

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

LIQUID AMMONIA AS A SOLVENT. I. THE SOLUBILITY OF INORGANIC SALTS AT 25°

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The tremendous importance of liquid ammonia as a solvent has been pointed out by E. C. Franklin and his students and has prompted the determination of physical data in this fundamental field of chemistry. The object of this paper is to present solubility data at the same temperature as similar data available for other solvents so that comparisons may be made in the chemistry of various solutions. This basic work on solubilities will be followed by data on vapor pressures, rates of reactions and other constants.

Gore, Franklin and Kraus¹ have determined qualitatively the solubilities of about seven hundred organic and inorganic substances in liquid ammonia at -33° . This large mass of information has enabled Franklin and Kraus to group the substances according to their relative solubilities. Their work has been augmented by the researches of Divers, Cady, Kuriloff, Moissan, Abegg and Riesenfeld, de Carli, Fredenhagen and Scherer.²

Experimental

Thermostat.—The temperature of the bath was kept at $25.00 + 0.025^{\circ}$. The thermometer was calibrated against a U. S. Bureau of Standards thermometer.

Salts.—The salts were Baker's c. p. chemicals, which were recrystallized and carefully dried.

Ammonia.—The ammonia was the anhydrous ammonia of commerce. It was transferred from the storage tank to small three-liter cylinders of the type described by Fernelius and Johnson and allowed to stand in these cylinders with metallic sodium for several weeks before use.

Two methods were used for determining the amount of salt present in a given amount of solvent. The methods were found to check within 0.5% of each other. Method I was more satisfactory for the less soluble salts while Method II was necessary in the case of some salts whose solutions attack cotton.

Method I.—The measurements were made in 25 mm. Pyrex tubes. The tubes were filled by placing part A in a carbon dioxide-alcohol bath at -60° and distilling the ammonia from the cylinder into it. The B end of the tube was fitted with a two-holed rubber stopper and the exit tube was guarded with calcium chloride to prevent moisture from condensing in the cold tube. From ten to twenty-five grams of ammonia was used in each experiment. When this volume of ammonia was condensed the carefully

¹ G. Gore, *Proc. Roy. Soc. (London)*, **21**, 140 (1873); E. C. Franklin and C. A. Kraus, *Am. Chem. J.*, **20**, 820 (1898).

² E. Divers, *Phil. Trans.*, **163**, 359 (1873); H. P. Cady, *J. Phys. Chem.*, **1**, 707 (1897); Kuriloff, *Z. physik. Chem.*, **25**, 109 (1898); H. Moissan, *Compt. rend.*, **133**, 713 (1901); Abegg and Riesenfeld, *Z. physik. Chem.*, **40**, 84 (1902); T. de Carli, *Gazz. chim. ital.*, **57**, 347 (1927); K. Fredenhagen, *Z. anorg. allgem. Chem.*, **186**, 1 (1930); P. C. Scherer, Jr., *This Journal*, **53**, 3694 (1931).

dried salt was quickly introduced into A, the bulbs C and D dropped in place and B was drawn down to a tip and sealed off.

The tube was then kept in position II, Fig. 1, in the thermostat, from one to three weeks with occasional shaking, being inverted during the shaking so that the solution in C filtered into A. The amount of salt placed in direct contact with the solvent was previously roughly determined so that it was never quite enough to saturate the solution. The end of C was closed with a very closely woven cotton cloth. This permitted salt to dissolve in the ammonia which enters C, and the solution to flow out, the undissolved salt being held back.

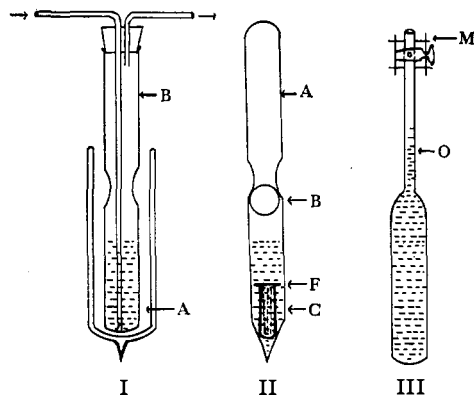


Fig. 1.—The solution and density tubes: F, filter cloth; M, clamp; O, calibration.

When the solution had been given ample time to reach equilibrium the tube was inverted in the bath and all of the solution drained into A. The tube was then removed to a freezing bath and sealed off at the neck between A and B. The tubes were so well drained that the volume change in A on chilling was only the change due to the vapor condensing. Since the tubes were uniformly about 80 cc. in volume and had about 30 cc. of free space the amount of vapor condensed was reduced to a minimum. The vapor pressures will vary from the most dilute to the most concentrated solutions in a manner which will tend to remove error from the final result. Because of this unavoidable error the results reported cannot have a precision greater than 0.5%. When A reached room temperature, it was rubbed dry and weighed on an analytical balance. The ammonia was boiled off, the tube and salt were warmed until all odor of ammonia was gone, and the salt deposited from the solution was weighed. This method gave the solubility in grams per grams of solvent. It has the advantage of being simple and of giving results which are reproducible, as shown in Table I.

