capillary tube *B* and the stopcock *C*. During the course of an experiment, *A* was closed by means of the loosely fitting cork *D*, covered with tin foil. The action of the electric current upon the solutions was studied by means of the small platinum electrodes shown in Fig. 2. These electrodes, fused into the ends of glass tubes of small

-Fig. 2-

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[1] *Ber.*, 43, 1927 (1910).

[2] *Rec. trav. chim.*, 14, 458 (1895); 15, 174–84 (1896); see also Hale and Shetterly, This Journal, 33, 1071–6 (1911).

[3] *Loc. cit.*

TABLE I.

Solutes.	Grams of solute dissolved in 1 cc. N_2H_4.	Action observed.	Phenomena observed at cathode.	Remarks.
Aluminum	..	......	.....	Insoluble
Aluminum chloride	0.01	None	Gas	M. C.
Aluminum iodide	..	Gas evolved, slight explosion	.....	
Ammonium bromide	1.10	NH_3 evolved	Gas	G. C. Decomp.
Ammonium chloride	0.75	NH_3 evolved	Gas	G. C. (de Bruyn, *Loc. cit.*) Decomp.
Ammonium nitrate	0.78	NH_3 evolved	Gas	G. C. Decomp.
Ammonium oxalate	0.44	NH_3 evolved	Gas	G. C. Decomp.
Tertiary ammonium phosphate	0.00	None	Gas	Slightly conducting. No decomp.
Ammonium meta-vanadate	0.02	Brown ppt. and brown soln.	Gas	P. C. Slight decomp.
Antimony	0.00	None	Gas	Insoluble
Antimony trioxide	0.01	Brown soln.	Gas	P. C. Partially decomp.
Antimony oxychloride	0.01	None	Gas	M. C.
Antimony pentasulfide	0.00	White ppt. Bluish green soln.	Gas	P. C.
Arsenious acid	0.01	Black ppt.	Black deposit	P. C. Decomp.
Barium chloride	0.31	None	Gas	G. C.
Barium nitrate	0.03	None	Gas	G. C. (de Bruyn, *Loc. cit.*)
Barium oxide	0.00	None	Gas	P. C.
Barium sulfate	0.00	None	Gas	P. C.
Bismuth chloride	0.32	Black ppt.	Gas	See discussion of results
Boric acid	0.55	None	Gas	M. C.
Boron nitride	0.00	None	Gas	P. C.
Cadmium bromide	0.40	None	Black deposit	M. C.
Cadmium carbonate	0.00	None	Gas	P. C.
Cadmium iodide	0.84	None	Black deposit	G. C.
Cadmium sulfide	0.00	None	Gas	P. C.
Calcium	..	None	.....	Insol. Dissolves on add. of $N_2H_4.H_2SO_4$

Calcium acetate	0.01	None	Slight grey deposit	P. C.
Calcium chloride	0.16	None	Slight grey deposit	G. C. White needlelike cryst. on standing
Calcium oxide	0.00	None	Gas	P. C.
Cerous chloride	0.03	Gas	Reddish brown deposit	M. C.
Cerous ammonium nitrate	0.00	White suspens.	Gas	P. C. Slight brown ppt. in solution
Cerous sulfate	0.00	Gas	Gas	P. C.
Chromium chloride (anhydrous)	0.13	Gas, red soln.	Gas	G. C. See discussion of results
Chromium sesquioxide	0.00	Gas	Gas	P. C. Slaking action
Chromium trioxide	0.01	Gas. Black ppt.	Gas	P. C.
Cobalt acetate	0.01	Gas. Brown soln.	Brown deposit	M. C.
Cobalt chloride	0.01	Gas	Black deposit	P. C.
Copper	..	....	......	Insoluble on addition of $N_2H_4.H_2SO_4$
Copper hydrogen arsenite	0.00	Black ppt. Brown soln.	Brown deposit sol. in HCl	P. C. Cu and As are probably precipitated
Copper chloride	0.05	Brown soln. Brown ppt.	Red deposit sol. in HNO_3	G. C.
Copper nitrate	0.01	Black ppt.	Red deposit	P. C.
Copper sulfate	0.02	Black ppt.	Black deposit	G. C.
Copper sulfide	0.00	Brown ppt.	Brown deposit	P. C.
Ferrous sulfate	0.01	Gas, yellow ppt.	Black deposit sol. in HCl	P. C.
Ferrous sulfide	0.09	Gas. Green soln.	Black ppt., sol. in HCl	P. C.
Lead acetate	0.00	Black ppt. on standing	Black ppt.	P. C.
Lead fluoride	0.06	Gas. Black ppt. on standing	Black ppt.	G. C.
Lead metaborate	0.02	None	Black ppt., sol. in HCl	P. C.
Lead chloride	0.03	Black ppt.	Black ppt., sol. in HCl	G. C.
Lead iodide	0.02	Gas. Black ppt.	Black ppt., sol. in HCl	P. C.
Lead nitrate	0.52	Yellow ppt.	Black deposit, sol. in HCl	G. C.

