No lithium alum has been found at 0°. Its formation at lower temperatures is still a possibility. In this study only two solid phases were found to exist. One is definitely lithium sulfate monohydrate. On the aluminum sulfate side, in addition to being too few in number, the extrapolations are too scattered due to slight variations in the composition of the aluminum sulfate used in making up the complexes as well as accidental errors in the analyses to be significant in the designation of the formula of the hydrate in equilibrium with the saturated solutions. Similar scattering in the extrapolations was found by Hill and Kaplan[9] when working with aluminum sulfate.

In previous ternary investigations involving aluminum sulfate as one of the phases, the octadecahydrate has been assumed to be the solid phases over a considerable range of temperatures although in the few cases where the tie lines were extrapolated, large deviations from the theoretical values were evident.

Additional work is being carried out in this Laboratory in an attempt to decide the hydration of aluminum sulfate at 0° as well as at other temperatures. The results of this work will be reported later.

The isothermally invariant point for this system has been found to be 16.83% aluminum sulfate and 14.45% lithium sulfate. This is considerably different than the previously reported value[2] at this temperature.
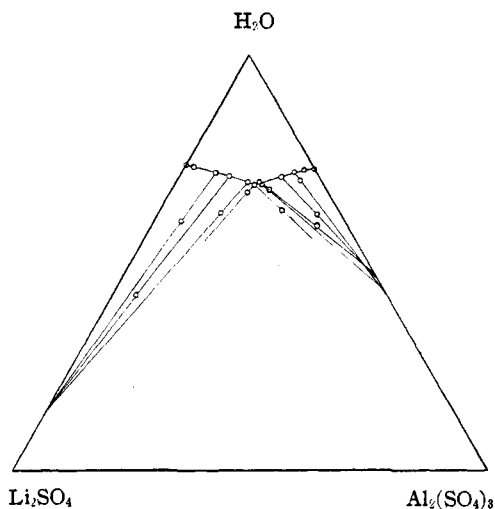

Fig. 1.—0° Isotherm: Li_2SO_4–$Al_2(SO_4)_3$–H_2O.

Summary

Solubility measurements are given for the system Li_2SO_4–$Al_2(SO_4)_3$–H_2O at 0°. There is no evidence of double salt formation or solid solution.

A new value for the solubility of aluminum sulfate at 0° is given.

The degree of hydration of aluminum sulfate in contact with a saturated solution at 0° has not been determined with certainty. The previous assumptions of the existence of the octadecahydrate at this temperature have been questioned.

Binary Liquid Systems. I. Vapor–Liquid Equilibria in the System Carbon Tetrachloride–Ethyl Acetate

By PHILIP W. SCHUTZ

In a survey of the behavior and properties of homogeneous binary liquid systems it became of interest to investigate the system carbon tetrachloride–ethyl acetate. A careful search of the literature showed that the only vapor–liquid equilibria data available, covering the complete range of composition for this system, were those due to Tyrer.[1] These data have been quoted in the "International Critical Tables" and other similar compilations. Unfortunately, a careful scrutiny of these data shows that they are most probably in error. When the vapor and liquid

(1) Tyrer. J. Chem. Soc., 101, 81 (1912).

compositions given are plotted against the boiling temperature (at 745 mm. in this case) as the concentration of carbon tetrachloride increases from zero mole per cent., both curves show the normal behavior for a system which exhibits a minimum boiling mixture. The behavior continues normal until the composition of the azeotropic mixture is reached (about 51 mole per cent.) at which point the vapor and liquid curves *cross* instead of becoming *tangent*. The vapor curve then continues to lie below the liquid curve through the rest of the concentration range. This behavior leads to the theoretically impossible situation of a system ex-

hibiting a minimum boiling point and at the same time giving at all concentrations, except that of the azeotropic mixture, a vapor which is richer in one component, carbon tetrachloride in this case, than the liquid in equilibrium with it. Because of these facts, it was deemed advisable to repeat the equilibrium measurements on this system.
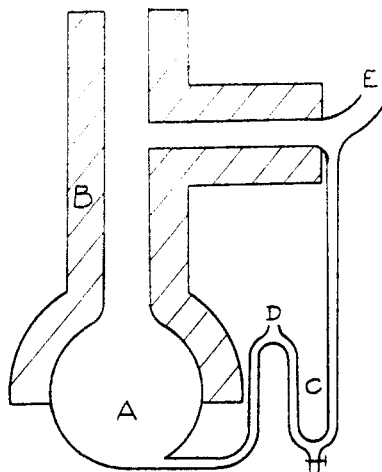

Fig. 1.—Cross section of apparatus: A, boiling flask; B, asbestos lagging; C, condensate receiver and return to boiling flask; D, pressure equalizing vent, kept loosely covered during operation; E, condenser attached here. Thermometer and internal electrical heater not shown.

