

velopment of a theory of the salting-out or salting-in phenomenon. Such an approach appears adequate for the non-polar solute benzene which is considered. Their method is of such generality that it promises to provide the necessary foundation from which a more complete theory including the effects (1) and (3) discussed above may be formulated.

The treatment of McDevit and Long is somewhat reminiscent of the much earlier concept of Tammann¹⁴ of an "internal pressure" (Binnendruck). He defined the increase in internal pressure of a salt solution in terms of the external pressure that would have to be applied to pure water in order to make properties such as the temperature of maximum density the same as for the salt solutions. Attempts were made by Euler¹⁵ and Geff-

(14) G. Tammann, *Z. physik. Chem.*, **11**, 676 (1893).

(15) H. Euler, *ibid.*, **31**, 369 (1899).

cken¹⁶ to correlate the solubility of various substances in salt solutions with increases in internal pressure as calculated by Tammann.

However the values of the lowering of the maximum density of water as given by Geffcken¹⁶ show poor correlation with our data for the salting-out of benzene by NaCl, KCl, LiCl, KBr and NH₄Br. Somewhat better correlation is found with the data for the relative compressibility of the salt solutions. Of perhaps more importance is the difficulty that this earlier concept of "internal pressure" does not appear to be capable of predicting the existence of the "salting-in" such as found in the case of nitrobenzene.¹⁷

(16) G. Geffcken, *ibid.*, **49**, 289 (1904).

(17) We are grateful to the reviewer, Dr. J. H. Hildebrand, for recalling to our attention this earlier "internal pressure" concept of Tammann, *et al.*

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Heat of Vaporization and Other Properties of Dioxane, Water and Their Mixtures

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The water-dioxane system has been studied with respect to refractive indices, specific heats, absorption of dioxane by sulfuric acid, and both total and partial specific and molal heats of vaporization. Various plots of different types of heats against compositions and dielectric constants have been discussed. An attempt has been made to explain the forms of the curves relative to the various types of intermolecular forces involved in the liquid mixture. Empirical equations relating the composition of the solutions to some of the variables have been evolved by methods of least squares and of averages.

Introduction

It was thought to be of interest to study the dioxane-water system with respect to certain thermodynamic and other properties. This system was selected because of the prominence it has received in mixed solvent studies of chemical kinetics, conductivity of electrolytes, and physical properties of liquids. Data are available in the literature on dielectric constants, densities and other physical properties of the liquids and their mixtures. Furthermore, dioxane is a good solvent for a wide variety of substances and is miscible with water in all proportions.

Apparatus.—The apparatus consisted of five main subdivisions; the pressure regulating devices, the air-drying and purification trains, the air-tempering or preconditioning system, the calorimeter proper with the appended electrical systems, and the freezing trap for the collection of the sample.

The pressure mechanism consisted of three 20-liter carbons in series (see Fig. 1), each provided with an escape valve consisting of a 10-mm. tube, the end of which is immersed under a layer of mercury, the pressure in the system being regulated by the depth of the mercury. Fine adjustment is achieved by adding a layer of water above the mercury. The large volume of the system makes any sudden fluctuation in pressure almost impossible, although small fluctuations (about 0.5 mm. on a sulfuric acid filled manometer, M) do occur due to bubbling through the mercury. Further regulation is achieved by a screw-clamp, S₁, and the needle valve, v. The air, now at constant pressure, is passed to the drying train, which consists of three towers filled with soda lime, calcium chloride and phosphorus pentoxide, in that order. These are of glass, sealed with paraffined cork stoppers. After passing the phosphorus pentoxide tube, all connecting tubing is of glass or metal with the minimum of rubber tubing for joints. Leaving the purifying train, the air enters the tempering system

through the Y-tube, Y, the pinch clamp S₂ being closed in normal operation, and the three way stopcock, W₁, being thrown so as to by-pass the presaturator, P, which is needed only in the determination of heat capacity at the end of the determination. The pressure inside the system may be read at any instant on the manometer, M.

Within the tempering system, the air is passed down the internal ³/₁₆" copper tube, and out through the space between the inner and the 1.5" thin-walled copper outer tube. The space between the two concentric pipes is filled with a roll of copper screen, to stir the ascending air and assist in the attainment of a thermal equilibrium with the bath. To ensure that the air is at the temperature of the thermostat, it is then passed through the coil, C, consisting of twenty feet of ³/₁₆" copper tubing.

Thence it enters the calorimeter proper, through the water-jacketed inlet tube, I, and passes through the liquid, and out of the water-jacketed outlet tube, O, through the electrically heated conveyor tube, F, to the sample trap, J, immersed in an acetone-carbon dioxide refrigerating mixture contained in the dewar flask, D₂. On the air outlet side of the calorimeter and beyond, all connections are made with lightly greased standard taper glass joints.

It was found in the calibration with water that this apparatus gave results that were consistently about 1.5 to 2.5% too high, as referred to the Bureau of Standards figures for water. The high results were due to heat leakage out of the top of the system. It was not found practicable to correct heat leakage out the top of the system except by extensive remodeling of the apparatus, but a correction factor was worked out which, when applied to subsequent results, gave a satisfactory calibration.

The calorimeter is seated on a cork block inside the dewar flask, D₁, being held concentric with it by the insulating rings of cork, X. The dewar flask itself is contained in the copper submarine, G, being held in place by the masonite spacer discs, E, and rests on cork blocks to insulate it further from the submarine. To prevent convection within the submarine, the space between the dewar flask and the walls of the submarine is packed with glass wool. A cardboard collar, not shown in the drawing, serves to keep the glass wool from overflowing into the mouth of the dewar