TABLE I (*continued*).

Solutes.	Grams of solute dissolved in 1 cc. N_2H_4.	Action observed.	Phenomena observed at cathode.	Remarks.
Red lead	0.01	None	Black deposit, sol. in HCl	P. C.
Lithium	..	Slightly soluble	.....	More sol. on add. of $N_2H_4.H_2SO_4$
Lithium carbonate	0.00	None	Gas	P. C.
Lithium chloride	0.16	None	White deposit, probably solute	M. C. White deposit on anode, probably solute
Magnesium (powder)	..	None	.....	Insol. Dissolves on addn. of $N_2H_4.H_2SO_4$
Magnesium (ribbon)	..	None	.....	Insol. Dissolves on addn. of $N_2H_4.H_2SO_4$
Magnesium carbonate	0.00	None	Slight white deposit	P. C.
Magnesium chloride	0.02	Flocculent ppt. on standing	Slight white deposit	G. C.
Magnesium nitride	0.00	None	Gas	P. C.
Magnesium phosphate	0.00	None	Gas	P. C.
Magnesium sulfate	0.00	None	Slight white deposit	P. C.
Manganese	0.00	None	Gas	Insoluble
Manganese chloride	0.13	None	Black deposit, sol. in HCl	G. C.
Manganese sulfate	0.01	None	Black deposit	P. C.
Mercury	..			Insoluble
Mercurous acetate	0.02	Hg ppt.	Gas	M. C.
Mercurous chloride	0.01	Hg ppt.	Gas	M. C.
Mercurous nitrate	0.02	Hg ppt.	Gas	M. C.
Mercuric chloride	0.01	Hg ppt.	Gas	M. C.
Mercuric iodide	0.69	Hg ppt.	Gas	G. C.
Mercuric oxide (yellow)	..	Hg ppt.	Gas	
Mercuric sulfide	..	None	Gas	P. C.
Nickel chloride	0.08	Violet soln.	Black deposit, sol. in HCl	G. C.

