

[CONTRIBUTION FROM THE BUREAU OF STANDARDS, U. S. DEPARTMENT OF COMMERCE.]

EQUILIBRIA IN THE SYSTEMS CARBON DISULFIDE:METHYL ALCOHOL, AND CARBON DISULFIDE:ETHYL ALCOHOL.¹

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Received October 31, 1921.

Introduction.

The occasion for the determination of the data presented in this paper arose several years ago in connection with work on the preparation of pure anhydrous alcohols to be used in density determinations. As is well known, in certain cases of limited miscibility between two liquid components, the critical solution temperature offers an extremely sensitive criterion of the purity or of changes in purity of either compound provided that the other component is either pure or of constant composition.

Mixtures of hydrocarbons, such as gasoline and kerosene, have been used extensively in testing the lower alcohols, but in order to obtain a fixed and easily reproducible point it is desirable to have a definite compound as the second component. Various hydrocarbons of the methane series, such as pentane, hexane or heptane, could be used for this purpose, but they are difficult to prepare with a sufficient degree of purity. Carbon disulfide is preferable because it is easily prepared pure and is fairly stable when kept under the proper conditions. It therefore appeared that more work should be done and more reliable values obtained on the equilibria in such common systems, of which the boiling-point curves have been the subject of study by many investigators.

General Principles.

The present discussion of equilibria in binary systems in which the components are only partially miscible will be confined to temperatures at which the vapor pressures of the components are small, far less than the critical pressures, and to cases in which only the upper critical solution temperature is realizable.

Consider two components such as A and B (Fig. 1) which are not completely miscible in the liquid state. Small quantities of B added to A, at the temperature T_c , will at first dissolve forming a homogeneous liquid phase. When the liquid has the composition represented by the point a , further quantities of B will not dissolve, but will take up some A from

¹ Published by permission of the Director of the Bureau of Standards, Washington, D. C.

² This investigation was practically completed prior to the death in November, 1919, of Mr. McKelvy, the senior author, and the manuscript was subsequently prepared by the junior author. Valuable suggestions were received from Mr. G. W. Morey, of the Geophysical Laboratory.

the liquid, forming a second liquid layer of composition b . As more and more B is added, the phase b will increase in amount, while the conjugate solution a will decrease until when the mass has the composition b the first liquid will have disappeared completely. Similarly, if the liquid A be added to B at the temperature T_a , the mixture will remain homogeneous until the composition b is reached, when a second liquid layer of the composition a will separate.

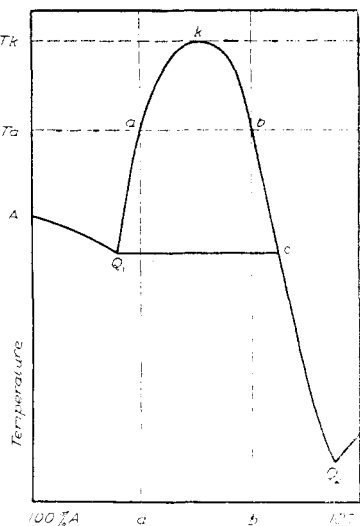


Fig. 1.—Typical equilibrium diagram for two partially miscible components.

As the temperature is changed the mutual solubility of the two liquids will change, the solubility increasing if the differential heat of solution is negative, decreasing if it is positive. We will consider the case that the solubility in each layer increases with temperature. The two conjugate liquids a and b will then approach each other in composition, until at the "critical solution temperature" T_k , the two solutions become identical in composition, and the curve has a horizontal tangent. At temperatures above the critical solution temperature the two components are completely miscible in the liquid state.

The effect of the introduction of a third component into a binary system exhibiting limited miscibility will depend on whether the added substance increases or decreases the mutual solubility of the two liquids. Consider a ternary system ABC (Fig. 2) in which the components A and B are partially miscible; K is the binary critical solution, a and b two binary conjugate liquid layers at a lower temperature T_a . If addition of C increases the mutual solubility of a and b , the two liquid layers will approach each other in composition, until at K' they become identical; T_a is the ternary critical solution temperature of the mixture of composition K' . Addition of C in this case lowers the critical solution temperature. The case in which addition of C diminishes the mutual solubility is shown in Fig. 3; the two curves aa'