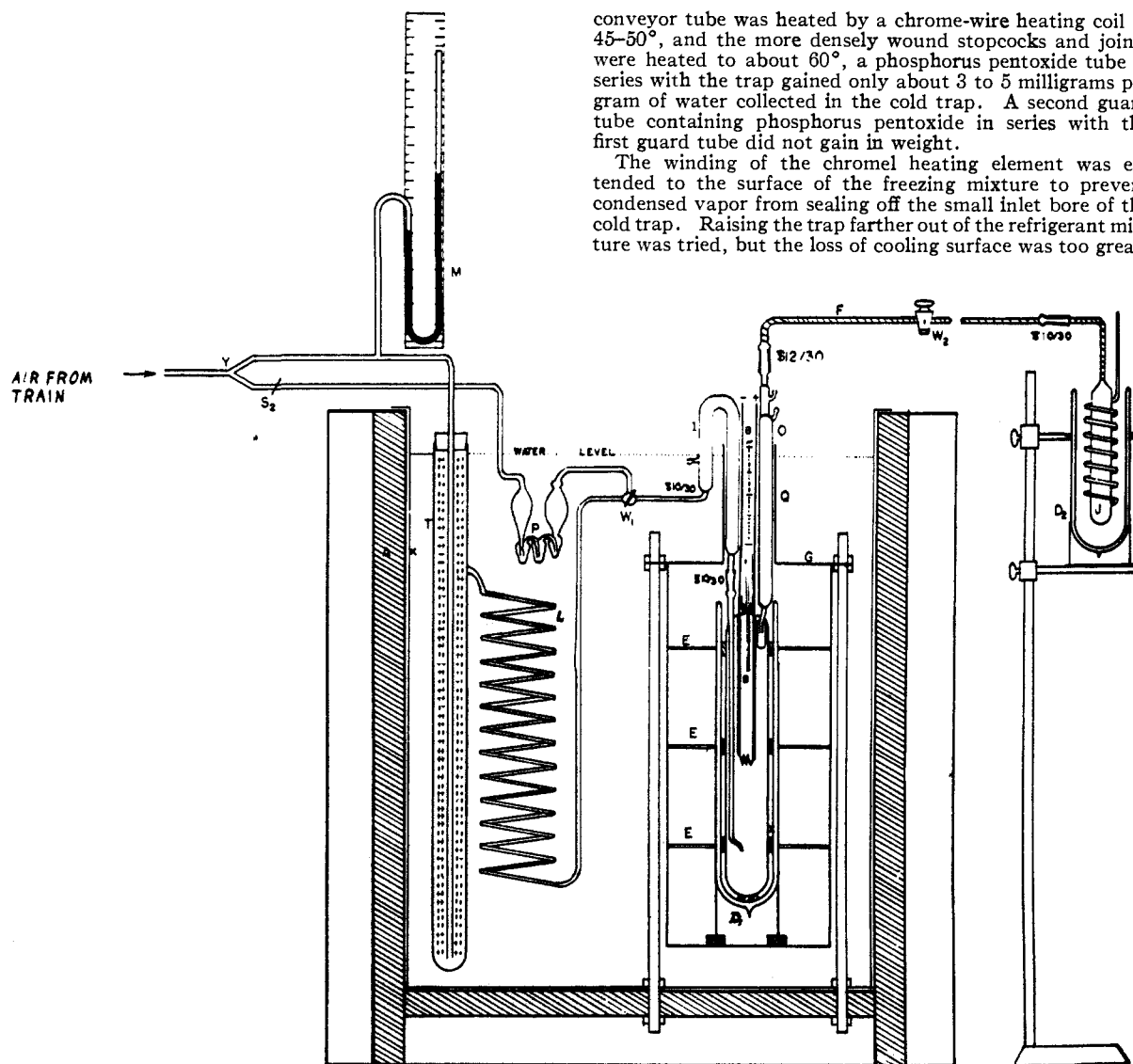


Fig. 1.—Semidiagrammatic sketch of thermostat, submarine, and calorimeter with appended drying train, A, and pressure regulating devices, B.

flask. The upper extension of the submarine, Q, is filled with ground cork, carefully screened so as to pass a U.S. Standard Sieve #16 but be retained on U.S. Standard sieve #40.

The air-tempering system and submarine were immersed in the water-bath to the level shown.

Temperature regulation in the thermostat was achieved with a Beckmann thermoregulator coupled to a Sargent zero current relay. A permanent heat of 250-watts output was put in series with a 20-ohm resistance and regulated so that the bath was held at constant temperature with an ordinary 75 watt light bulb as an intermittent heater controlled by the relay. The precision of the regulation of the temperature of the thermostat was to $\pm 0.01^\circ$ during any run.

The air conveyor tube needs little further discussion except that the stopcock, W_2 , is a three-way ninety degree stopcock arranged so that a trap can be connected to one side arm while a sample is being taken. By turning the stopcock, a second sample can be collected.

For samples of such volatility that there was a weighable loss past the first trap, a second glass coil, consisting of 10 feet of 4-mm. glass tubing wound on a 2" mandrell, was put in series with the first.

The heat evolved in the air conveyor tube prevented condensation between the calorimeter and the trap, and had to be regulated within certain limits since overheating the vapor laden air hindered condensation even in the acetone-solid carbon dioxide previously weighed cold trap. When the

conveyor tube was heated by a chrome-wire heating coil to $45-50^\circ$, and the more densely wound stopcocks and joints were heated to about 60° , a phosphorus pentoxide tube in series with the trap gained only about 3 to 5 milligrams per gram of water collected in the cold trap. A second guard tube containing phosphorus pentoxide in series with the first guard tube did not gain in weight.

The winding of the chromel heating element was extended to the surface of the freezing mixture to prevent condensed vapor from sealing off the small inlet bore of the cold trap. Raising the trap farther out of the refrigerant mixture was tried, but the loss of cooling surface was too great.

The air inlet tube, I, consists of a condenser made of two concentric glass tubes of 6-mm. and 10-mm. glass tubing.

The calorimeter is essentially a large capsule of Pyrex glass approximately 300 mm. long and 50 mm. in diameter. Through the upper end are fused a continuation of the air inlet tube, extending to within a few centimeters of the bottom of the calorimeter, the heating coil, the entrainment separator, or spray trap, of the air outlet tube and the outer section of the thermometer well. The heating coil was constructed by heating about 5 cm. of 8-mm. tubing and drawing it out to approximately 40 cm. length. The approximate internal diameter of the restricted portion of the coil was about 0.8 mm. After being filled with mercury, the resistance of the constricted portion was determined roughly by the current forced through the bore by a three-volt dry cell. A coil of optimum resistance of one and a half ohms was wound freehand and fused through the top of the calorimeter. The entrainment separator (spray trap) consists of a capsule of glass fused over the end of the outlet tube, holes being blown in the upper end to admit the air. Preliminary experiments showed that there is only a relatively small amount of spray formed in pure water if the rate of flow is below about 3.5 liters a minute, and that no droplets appear in a Tyndall beam 5 cm. above the surface of the water. Since this is several times the air flow employed in the experiment, it may be safely assumed that no spray passed the trap. Soon after leaving the interior of the calorimeter through the spray trap, the air entered

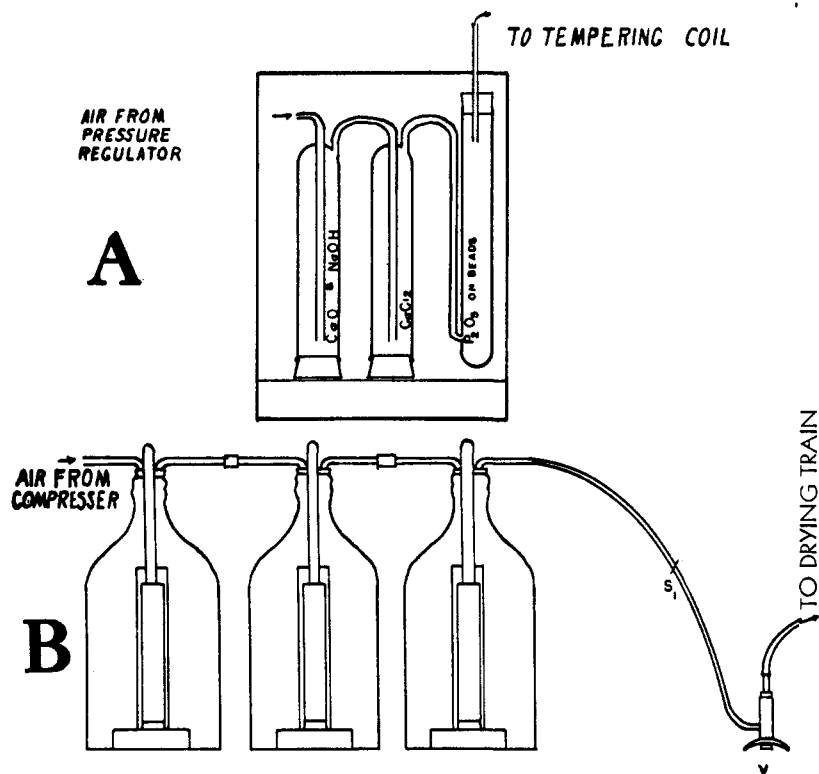


Fig. 1.—Continued

the water-jacketed portion of the air outlet tube, the length of the exposed portion of the glass being limited only by practical considerations of glass welding. An outlet tube, O, was constructed to maintain the temperature of the outgoing air at the temperature of the bath; thus preventing premature condensation of moisture. Water entered from the circulating pump into the outer-most of the three concentric tubes, rose in the space between the central and median tubes and returned to the bath thereafter. The vapor-laden air rises through the central tube.