TABLE I
REPRODUCIBILITY OF DETERMINATIONS

Salt	Experiment I G./100 g. NH ₃	Experiment II G./100 g. NH ₃	Experiment III G./100 g. NH ₃
NaNO ₃	97.65	97.60	97.55
NH ₄ NO ₃	390.0	390.0	390.0
NH ₄ CNS	311.9	312.4	311.6
KBr	13.50	13.55	13.45
KNO ₃	10.35	10.45	10.40
NaI	161.9	162.0	161.9

Method II.—A tube such as III, shown in Fig. 1, was used. Ammonia in excess was condensed upon the salt. The solution was brought to 25° in the thermostat and the ammonia was allowed to escape very slowly until a single crystal of the salt remained undissolved after long shaking. This method is quicker and gives results which are equally as reproducible as in the case of the highly soluble salts. The results given are the averages of three determinations which agree within 0.5%.

The solubilities expressed per 100 ml. of solvent were calculated using 0.604 as the density of ammonia at 25°.

TABLE II
THE SOLUBILITY OF INORGANIC SALTS IN LIQUID AMMONIA AT 25°

Salt	G./100 g. NH ₃	G./100 ml. NH ₃	Moles/10 moles NH ₃	Moles/10 moles ^a H ₂ O
NaF	0.35	0.21	0.0142	0.21
NaCl	3.02	1.82	.088	1.11
NaBr	137.95	83.32	2.28	0.848
NaI	161.90	97.78	1.835	2.214
NaNO ₃	97.60	58.95	1.95	1.927
NaCNS	205.50	124.12	4.313	...
Na ₂ SO ₃	0.17	0.102	0.0023	0.447
Na ₂ SO ₄	.088	.053	.001	.355
NH ₄ Cl	102.5	61.91	3.257	1.32
NH ₄ Br	237.9	143.69	4.13	1.45
NH ₄ NO ₃	390.0	235.56	8.2875	4.82
NH ₄ CNS	312.0	188.45	6.969	1.55
(NH ₄) ₂ C ₂ O ₄	0.00—	0.00—	0.0	0.0696
(NH ₄) ₂ SO ₄	.00—	.00—	.0	1.045
KCl	.04	.024	.0009	0.96
KBr	13.50	8.15	.192	1.025
KI	182.0	109.92	1.86	1.608
K ₂ CO ₃	0.00—	0.00—	0.0	1.458
K ₂ SO ₄	.00—	.00—	.0	0.1245
KNO ₃	10.4	6.28	.174	.664
KCNO	1.70	1.02	.0356	1.665

^a Taken largely from Seidell, "Solubilities of Inorganic and Organic Compounds," 1919.

The density of a saturated solution of ammonium nitrate in ammonia was found to be 1.212 g. per ml. at 25°. The volume of tube III, Fig. 1, was calibrated. The ammonium nitrate solutions were weighed in it and their densities were calculated from the weight-volume ratio.

TABLE III
SOLUBILITY OF NH₄NO₃ IN MIXTURES OF NH₃ AND H₂O AT 25°

G. H ₂ O per 100 g. mixture	G. NH ₄ NO ₃ per 100 g. solvent	G. H ₂ O per 100 g. mixture	G. NH ₄ NO ₃ per 100 g. solvent
0.00	390.0	13.2	351.9
1.78	383.7	15.9	337.4
2.80	381.0	18.6	331.8
3.40	378.6	21.8	316.8
4.82	372.8	47.5	247.0
6.86	368.6	68.0	220.0
10.1	354.7	100.0	214.2
12.7	352.1		

Discussion of Results

In general the solubility of the halides increases as the atomic weight of the halogen increases. The salts of ammonia are the most soluble, and salts of sodium are more soluble than salts of potassium. The sulfates,

carbonates and oxalates examined were insoluble. The sulfites and cyanates were only sparingly soluble. This is in agreement with Franklin and Kraus' work at low temperatures.

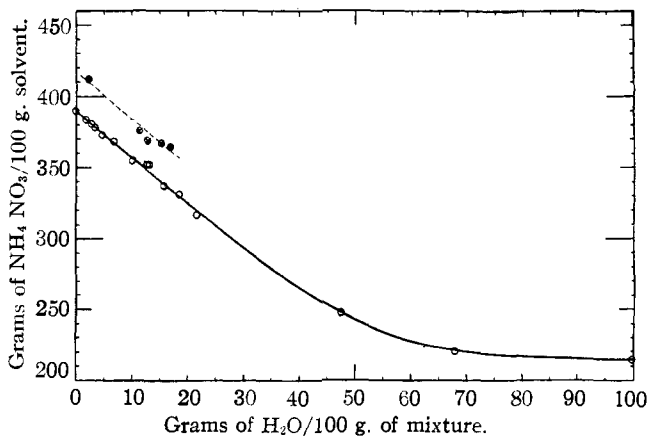


Fig. 2.—The solubility of ammonium nitrate in mixtures of ammonia and water: O, β -ammonium nitrate; \oplus , α -ammonium nitrate.

The order of solubility in water and ammonia is not regular. A calculation of the solubilities in ammonia based on the physical properties of the solvents cannot be made from the solubilities in water. The solubility must be coordinately determined by properties of the salts as well as of the solvents. If the solution of ammonium nitrate is raised above 33° the α -form will crystallize on slowly cooling to 25° and, since it is more soluble than the β -form, points were obtained which lie above the curve.

Summary

1. The solubilities of seventeen inorganic salts in liquid ammonia have been determined quantitatively at 25° .
2. The solubilities in ammonia and water are not always concordant with the physical properties of the solvents.
3. The progressive addition of water decreases the solubility of ammonium nitrate in liquid ammonia.

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