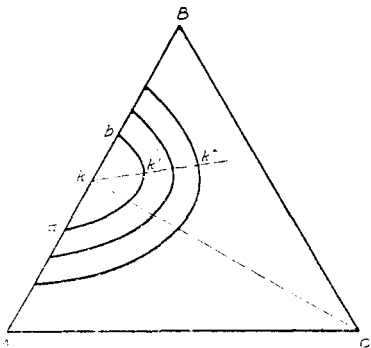
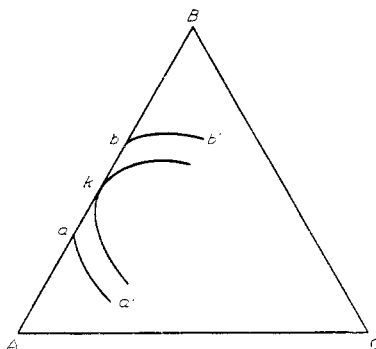


Fig. 2.—Three component system, in which addition of C increases the mutual solubility of A and B.

and bb' give the composition of the two liquid layers at the temperature T_a . In this case a higher temperature is necessary in order to make the two layers miscible, and addition of C will raise the critical solution temperature. Both the direction of the effect and its magnitude depend on the specific properties of the components; the first case will usually be found in systems in which the component C is miscible with both A and B, the second case in systems in which the component C is immiscible with either A or B, or with both. In the latter case the effect will be the more marked the more complete the immiscibility. An example is the effect of water on the critical solution temperature of the system ethyl alcohol-kerosene, in which 1% of water raises the critical solution temperature nearly 20° .

The effect of addition of the component C on the ratio A/B of the conjugate solutions and the critical solution should also be considered.

Addition of C will in general alter the proportion of A and B in the conjugate solutions (Fig. 2), and the curve passing through the critical compositions will not in general coincide with the curve KC, which represents the compositions of the solutions obtained by adding C to the binary critical mixture K. In other words, when increasing amounts of C are added to the mixture represented by the point K, the temperature at which the liquids become mutually soluble is not the critical temperature, but merely a point on the mutual solubility



surface of the ternary system. At the critical solution temperature, on the curve $KK'K''$ the two liquid phases become identical in composition; at a point on the line KC, a liquid of one (changing) composition becomes completely soluble in another of different (changing) composition. This distinction between points on the line KC and between true critical solution temperatures is one often disregarded.

Earlier Work.

Study of the earlier work showed wide discrepancies in values, which are probably almost totally ascribable to impurity of the materials used.

1. In the system carbon disulfide: methyl alcohol, Rothmund³ obtained 39.92° as the critical solution temperature and approximately 84.5% by weight of carbon disulfide as the critical concentration. Timmermanns⁴ in a very comprehensive paper

³ Rothmund, *Z. physik. Chem.*, **26**, 433 (1898).

⁴ Timmermanns, *Récherches Expérimentales sur les Phénomènes de Démixtion des Mélanges Liquides*. Thesis, University of Brussels, 1911.

reported 48.5° for the critical solution temperature of this system but gave no value for the concentration. He stated that the alcohol used contained traces of water. No values could be found in the literature for temperatures below zero.

2. In the system carbon disulfide:ethyl alcohol Guthrie⁵ gave -14.4° for the critical solution temperature. No value for the critical concentration can be read from a curve through the four points given by him. Kuenen⁶ gave -10.6° for the critical solution temperature, but no values for concentration. For this system values have been found for only five concentrations, probably because of the low temperature required for the complete investigation.

Purification of Materials.

The materials used were carefully purified and special attention was paid to the dehydration of the alcohols. Freezing points, densities, and the critical solution temperature itself were used as criteria of purity. (Hereafter the abbreviation c. s. t. will be used in place of the words critical solution temperature.)

Carbon Disulfide.—Preliminary tests were made in which samples were purified as follows: (a) by treatment with bromine; (b) by treatment with fuming nitric acid, one portion being further treated with phosphorus pentoxide and another portion with conc. sulfuric acid; (c) by distillation from a flask containing ceresin. The c. s. t. of each sample (see Table I) with the same test alcohol was used as a basis for comparing the different products.

TABLE I
PRELIMINARY TESTS ON CARBON DISULFIDE

Treatment	C. s. t. with test alcohol No. 1 °C
Bromine	35.27
Fuming HNO ₃	
(a) then P ₂ O ₅	34.99
(b) then H ₂ SO ₄	35.00
Distilled from ceresin	35.00

The carbon disulfide used was prepared by the third method which seemed to be simple as well as efficient. No satisfactory explanation has been offered of the mechanism by which the ceresin removes the impurities. Twelve liters of technical carbon disulfide was distilled from about 900 g. of ceresin. The middle fractions of this distillation were combined and redistilled from fused calcium chloride. The temperature of the vapor remained constant at 46.6° (uncorr.) during both distillations. The constancy of the c. s. t. of the fractions as shown in Table II indicates that the second distillation might not have been necessary.