The lower portion of the thermometer well is drawn extremely thin before sealing off the bottom. The thermometer bulb was inserted in the well and surrounded with mercury to ensure good thermal contact with the contents of the calorimeter.

The upper portions of the calorimeter were wrapped in asbestos tape, and all the free space between the mercury seal of the thermometer well, the inlet tube and the outlet tube, were filled with wet asbestos which was baked on and painted with a silver paint, after which it was waterproofed with melted paraffin. This heavy asbestos coating not only insulated the top of the calorimeter, but also braced the glass tubing and strengthened the system mechanically.

The trap is made of a thin-walled 26-mm. test-tube, onto which near the bottom is fused a coil of about five feet of 8-mm. tubing. To assist in stirring the air, and to provide an adequate surface for condensation, the body of the trap was filled with small helices of No. 20 B&S gage chromel wire. Preliminary experiments showed that the coil was much more effective with than without the metallic packing. For very volatile solutions two traps were placed in series.

The electrical circuit used is shown in Fig. 2. Current was produced by the six-volt lead storage battery, E, which was maintained at approximately half-charge, since the voltage was more constant at that point. A variable resistance, R_v , gave rough control of amperage, and a set of two 3-ohm variable resistors provided fine control. R_s is a Leeds and Northrup, 1-ohm, N.B.S. certified standard resistance, R_x the calorimeter heating coil, and A a Simpson milliammeter included for convenience in the initial setting. Leads from the resistances R_x and R_s were connected through the double-pole, double-throw switch, S, to the Fisher Type S Potentiometer, P. All connections in the switch and at the calorimeter were soldered to minimize variable contact resistances.

The potentiometer was calibrated against a Leeds and Northrup Type K-2 Potentiometer, using Eppley certified standard cells, and was used in conjunction with an Eppley certified cell, C, and a G.M. galvanometer, G, of sensitivity 0.10 microampere per mm. division. The electrical measurements were accurate within the limit of accuracy in reading the potentiometer, P, which is approximately one or two ten thousandths of a volt.

The submarine was similar to that described by Smith.¹ The heating coil was essentially that described by Wrewsky.²

Procedure.—All glassware was cleaned in chromic acid cleaning solution, rinsed with tap water, distilled water and acetone, in the order given, and dried in a stream of dry air. The traps and air tempering system were dried by sucking dry air through them while at an elevated temperature. The interior of the copper submarine and dewar flask were dried and carefully protected by a cover from splashing while replacing them in the bath.

The submarine, with the dewar flask in place, was first bolted into the thermostat. The calorimeter was joined onto the conveyor tube. The liquid being studied was pipetted into the calorimeter through the opening for the thermometer well. The electrical leads to the heating coil were seated and the coil tested for conductivity in order to be sure that the mercury filament was not broken by an air bubble. The outer cup of the thermometer well was filled with mercury and the thermometer well inserted. The entire assembly was seated in the dewar flask and the Beckmann thermometer inserted. The water-jacketed air inlet was connected to the air tempering coil, and the male 10/30 joint of the

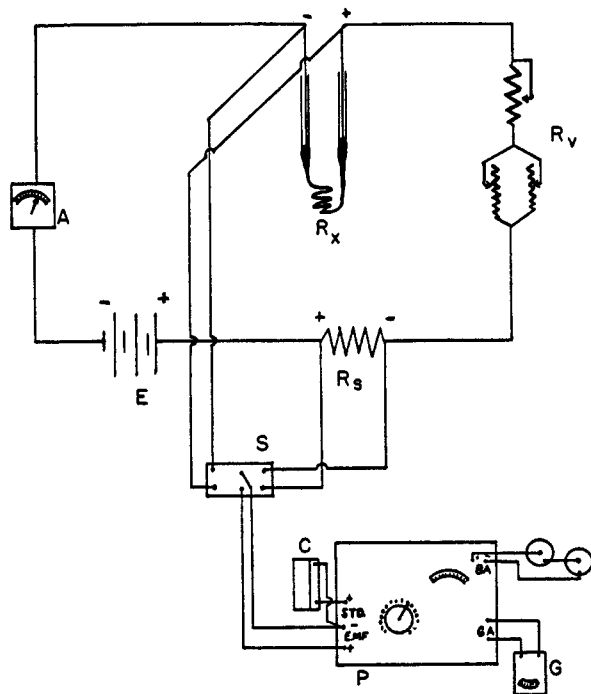


Fig. 2.—Details of the heating and potentiometric circuits.

(1) A. W. Smith, *Phys. Rev.*, **25**, 145 (1907).
 (2) M. S. Wrewsky (also Vredskii), *Z. physik. Chem.*, **144A**, 244 (1929).

air inlet tube firmly seated in the female joint on the calorimeter. The section containing the manometer was coupled on one side to the air tempering system, and on the other side to the air drying train. The resistance coils on the air conveyor tubes and the traps were connected in series, and the 110-volt a.c. heating current, properly controlled by a permanently connected rheostat, was turned on. The circulating pump was connected to the water-jacketed inlet, the exhaust therefrom being connected to the water jacket on the outlet tube, and the pump was turned on.

The heating circuit was connected to the d.c. source, and the current started at sufficient amperage to heat the calorimeter and contents to the temperature of the bath in about 20 minutes. During this time the chimney-like extension, Q, on the submarine, of Fig. 1, was packed thoroughly with cork shavings, to minimize heat loss out of the top of the calorimeter. The system was left to stand for not less than four or five hours to attain equilibrium with the surroundings. If the temperature as read on the Beckmann thermometer fell more than a few tenths of a degree below the temperature of the bath, the heating current was started until the equilibrium temperature was restored. In the last two hours of the seasoning period the temperature was held constant to within a few hundredths of a degree.

After adequate seasoning, the air stream and the electric current in the heating coil were started and adjusted so that the temperature remained constant. When a steady state had been reached, the determination proceeded. Simultaneously a stop-watch was started and the three-way stopcock W_2 was turned so as to direct the vapor into the trap coupled to the conveyor tubes. Every minute the temperature was noted and the voltage read across the heating coil in the calorimeter and the standard resistor in series with it in order to detect any changes in the current or in the resistance of the mercury-filled heating coil. A slow decrease in the resistance of the heating coil was often observed, due perhaps to the migration of small air bubbles from the smaller to the larger portions of the coil under the combined action of gravity and vibration. In case the temperature inside the calorimeter varied, the airflow was adjusted, since it was found more practicable to regulate air pressure than the current. After evaporation of approximately one gram of sample, the air was diverted from the first trap into a similar one coupled onto the other side arm of the three-way stopcock. Simultaneously the stop-watch timing the first run was stopped and the one timing the second run started. The procedure for the second sample was in every respect similar to the first. During the collecting of the second sample, the first trap was removed from the conveyor tube, so that vapor could be diverted from the second sample at the end of the determination without adding further condensate to the first. The traps were fitted with glass caps to prevent the loss of moisture while attaining balance room temperature. The stopcock grease was removed from the joints with swabs dipped in benzene, and the surface wiped clean and dry. It was found that no weighable amount of sample was lost in a time far in excess of that needed for a weighing.

