in the specific rate of the solvolysis. The magnitude of the effect is practically the same in the chloride and bromide cases, while the decrease in the presence of potassium iodide is quite a bit greater. The effect would appear to be of the same nature as that exerted by acetate ion upon the rate of production of benzyl alcohol from benzyl chloride[4] or that exerted by azide ion upon the rate of production of dimethylbenzhydrol from dimethylbenzhydryl chloride[14b] and to indicate that some at least of the hydrolysis goes by way of the ionic mechanism

$$\mathrm{EtTs} \longrightarrow \mathrm{Et^+} + \mathrm{Ts^-}$$
$$\mathrm{Et^+} + 2\mathrm{H_2O} \longrightarrow \mathrm{EtOH} + \mathrm{OH_3^+}$$

If the halide ion diverts part of the ethyl ion to the formation of ethyl halide

$$\mathrm{Et^+} + \mathrm{X^-} \longrightarrow \mathrm{EtX}$$

the total rate of formation of alcohol and of titratable acidity must decrease.

During the course of a hydrolysis the specific rate k_1 (see Table I) increases about as one would predict from the change in concentration of ethyl toluenesulfonate. This is consistent with previous observations[15] to the effect that the hydrolysis of toluenesulfonates is not catalyzed by acids, and indicates further that ethyl alcohol in small amounts has a negligible effect upon the rate of hydrolysis.

The lack of an appreciable general salt effect of the sort which perchlorates exert upon the hydrolysis of benzyl chloride suggests that the transition state in the hydrolysis of ethyl toluenesulfonate is less polar and corresponds to a smaller separation of charges than is the case with benzyl chloride.

Summary

The rates of the solvolytic reactions of ethyl toluenesulfonate and of ethyl chloride, bromide and iodide and the rates of the displacement of toluenesulfonate ion by chloride, bromide, iodide and hydroxyl ions have been measured in a 60.72% dioxane–39.28% water medium at 50°. Iodide ion displaces toluenesulfonate ion from ethyl toluenesulfonate at a greater rate than do the other halide ions; nevertheless, ethyl iodide, of all the ethyl halides, is most rapidly decomposed by hydrolysis. This apparent paradox may be accounted for in terms of the fact that the lower solvation energy of iodide ion approximately compensates for its weaker binding to carbon. The equilibrium constants for the displacement of toluenesulfonate ion by bromide and by iodide ion are of the order of 10^2. Halide ions decrease the rate of formation of ethyl alcohol from ethyl toluenesulfonate, an effect which is consistent with an ionic mechanism of solvolysis.

New York, N. Y. Received June 2, 1941

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[15] Praetorius, *Monatsh.*, **26**, 1 (1905); Wegscheider, *Z. physik. Chem.*, **41**, 52 (1902).

[Contribution from the Department of Chemistry of Haverford College and the Department of Chemistry and Chemical Engineering of the University of Pennsylvania]

Transition Phenomena Involving Decahydrated Mixed Crystals of Sodium Sulfate and Sodium Chromate[1]

By William E. Cadbury, Jr.,[2] William B. Meldrum and Walter W. Lucasse

The temperature of transition of sodium sulfate decahydrate into the anhydrous form is 32.383° on the International Hydrogen Scale,[3] while that of sodium chromate decahydrate into the hexahydrate is 19.525°, and into the tetrahydrate is 19.987°.[4] It is known that sodium chromate lowers the transition temperature of sodium sulfate decahydrate. Richards and Kelley[4] have reported that sodium sulfate *raises* the temperature of transition of sodium chromate decahydrate into the hexahydrate. They reported an elevation of as much as 4°.

At sufficiently low temperatures sodium sulfate and sodium chromate decahydrates form mixed crystals in all proportions. When these mixed crystals are warmed they undergo transition, losing water of crystallization and forming another solid phase and a saturated solution. The temperature at which solution and two solid

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[1] Part of the material in this paper was presented before the Philadelphia Meeting of the American Association for the Advancement of Science, December 28, 1940.

[2] This paper is abstracted from part of a dissertation presented by William E. Cadbury, Jr., to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1940.

[3] Richards and Wells, *Proc. Am. Acad. Arts Sci.*, **38**, 43 (1902); *Z. physik. Chem.*, **43**, 465 (1903).

[4] Richards and Kelley, This Journal, **33**, 847 (1911).

phases are in equilibrium at atmospheric pressure is dependent upon the composition. The present paper reports the results of a study of the relation between composition and equilibrium temperature, and attempts to interpret the data obtained in the light of the phase rule.

