

[CONTRIBUTION FROM THE VIRGINIA POLYTECHNIC INSTITUTE]
SOLUBILITY OF SALTS IN LIQUID AMMONIA¹

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An investigation recently undertaken at this Laboratory made necessary the preparation of saturated solutions of salts in liquid ammonia. No data for the preparation of such solutions could be found in the literature. Franklin and Kraus² have made measurements of the solubility of some salts but their values are merely relative and most of them are for the purpose of conductivity measurements and these are only for dilute solution. Values given by Cady,³ Abegg and Riesenfeld,⁴ Raoult,⁵ and Moissan⁶ are all for dilute solutions or only state the relative solubility of the salts without definite numerical values.

Ammonium nitrate has been measured in the form of Diver's liquid⁷ but from the point of view of possible compound formation rather than merely for its solubility in liquid ammonia.

In the present investigation four sodium salts and four ammonium salts were tested for their solubility and curves showing the relation between solubility and temperature were determined. The method in general, consisted in dissolving a definite weight of the salt up to a definite volume by condensing ammonia to complete solution. By lowering the temperature of the solution a trace of crystals was separated out. On raising the temperature slowly and with constant stirring, the point at which cloudiness disappeared was taken as the saturation point. The volume and temperature were read at this point. By condensing or removing ammonia, the concentration could be varied at will and points determined on the curve. The readings for each point were checked several times. The results are given in grams per 100 cc. of solution, since such values are useful in work with liquid ammonia, owing to the fact that solutions are usually prepared by condensing ammonia upon the salt employed. Results in per cent. would have involved the determination of the specific gravity of each solution and this point was not undertaken.

In general, all the curves obeyed normally, *i. e.*, the solubility of the salt increased with increasing temperature. In the case of sodium nitrate

¹ The author is indebted to Robert E. Hussey for certain aid in the preliminary work for this article.

² Franklin and Kraus, *THIS JOURNAL*, **27**, 820 (1905); **29**, 1274, 1557 (1907); **30**, 653, 1197 (1908); **37**, 2279 (1915); **43**, 749 (1921); *Am. J. Sci.*, [4] **23**, 277 (1900); [4] **24**, 83 (1900).

³ Cady, *J. Phys. Chem.*, **1**, 707 (1897).

⁴ Abegg and Riesenfeld, *Z. physik. Chem.*, **40**, 84 (1902).

⁵ Raoult, *Ann. chim. phys.*, [5] **1**, 262 (1873).

⁶ Moissan, *Compt. rend.*, **133**, 713 (1901).

⁷ E. Divers, *Phil. Trans.*, **163**, 359 (1873).

a most peculiar curve resulted which could only be ascribed to the formation of a compound between the salt and ammonia. A further extension of this curve may be of interest but not for the purpose of this investigation.

Experimental Part

Materials.—The salts used were all Baker's Analyzed Chemicals, c. p., which had been recrystallized from distilled water. The sodium salts were dried by heating over a Fletcher burner for one hour, in an oven at 110° for twelve hours, and then kept in a desiccator over concentrated sulfuric acid for one week before using. The ammonia salts were recrystallized and dried in an oven at $50\text{--}60^\circ$ for twenty-four hours. They were then placed in a vacuum desiccator over concentrated sulfuric acid for one week and kept over concentrated sulfuric acid for one week before using.

The ammonia was the ordinary ammonia of commerce, dried by distillation from metallic sodium, and further dried by passing through a gas train consisting of two towers containing fused potassium hydroxide and one tower containing dried Bentonite.

Apparatus.—The sketch illustrates the apparatus used. (A) is a Dewar tube which serves to hold a bath of liquid ammonia. By applying a vacuum on tube (I) the temperature of the bath may be lowered to between -50 and -55° . A current of ammonia passed through tube (H) will serve to heat the bath to the boiling point or about -33° . If pressure be applied about -30° can be obtained.

The reaction tube (B), consisting of a large Pyrex test-tube, was calibrated with thermometer (C) and glass stirrer (D) in place. This calibration was done with pure mercury at 21° and calculated to -30° by the use of the formula given by Chappuis.⁸ Values could be estimated to 0.50 cc. The thermometer used was a toluene thermometer with Bureau of Standards certificate. The stirrer (D) was passed through a T-tube (E) which bore a short piece of gum rubber tubing (F). To the upper end of this was fastened, by a rubber stopper, the end of the stirrer. By stretching the tubing an up and down motion could be imparted to the stirrer. The T-tube (E) also served to make connection to a mercury manometer which was closed to moisture by a tube filled with dried Bentonite. Ammonia could be condensed in the tube by means of tube (G).

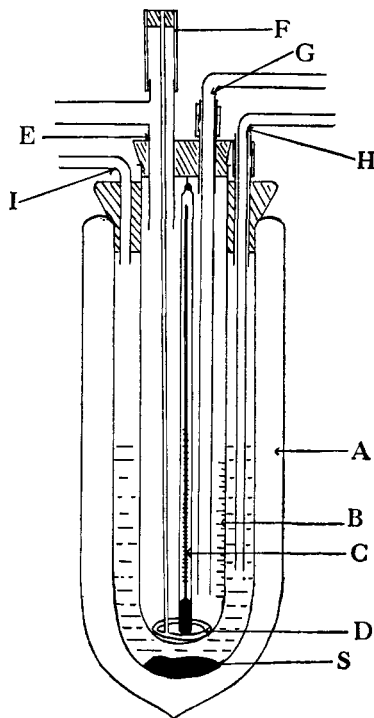


Fig. 1.—S, silica gel.