For volatile liquids, which required two cold traps in series to ensure complete condensation, the entire sample was collected in the first cold trap in the following manner. After the outlets to the atmosphere had been closed, the first trap was left immersed in the carbon dioxide-acetone refrigerant and the second trap immersed in a large beaker of boiling water. In the case of mixed liquids it was necessary that the condensate be obtained in one sample in order that its composition might be determined by its refractive index.

After the second sample had been collected, the air and the heating current were stopped, and the system allowed to stand. The rate of temperature change due to heat leakage through the insulation was observed over a period of about an hour. The screw clamp S_2 and the three-way stopcock W_1 were then moved so as to by-pass the tempering system and send air through the presaturator into the calorimeter. In case the composition of the liquid in the presaturator was not the same as that in the calorimeter, or if the rate of air flow was such that the air was not saturated in one pass through, the temperature in the calorimeter dropped. The rate of fall was observed for two minutes.

The air was shut off and the heating current started. The temperature rose rapidly. After several minutes,

during which the voltage was read across the standard resistor every 30 seconds, the air was passed through the presaturator and the calorimeter for two minutes. The resulting stirring equalized the temperature throughout the solution and allowed a reasonably accurate value for the temperature increase to be had. This, corrected for the leakage, and for the cooling induced by the passage of the air stream, permitted a calculation of the heat capacity of the system, which in turn allowed a correction to be calculated for the heat leakage in the vaporization experiments.

The apparatus was now dismantled for cleaning. The temperature of the remaining liquid and its depth in the calorimeter were simultaneously determined, the depth being converted to volume by a previous calibration. Volume was converted to mass by the density data of Herz and Lorenz.³ A sample was pipetted out for the determination of the composition by the refractive index measured as described below.

After weighing, the condensed sample was well mixed by shaking in the trap, and by rotating to work the body of the sample over the entire surface and pick up any liquid that was condensed in the coils. Samples of the well-mixed liquid were pipetted out for the determination of index of refraction. This was taken with the Abbe refractometer using a sodium lamp for illumination. The lamp was allowed to run for several minutes before a reading was taken. Tap water was circulated through the prisms of the refractometer to keep them cool. The temperature was read from a thermometer calibrated in 0.1° inserted in the thermometer well of the refractometer. With the aid of calibration data, taken at three widely separated temperatures, covering the ordinary range of room temperature, it was possible to interpolate for temperature and determine composition. In taking the calibration data, the temperature was maintained constant to $\pm 0.01^\circ$ by circulating water from the thermostat through the refractometer prisms. All thermometers were calibrated against N.B.S. certified thermometers.

The air-purifying train did not need changing more often than once every five or six runs.

Data.—In order to determine the composition of the liquid and the vaporized samples, calibration curves of the composition *versus* the refractive index had to be made for the dioxane-water system. Herz and Lorenz³ had measured the refractive index at five different volume per cents. over the entire composition range, at a temperature of 17.5°. Gillis and Delanois⁴ measured the refractive index of the dioxane-water system as a function of weight per cent. at 20°. However, their data were not consistent enough to be dependable. Makowiescki⁵ made a series of determinations on mixtures by mole per cent. at 16°. Since these earlier determinations were all confined to a very narrow range of temperature, and since the newer methods of purifying dioxane, which stem mainly from the work of Hess and Frahm,⁶ produce a material with physical constants which are entirely different from those of the material purified by mere drying and distillation, it was thought necessary to repeat the determinations at lower temperatures and extend them to higher temperatures over all concentrations.

The solutions of known weight compositions were prepared from the carefully purified dioxane and redistilled water. Sufficient readings on a Abbe refractometer were taken so that the mean deviation was ± 0.0001 or less.

Equations of the form

$$n^2D = a + bx + cx^2 \quad (1)$$

(3) W. Herz and L. Lorenz, *Z. physik. Chem.*, **140A**, 406 (1929).

(4) J. Gillis and A. Delanois, *Rec. trav. chim.*, **53**, 186 (1934).

(5) A. Makowiescki (also Makovetzki), *Chem. Centr.*, **79**, IV, 1567 (1908).

(6) K. Hess and H. Frahm, *Ber.*, **71B**, 2627 (1938).

were calculated by the method of least squares to fit the data taken at the different temperatures. The constants for each of the equations may be found in Table I. The curves representing the experimental data, together with the curves showing the deviation of the observed values from those calculated according to the appropriate equation may be seen in Fig. 3.

TABLE I

COEFFICIENTS OF THE EMPIRICAL EQUATIONS FOR INDEX OF REFRACTION, n_D , AT TEMPERATURE, t , AS A FUNCTION OF PER CENT. BY WEIGHT OF DIOXANE, x

t	a	b	c
14.87	1.33250	0.0010950	-0.0000018105
24.70	1.33130	.0010854	-.0000020016
35.00	1.33025	.0010597	-.0000020315

In actual practice the values of index of refraction were calculated at intervals of 2% weight composition by use of the equations together with the deviation curves, and the results plotted on a very large scale so that interpolation over a narrow range of concentration could be made graphically.

In order to correct the heats of vaporization for heat leakage from the calorimeter, it was found necessary to determine the heat capacity of the calorimeter and contents, under conditions as nearly paralleling the conditions of the run as possible. Column 2 of Table II contains the calculated values of the heat capacity. Total heat capacity was calculated using equation 2.

$$C = \frac{60S \sum \frac{E_s^2 R_x}{R_s^2}}{\Delta t + \left(\frac{\Delta t}{\Delta s}\right)_1 s + \left(\frac{\Delta k}{\Delta s'}\right)_e s'} \quad (2)$$

TABLE II

A TABLE OF HEAT CAPACITY, C ; OBSERVED AND CALCULATED SPECIFIC HEATS, c_p , AND THEIR DIFFERENCES; AND WEIGHT PER CENT. DIOXANE, x_v , COMING FROM THE LIQUID OF WEIGHT PER CENT. DIOXANE, x

x	C	c_p , obsd.	c_p , calcd.	Difference, obsd.-calcd.	x_v
7.05	1657.1				41.03
7.43	1689.8				41.07
16.14	1575.8	4.04	3.96	0.08	58.65
18.16	1535.3	3.84	3.91	-.07	60.47
18.50	1545.0	4.01	3.90	.11	61.72
26.84	1445.6	3.75	3.73	.02	70.70
27.67	1486.3	3.68	3.71	-.03	71.13
38.62	1452.0	3.58	3.46	-.12	77.16
39.18	1416.1				77.67
49.45	1271.3	3.14	3.20	-.06	81.46
66.93	1173.0	2.83	2.75	.08	86.75
77.00	1037.4	2.36	2.46	-.10	86.02
91.72	890.6	1.91	2.02	-.11	89.35
95.06	855.2	1.89	1.92	-.03	92.55
95.10	880.1	1.88	1.92	-.04	93.33
97.94	845.2	1.75	1.83	-.08	92.55
100.00	805.2	1.76	1.77	-.01	100.00
100.00	822.4				100.00

In this equation, C is the total heat capacity, s is the time the current ran in minutes, E_s is the voltage observed across the standard resistor, R_x is the resistance of the calorimeter heating coil, t is the observed temperature, $(\Delta t/\Delta s)_1$ is the rate