Experimental

Purification of Reagents.—Pure sodium sulfate was obtained by recrystallizing reagent grade salt three times as the decahydrate. Sodium chromate free from impurities other than sodium sulfate was prepared in a similar manner. Sodium sulfate cannot be removed completely from sodium chromate by this method, since it is isomorphous with the latter salt, whether as decahydrate, tetrahydrate, or hexahydrate, as will be shown later. However, since the two salts were used as mixtures, this impurity introduced no difficulty.

Preparation of Mixed Crystals.—Mixed crystals of various compositions were prepared as follows. The desired quantities of the two salts were dissolved in water and the solution was evaporated by boiling until a slight scum formed on the surface. The vessel was then covered with a watch glass, cooled to below 15°, and inoculated with a decahydrated crystal of one of the salts, or with a decahydrate mixed crystal. Mixed crystals of these two salts are richer in sodium sulfate than the solution from which they separate. The composition of the crystals consequently changes during crystallization. Lack of uniformity of the crystals, however, introduces no difficulty, as is explained below. The crystals were separated centrifugally from the mother liquor in large aluminum crucibles of the Gooch type. In some cases they were used moist, just as they came from the centrifuge; in others, they were exposed to the air until they had effloresced appreciably.

Determination of Equilibrium Temperature.—The equilibrium temperatures were determined by a method similar to that of Richards and his co-workers[3,4] in their investigations of the transition temperatures of salt hydrates. The apparatus resembled the familiar Beckmann freezing point apparatus. The crystals were placed in a test-tube, 150 mm. × 25 mm., held by a cork ring around the neck within a second test-tube, 200 mm. × 38 mm., which acted as an air-bath. The crystals were warmed by the heat of the hand on the inner tube until they had undergone partial transition, so that a suitable quantity of solution was formed. The apparatus was then introduced into a thermostat, set at a temperature within the transition range of the crystals at hand, as indicated by a thermometer immersed in the mixture. The mixture was stirred gently and continuously by a mechanical stirrer with a vertical motion. After an hour or more, which was sufficient time for the composition of the mixture to have become adjusted to its equilibrium value at this temperature, the temperature as measured by the accurate thermometer immersed in the mixture was recorded.

Removal of Sample of Solution for Analysis.—A sample of the equilibrium solution formed during transition was separated from the crystals for analysis. A pipet was made from 10-mm. glass tubing, with a constriction near the tip, so that a piece of cloth, through which the solution could be filtered, could be tied over the end. Bolting cloth of suitable mesh was found to permit sufficiently free passage of solution, but to prevent passage of any crystals. Before use, the pipet was always placed for some time in a test-tube immersed in the thermostat so that the temperature of the mixture would not be changed when the pipet was introduced. After the solution was withdrawn, the cloth was removed quickly from the pipet and a few drops of the solution were run into each of four weighing bottles to obtain the weight of the sample.

Determination of the Transition Product.—The nature of the solid phase formed from the decahydrate by transition, the transition product, was determined. The temperature of the bath was raised about a degree above the equilibrium temperature, *i. e.*, just above the upper limit of the transition range of the crystals, and maintained at this temperature until transition was complete, as shown by a rapid rise in the temperature of the mixture to the temperature of the bath. The solid remaining was separated rapidly from the mother liquor by centrifuging and then analyzed. If room temperature was much below the equilibrium temperature there was danger that the decahydrate might be re-formed during the process of separating. Consequently, the determinations of transition product were all made when room temperature was above the temperature of the bath. The transition product was not determined after every transition study, but only after a sufficient number to establish the phases in equilibrium along each curve.

Method of Analysis.—The samples to be analyzed were in all cases solutions or easily soluble mixed crystals. Chromate was determined by the familiar iodometric method. Separate samples were analyzed for sulfate. This was done by the method suggested by Meldrum, Cadbury and Lucasse[5] for the determination of sulfate in the presence of chromate. Water was determined directly, where necessary, from the loss in weight when the sample was heated for ten to twelve hours at 180°. All analyses were made in duplicate.

Results

The results obtained are shown in the accompanying graphs, Figs. 1 and 2, in which equilibrium temperature is plotted against the composition of solution, expressed as mole fraction of sodium sulfate in the dried salt from solution. Results over the entire range of concentration are shown in Fig. 1. The points plotted on this graph were selected at random from among the many points obtained, and the resulting curve is identical in form with a large scale plot on which all of the points were included.