Experimental

Carbon Tetrachloride.—Merck technical carbon tetrachloride was treated with a mixture of 50% potassium hydroxide solution and ethyl alcohol and subsequently with concentrated sulfuric acid as suggested by Fieser.[2] After removing the dissolved acid by washing with water, the material was dried for several hours over calcium chloride and finally for twenty-four hours over phosphorus pentoxide. The dried material was distilled through a twenty-inch (51-cm.) packed column under heavy reflux, and a fraction boiling at 73.50° under 687.0 mm. collected for use. The boiling range was not detectable on a thermometer graduated in 0.1°. The refractive index of this product (n^{20}D) was 1.46023.

Ethyl Acetate.—Merck technical ethyl acetate was washed with saturated sodium carbonate and then with saturated calcium chloride. After drying for twenty hours over calcium chloride, it was distilled in the column mentioned above. A fraction boiling between 73.9 and 74.2° at 685 mm. was then dried over phosphorus pentoxide for several weeks and refractionated. Material taken as product from this fractionation boiled at 74.10 ± 0.05° under 685.0 mm. and had a refractive index (n^{20}D) of 1.37239.

Apparatus and Method.—The apparatus used consisted of a 250-cc. round-bottomed distilling flask on which the

(2) Fieser, "Experiments in Organic Chemistry," D. C. Heath and Company, 1935, p. 308.

usual side-arm was replaced by a piece of 12 mm. i. d. glass tubing. It was so arranged that the condensed vapor was returned continuously to the distilling flask. The detail of this arrangement is shown in Fig. 1. The entire vapor space, up to the point at which the condensate return line was attached, was enclosed in three-quarters of an inch (2 cm.) of asbestos paper in order to minimize fractionation in this section. That this was accomplished is indicated by the fact that the results obtained were not affected by a two-fold change in the rate of distillation. Had there been an appreciable amount of fractionation, this would not have been true. The condensate trap had a volume of about 2 cc. In order to avoid the possibility of error due to condensate from the beginning of a run being trapped in the short length of tubing (volume about 0.25 cc.), leading to the ungreased stopcock, a small volume of condensate was drawn off slowly about the middle of the run and discarded. In no case did this amount to more than 0.5 cc. In making a run the flask was charged with 100–125 cc. of mixture and heating begun with the internal electrical heater. After distillation had attained its maximum rate, it was continued for forty-five minutes, when the heating was stopped and the condensate sample withdrawn into a small tightly stoppered vial. The boiling liquid sample was removed by tilting the whole apparatus and filling the condensate trap. This was done three or four times, and the material drawn off was discarded in order to rinse the trap. The next filling was then withdrawn as a sample. Both samples were put into a thermostat at 20.00 ± 0.02° and analyzed by means of a Pulfrich refractometer whose temperature was controlled by a stream of water from the same thermostat. All of the concentrations are judged to be accurate to at least ±0.1 mole per cent. Temperatures were measured with a mercury-glass thermometer which was checked against a Bureau of Standards calibrated thermometer. The recorded temperatures are accurate to ±0.03°. No effort was made to control the pressure, all runs being made at the normal barometric pressure here. During the period of these runs, it did not vary by more than 1 mm. from 685 mm. (corrected to 0°).

Discussion of Results

TABLE I

VAPOR–LIQUID EQUILIBRIA AT 685 MM.