Fraction 5 of the second distillation was used in this investigation. Its freezing point was determined as follows.

⁵ Guthrie, *Phil. Mag.*, [5] 18, 495 (1884).

⁶ Kuenen, *Phil. Mag.*, [6] 6, 637 (1903).

TABLE II
FINAL PURIFICATION OF CARBON DISULFIDE

Distilled from ceresin Fraction	C. s. t. with test alcohol No. 2 °C	Fractions 2 to 6 combined and distilled from CaCl ₂ Fraction	C. s. t. with test alcohol No. 3
1	34.15	1	34.80
2	34.80	2	34.78
3	34.75	3	34.65
4	34.70	4	34.75
5	34.60	5	34.65
6	34.90	

The carbon disulfide was first frozen by means of liquid air in a bulb to which was attached by a glass-to-metal joint⁷ a diaphragm valve through which the bulb was connected to the freezing-point apparatus, illustrated in Fig. 4. The valve was then opened and after the entire system had been evacuated the carbon disulfide was melted and condensed into the freezing-point tube. During the measurement of the freezing point the liquid was stirred with a platinum stirrer fastened to a gold-plated iron ring which in turn was moved up and down by a large permanent magnet outside. Temperatures were measured by means of a platinum resistance thermometer⁸ which extended into the carbon disulfide. The freezing point obtained was -112.0° , which agrees with that given by Henning⁹ (-112.0°) as the mean of 17 determinations on different samples.

This thermometer was standardized in ice, steam and sulfur vapor, in the customary way, the temperatures being calculated by the Callendar formula. Below -40° , temperatures calculated by this formula are too low, and the calculated temperatures were corrected to the hydrogen scale, using the deviation curve found by Henning.⁹ Since the platinum used in this thermometer was of the same high purity as that used by Henning, the use of his correction curve could introduce no significant error, especially since the total correction at the lowest temperature measured (-112°) amounts to only 0.3° .

Methyl Alcohol.—Preliminary drying of the methyl alcohol was accomplished by distillation from lime, but the last traces of water were removed by treatment with sodium, since when lime was used for the final dehydration, great swelling of the lime occurred and loss of alcohol resulted. Two distillations from sodium were necessary before a constant composition was obtained as shown by the constant c. s. t. of the fractions with a test gasoline. (See Table III).

The second fraction of the third distillation was used in this work. Its

⁷ McKelvy and Taylor, *THIS JOURNAL*, **42**, 1364 (1920).

⁸ *Bur. of Standards Bull.*, **6**, 154 (1909).

⁹ Henning, *Ann. Physik.*, **40**, 653 (1913).

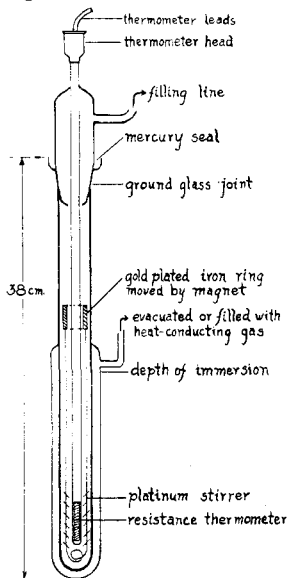


Fig. 4.—Freezing-point apparatus.

density (d_4^{25}) was 0.78658 and its freezing point -97.7° . Timmermann's¹⁰ value for the melting point is -97.1° and Young's¹¹ value for d_4^{20} is 0.7915 and for d_4^{30} is 0.7825.

Ethyl Alcohol.—This alcohol was originally prepared from ivory nuts, which source gives a product especially free from aldehydes. It was dehydrated by prolonged refluxing with fine freshly calcined lime. A slow stream of dry air was passed through the very top of the condenser and the condenser water was kept at about 55° . By this means the alcohol was condensed, but aldehydes, if present, passed through and were swept away. Constancy of the c. s. t. as shown in Table IV with a test kerosene oil was the criterion of constant composition of the fractions.