At the point J, sodium sulfate decahydrate undergoes transition into anhydrous sodium sulfate and solution. As the concentration of sodium chromate in the solution formed by transition increases, the temperature at which anhydrous and

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[5] Meldrum, Cadbury and Lucasse, *Ind. Eng. Chem., Anal. Ed.*, **13**, 456 (1941).

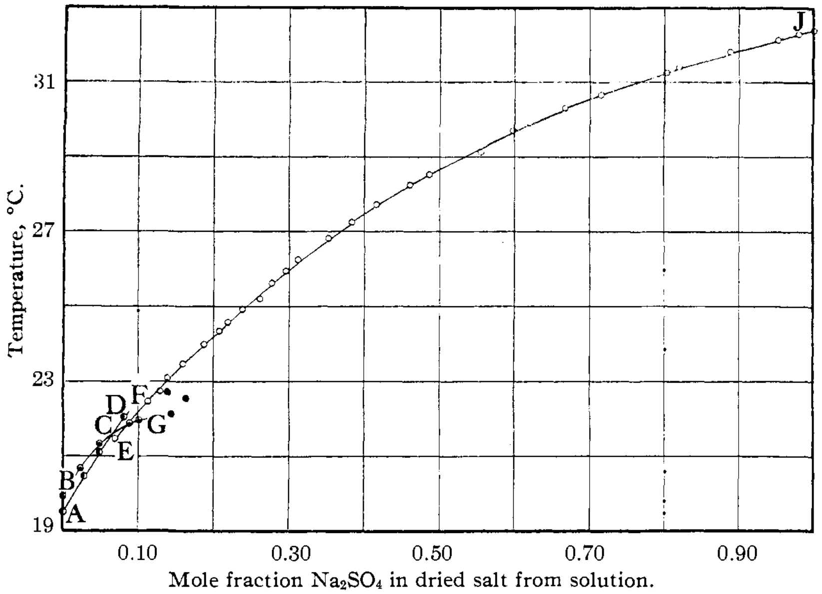

Fig. 1.—Variation of equilibrium temperature with concentration: O, transition product anhydrous; ◐, transition product hexahydrate; ◓, transition product tetrahydrate; ●, transition product uncertain.

decahydrate crystals can coexist in equilibrium with solution falls, as is shown by the curve JF.

At still higher concentrations of sodium chromate the situation is more complex. This can be seen from Fig. 1, and more clearly from Fig. 2, where the results are shown on a larger scale. The lettering of the two graphs corresponds. All the points obtained within the region covered by Fig. 2 are included on the plot.

The point A represents the temperature of transition of sodium chromate decahydrate into hexahydrate and solution. The temperature at which decahydrate, hexahydrate and solution are in equilibrium rises along the curve ACD, possibly continuing on toward H, as the concentration of sodium sulfate increases.

The point B represents the temperature of transition of sodium chromate decahydrate into

