

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

**The System Cadmium Sulfate-Acetic Acid-Water at 25<sup>o</sup>**

BY WILLIAM C. CAGLE, GRADY TARBUTTON AND W. C. VOSBURGH

This investigation was undertaken to determine the solubility of the octotrihydrate of cadmium sulfate in mixtures of acetic acid and water and also the range of concentrations within which this hydrate is stable. This was of interest in connection with the construction of some Weston cells with large concentrations of acetic acid in the electrolyte.

Some interest is attached also to the lower hydrate, which can exist in stable equilibrium with the more concentrated acetic acid solutions. While this hydrate is commonly considered to be the monohydrate,<sup>2</sup> the values reported for the percentage of water vary from 7.78 to 8.80% with only one near the theoretical (which is 7.96%) and that questionable.<sup>3</sup> More precise analytical data are therefore desirable.

Twice recrystallized cadmium sulfate ( $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ ) or the monohydrate prepared as described below and various mixtures of acetic acid and water were sealed in glass tubes and the tubes rotated in a thermostat at  $25 \pm 0.02^\circ$  for a week or more. Analysis of duplicate samples rotated for different periods showed that saturation was attained within the time of rotation. Samples of the saturated solution and wet solid were taken essentially as described by Tarbutton and Vosburgh<sup>4</sup> and analyzed.

It was found desirable in making up a mixture to use the particular solid phase capable of existing in equilibrium with the acetic acid solution. The higher hydrate in contact with a solution of high acetic acid content was dehydrated rather slowly, and the monohydrate in contact with a solution of too high water content was hydrated so slowly that after two or three months the reaction was far from complete. It was important therefore to prepare the monohydrate in as nearly a pure form as possible.

(1) Part of a thesis submitted by William C. Cagle in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences of Duke University.

(2) (a) Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, 1923, Vol. IV, p. 616. (b) Benrath and Benrath, *Z. anorg. Chem.*, **179**, 371 (1929).

(3) (a) V. Hauer, *J. prakt. Chem.*, [I] **64**, 477 (1855), seems to have heated only to  $100^\circ$  in his analysis. See (b) Hackspill and Kieffer, *Ann. chim.*, [10] **14**, 272 (1930).

(4) Tarbutton and Vosburgh, *THIS JOURNAL*, **54**, 4537 (1932).

The monohydrate was best prepared by precipitation. Solutions of cadmium acetate and sulfuric acid in 95% acetic acid were added alternately in small portions to some 95% acetic acid which was mechanically stirred. For analysis, samples were drained in a centrifuge and dried in a desiccator over anhydrous cadmium sulfate. Six samples gave an average of 8.07% water. On drying for three days at  $50^\circ$  four samples of another preparation gave 8.85% water, while two samples dried for a month at  $50^\circ$  gave 7.90 and 7.97, respectively. The latter agree with the results obtained in the solubility determinations.

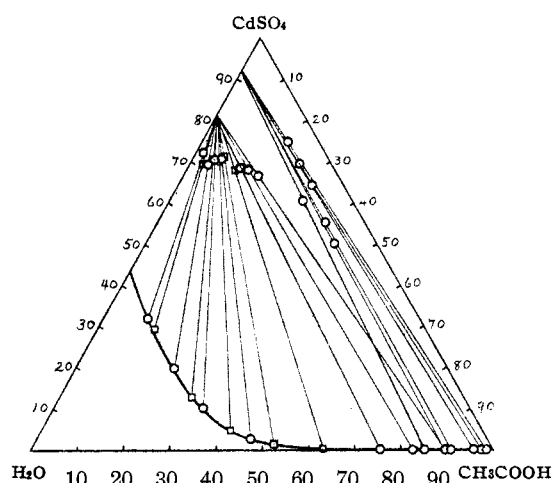


Fig. 1.—Solubility of cadmium sulfate in mixtures of acetic acid and water. The compositions are given in weight percentage. Circles represent results at  $25^\circ$  and squares at  $30^\circ$ .

Acetic acid was determined by titration after precipitating the cadmium by neutralized potassium oxalate solution. Cadmium sulfate was determined by evaporation to dryness with the addition of small quantities of nitric and sulfuric acids and weighing as anhydrous cadmium sulfate.<sup>5</sup> From the analytical results for the saturated solutions and the wet solid phases the composition of the dry solid was found graphically (Fig. 1) and by algebraic extrapolation,<sup>6</sup> for which the results are given in the last column of Table I.

(5) Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, New York, 1929, p. 205. No trouble was experienced in expelling all of the sulfuric acid in one evaporation.

(6) Hill and Ricci, *THIS JOURNAL*, **53**, 4308 (1931).