Nickel nitrate	0.03	Violet soln., black ppt.	Black deposit, sol. in HCl	M. C.
Nickel sulfate	0.00	Salt assumes lavender color	Slight black deposit	P. C. $NiSO_4.2N_2H_4$ probably formed
Potassium	..	Explosion takes place at once	.....	.....
Potassium bichromate	0.01	Grey ppt.	Gas	P. C.
Potassium bromide	0.60	None	Gas	G. C. (de Bruyn, *Loc. cit.*).
Potassium chloride	0.09	None	Gas	M. C. (de Bruyn, *Loc. cit.*).
Potassium carbonate	0.01	None	Gas	P. C.
Potassium chromate	0.01	None	Gas	P. C.
Potassium iodate	0.01	Gas	Gas	P. C.
Potassium iodide	1.75	None	Gas	G. C. (de Bruyn, *Loc. cit.*).
Potassium ferricyanide	0.02	Gas, white residue	Gas	M. C.
Potassium nitrate	0.14	None	Gas	G. C. (de Bruyn, *Loc. cit.*)
Potassium permanganate	0.02	Gas, brown ppt.	Gas	P. C.
Potassium sulfate	0.05	None	Gas	M. C.
Silver chloride	0.00	Ag mirror	Gas	G. C. Decomp.
Silver nitrate	0.01	Gas, Ag mirror	Gas	M. C.
Sodium	..	Soluble	.....	....
Sodium acetate	0.06	None	White deposit, probably solute	M. C.
Sodium bromate	0.01	Gas, yellow solution	Gas	P. C.
Sodium bromide	0.37	None	White deposit, probably solute	G. C.
Sodium carbonate	0.00	None	Gas	P. C.
Sodium chlorate	0.66	None	White deposit, probably solute	G. C. (de Bruyn, *Loc. cit.*)
Sodium chloride	0.08	None	Gas	G. C.
Sodium nitrate	1.00	None	White deposit, probably solute	G. C. (de Bruyn, *Loc. cit.*)
Sodium iodide	0.64	None	White deposit, probably solute	G. C.

TABLE I (*continued*).

Solutes.	Grams of solute dissolved in 1 cc. N_2H_4.	Action observed.	Phenomena observed at cathode.	Remarks.
Sodium sulfate	0.00	None	White deposit, probably solute	P. C.
Strontium chloride	0.08	None	Gas	M. C.
Strontium nitrate	0.05	None	Gas	M. C.
Strontium sulfate	0.00	None	Gas	P. C.
Tin	..	None	.....	Insol., even on addn. of $N_2H_4.H_2SO_4$
Zinc	..	None	.....	Insol. Dissolved slightly on addn. of $N_2H_4.H_2SO_4$
Zinc acetate	0.04	White suspension	Grey deposit, sol. in HCl	M. C.
Zinc carbonate	0.00	White suspension	Gas	P. C.
Zinc chloride	0.08	None	Black deposit	G. C.
Zinc sulfate	0.00	White suspension	Grey deposit	P. C.
Zinc phosphate	0.00	None	Gas	P. C.
Zinc sulfide	0.00	None	Gas	P. C.
Iodine	..	Gas explosion	Gas	....
Lanthanum chloride	0.00	None	Slight deposit	M. C.
Neodymium chloride	0.00	None	Slight brown deposit, sol. in HCl	M. C.
Palladium chloride	0.01	Gas. Black ppt.	Black deposit	M. C. Decomp.
Platinic chloride	0.01	Black ppt.	Gas	M. C. Decomp.
Praseodymium chloride	0.00	None	Slight brown deposit	M. C.
Samarium sulfate	0.01	None	Slight white deposit	P. C.
Rubidium chloride	0.05	None	Gas	M. C.
Sulfur	0.54	Brown soln., H_2S and NH_3 formed	Gas	G. C. (de Bruyn, *Loc. cit.*) (Ephraim and Piotrowski, *Ber.*, 44, 386 (1911))

diameter, had an area of 32 sq. mm., were 4 mm. apart, and were mounted in a cork covered with tin foil and fitted to the tube *A*. The electrodes were connected to the source of current through a reversing switch, a voltmeter and a milliammeter, both of which could be temporarily cut out of the circuit. A number of solubility vessels were mounted on a wooden support and one pair of electrodes used interchangeably.

General Procedure.