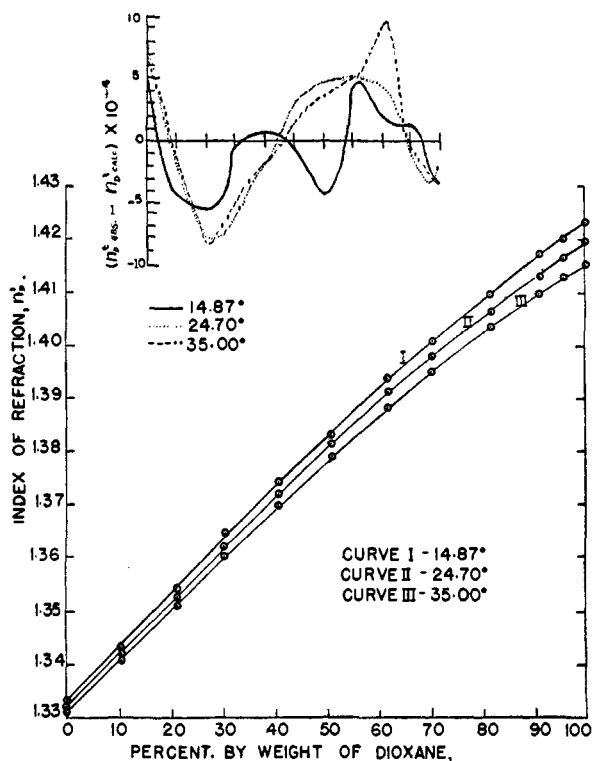


Fig. 3.—Index of refraction versus per cent. by weight of dioxane. Also deviation of calculated from observed values of refractive index.

of change of temperature due to leakage, $(\Delta t/\Delta s')_e$ is the rate of change of temperature during the air stirring, and s' is the duration of the stirring in minutes.

The average loss of heat from the calorimeter during a run was equivalent to a positive error of about 1.5 to 2.5% of the measured heat of vaporization. Since the precision of measurement of heat capacity was roughly $\pm 3\%$, the uncertainty introduced in the measured heat of vaporization was about 0.02×0.03 or ± 0.0006 or about 1 part in 1600.

Making use of the calculated heat capacities and other data, it was possible to obtain the approximate specific heats of the various dioxane-water mixtures. The heat capacity of the calorimeter, C' , was determined by a measurement involving a weighed amount of distilled water. An average of several measurements yielded 261 joules/degree. Column 1, Table II, contains the resulting specific heats, c_p , of the solutions at 40° calculated from equation 3

$$c_p = \frac{C - C'}{vd} = \frac{C - C'}{w} \quad (3)$$

wherein v is the volume obtained by a previous calibration from the observed depth of the liquid in the calorimeter; d is the density, calculated from the data of Herz and Lorenz³ for the temperature t ; w is the calculated weight of the solution. C and C' have been previously defined.

Since pure water was used as a calibrating substance, it is not possible to state the accuracy of the measurements at the upper limit. But Makowieski⁵ reported mean specific heat of 0.43

calories or 1.80 joules per gram between 0 and 100° and Herz and Lorenz³ reported 0.42 calories or 1.76 joules per gram at 23° for pure dioxane. Hence, the observed value of 1.76 joules per gram for pure dioxane at 40° is a satisfactory check with the literature values.

The specific heats of the various solutions are plotted as a function of both weight per cent. and mole per cent. of dioxane in Fig. 4. The mole per cent. curve is drawn by estimation, but the weight per cent. curve is the graph of the equation calcu-

$$c_p = 4.250 - 0.017554x - 0.00007356x^2 \quad (4)$$

lated by the method of averages. In this equation x is the mole per cent. of dioxane. At 0% dioxane the calculated value is somewhat too high. In columns 3 and 4 of Table II the observed and calculated values, respectively, of specific heat are recorded and the deviations of the calculated from the observed values are recorded in column 5 of the table.

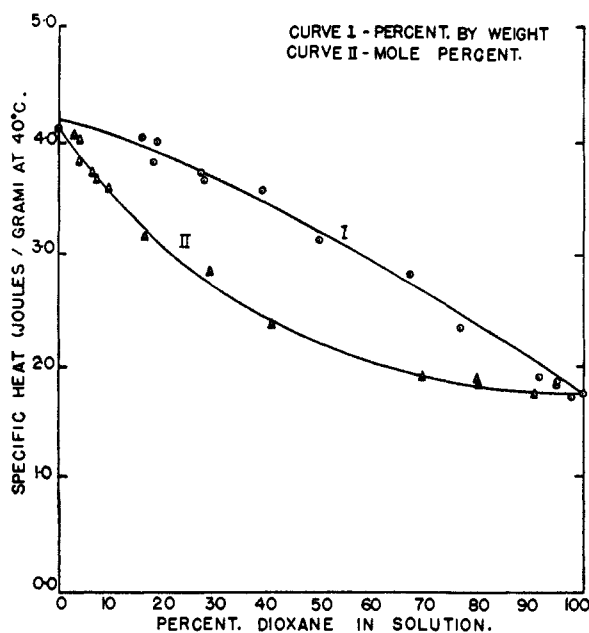


Fig. 4.—Specific heat versus per cent. dioxane in solution.

Composition of vapor samples in weight per cent. of dioxane, x_v , coming from liquids of various compositions are recorded in column 6 of Table II and a plot of these data is given in Fig. 5. The form of the curve is very similar to that obtained by Makowieski at 50°.

The work of Paterno and Apallina⁷ showed that dioxane formed a very stable compound with sulfuric acid, which could be isolated and purified by recrystallization from benzene. Furthermore, Lindenberg⁸ made a micro-determination of dioxane by refluxing it with standard dichromate in the presence of sulfuric acid and determining the excess dichromate by an iodometric procedure. These experiments indicated that the composition of the dioxane-water sample could be obtained by absorbing the weighed amount of vapor in sulfuric acid of the proper concentration, and then an-

alyzing for dioxane, using the procedure described above. This method was considered in the early part of this investigation.

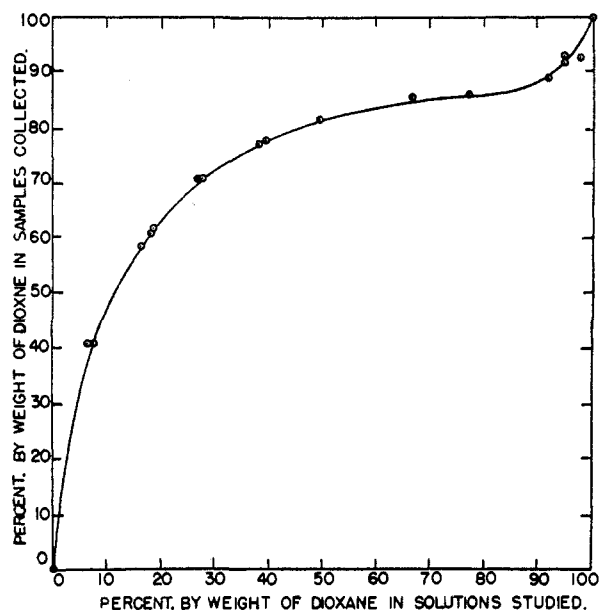


Fig. 5.—Per cent. by weight of dioxane in vapor versus per cent. by weight of dioxane in solution.

