ethane in excess, to the mixture with two condensed phases. The other approach is not included because the ethane is so slightly soluble in the carbon dioxide that the quantity of dissolved ethane could not be measured in our apparatus with reasonable accuracy. However, the measurements indicated that the condensed mixture in the carbon dioxide-rich part of the diagram developed two phases before the mole fraction of ethane in the condensed phase reached 0.03.

In the region with two condensed phases the measured partial relative pressure of carbon dioxide slightly exceeds 1.0, an obvious thermodynamic impossibility. The discrepancy is, however, within the expected error of the measurements.

The comparison between the theoretical and experimental adsorptions is shown in Figs. 2 and 3. Both graphs show isotherms of the volume of one gas adsorbed as function of its partial pressure, with the partial pressure of the other gas constant. It is obvious that the experimental procedure previously described does not measure directly isotherms in which one partial pressure is held constant. However, from each directly measured isotherm in which the quantity of one component was held constant, there could be extracted points for several isotherms of the type shown. Thus no two points of any single isotherm from mixtures were obtained in the same experimental run.

In Figs. 2 and 3 the curves are the predictions calculated from the theory, and the circles are the measured points. The completely open circles are points measured with only one gas present. The half-blackened circles are points of the isotherm in which the relative pressure held constant is 0.1; the circles with only a dividing line are points of the isotherm in which the constant relative pressure is 0.3. The direction of the dividing line in any circle indicates which gas was added first (and held constant) during the run from which the point was obtained. A horizontal dividing line means that ethane was added first; a vertical line, that carbon dioxide was first.

The values of the BET constants used in the theoretical calculations are as follows:

	C	V_m, ml. at S.T.P.
Ethane	48.6	82.4
Carbon dioxide	106.0	94.4

Hill's equation (14), which assumes unrestricted adsorption, was used for the calculations.

For carbon dioxide, the saturation pressure used was that of the solid.

Discussion

The disagreement between theory and experiment is considerable. Because this investigation was originally proposed as a means of verifying the BET assumption that adsorbed layers after the first have the evaporation–condensation properties of the bulk liquid, a few of the calculations were repeated with the assumption that the liquid mixture obeys Raoult's law. This assumption improves the situation for carbon dioxide, but aggravates it more for ethane than it improves it for carbon dioxide. However, there is not much difference in the over-all accuracy of prediction whether Raoult's law or the observed vapor pressure data are used. Thus the experimental results cannot be said to verify the BET assumption in question.

At the same time, it is not at all clear that the results disprove the assumption. The discrepancies first appear, and very strongly, at low pressures where it is unlikely that the properties of the second and higher adsorbed layers have very much effect. The discrepancies in these regions suggest some other limitation of the theory, probably the assumption that there are no horizontal interactions in the first layer.

Part of the disagreement may be due to the fact that the saturation pressure used for carbon dioxide was that of the solid. If the assumption that layers of adsorbate after the first have the vapor-pressure properties of the bulk material is correct, then certainly the saturation pressure of the solid is appropriate for these layers, since that is the stable phase in bulk under these conditions. Even if the vapor pressure of the liquid is more appropriate for the first layer, the choice we have made yields a value for C which must partially compensate for the error in P_0.

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D-Fructose Hemihydrate

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D-Fructose frequently crystallizes from concentrated solutions as spherulitic aggregates of fine needles. Although these spherulites were reported to be D-fructose hemihydrate by Honig and Jesser in 1888[1] their conclusion, based on meager evidence, has not since been verified. Wolfrom and Thompson[2] recently suggested that this phase is an unstable dimorph of anhydrous D-fructose rather than the hemihydrate, as a result of their work on the corresponding phase of L-fructose. The existence of D-fructose hemihydrate is established by the work reported here, in which its preparation is also described.

