[Contribution from the Baker Laboratory of Chemistry at Cornell University]

Ammonium Trinitride[1]

By W. S. Frost, J. C. Cothran and A. W. Browne

In connection with a current investigation of the nitridizing action of ammonium trinitride in solution and in the vapor state, determinations have been made of various properties of this substance, including (1) its solubility in water, methanol, ethanol, benzene and ether, (2) its qualitative behavior toward numerous organic liquids, (3) its specific gravity and the specific gravity of its saturated solutions and (4) its vapor tension at temperatures from 15 to 134°.

Preparation of Ammonium Trinitride.—The ammonium trinitride used throughout the present investigation was prepared either by the method of Browne and Houlehan,[2] or by the following procedure: 65 g. of sodium trinitride was placed in a 500-cc. round-bottomed flask connected through a Reitmeier bulb with a suitable condenser and a receiver containing 200 cc. of ether and cooled with ice. Two hundred cc. of water and 200 cc. of ether were added, and 60 cc. of concentrated sulfuric acid was slowly introduced, from a dropping funnel, beneath the surface of the solution. The greater part of the hydrogen trinitride, diluted with ether vapor, passed over into the receiver during this operation. The remainder was distilled by heating the flask for a short time over the steam-bath. The ethereal distillate was refluxed for thirty minutes over calcium chloride, and was finally redistilled from the desiccant. Dry ammonia gas was bubbled through the ethereal hydrogen trinitride until complete precipitation of the ammonium salt had been effected. The final product was readily freed from residual ether by storage over sulfuric acid.

Solubility of Ammonium Trinitride.—Curtius[3] observed that ammonium trinitride is soluble in water and in 80% ethanol, slightly soluble in 100% ethanol, and insoluble in ether and in benzene. Qualitative experiments have been performed by the authors with a number of other liquids at room temperature, including methanol, pyridine and glycerol, in which the salt is soluble; allyl, butyl and isobutyl alcohols, in which it is slightly soluble; and acetone, aniline, benzaldehyde, carbon disulfide, chlorobenzene, chloroform, ethyl acetate, ethyl methyl ketone, isoamyl alcohol, methyl acetate, nitrobenzene, tetrachloroethane, toluene and xylene, in which it is insoluble.

Quantitative determinations of the solubility of ammonium trinitride in carefully purified benzene, ether, ethanol, methanol and water have been made by a method and with an apparatus especially designed for systems in which both solvent and solute are

Table I

Solubility of Ammonium Trinitride

Solvent	Grams NH_4N_3 per 100 cc. soln. 0°	20°	40°	*d* of satd. soln. 0°	20°	40°
Benzene	...	0.0032	0.0078	....	0.8778	0.8609
Ether	...	.0063	.....	....	.7129	....
Ethanol	...	1.060	1.325	....	.7972	.7803
Methanol	...	3.268	3.984	....	.8166	.7986
Water	13.80	20.16	27.07	1.0435	1.0473	1.0554

---

(1) This article is based upon parts of the theses presented by Walter Sprague Frost and John Cleveland Cothran to the Faculty of the Graduate School of Cornell University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Browne and Houlehan, This Journal, **33**, 1742 (1911).

(3) Curtius, *Ber.*, **24**, 3341 (1891).

volatile.[4] The results are summarized in Table I. Each datum is the average of at least two satisfactorily concordant determinations.

Specific Gravity of Solid Ammonium Trinitride.—Determinations of the specific gravity made with the aid of a pycnometer containing a saturated solution of the salt in benzene yielded the result d_{20} (compared with water at 4°) = 1.3459.

Vapor Tension of Ammonium Trinitride.—Curtius[3,5] and his co-workers have repeatedly called attention to the volatility of ammonium trinitride. From vapor density determinations Curtius and Rissom[5c] concluded that the vapor was completely dissociated at 100°.

The results of a series of measurements of the vapor tension of freshly sublimed ammonium trinitride at temperatures ranging from 15 to 134° are recorded in Table II. For this work a constant volume tensimeter with compact, completely immersible cell was designed.[6]