Two Geissler potash bulbs were prepared by pipetting about 15 cc. of concentrated acid into each bulb, and adding about 0.5 cc. of water to the first bulb of one of the potash bulbs. This water was to prevent formation of a solid compound of dioxane and sulfuric acid, and consequent stoppage of air flow. The bulbs were weighed and connected in series with each other and with a weighed bottle of pure dioxane. The connections were made with the minimum amount of rubber, since it was found that as little as two inches of rubber tubing caused the loss of about 2% of a 0.5000-g. sample. An aspirator connected to the second of the two potash bulbs drew air slowly through the vaporizer and absorption train. Preceding the vaporizer was a presaturator filled with water followed by an absorber containing sulfuric acid, so that the volume of air passing through the train per unit time could be determined by the gain in weight of the absorber, using handbook data for the weight of water vapor per liter at t° .

Table III contains the data for the absorption of dioxane in the sulfuric acid. The average dioxane lost per sample was 0.25%. It was found that a 15-cc. sample of sulfuric acid adsorbed dioxane quantitatively even after about 6.4 g. had been absorbed. The data show that the major portion of the samples were absorbed in the first bulb.

The central purpose of this investigation was to study heats of vaporization and partial molal heats of vaporization of dioxane-water mixtures as a function of composition and of the dielectric constant of the mixtures. Column 4 of Table IV contains the calculated specific heats of vaporization in joules per gram for the isothermal-isobaric transformation of the liquid into the vapor phase of the pure substances and of their mixtures. The method used in this investigation yields a heat of

(7) E. Paterno and R. Apallina, *Atti. Accad. Lincei*, **16**, 87 (9108).

(8) A. B. Lindenberg, *Bull. soc. chim. biol.*, **28**, 451 (1946).

TABLE III
ABSORPTION OF DIOXANE BY SULFURIC ACID

Sample No.	Time	Air flow l./min.	Weight evaporated	Weight recovered 1st bulb	Weight recovered 2nd bulb	Weight lost	Percentage recovery 1st bulb	Percentage recovery 2nd bulb	Loss, %
1	6	0.45	0.5784	0.5758	0.0010	0.0016	99.6	0.17	0.28
2	5	.45	.4748	.4739	.0009	.0000	99.8	.18	.00
3	5	.40	.4226	.4221	.0004	.0001	99.9	.09	.02
4	5.5	.44	.5192	.5180	.0002	.0010	99.8	.04	.19
5	5.25	.43	.4790	.4752	.0007	.0031	99.2	.15	.65
6	8	.53	.9002	.8962	.0006	.0033	99.4	.07	.37

vaporization identical with that found from vapor pressure data and using the Clausius-Clapeyron equation.⁹ Plots of these specific heats of vaporization *versus* per cent. dioxane in the solution are given in Fig. 6. The curves for both mole per cent. and weight per cent. in Fig. 6 show that the specific heats of vaporization of the mixtures fall rapidly from the value of that of pure water with the first

small additions of dioxane. The rate of change becomes more gradual with the further addition of dioxane. At a point corresponding to about 95% by weight of dioxane, the heat of vaporization falls precipitously to the value for pure dioxane. The sharp fall in the heat of vaporization when small amounts of non-polar dioxane are added to water is perhaps due to the lessening of dipolar-dipolar forces and hydrogen bonding among the water molecules. The increasingly smaller rate of change which is observed between about 20 and 90% by weight is probably due to the increasing predominance of the dipole-induced dipole forces among the dioxane and water molecules. The rapid fall beyond 95% by weight of dioxane can be interpreted as due to the predominance of the weak induced dipole-induced dipole forces in the very concentrated dioxane solutions.

TABLE IV

SPECIFIC HEAT, λ , AND MOLAL HEAT, L , OF VAPORIZATION OF DIOXANE, WATER AND THEIR MIXTURES FOR THE ISOTHERMAL-ISOBARIC TRANSFORMATION OF THE LIQUID INTO VAPOR

The values of L were calculated from average values of λ

Weight per cent. dioxane, x	Mole per cent. dioxane	Apparent molecular weight $\frac{ND.MD}{NH.MH} +$	Specific heat of vaporization, λ	Molal heat of vaporization, L
0.00	0.00	18.016	2403.0	43,340
7.05	1.53	19.087	1608.6	30,710
7.43	1.62	19.151	1618.8	30,990
16.14	3.79	20.672	1276.7	26,430
18.16	4.34	21.057	1201.8	25,310
18.50	4.44	21.128	1220.5	25,840
26.84	6.98	22.907	1018.8	23,560
27.67	7.25	23.097	1018.6	23,580
38.62	11.40	26.005	884.4	23,050
39.18	11.64	26.174	880.8	23,110
49.45	16.67	26.699	783.1	23,260
66.93	29.27	38.530	736.3	28,380
77.00	40.64	46.498	700.1	32,500
91.72	69.37	66.633	667.5	44,450
95.06	79.74	73.901	642.5	47,310
95.10	79.87	73.991	658.1	48,780
97.94	90.67	81.561	571.5	46,670
100.00	100.00	88.104	440.6	38,590
			436.4	
			437.2	

(9) Coon and Daniels, *J. Phys. Chem.*, **37**, 1 (1933), particularly page 6 of this article.

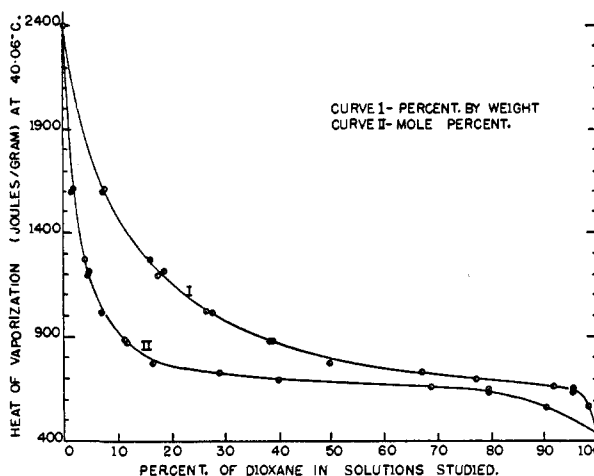


Fig. 6.—Heat of vaporization *versus* per cent. of dioxane in the solutions.

The precision of the calibrating measurements on pure water was about $\pm 0.5\%$ and the average of the determinations was about 0.2% less than that reported by the National Bureau of Standards¹⁰ for the same temperature. The accuracy of the other values cannot be determined since the data are not available in the literature. The over-all average precision of all the runs was about $\pm 0.6\%$. These heats were calculated by the equation

$$\lambda = \frac{60 \sum \frac{E_1^2 E_2}{R_s} \Delta s - \left(\frac{\Delta t}{\Delta s}\right)_1 s C}{g} \quad (5)$$

in which λ is the specific heat of vaporization, g is the weight of the sample in grams, and Δs is the time interval corresponding to the voltages E_s ,

(10) N. S. Osborne, *Bur. Standards J. Research*, **4**, 609 (1930).

and E_x . The other terms have been defined previously.

Relative to the duplication of the results of a run, it is observable that one or both samples are very large when the discrepancy is greater than about 1%. This can be explained on the grounds that the vapor has a different composition from the solution, since there is a selective evaporation of either dioxane or water from all solutions except the azeotrope composition. Hence

$$x_f = \frac{x_i w - x_v g}{w - g} = \frac{x_i - s_v \left(\frac{g}{w}\right)}{1 - \frac{g}{w}} \quad (6)$$

wherein x_f is the concentration of dioxane in the solution at the end of the run, x_i the concentration at the start of the run and x_v the concentration of dioxane in the vapor. It can be seen that if the ratio g/w is very small, or if the x_v is nearly equal to x_i the final concentration is nearly equal to the initial concentration, otherwise the concentration may change during the run, and the two samples are taken from two solutions of slightly different composition. As a first approximation, the total weight of the sample should not exceed 1% of the total weight of liquid in the calorimeter for good results.