TABLE III

FINAL PURIFICATION OF METHYL ALCOHOL

Third distillation from sodium Fraction	C. s. t. with test gasoline °C.
1	29.68
2	29.49
3	29.48
4	29.47

TABLE IV

FINAL PURIFICATION OF METHYL ALCOHOL

Fourth distillation from lime Fraction	C. s. t. with test oil No. 5 °C.
1	23.30
2	23.23
3	23.11
4	23.00
5	22.95
6	23.00

Fraction 5 of the fourth distillation was used in this work. Its density (d_4^{25}) was 0.78506, which is identical with the value previously determined at this Bureau.¹²

General Description of Apparatus and Methods.

Temperature Baths.—For ordinary temperatures a water-bath was used. It consisted of an inverted bell jar provided with an efficient stirrer, a steam heating-coil and a cold water cooling-coil. The low-temperature bath consisted of a 500cc. Dewar cylinder fitted with a stirrer and a cooling coil into which liquid air could be siphoned in small quantities. Petroleum ether was used for the contact liquid because it can be cooled to -125° before it freezes or becomes cloudy. In using this type of bath every possible precaution must be taken to avoid introducing liquid air directly into the bath itself, and to avoid mixing the vapors from the bath liquid with those from the liquid air, especially as the latter may be nearly pure oxygen. Care must also be taken to eliminate as far as possible any means such as sparks from motors, frictional electricity, etc., which might ignite the vapors. Neglect of these precautions

¹⁰ Timmermann, *Proc. Roy. Soc. Dublin N. S.*, **13**, 339 (1912).

¹¹ Young, *ibid.*, **12**, 374 (1910).

¹² *Bur. Standards, Bull.*, **9**, 327 (1913).

may cause serious trouble. The death of Mr. McKelvy,¹³ the senior author, resulted from an explosion while working with a bath of this type. The exact cause of this explosion is unknown.

Temperature Measurements.—Temperatures in the water-bath were measured with a mercury thermometer. The low temperatures were measured with a single-junction copper-constantan thermocouple, using a potentiometer of the White type.

The wire used for this thermocouple was taken from a stock of B. and S. gage No. 36 wire (0.127 mm. diam.) which was known to be exceedingly homogeneous, different couples made from this stock differing in their indications by less than 1 part in 1000. Two 10-junction thermocouples made from this wire had been calibrated by comparison with platinum-resistance thermometers. These platinum resistance thermometers had been standardized to reproduce the scale of Henning's hydrogen thermometer.¹⁴ The results of the intercomparisons with the platinum-resistance thermometers, and a separate measurement at the freezing point of mercury, were in agreement within 0.02° with those given by the empirical equation, for a single junction

$$E = 38.836t + 0.04576t^2 - 0.00004243t^3$$

where E is e. m. f. in microvolts, and t is the temperature in centigrade degrees, the cold junction of the couple being at 0° .

It seems probable that the single junction couple used could, by means of the equation given, be used to reproduce the scale of Henning's hydrogen thermometer with an accuracy of a few hundredths of a degree down to -40° , and to within 0.1° at the lowest temperatures, (-112°) reached in the measurements given in this paper.

Procedure.—All determinations were made with the mixtures contained in glass bulbs of about 5 cc. capacity blown at the end of a short piece of tubing. Preliminary data were obtained with cork-stoppered bulbs, the liquids being measured from burets.

Mixtures for the final measurement were made by a different method, using bulbs fastened to valves by glass-to-metal joints. The alcohol and carbon disulfide were contained in long graduated bulbs (burets) also attached to the line by metal valves. The bulb to contain the mixture was fastened to the line and the whole system evacuated. By immersing the bulb in liquid air any desired amount of either liquid was distilled over. With the valves and unions used the bulb could be detached, weighed and again attached repeatedly without change in weight, as shown by McKelvy and Taylor.⁷ The system was again evacuated and after the liquid in the bulb was frozen the valves were opened and the desired amount of the other component distilled over. After weigh-

¹³ McKelvy, *J. Ind. Eng. Chem.*, **12**, 94 (1920).

¹⁴ Henning, *Ann. Physik.*, **40**, 635 (1913); **43**, 282 (1914).

ing the bulb the mixture was again frozen in liquid air and the tube sealed as close as practicable to the bulb. It is to be noted that by this method, which excluded contact with air and moisture, the liquids received a final distillation not long before the c. s. t. was determined.