TABLE II

VAPOR TENSION OF AMMONIUM TRINITRIDE

Temp., °C.	Pressure Obs., mm.	Pressure Calcd., mm.	Diff., mm.	Temp., °C.	Pressure Obs., mm.	Pressure Calcd., mm.	Diff., mm.
15.0	0.2	0.3	−0.1	77.9	38.5	35.8	2.7
27.5	.6	.8	− .2	85.0	55.1	56.0	− 0.9
32.5	1.0	1.3	− .3	91.0	80.1	80.5	− .4
37.5	1.9	1.9	.0	96.0	108.3	107.9	.4
42.0	2.9	2.8	.1	102.9	160.9	160.0	.9
48.0	4.5	4.4	.1	109.0	222.7	223.9	− 1.2
54.0	6.7	6.9	− .2	114.0	292.3	291.8	0.5
58.4	9.5	9.5	.0	119.0	377.9	379.3	− 1.4
61.9	12.0	12.2	− .2	125.0	508.1	512.9	− 4.8
67.5	18.5	18.0	.5	132.1	709.9	727.8	−17.9
71.9	24.4	24.2	.2	134.2	782.1	803.5	−21.4

The equation used in calculating the pressures was: $\log p = -(3428.6/T) + 11.325$.

The rectilinear character of the logarithmic curve indicates the nonexistence of isomeric forms[7] of ammonium trinitride under the conditions prevailing in the experiments. This negative conclusion was strongly substantiated by the identity of the vapor tension curves successively obtained with samples of ammonium trinitride that had been (1) freshly prepared, but not sublimed, (2) stored for five months over calcium chloride, (3) stored for eight months in dry air containing ammonia gas and (4) freshly sublimed.

---

(4) A detailed description of the method and apparatus used in this work will be found in the thesis, "A Study of Ammonium Trinitride," by W. S. Frost, of which a typewritten copy has been deposited in the Library of Cornell University, Ithaca, N. Y.

(5) Curtius, (a) *Ber.*, **23**, 3033 (1890); (b) Curtius and Radenhausen, *J. prakt. Chem.*, **43**, 208 (1891); (c) Curtius and Rissom, *ibid.*, **58**, 273 (1898).

(6) Thesis, "A Study of Certain Compounds Containing Chains of Four Nitrogen Atoms," by J. C. Cothran. A typewritten copy is on file in the Library of Cornell University, Ithaca, N. Y.

(7) Mendeléeff, *Ber.*, **23**, 3464 (1890).

When samples that had been stored for a long time over phosphorus pentoxide were sublimed, however, appreciable amounts of a white, vesicular, relatively non-volatile residue were obtained. This may be identical with the residual traces noted by Curtius and Rissom.[5c] It was at first surmised that this residue might be the long-sought isomer predicted by Mendeléeff.[7] Analysis by the Pregl method, however, proved that the substance was not a hydronitrogen, but rather, in all probability, an ammonium salt of hypophosphorous acid. It is interesting to note, further, that storage of ammonium trinitride over phosphorus pentoxide, calcium chloride or any other desiccant capable of absorbing ammonia but not hydrogen trinitride, soon results in the accumulation of considerable amounts of the latter substance in the vapor phase. The reverse is true for alkaline desiccants that selectively absorb hydrogen trinitride.

Summary

The solubility of ammonium trinitride (1) in water, methanol, ethanol, benzene and ether has been determined quantitatively and (2) in numerous organic liquids has been studied qualitatively. The specific gravity of solid ammonium trinitride and of various saturated solutions has been determined. The vapor tension of the solid has been measured over a temperature range of 15 to 134°.

Ithaca, N. Y.

Received April 10, 1933
Published September 5, 1933

[Contribution from the Department of Chemistry of the University of Michigan]

Solid–Liquid–Air Contact Angles and their Dependence upon the Surface Condition of the Solid

By F. E. Bartell and Allan D. Wooley

Introduction

Several investigators[1] have observed that the angle formed when a contact angle forming liquid has advanced to rest over a dry solid surface is larger than the angle formed when the liquid has receded to rest from a wetted surface. Sulman[1d] called this phenomenon "hysteresis of contact angle," which term was used to imply that advancing and receding contact angles are unstable forms of a definite equilibrium contact angle. Later workers,[1e,2] holding similar views, have attempted to evaluate equilibrium contact angles by relating them mathematically to the advancing and receding contact angles. Thus Ablett, believing that the so-called

(1) (a) Edser, Fourth Report of Colloid Chem., 284 (1922); (b) Rayleigh, *Phil. Mag.*, **30**, 397 (1890); (c) Pockels, *Physik. Z.*, **15**, 39 (1914); (d) Sulman, *Trans. Inst. Min. & Met.*, Nov. (1920); (e) Adam and Jessop, *J. Chem. Soc.*, **127**, 1865 (1925).

(2) Ablett, *Phil. Mag.*, **46**, 244 (1923); Nietz, *J. Phys. Chem.*, **32**, 255 (1928).