ing point of pentyne-2 is 20° above that of pentene-2, there would not be enough in the vapor to affect the absorption spectrum measurements which are made at a pressure of from 3–6 mm.

The absorption spectra measurements and physical constants for hexene-3 and heptene-3 are reported in earlier publications.[4,12]

Summary

The ultraviolet absorption spectra of *cis*- and *trans*-butene-2, cyclohexene and different samples of pentene-2 have been examined in vapor phase in the Schumann region. The marked similarity between the spectra of the higher boiling butene-2 and cyclohexene confirms the earlier assignment of the *cis* configuration to this isomer.

The absorption curves for two samples of pentene-2, which from their methods of preparation should give two different geometrical isomers, showed intensity relationships which were entirely analogous to those shown by the *cis* and *trans* isomers of butene-2. These differences were sufficiently marked to serve as a basis for identification of the two isomers; the higher boiling pentene-2 is the *cis* form.

The comparative yields of the two isomers of pentene-2 prepared by four other methods have been estimated from their absorption spectra.

SOUTH HADLEY, MASS. RECEIVED AUGUST 11, 1937

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[12] E. P. Carr and G. F. Walter, *J. Chem. Phys.*, **4**, 757 (1936).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

The System Lithium Sulfate, Cadmium Sulfate and Water at 30°

BY HELEN PARKS, MILDRED PATTERSON, AND W. C. VOSBURGH

The solubilities and the identity of the solid phases in the system lithium sulfate, cadmium sulfate and water were of interest in connection with the preparation of a modified Weston Cell. Calgagni and Marotta[1] have determined the freezing point curve of the anhydrous system lithium sulfate and cadmium sulfate and found no evidence of a double salt. In the present investigation also no evidence of a double salt was obtained.

Most of the mixtures were prepared from carefully weighed quantities of monohydrated lithium sulfate, selected crystals of hydrated cadmium sulfate and water. The mixtures were rotated in an air-bath at 30 ± 0.05° from one to several days. The agreement of the results when the time of rotation varied showed that equilibrium could ordinarily be attained in one day. The cadmium in the saturated solutions was determined electrolytically[2] and the total sulfate gravimetrically, by the procedure of Friend and Wheat.[3]

Trial of the sulfate determination on known samples of cadmium sulfate gave results about two parts in a thousand too low. There was considerable co-precipitation of cadmium sulfate, and the most nearly correct results were obtained when loss of cadmium oxide was prevented by the avoidance of too high temperatures and sulfuric acid was added to convert any cadmium oxide entirely to sulfate. Ignition was carried out in a muffle at 500°. The cadmium determination was found to give slightly high results, especially with small samples. It is believed that analytical errors were well within ten parts in a thousand.

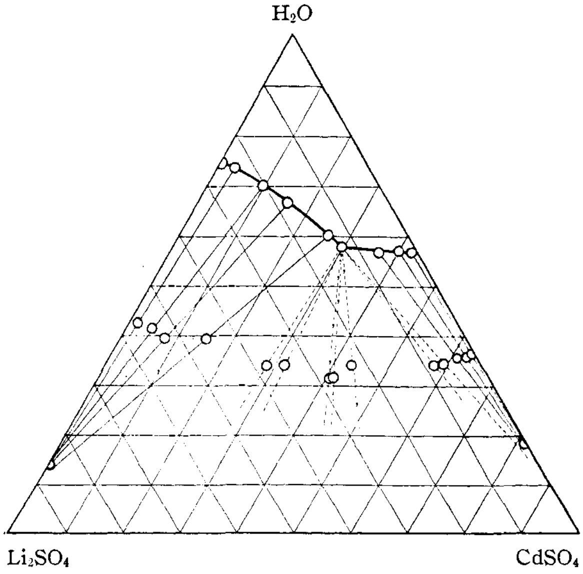

Fig. 1.

The solid material for a few of the mixtures was prepared by slow addition of lithium sulfate to a saturated cadmium sulfate solution. Since the

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[1] Calgagni and Marotta, *Gazz. chim. ital.*, **44**, I, 488 (1914).

[2] Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, 1929, p. 206.

[3] Friend and Wheat, *Analyst*, **57**, 559 (1932).

weight of the components in these original mixtures could not be obtained, the wet solid phases were analyzed.

The results are given in Table I and are shown graphically in Fig. 1. The solid phases were hydrated cadmium sulfate, $3CdSO_4 \cdot 8H_2O$, and hydrated lithium sulfate, $Li_2SO_4 \cdot H_2O$, and no evidence of a double salt was obtained.