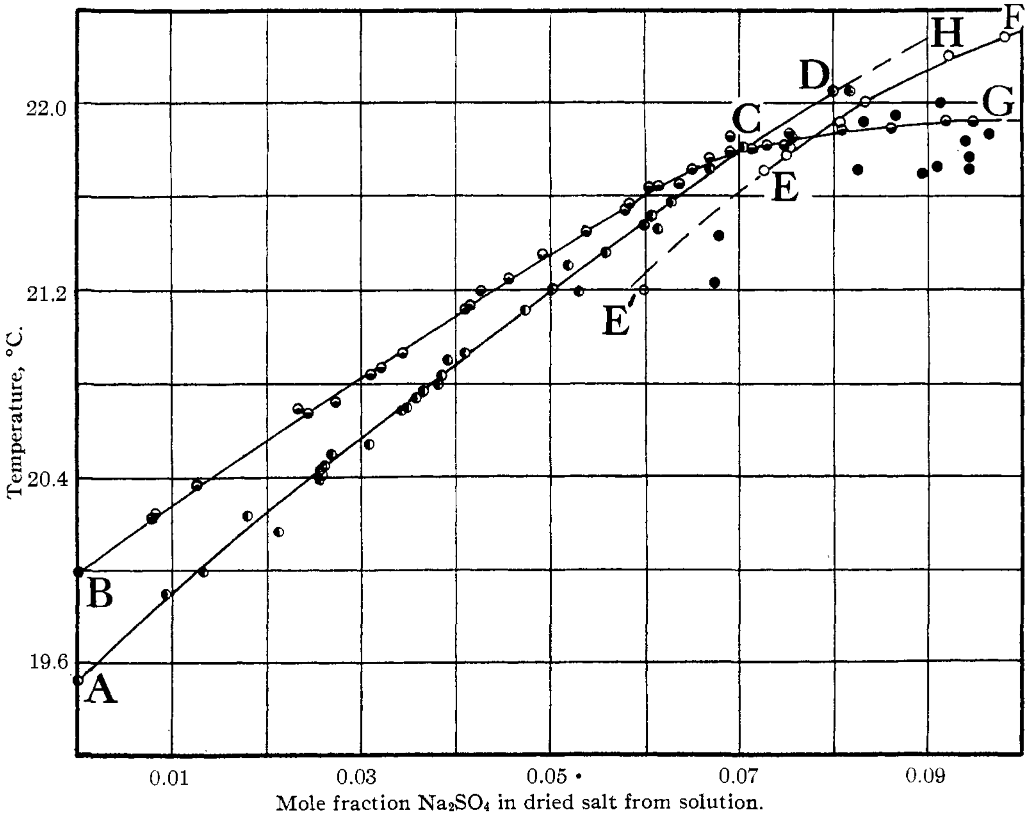

Fig. 2.—Variation of equilibrium temperature at low sodium sulfate concentrations: O, transition product anhydrous; ◐, transition product hexahydrate; ◓, transition product tetrahydrate; ●, transition product uncertain.

tetrahydrate and solution. The temperature at which decahydrate, tetrahydrate and solution are in equilibrium rises with increasing sulfate concentration along the curve BC, and probably along the continuation of this curve CG.

The curve FE is a continuation of the decahydrate–anhydrous curve, JF, shown on Fig. 1, and may extend toward E′. Since the last point obtained experimentally is not necessarily the last point which could be obtained along the metastable portion of such a curve, it is proper to indicate such continuations as DH and EE.′

Each of the lines on the accompanying diagrams corresponds to a single degree of freedom in a three-component system at constant pressure, where two solid phases and solution are in equilibrium. The temperature of the system depends on the composition. The point C, where four phases: solid decahydrate, solid hexahydrate, solid tetrahydrate and solution are in equilibrium, is a quadruple point in a three-component system, an invariant point at constant pressure. The temperature at this point is 21.80° and the composition 0.070 mole fraction sodium sulfate in the dried salt from solution. The intersection of CG with EF in Fig. 2 represents the equilibrium established by solution and decahydrate, tetrahydrate and anhydrous crystals. Experimental difficulties in this region, however, make the location of this point less certain than that of the point C. Other quadruple points are theoretically possible in this system, but were not realized experimentally, possibly because they lie in metastable or in unstable regions.

The Products of Transition

When the transition product is hexahydrate or tetrahydrate, separation of the crystals from practically all of the mother liquor is achieved by centrifuging, and the crystals can be analyzed readily. The anhydrous crystals, on the other hand, are so fine that they retain a large quantity of mother liquor on the surface even after prolonged centrifuging. The moist crystals were therefore examined by the method of wet residues. Data for three of these analyses are given in Table I. Graphical extrapolation from these data indicates clearly that the crystals are anhydrous, and that they contain no sodium chromate. They are therefore not mixed crystals, but anhydrous sodium sulfate.

TABLE I

DETERMINATION OF SOLID PHASE BY METHOD OF WET RESIDUES

% Na_2SO_4		% Na_2CrO_4		% H_2O	
Soln.	Residue	Soln.	Residue	Soln.	Residue
4.6	70.5	39.6	12.6	55.8	16.7
5.0	75.1	37.0	10.2	56.5	14.2
5.8	71.7	36.5	11.1	57.5	17.1

Analysis of the samples of transition product obtained when the concentration of chromate was high showed that these crystals were hydrates: in some cases tetrahydrate and in others hexahydrate. The analyses also indicated an appreciable quantity of sodium sulfate in both tetrahydrate and hexahydrate crystals. Sodium sulfate does not exist alone as either tetrahydrate or hexahydrate. However, Richards and Meldrum[6] showed that sodium sulfate tetrahydrate, although otherwise unknown, exists in the form of mixed crystals with sodium chromate tetrahydrate when the ratio of sodium sulfate to sodium chromate is not too large.