The temperature of complete mutual solubility, or the unmixing temperature, of any mixture can be found by noting either the temperature

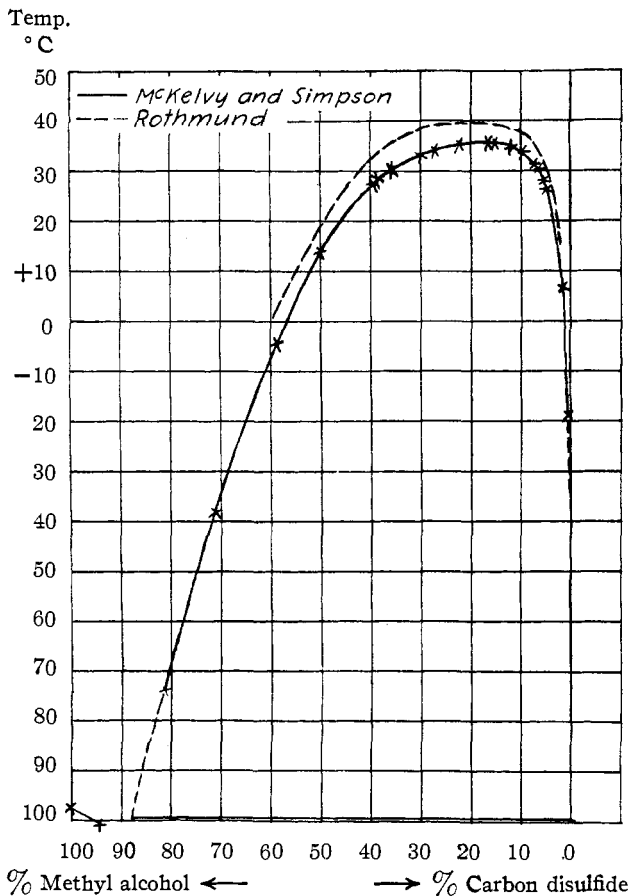


Fig. 5.—Temperature of complete mutual miscibility of mixtures of carbon disulfide and methyl alcohol.

at which the cloudiness of the mixture disappears when shaken in a bath whose temperature is gradually rising, or the temperature at which cloudiness appears when the temperature of the bath is falling. The temperature of the bath was changed so slowly that the bulb was considered to be at the same temperature as the bath. In the systems studied the opalescence is so great that it obscures the clouding point, especially by the first method. By the second method, when the bulb is shaken with

a swirling motion a cloudy wisp appears and is followed immediately by complete cloudiness. Trials were made to determine the clouding point by looking through the bulb at a scale immersed in the bath, and also looking directly at a light suspended behind the bath.

The procedure finally adopted was as follows. Having found approximately the mutual solubility temperature while warming the bath, the accurate readings were made when the temperature was falling very slowly. By looking directly at the light the formation of the cloudy wisp

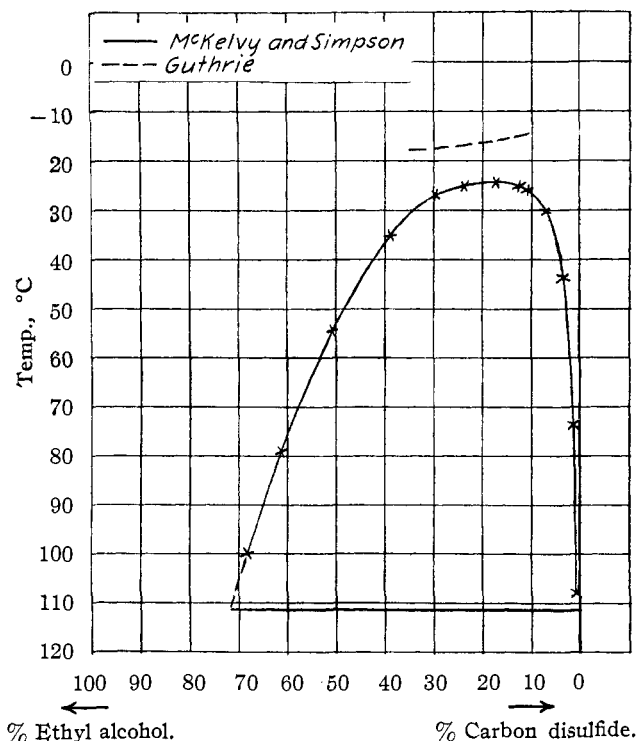


Fig. 6.—Temperatures of complete mutual miscibility of mixtures of carbon disulfide and ethyl alcohol.

could be observed, even through the troublesome opalescence. The temperature at which the wisp appeared was considered to be the true unmixing temperature and successive determinations on the same mixture were constant to 0.01° or 0.02° . The determinations on different mixtures are presented in Tables V and VI and Figs. 5 and 6. The critical solution temperature and composition were interpolated from these data.

Discussion of Results.