In Fig. 7 is the specific heat of vaporization *versus* the per cent. of dioxane in the vapor samples. Here the specific heat of vaporization is apparently a linear function of the per cent. by weight of dioxane in the vapor sample, whereas the mole per cent. curve has the same general shape as, but less marked curvature than, the curve for specific heats of vaporization *versus* the composition of the liquid. The data appear to be less precise than in the case of the liquid composition and this is due to a less accurate determination of the composition of the vapor. The lesser precision obtained in the determination of the vapor arose from the difficulty encountered in mixing the sample in the cold trap filled with the helices of Chromel wire.

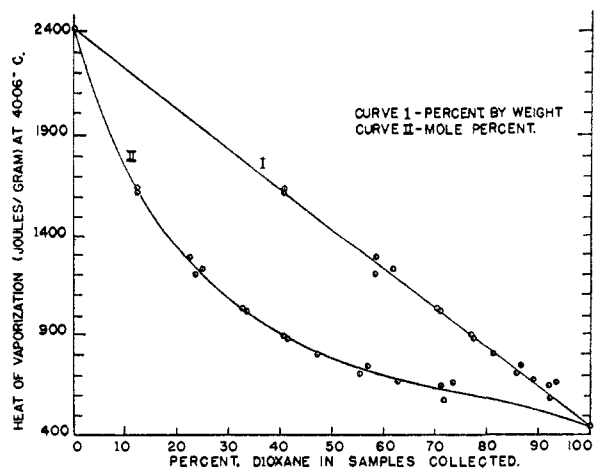


Fig. 7.—Heat of vaporization *versus* per cent. dioxane in the vapor samples.

Total molal heats of vaporization, L , were calculated by the equation

$$L = (N_D M_D + N_H M_H) \lambda \quad (7)$$

In this equation N_D and N_H are the mole fractions and M_D and M_H are the molecular weights of dioxane and water, respectively, and λ is the total specific heat of vaporization. The total molal heats of vaporization are recorded in column 5 of Table IV. A plot of the total molal heat of vaporization for the isothermal-isobaric transformation of the liquid into the vapor phase *versus* mole per cent. of dioxane in the liquid phase is given in Fig. 8. The shape of this curve is hard to explain in view of Fig. 6. In conjunction with Fig. 5, however, Fig. 8 does make sense. The initial rapid decrease of molal heats of vaporization with the mole per cent. dioxane in the liquid is attributable to the lessened hydrogen bonding and dipolar forces among the water molecules. This is similar to Fig. 6. The fact that the molar heat of vaporization after passing through a minimum, increases with further addition of dioxane could be due to the rapid proportionate increase of water coming off as vapor as is shown in Fig. 5. The greater proportionate amount of water with its higher heat of vaporization causes an increase in the molar heat. At higher percentages of dioxane the proportionate amount of dioxane in the vapor again increases (see Fig. 5) and the molar heat falls in this region as is shown by Fig. 8. This decrease is also partly due to the predominance of weak induced dipole-induced dipole forces in the solutions rich in dioxane.

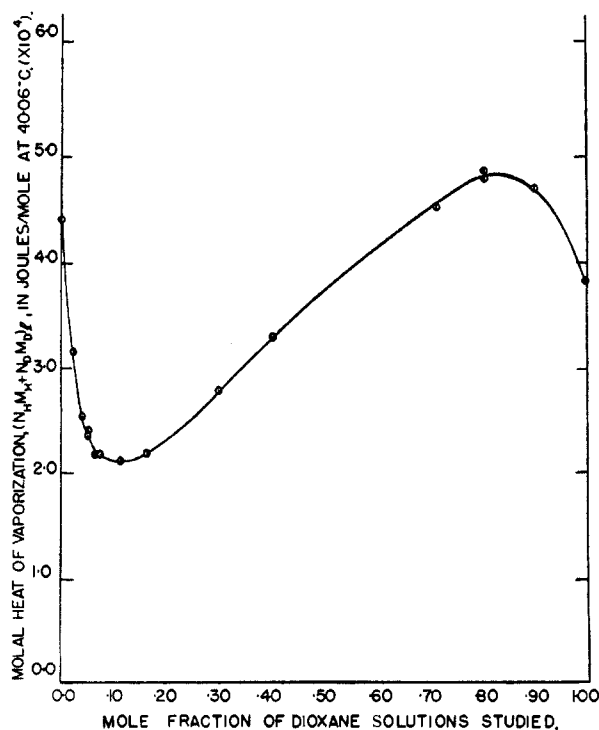


Fig. 8.—Molal heat of vaporization *versus* mole fraction of dioxane in the solutions.

The partial molal heats of vaporization of the two components at various compositions of solution were calculated from the partial specific heats of vaporization by multiplying these at the various compositions by the respectively mole weights of the components. The partial specific heats of the components were determined by drawing tangents

to the curves of total specific heat against per cent. by weight dioxane in solution, Fig. 6, at various weight percentages of dioxane, and finding the intercepts of the tangents on the 100% water and 100% dioxane ordinates. The partial specific heats of vaporization, $\bar{\lambda}_D$ and $\bar{\lambda}_H$, of dioxane and water, respectively, and the partial molal heats of vaporization, \bar{L}_D and \bar{L}_H , of dioxane and water, respectively, are recorded in Table V. The precision of these data are dependent on the precision of drawing tangents to the curve using a tangentimeter and of obtaining their intercepts. The intercepts of tangents were reproducible to within $\pm 3.9\%$ as was shown by repeated attempts to reproduce values, at least five trials being made on each tangent.

TABLE V

PARTIAL SPECIFIC AND PARTIAL MOLAL HEATS OF VAPORIZATION OF DIOXANE AND WATER FROM SOLUTIONS OF WEIGHT PER CENT. x

x	Tangent	$\bar{\lambda}_D$	$\bar{\lambda}_H$	$\bar{L}_D \times 10^3$	$\bar{L}_H \times 10^3$
0	205.6 \pm 21.3	-18,155	2403	-1599.45	43.34
5	71.5 \pm 2.4	-5,047	2103	-444.60	37.89
10	38.9 \pm 0.2	-2,016	1874	-176.61	33.77
20	24.5 \pm 0.2	-785	1665	-69.16	30.00
30	13.8 \pm 0.1	24	1404	2.11	25.30
40	10.4 \pm 0.1	251	1291	22.11	23.26
50	6.92 \pm 0.11	449	1141	39.56	20.56
60	3.60 \pm 0.04	611	971	53.83	17.50
70	2.75 \pm 0.04	634	907	55.81	16.34
80	2.00 \pm 0.035	655	855	57.71	15.41
90	0.80 \pm 0.17	667	747	58.76	13.46
95	11.23 \pm 0.93	594	1714	52.33	30.89
97.5	33.6 \pm 0.6	526	3276	46.34	59.03
100.0	87.6 \pm 8.5	438	9188	38.59	165.57

The accuracy of these partial specific properties were checked by using their values to recalculate the specific heats at the points to which the tangents were drawn according to the equation

$$\bar{\lambda}_{HxH} + \bar{\lambda}_{DxD} = \lambda \quad (8)$$

The agreement was exact except at two points that differed by about 1% from the ordinates read from the graph.