The existence of mixed crystals of the hexahydrates of these two salts has not, however, been reported in the literature. In fact, Takeuchi[7] has stated that sodium chromate hexahydrate is unable to take up any sodium sulfate. As was mentioned above, preliminary examination of the hexahydrate crystals formed by transition indicated appreciable quantities of sulfate in the crystals. Since Takeuchi's statement directly contradicts this observation, it was necessary to examine the hexahydrate crystals more carefully in order to determine whether they were pure sodium chromate or mixed crystals of sodium chromate and sodium sulfate. Crystals for this investigation were obtained in two ways: by transition from the decahydrate, and by crystallization of hexahydrate from supersaturated sodium chromate solutions containing some sodium sulfate.

Four samples of decahydrate mixed crystals which underwent transition into hexahydrate gave crystals containing 1.3, 1.5, 1.6 and 2.0% sodium sulfate. By crystallization from supersaturated solutions crystals were obtained containing up to 8.5% sodium sulfate. When the slightly moist crystals were analyzed, just as they came from the centrifuge, the water content varied from 6.14 to 6.37 moles of water per mole of dry salt, the average being 6.24. When the crystals before analysis were dried in the air until

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[6] Richards and Meldrum, THIS JOURNAL, **43**, 1543 (1921).

[7] Takeuchi, *Mem. Coll. Sci., Kyoto Imp. Univ.*, **1**, 249 (1915).

the first traces of efflorescence became visible with a magnifying glass, the water content varied from 5.61 to 6.07 moles of water per mole of dry salt, the average being 5.91. Thus it is established that these crystals are hexahydrate. Rough measurements indicated that sodium sulfate is about evenly distributed between the crystals and the mother liquor. Since the quantity of sodium sulfate found was much more than could be accounted for by the small quantity of adhering mother liquor, the crystals themselves must contain sodium sulfate, and are mixed crystals. The absence of decahydrate, small quantities of which might have accounted for the sodium sulfate found, was proved in each case by inoculating a supersaturated solution of sodium sulfate with some of the crystals. Failure of the solution to crystallize proved that no decahydrate was present.

Further transition of the hexahydrate mixed crystals into tetrahydrate mixed crystals and solution takes place on warming. Pure sodium chromate hexahydrate undergoes transition into tetrahydrate and solution at 25.90°.[4] The presence of sulfate was found to lower the temperature at which hexahydrate, tetrahydrate and solution are in equilibrium, as is shown by the results of measurements summarized in Table II.

Table II

Effect of Sodium Sulfate on Temperature of Equilibrium among Hexahydrate, Tetrahydrate and Solution

Equil. temp., °C.	Mole fract on Na_2SO_4 in dried salt from solution
25.90[4]	0.000
25.40	.046
25.15	.070
24.97	.082
24.83	.092

From the observations made above it is evident that when decahydrate mixed crystals undergo transition, the transition product when anhydrous is pure sodium sulfate, and when either tetrahydrate or hexahydrate is a solid solution of sodium sulfate and sodium chromate.

Discussion

The transition temperature of a pure salt hydrate is an invariant point at constant pressure, since there are two components, salt and water, and three phases, two solid phases and solution.[8] When, however, a second salt is added, the system becomes univariant, provided that no new solid phase is added. The transition temperature of a salt hydrate is therefore altered by addition of a new component and depends upon the composition of the solution formed. If the second salt is isomorphous with the first, some of the second salt enters into the crystals of the first, giving mixed crystals. The transition of such hydrated mixed crystals in general occurs over a range of temperatures, the actual temperature during transition being directly related to the composition of the liquid solution at equilibrium.

To fix a point on the phase diagrams it was necessary to determine both composition and temperature. More than one such point could be, and in some cases was, obtained from a given batch of crystals by allowing transition to proceed for a while, taking off a sample, raising the temperature and, after a new equilibrium had been reached, taking off another sample. However, if transition were complete, or if so much solution were formed that all of one solid phase was dissolved, the point thus obtained would not represent equilibrium among two solid phases and solution.

Throughout this investigation care was exercised not to permit transition to proceed so far as to destroy all the decahydrate or to form so much solution as to dissolve all of one solid phase. In the composition range 0.10 to 0.15 mole fraction of sodium sulfate, a number of points were obtained which did not fit on any of the curves here given. Experimental evidence indicates that this scattering of points is not due to lack of equilibrium among three phases but to some other cause, such as the existence of unstable or metastable phases in this region.