TABLE I  
SOLUBILITY OF CADMIUM SULFATE IN ACETIC ACID  
SOLUTIONS. 25°

Rotation time, days	Satd. soln.		Wet solid		Solid <sup>a</sup> Wt., % H <sub>2</sub> O
	Wt., % HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	Wt., % CdSO <sub>4</sub>	Wt., % HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	Wt., % CdSO <sub>4</sub>	
39	71.34	0.11	9.58	70.17	18.90
7	9.78	31.72	1.79	72.09	19.08
7	21.25	19.69	4.00	69.33	18.76
15	20.85	19.87	3.69	70.50	18.61
14	46.34	2.77	6.32	70.69	18.53
29	32.39	10.05	4.91	70.60	18.58
25	75.48	0.06	11.56	68.43	19.16
38	76.35	.05	19.52	60.38	18.90
38	82.92	.01	13.52	67.96	18.80
26	89.77	.01	16.14	66.74	18.61
36	85.13	.02	28.89	60.62	8.24 <sup>b</sup>
64	85.49	.02	32.72	56.61	8.28 <sup>b</sup>
53	90.91	.007	36.33	55.32	7.89 <sup>b</sup>
72	89.52	.007	40.85	50.09	7.88 <sup>b</sup>
63	95.79	.015	28.90	64.29	7.93
20	95.87	.004	27.26	65.87	7.92
24	97.53	.016	23.86	69.42	8.01
24	98.59	.025	18.45	74.81	7.97

<sup>a</sup> Calculated for 3CdSO<sub>4</sub>·8H<sub>2</sub>O, 18.73% H<sub>2</sub>O and for CdSO<sub>4</sub>·H<sub>2</sub>O, 7.96% H<sub>2</sub>O.

<sup>b</sup> The solid introduced was 3CdSO<sub>4</sub>·8H<sub>2</sub>O. In the two with 85% acetic acid transition was probably incomplete. The transition point is probably near 85% acetic acid.

A number of determinations were made at 30° in solutions of between 12 and 66% acetic acid. The solubility was practically the same as at 25° throughout the entire range.

#### Summary

The solubility of the octotrihydrate of cadmium sulfate in mixtures of acetic acid and water decreases rapidly as acetic acid is added and is very small when the solvent is above 55% acetic acid. The octotrihydrate is the stable solid phase when the percentage of acetic acid in the solution is less than 85%.

The composition of the monohydrate of cadmium sulfate has been confirmed.

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[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

## Behavior of the Hydronitrogens and their Derivatives in Liquid Ammonia. IX. Equilibria in the System Ammonium Trinitride-Ammonia<sup>1,2</sup>

BY D. H. HOWARD, JR., F. FRIEDRICHS AND A. W. BROWNE

As a preliminary to an extended study and comparison of the structural and genetic relationships that may exist between the various solvated saline hydronitrogens,<sup>3</sup> which are probably of the nature of coördination compounds, and their respective nitrogen-chain empirical isomers of the diazene<sup>4</sup> and monazane series, the present investigation of the binary system ammonium trinitride-ammonia from the viewpoint of the phase rule has been undertaken. In this work the number, composition, stability, and fields of existence of the ammonates of ammonium trinitride have been determined, as well as all inversion and other transition points of the system. While many ammonates of a large variety of

substances have been described previously,<sup>5</sup> the investigations in nearly all cases have covered but a limited range of temperature and pressure, and the phase relations have been studied only incompletely.

In the current investigation, pressure has been varied from 0 to 4000 mm., temperature from -90 to +30°, and concentration from 0 to 100% ammonia.

#### Apparatus and Materials

The apparatus (Fig. 1) is of the latest form employed in this Laboratory for the phase rule investigation of binary systems with one volatile component. Ammonia from a steel cylinder (A) is passed through a series of tubes (C) filled with soda-lime and metallic sodium, and is condensed at -78° in a reservoir (D) from which are pumped out the small volumes of non-condensable gases present in the ammonia. This reservoir contains a soluble salt, such as ammonium iodide, the saturated solution of which has a vapor tension of about one atmosphere at room temperature, and serves as a convenient source of highly purified ammonia gas.

(5) See for example Ephraim, *Ber.*, **52**, 940 (1919); Biltz, *Z. anorg. allgem. Chem.*, **180**, 93 (1923).

(1) For references to Articles I to VII of this series see Howard and Browne, *THIS JOURNAL*, **55**, 1968 (1933). For VIII see *ibid.*, **55**, 3211 (1933).

(2) The current article is based chiefly upon a part of the thesis presented to the Faculty of the Graduate School of Cornell University by David H. Howard, Jr., in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Dresser and Browne, *THIS JOURNAL*, **55**, 1963 (1933).

(4) These compounds are now under investigation in this Laboratory.