Procedure

A carefully weighed sample of the salt to be tested was placed in the reaction tube and after surrounding the tube with liquid ammonia, care-

⁸ Chappuis, *Trav. Bur. int.*, 13 (1903).

fully dried ammonia was condensed therein against a pressure of about 15 cm. of mercury in the manometer. When, with stirring, the salt had

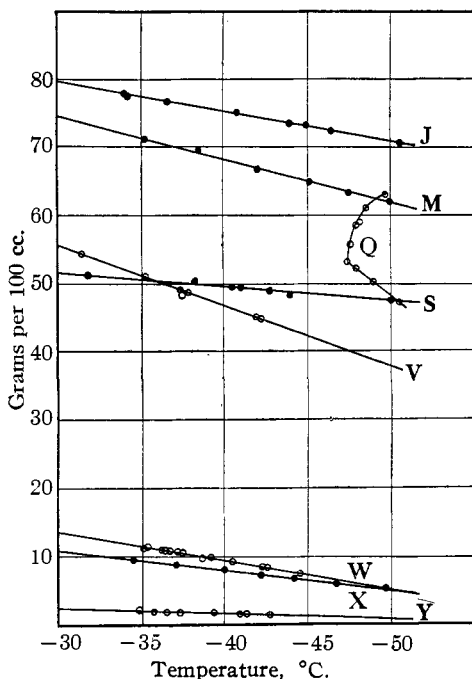


Fig. 2.—Solubility of salts in liquid ammonia: O, sodium salts; ●, ammonium salts. J, NH_4NO_3 ; M, NH_4I ; Q, NaNO_3 ; S, NH_4Br ; V, NaI ; W, NaBr ; X, NH_4Cl ; Y, NaCl .

completely gone into solution, the pressure was removed and, if necessary, the solution concentrated by applying a vacuum at (E). The temperature of the bath (A) was reduced by a vacuum until with constant stirring a cloudiness from precipitated crystals occurred. The vacuum was removed from the bath and the temperature was raised with constant stirring at the rate of one degree per minute by means of an ammonia stream through (H). The point at which the cloudiness disappeared was taken as the saturation point and the volume and temperature were read. The points were checked several times and the values calculated to grams of salt per 100 cc. of solution. By condensing one or two cubic centimeters more of ammonia, the concentration of the solution

TABLE I

SOLUBILITY DATA

Temp., °C.	G. per 100 cc.	Temp., °C.	G. per 100 cc.	Temp. °C.	G. per 100 cc.
(A) Sodium Chloride		(B) Sodium Bromide		(C) Sodium Iodide	
-42.8	1.35	-44.6	7.37	-42.2	44.8
-41.4	1.48	-42.6	8.03	-41.9	45.5
-41.0	1.53	-42.3	8.34	-37.5	48.4
-39.4	1.69	-40.5	9.09	-37.8	48.8
-37.4	1.87	-38.7	9.64	-37.4	49.0
-36.6	1.95	-39.3	9.62	-35.2	51.3
-35.8	2.05	-37.5	0.23	-31.5	54.6
-34.9	2.18	-37.2	10.32		
		-36.6	10.56		
		-36.8	10.64		
		-36.3	10.88		
		-35.2	11.24		
		-35.3	11.53		

TABLE I (Concluded)

Temp., °C.	G. per 100 cc.	Temp., °C.	G. per 100 cc.	Temp., °C.	G. per 100 cc.
(D) Sodium Nitrate		(E) Ammonium Chloride		(G) Ammonium Iodide	
-50.5	47.3	-49.6	5.2	-50.0	62.1
-49.0	50.3	-46.8	5.9	-47.5	63.3
-48.0	52.3	-44.2	6.5	-45.2	64.6
-47.5	53.3	-42.2	7.0	-42.0	66.7
-47.6	55.8	-40.1	7.6	-38.6	69.2
-48.0	58.5	-37.2	8.6	-35.3	71.2
-48.2	59.0	-34.6	9.6	(H) Ammonium Nitrate	
-50.2	59.9	(F) Ammonium Bromide		-50.6	70.1
-48.6	61.2	-50.0	47.1	-46.5	72.6
-49.8	63.1	-44.0	48.2	-45.0	73.4
		-41.2	48.9	-44.0	73.5
		-42.8	49.0	-40.8	75.1
		-40.5	49.7	-36.6	77.0
		-38.2	50.6	-34.2	77.4
		-31.8	52.0	-34.0	9.77

could be varied and a further determination made upon the same substance. The experimental data are given in Table I. In general, the experiments were run in a volume of approximately 25 cc., although in individual cases the volumes varied from 16.4 to 43.4 cc. Each value given in the table is the result of at least three check readings.

Summary

1. The solubility of four sodium and four ammonium salts in liquid ammonia has been determined over a temperature range from -30 to -50° .

2. Solubility and temperature curves are given. The curves are normal except in the case of sodium nitrate.

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