T, °C.	Mole % CCl₄ in vapor	Mole % CCl₄ in liquid	n^{20}D of liquid
73.40	100	100	1.46023
72.57	87.1	89.4	1.45044
72.12	76.5	79.2	1.44122
71.81	67.5	69.3	1.43238
71.62	61.0	61.3	1.42527
71.57	58.7	58.8	1.42277
71.57	57.7	57.2	1.42157
71.63	52.8	51.3	1.41627
71.74	45.9	42.9	1.40893
71.95	38.9	35.2	1.40223
72.20	32.4	28.0	1.39607
72.76	20.2	15.9	1.38569
73.30	10.0	7.3	1.37836
74.01	0.8	0.5	1.37280
74.10	0.0	0.0	1.37239

The data are presented in Table I. Because of the difficulty of reproducing on a small scale a plot of temperature vs. composition when the liquid and vapor are so nearly alike, this plot has been omitted. On a large-scale plot all of the points fall on smooth curves with no deviations as large as those given above. It is evident from these data that this system behaves in the normal manner for systems exhibiting a minimum boiling mixture. The azeotropic mixture contains 58.2 mole per cent. carbon tetrachloride and boils at 71.56° under 685 mm. pressure.

In Table II are given the various data available on the azeotropic constants for this system at different pressures. The values attributed to Tyrer were obtained after a careful consideration of his data and do not agree with those given in the International Critical Tables.[3]

Inspection of Table II shows that the rate of change of composition of the azeotrope with pressure is decreasing as the pressure decreases. This behavior is just the reverse of that found in numerous other systems which have been investigated over a range of pressures.[4] Because of this

(3) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., 1928, Vol. III, p. 312.

(4) (a) Wade and Merriman, J. Chem. Soc., 99, 997 (1911). (b) Merriman, ibid., 103, 628, 1790 (1913); (c) Vrevsky, Z. physik. Chem., 81, 1 (1912); 83, 551 (1913).

TABLE II

AZEOTROPIC DATA AT DIFFERENT PRESSURES

P, mm.	B. p., °C.	Mole % CCl_4	Observer
760	74.75	43	Young,[5] Lecat[6]
745	74.04	51.0 ± 0.5	Tyrer[1]
685.0	71.56	58.2	This paper
318.8	49.99	67.4	Zawidzki[7]

apparent difference in behavior, this system is being investigated over a wide pressure range in order to verify this difference with a single set of data.

The refractive index–composition curve falls just slightly below the straight line joining the indices of the two pure components. The maximum deviation comes at 50 mole per cent., and the curve appears to be symmetrical about this point.

Summary

The system carbon tetrachloride–ethyl acetate has been investigated at 685 mm. and found to behave as expected for a system having a minimum boiling mixture, contrary to indications from other data.

(5) Young, "Distillation Principles and Processes," Macmillan and Company, London, 1922, p. 52.

(6) Lecat, "L'azeotropisme," Lamertin, Brussels, 1918, p. 136.

(7) Zawidzki, Z. physik. Chem., 35, 129 (1900).

The Peroxide Effect in the Addition of Reagents to Unsaturated Substances. XXII. The Addition of Hydrogen Bromide to Trimethylethylene, Styrene, Crotonic Acid, and Ethyl Crotonate

By CHEVES WALLING,[1] M. S. KHARASCH AND F. R. MAYO

Recently we described an abnormal addition of hydrogen bromide to 2-bromo-2-butene under peroxidic conditions in dilute pentane solution, and commented upon the efficacy of this method of obtaining the abnormal addition of this reagent.[2] Further interesting results, with the aid of this technique, now have been obtained with several more olefins.

Addition of Hydrogen Bromide to Trimethylethylene.—In 1904 Ipatieff and Dechanov[3] observed that, while treatment of trimethylethylene with hydrogen iodide or aqueous hydrobromic acid yielded exclusively the tertiary halide, addi-

tion of hydrogen bromide in 60% acetic acid gave 10–25% of s-isoamyl bromide (2-methyl-3-bromo-butane). A similar result was reported by Michael and Zeidler.[4] Recently, however, Smith[5] has indicated that t-amyl bromide is the sole product of the addition of hydrogen bromide to this olefin and that peroxides are without effect upon the course of the reaction, but unfortunately he does not describe the experimental conditions employed. The latter conclusion is contradicted by the results of this investigation, as shown in Table I. In the absence of a solvent and air and in the presence of an inhibitor, a

(1) Du Pont Fellow 1938–1939.

(2) Walling, Kharasch and Mayo, THIS JOURNAL, 61, 1711 (1939).

(3) Ipatieff and Dechanov, Chem. Zentr., 75, II, 961 (1904).

(4) Michael and Zeidler, Ann., 385, 271 (1911).

(5) Smith, Chemistry and Industry, 57, 561 (1938).