The solubility vessels were thoroughly cleaned and dried, one cc. of anhydrous hydrazine introduced, and the vessel tightly corked. The finely powdered solute was then introduced in successive small portions taken from a weighed amount contained in a small glass bottle. Nitrogen was allowed to bubble slowly through the apparatus in order to provide thorough stirring, care being taken that the cork did not fit tightly enough to prevent the escape of gas. This procedure was continued until no more of the solute would dissolve. In the course of the experiments the solutions were closely observed for evolution of gas and other accompanying phenomena. The action of the electric current was then studied by removing the cork *D*, and substituting for it the cork supporting the electrodes, as previously described. In those cases where a noticeable deposit was formed on an electrode, the direction of the current was reversed and the effect upon the deposit was noted under these conditions. No great accuracy is claimed for the solubility determinations, as weighings were made only to the second place and the temperature was not kept constant, and furthermore, it was very difficult to prevent slight oxidation of the hydrazine taking place, and the introduction of slight amounts of moisture with the apparatus at hand. The chief object of the research has been to obtain qualitative and approximate quantitative data concerning the behavior of various substances toward hydrazine. In Table I the third column contains the results of observations upon the behavior of the substances when introduced into hydrazine. In the fourth and fifth columns are recorded chiefly the facts noted during electrolysis. The abbreviations "G. C.," "M. C.," and "P. C.," signify, respectively, that the solutions under consideration are good, medium, or poor conductors of the electric current. A four volt circuit was used and where the current was less than 15 m. amp. it was designated as "P. C.," between 15 and 50 m. amp. as "M. C.," and above 50 m. amp. as "G. C."

Summary.

The principal results of this investigation, the details of which have been recorded in the foregoing table, may conveniently be summed up under the following headings:

Elements.—Of the metallic elements employed, the alkali metals are the only ones that are appreciably acted upon and dissolved. The solubility increases with rise of atomic weight. Sulfur and iodine are both very soluble and chemical decomposition of the solvent takes place with rapidity, especially in the latter case.

Halogen Compounds.—The solubility of these compounds appears to increase with the increase of atomic weight of the halogen. In the case of the alkaline earth metals, crystals separate out from the solutions on standing, which are probably hydrazinated salts.[1] This was especially noticeable in the case of calcium chloride. The iodides are much more readily soluble than the corresponding bromides.

Carbonates.—The carbonates are insoluble or at most only very slightly soluble.

Oxides.—The oxides are apparently all insoluble.

Nitrates.—The nitrates, with the exception of those which react with the solvent, are in the majority of cases soluble.

Sulfates and Sulfides.—Both of these classes of compounds are only slightly soluble.

Ammonium Compounds.—These are all soluble with the exception of tertiary ammonium phosphate. Solution is accompanied by the evolution of large amounts of ammonia gas. Liberation of ammonia from ammonium salts by the action of free hydrazine has already been noted by de Bruyn.[2] This process, which is essentially one of *hydrazinolysis*, is the reverse of the decomposition of hydrazine salts in liquid ammonia already studied in this laboratory.[3]

Bismuth Compounds.—Bismuth chloride dissolves and reacts with the solvent, giving a quantitative precipitation of metallic bismuth.

Cadmium Compounds.—The carbonate and sulfide are insoluble. The halogen compounds are very soluble without visible chemical action.

Miscellaneous Compounds.—The mercury compounds, with the exception of mercuric sulfide which is insoluble, react chemically with the solvent immediately on being introduced, with formation of metallic mercury.

It is very probable that nickel and cobalt compounds are dissolved and react chemically with the solvent giving hydrazine addition products. In the case of cobalt chloride, a slow continuous decomposition was noticed with formation of a cobalt mirror on the tube.

The copper and lead compounds are all soluble with more or less decomposition. With the silver salts, the formation of a silver mirror was noted in each case.

This investigation was undertaken at the suggestion of Professor A. W. Browne and was carried out in coöperation with him.

ITHACA, N. Y.

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[1] Curtius and Schrader, *J. prakt. Chem.*, [2] 50, 311.

[2] *Loc. cit.*

[3] Browne and Welsh, THIS JOURNAL, 33, 1728 (1911); Browne and Houlehan, *Ibid.*, 33, 1734 (1911); Friedrichs, *Ibid.*, 35, 244 (1913); *Z. angew. Chem.*, 26, 201 (1913).