Table I

Compositions of Saturated Solutions and Original Mixtures

Solution		Original mixture	
$CdSO_4$, wt. %	Li_2SO_4, wt. %	$CdSO_4$, wt. %	Li_2SO_4, wt. %
42.5	0.9	63.2	0.5
40.0	2.9	62.6	1.7
36.7	6.6	61.0	3.2
29.5	12.7	59.2	6.2
29.6	12.6	57.7	8.1
29.6	12.5	43.3	22.6
29.5	12.4	41.3[a]	27.2[a]
29.6	12.5	40.6[a]	28.0[a]
29.6	12.5	31.5[a]	34.3[a]
29.7	12.4	28.4[a]	37.6[a]
26.0	13.9	15.0	45.3
15.7	17.8	7.6	52.8
9.7	20.3	4.5	54.0
2.9	23.2	1.3	56.0

[a] These are compositions of wet solid phases as found by analysis.

Summary

The solubility of hydrated cadmium sulfate in solutions containing lithium sulfate and of hydrated lithium sulfate in solutions containing cadmium sulfate have been determined. A solution containing 29.6 wt.-% $CdSO_4$ and 12.5 wt.-% of Li_2SO_4 is saturated with both salts. No evidence of a double salt was obtained.

Durham, N. C. Received August 21, 1937

[Contribution from the Department of Chemistry, Oregon State College]

Studies on Hydrazine: Heats of Solution of Hydrazine and Hydrazine Hydrate at 25°

By V. C. Bushnell,[1] Albert M. Hughes and E. C. Gilbert

Calorimetric determinations of the heat of solution of a number of hydrazonium salts and heat capacities of the solutions previously have been reported from this Laboratory.[2] In this paper are presented data on the heat of solution or dilution of the hydrate (hydrazonium hydroxide), the heat capacity of its solutions, and the heat of solution of anhydrous hydrazine, in water at 25°.

Experimental

Apparatus.—The calorimeter was essentially the same as previously used[2b] but was modified by improvement of the pipet in which the solute was held. In place of the glass pipet used in work with the salts, a new gold-plated brass one of smaller capacity was constructed. This pipet consisted of a cylinder of 12-ml. capacity the upper and lower ends of which, fixed on a metal rod passing through their centers, served as valves. They opened and closed simultaneously and their movement could be regulated closely by means of a knurled nut at the upper end of the bakelite tube which served as the support for the pipet in the chimney of the submarine lid. The calorimeter constant, by reason of these changes, became 108 joules per degree, in good agreement with that calculated from the weight of the new parts.

Materials.—Most of the hydrate used was a fresh Kahlbaum product, *pro analysi*, which proved by analysis to have a slight excess of hydrazine over that required for the monohydrate. It was diluted exactly to 100.0% by the addition of water and preserved in a weight buret from which the calorimeter pipet was filled. Some hydrate was prepared by the method of Hurd and Bennett.[3]

Anhydrous hydrazine was prepared by repeated refluxing and distillation of the hydrate either from potassium hydroxide or barium monoxide in an all glass apparatus, in a vacuum or with the air replaced by hydrogen; b. p. (corr.) 112.9° at 756 mm. Barium monoxide, recommended by Hale and Shetterly,[4] seemed to serve more efficiently as a dehydrating agent but there was a greater loss of material. The purity of the material was also checked by titration with standard acid, using methyl orange.

Conductivity water was used for the dilutions. It had been redistilled from a Pyrex still to ensure absence of copper ions. It was de-oxygenated by repeated saturation with hydrogen followed by boiling at reduced pressure. It was maintained under an atmosphere of hydrogen. In this way decomposition or oxidation was reduced to a minimum.

Manipulation.—Hydrazine or the hydrate was introduced into the reaction pipet from the weight buret into

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(1) This paper is taken in part from a thesis submitted by V. C. Bushnell in partial fulfilment of the requirements for the M.S. degree, Oregon State College, 1936.

(2) (a) Cobb and Gilbert, This Journal, **57**, 35 (1935); (b) Gilbert and Cobb, *ibid.*, **57**, 37 (1935); (c) Gilbert and Bushnell, *ibid.*, **57**, 2611 (1935).

(3) Hurd and Bennett, *ibid.*, **51**, 265 (1929).

(4) Hale and Shetterly, *ibid.*, **33**, 1071 (1911).