Carbon Disulfide : Methyl Alcohol.—The c. s. t. of this system is 35.7°

and the critical concentration is approximately 85% by weight of carbon disulfide.

The temperature at which solid methyl alcohol separates from the alcohol-rich layer is -99.6° . This corresponds to temperature Q_1 of Fig. 1; the compositions of the two conjugate solutions Q_1 and c were not determined. The unmixing temperature of a solution containing only 0.36% of methyl alcohol is -18.95° , and the liquid c would be at even smaller methyl alcohol concentration; the binary eutectic Q_2 would contain even less alcohol. More complete study of mixtures rich in carbon disulfide was prevented by the accidental destruction of the low-temperature bath.

TABLE V
TEMPERATURES OF COMPLETE MUTUAL MISCIBILITY OF MIXTURES OF CARBON DISULFIDE AND METHYL ALCOHOL

CS ₂ %	Unmixing temperature °C.	CS ₂ %	Unmixing temperature °C.	CS ₂ %	Unmixing temperature °C.
99.64	-18.85	88.43	34.82	61.03	28.60
98.47	+ 6.46	84.73	35.75	60.53	27.34
95.27	26.50	83.89	35.63	49.93	+13.80
94.74	28.00	77.65	35.30	41.29	- 4.43
93.55	30.58	72.85	34.09	28.78	-38.37
93.40	31.08	70.13	33.35	18.70	-73.60
90.22	33.80	64.12	30.70	6.39	Freezes at -100.7°

Carbon Disulfide:Ethyl Alcohol.—The c. s. t. of this system is -24.4° and the critical concentration is approximately 83% by weight of carbon disulfide. The temperature at which all mixtures freeze is -111.7° . Since the freezing point of carbon disulfide is -112° , the solid phase is probably this substance, and the eutectic lies on the ethyl alcohol side. In this system carbon disulfide corresponds to component A and ethyl alcohol to component B. The composition of the two co-existing liquid phases at the quadruple point Q_2 was not determined. On the alcohol side complete study of the curve was impossible because of vitreous solidification.

TABLE VI
TEMPERATURES OF COMPLETE MUTUAL MISCIBILITY OF MIXTURES OF CARBON DISULFIDE AND ETHYL ALCOHOL.

CS ₂ %	Unmixing temperature °C.	CS ₂ %	Unmixing temperature °C.	CS ₂ %	Unmixing temperature °C.
99.09	-108.04	87.48	-25.07	61.23	-35.17
98.55	-73.68	82.71	-24.31	49.46	-54.58
96.78	-43.71	76.25	-25.13	38.75	-79.26
93.05	-30.16	70.39	-26.88	31.96	-100.07
89.57	-25.76

Applications of the above data have not been worked out. McKelvy¹⁵

¹⁵ McKelvy, Ref. 12, pp. 330-370.

has confirmed the results of earlier investigators on the estimation of small amounts of water in ethyl alcohol by its effect on the critical solution temperature of a test kerosene. The effect of water on the critical solution temperatures of methyl alcohol-carbon disulfide and of ethyl alcohol-carbon disulfide mixtures could be similarly applied to the estimation of water in methyl or ethyl alcohol, and would offer the advantage of making use of a definite compound instead of an indefinite mixture of hydrocarbons such as kerosene. It has been found that the addition of 1% of water raises the c. s. t. about 10°. As early as 1871,¹⁶ the possibility of determining the purity of ethyl alcohol by measuring the solubility of carbon disulfide in it at a fixed temperature (*e. g.*, 17°) was pointed out, and suitable equations were derived. This method is not, however, as sensitive as the measurement of the c. s. t. By using the proper components the c. s. t. method can be used for testing products in many processes. In fact, Orton and Jones¹⁷ have reported on c. s. t. as a criterion of purity of organic liquids of industrial importance.

Summary.

Earlier work on the critical solution temperature of carbon disulfide with methyl and ethyl alcohol is reviewed. Methods of purification of these substances are given, and a freezing-point apparatus is described.

A detailed description is given of the method used in preparing the mixtures for critical solution temperature measurement.

The values obtained are as follows.

	Crit. sol. temp. ° C	Crit. concentration % CS ₂
Carbon disulfide : methyl alcohol	35.7	85
Carbon disulfide : ethyl alcohol	-24.4	83

Some applications of the critical solution temperature are suggested.

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¹⁶ Tuchschnid and Follenius, *Ber.*, **4**, 583 (1871).

¹⁷ Orton and Jones, *J. Chem. Soc.*, **115**, 1194 (1919).