Experimental

Preparation.—Seed crystals of fructose hemihydrate usually can be obtained at 0° from a solution containing over 75% fructose seeded with powdered anhydrous fructose. Vigorous stirring of this solution must be avoided because it would result in a transformation to fructose dihydrate instead of the hemihydrate.[3] The hemihydrate also frequently crystallizes spontaneously at about 25° from solutions containing about 83% fructose. Although it is metastable under these conditions, the hemihydrate sometimes may be kept for months before anhydrous fructose appears. In either case, it crystallizes as densely packed spherulitic

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(1) M. Honig and L. Jesser, *Monatsh.*, **9**, 563 (1888).

(2) M. L. Wolfrom and Alva Thompson, THIS JOURNAL, **68**, 791 (1946).

(3) F. E. Young, F. T. Jones and H. J. Lewis, *J. Phys. Chem.*, **56**, 738 (1952).

masses of fine filaments. After seed crystals have been obtained, fructose hemihydrate free from both anhydrous fructose and fructose dihydrate can be crystallized at 20 to 21° from a slowly stirred, seeded solution containing about 81% fructose.

Composition.—Material crystallized as described above was filtered by suction and stored over anhydrous fructose seeded with fructose hemihydrate at 0°. This desiccant was selected because, at this temperature, it should take up the excess water by forming additional hemihydrate without danger of overdrying the sample. After six days, during which lumps were crushed occasionally, the water content was reduced from over 10 to 5.2%,[4] and the sample changed from a pasty mass to a dry crystalline powder. The water content of the sample was further reduced to 4.93% by fresh anhydrous fructose desiccant over which the sample was stored at 0° for 5 months. Consideration of the agreement of this value with the theoretical value for fructose hemihydrate (4.73%), and of the method of drying, leads to the conclusion that this material is fructose hemihydrate. This conclusion was confirmed by drying the sample at 0° for an additional month over anhydrous calcium chloride. During the first two weeks the water content decreased to 4.68%, at which it remained, in excellent agreement with the theoretical value. At no time in the history of this product was any anhydrous fructose observed in it, either microscopically or by X-ray diffraction.

Discussion

The agreement of our X-ray powder data with those reported by Wolfrom and Thompson[2] indicates that the sample which gave their X-ray data was L-fructose hemihydrate and not an anhydrous dimorph as they suggested. Since it is very improbable that stable and metastable forms of a pure substance would show identical melting points, the agreement they found between the melting points of their L-fructose and anhydrous D-fructose suggests further that the material used for that determination had also been dehydrated during their purification treatment.[5] Their purification step of soaking the crystals overnight in ethanol at 25° appears to be the most likely place for dehydration to occur. Our observations show that such dehydration occurs readily at 25° in 95% ethanol. It will occur slowly, even at 0°, in more concentrated ethanol.

The initial specific rotation (−129°) and mutarotation constant (0.074) of fructose hemihydrate are in sufficiently good agreement with accepted values[6] to indicate that D-fructose has the β-pyranose configuration in the hemihydrate.

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[4] Calculated from refractive indices of solutions containing weighed amounts of the hemihydrate and water. The tables of R. F. Jackson and J. A. Mathews, *J. Research Natl. Bur. Standards*, **8**, 412 (1932) (RP 426), were used to convert refractive indices to fructose percentages.

[5] In a private communication, Professor Wolfrom and Dr. Thompson agree that their original material must have been L-fructose hemihydrate and that dehydration had occurred in the samples they used for analysis and melting point determinations.

[6] H. S. Isbell and W. W. Pigman, *J. Research Natl. Bur. Standards*, **20**, 773 (1938). (RP 1104.)

NEW COMPOUNDS

Some Thiazole, Benzenesulfonamide and *n*-Hexylresorcinol Derivatives

2-Acetamido-5(?)-thiazolesulfinic Acid.—When 2-acetamido-5(?)-thiazolesulfonyl chloride[1,2,3] was reduced with sodium bisulfite solution similar to the procedure used in preparing *p*-acetamidobenzenesulfinic acid,[4] the corresponding sulfinic acid was obtained (62% yield). After it was freshly precipitated from a neutral solution of its sodium salt by acidification, or after rapid crystallization from water, it decomposed at 203°[5] when heated from 195°. However, the decomposition point was no criterion of purity inasmuch as analytical results of it and its barium salt were erratic. The first analyses of such a sample[2] indicated incorrectly that the compound was 2-acetamido-5-mercaptothiazole, which has subsequently been made by Hurd and Wehrmeister.[3] The sulfinic acid lost sulfur dioxide upon standing at room temperature or when boiled with water. It decolorized iodine in aqueous solution.