Since the decahydrate mixed crystals are relatively richer in sodium sulfate than the solution formed from them by transition, it is evident that as transition proceeds the composition of the solution and of the crystals changes. Diffusion in the solid phase being very slow, internal equilibrium is probably not attained in the crystals in the time allowed. Consequently the whole mass of crystals is not in equilibrium with the solution. However, the crystals soon become coated with a layer of mixed crystals of the equilibrium composition, and equilibrium between the surface of the crystals and the solution is established in a relatively short time. Because of the establish-

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[8] Since atmospheric pressure is greater than the vapor pressure of the system, such a system may be considered to behave as if the vapor phase were absent, as it would be if the same pressure were applied by a mechanical piston on the surface of the liquid.

ment of this surface equilibrium, the fact that the crystals are not of uniform composition when formed, as was mentioned above, introduces no difficulty. Indeed, even if the crystals were originally uniform, they would lose this uniformity during transition.

At low sulfate concentrations, transition may take place to either the hexahydrate or the tetrahydrate. It is of interest to consider which of these transitions will actually take place under given conditions. The hexahydrate is more stable than the tetrahydrate at any temperature below that at which the hexahydrate undergoes transition into the tetrahydrate. Consequently, if any hexahydrate is present, the transition is from decahydrate into hexahydrate, provided the concentration of sodium sulfate is not too high. In the absence of hexahydrate, the transition may be into the tetrahydrate, although this cannot readily be controlled. If any hexahydrate crystals have been in the room recently, it is almost impossible to prevent the hexahydrate from forming, as was mentioned in a different connection by Richards and Kelley.[4] Sometimes tetrahydrate forms first, and then changes spontaneously to the hexahydrate. To obtain transition to the tetrahydrate, it is necessary to exclude completely any hexahydrate nuclei from the atmosphere and to warm the system fairly rapidly past the temperature of transition into the hexahydrate. Under these conditions tetrahydrate may be obtained.

Summary

1. The transition of mixed crystals of sodium sulfate and sodium chromate decahydrate into hexahydrate, tetrahydrate or anhydrous crystals and solution has been investigated. The relation between temperature and the composition of the solution in equilibrium with decahydrate and another solid phase has been determined.

2. The existence of sodium sulfate hexahydrate in mixed crystals with sodium chromate hexahydrate has been established. Addition of sodium sulfate to sodium chromate hexahydrate lowers the temperature at which hexahydrate, tetrahydrate and solution are in equilibrium.

3. When the concentration of sodium sulfate is low, the solid formed from the decahydrate by transition is usually mixed crystals of sodium chromate and sodium sulfate hexahydrate. Under some conditions the transition product is mixed tetrahydrate crystals. When the sodium sulfate concentration is high, the transition product is anhydrous sodium sulfate.

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RECEIVED MARCH 4, 1941

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Heat Capacity and Entropy, Heats of Fusion and Vaporization, and the Vapor Pressure of Dimethyl Ether. The Density of Gaseous Dimethyl Ether

BY R. M. KENNEDY, MALCOLM SAGENKAHN AND J. G. ASTON

The comparison of the gaseous heat capacity of dimethyl ether with that calculated from spectroscopic and molecular data has indicated a potential of 2500 cal. hindering the internal rotation of the methyl groups.[1] This paper presents the results of an investigation of the thermal properties of dimethyl ether from 14.13°K. to its normal boiling point which yields a value of 3100 ± 150 cal. for the hindering potential. This latter value is probably more nearly correct for reasons which will be presented presently.

Preparation and Purification of Dimethyl Ether.—Somewhat to our surprise, a preliminary and rather hasty preparation of dimethyl ether by dehydration of methyl alcohol over alumina gave a product which, for some reason unknown, could not be purified readily by fractional distillation. On the other hand, the reaction of methyl iodide with sodium methylate gave a product which was purified readily to yield the purest organic compound yet prepared in this Laboratory.

Four moles of methyl iodide was added to a solution of four moles of sodium in one liter of aldehyde-free alcohol, which had been distilled from magnesium, then from an equal atomic mixture of aluminum and zinc. The solution was contained in a 3-necked flask fitted with a mercury seal stirrer, a dropping funnel and a reflux condenser. The condenser outlet led to a carbon dioxide-snow trap through drying towers of calcium chloride and potassium hydroxide. The solution of sodium methylate was surrounded by a water-bath at 25° and the methyl iodide was added over a period of three hours. The bath was heated to 75–80° to obtain a reasonable rate of gas evolution. When the rate of gas evolution slowed down, the reaction was discontinued. The yield was approximately 180–190 g.

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(1) Kistiakowsky and Rice, *J. Chem. Phys.*, **8**, 618 (1940).