Anal.[6] Calcd. for $C_5H_6N_2O_3S_2$: C, 29.12; H, 2.93. Found: C, 29.30; H, 2.85.

The acid was characterized further by a derivative, **2-acetamido-5(?)-thiazolyl 2,4-dinitrophenyl sulfone**, prepared as follows: to a solution of 2.06 g. (0.01 mole) of the sulfinic acid in 23 ml. of ethanol, 5 ml. of water and 4 ml. of 2.5 *N* sodium hydroxide solution, was added 2.02 g. (0.01 mole) of 2,4-dinitrochlorobenzene. After 15 minutes of refluxing, the precipitate was filtered off and recrystallized from glacial acetic acid. The product weighed 1.85 g. (50%), m.p. 291–292.5°. No success was had in treating the sulfinic acid with *p*-nitrobromobenzene for the purpose of obtaining a known derivative.

Anal. Calcd. for $C_{11}H_8N_4O_7S_2$: C, 35.48; H, 2.17; S, 17.22. Found: C, 35.63; H, 2.09; S, 16.94.

Methyl 2-Amino-5-thiazolecarboxylate.—Methyl formylchloroacetate was made by condensing 208 g. of methyl chloroacetate in 450 ml. of toluene with dry methyl formate (121 g.) in the presence of sodium methoxide (109 g.) which was added over 1.5 hours at 0°. The mixture was stirred for four hours at 0° and was then stirred with 600 ml. of cold water to dissolve the sodium methyl formylacetate. The aqueous solution was neutralized with 128 ml. of concd. hydrochloric acid; 190 g. of thiourea was added and the mixture was refluxed for one hour and 45 minutes. Next, the solution was stirred with 15 g. of activated carbon and filtered. By neutralizing with sodium hydroxide solution, 156 g. of the ester was obtained, m.p. 187–188°. When recrystallized from water, it melted at 192–193.5°. The yields, based on the methyl chloroacetate employed, varied from 40 to 50%.

Anal. Calcd. for $C_5H_6N_2O_2S$: C, 37.96; H, 3.82. Found: C, 37.91; H, 3.45.

2-Amino-5-thiazolecarboxamide.—Methyl 2-amino-5-thiazolecarboxylate (200 g.) was stirred for 10 hours at 50° in 2.5 l. of concd. ammonium hydroxide solution. The mixture was cooled, filtered, and the filtrate was concentrated under reduced pressure. Then it was chilled to precipitate the product (m.p. 230°, dec.), which was washed with water. An analytical sample, washed with benzene, acetone and then recrystallized from water melted at 231–232° (dec.); yield 121 g. (54%).

Anal. Calcd. for $C_4H_5N_3OS$: N, 29.36. Found: N, 29.13.

2-Sulfanilamido-5-thiazolecarboxamide.[7]—2-Amino-5-

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[1] H. J. Backer and J. A. K. Buisman, *Rec. trav. chim.*, **63**, 228 (1944).

[2] H. E. Faith, THIS JOURNAL, **69**, 2063 (1947).

[3] C. D. Hurd and H. L. Wehrmeister suggest the possibility of the sulfonyl group being attached to the amino nitrogen, *ibid.*, **71**, 4008 (1949).

[4] H. Gilman and A. H. Blatt, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 7.

[5] All melting points are uncorrected.

[6] Microanalyses by Dr. Carl Tiedcke, Laboratory of Microchemistry, Teaneck, N. J.

[7] For biological data see H. J. Florestano and M. E. Bahler, *J. Pharmacol.*, **92**, 196 (1948).