It is worthwhile to note here that all attempts to fit an empirical equation to the curve of Fig. 6 have been futile. Tangents taken for the determination of the partial molal heats of vaporization were plotted, giving a curve of $d\lambda/dx$ versus composition, the tangents to which were $d^2\lambda/dx^2$, which, when plotted against composition, gave a curve the tangents to which were $d^3\lambda/dx^3$, and so on to the fourth graphical derivative. Since the n th derivative of an algebraic polynomial of the n th degree is a constant, the fact that the fourth graphical derivative of the curve has pronounced curvature will indicate that a polynomial of at least the fifth degree, and more probably of the sixth degree, will be necessary to approximate the curve. If the graphical tangents were accurate, the necessary degree of the polynomial could be stated with certainty. Other types, such as an exponential term plus a polynomial, a product of exponential and trigonometric terms, and the doubly exponential equations of Gompertz, were all considered, but were found too burdensome to compute to the desired degree of accuracy. Therefore, the graphical method was selected.

In Fig. 9 the partial molal heats of dioxane and of water are plotted as ordinates against the dielectric constant of the liquid solution as abscissas. The dielectric constant data were taken from Akerlöf and Short.¹¹ In Fig. 9 the percentage composition is written as a second abscissa so that interpolation can readily be made from dielectric constant to weight per cent. dioxane and *vice versa*.

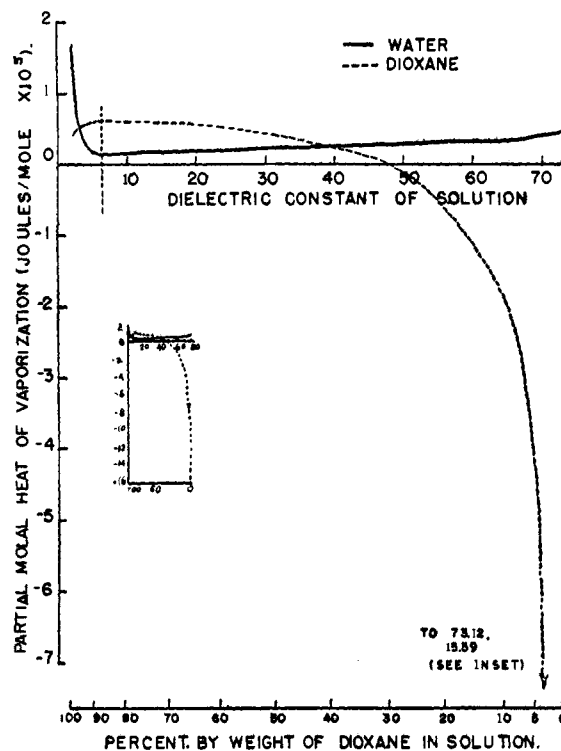


Fig. 9.—Partial molal heat of vaporization versus per cent. by weight of dioxane in the solutions.

Figure 9 demonstrates that the partial molal heat of vaporization of water falls rapidly with increased dielectric constant up to a dielectric constant of about 5, and then increases linearly with dielectric constant up to a value of dielectric constant of 65. Above a dielectric constant of 65 the partial molal heat of vaporization of water increases slightly more rapidly. Since the partial molal heat of vaporization of water falls and that of dioxane rises in solutions rich in dioxane, the water apparently is responsible for the sharp decrease in total heat of vaporization in strong dioxane solutions noted in Fig. 6.

When there are very few water molecules in a large excess of dioxane, each water molecule exerts its maximum induction effect on non-polar dioxane molecules producing the maximum number of dipole-induced dipole bonds. In addition there is perhaps a strong hydrogen bonding as is indicated by the existence of a water-dioxane azeotrope at about 85% by weight dioxane. Thus the relative partial molal heat of vaporization of water will be high. As more water is added there are fewer dioxane molecules to be polarized by each water molecule. The dipole-induced dipole effect will be lessened without a lessening of hydrogen bonding effect or an appreciable appearance of

(11) G. Akerlöf and O. Short, THIS JOURNAL, 58, 1242 (1936).

dipole-dipole effect. Thus the partial molal heat of vaporization of water falls. This trend continues until dipole-dipole effects become increasingly significant, when the partial molal heat of vaporization of water increases linearly with dielectric constant up to about 90% by weight of water. In solutions more concentrated in water than 90% by weight an accelerated increase of partial molal heat of vaporization of water is observable. This increase is due perhaps to the increased magnitude of dipole-dipole forces relative to dipole-induced dipole forces and perhaps also due to increased hydrogen bonding among water molecules alone.

With reference to the dioxane curve, the initial increase of the partial molal heat of vaporization of dioxane can be explained by the increased forced holding each dioxane molecule as the proportion of water increases. The increased forces arise perhaps from both induced polarity in dioxane molecules and hydrogen bonding between water and dioxane molecules. These increased forces reach a maximum at the azeotrope composition

shown by the dotted line in Fig. 9. Beyond the azeotrope composition, dipole-dipole forces among water molecules become increasingly important relative to dipole-induced dipole forces among the water and dioxane molecules. Thus the restraining forces on dioxane becomes less and the partial molal heat of vaporization of dioxane falls, less rapidly at first and then more rapidly and finally precipitously as predominant dipole-dipole interacting molecules, in a sense, squeeze out the dioxane.

A further study of the heats of vaporization of the dioxane-water system at several temperatures is planned, since the rate of change of heat of vaporization with temperature at any given composition would be theoretically useful, and the data taken at other temperatures would tend to check the present study qualitatively without the labor of repeating it.

Since the calorimeter was designed for the most general applicability, it is planned to study other types of liquid mixtures.

FAYETTEVILLE, ARKANSAS RECEIVED SEPTEMBER 21, 1951

[CONTRIBUTION FROM THE SIR WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES, UNIVERSITY COLLEGE, LONDON]

The Reaction of Cyanogen and Related Nitriles with 1,3-Dienes. III. Kinetic Study of the Cyanogen-Butadiene Cyclization Reaction¹

BY P. J. HAWKINS AND G. J. JANZ²

The reaction of cyanogen with butadiene at moderately high temperatures in the gas phase yields 2-cyanopyridine as product. The present communication reports on a kinetic study of this cyclization-dehydrogenation reaction. The constant pressure continuous flow method was used to obtain the kinetic data for the temperature range of 325 to 450°. The reaction is homogeneous and over-all second order, first order with respect to each of the reactants. The energy of activation is 31.6 ± 0.2 kcal./mole, and the frequency factor, 1.6×10^{-12} sec.⁻¹ g. mole⁻¹ l. A comparison of these data with those reported for diene reactions at high temperatures is made.

It has been seen in Parts I and II of this series³ that the reaction of cyanogen with butadiene to give 2-cyanopyridine previously reported⁴ is one of a more general group of reactions of organic nitriles with conjugated dienes. This generality favors a Diels-Alder type of mechanism for this cyclization-dehydrogenation reaction. The (C≡N) group thus has the role of the dienophilic component of the dienophile, and because the conditions are favorable for aromatization, the reaction is accompanied by a simultaneous dehydrogenation, giving the pyridinic derivative as product. Alder⁵ has mentioned in his observations on the formation of pyridinic nuclei by this reaction that when hydrogen is present in the 2- and 5-positions of the adduct, dehydrogenation to a pyridine derivative takes place under the normal conditions of the reaction. A kinetic study of the cyanogen-buta-

diene cyclization was thus undertaken to gain quantitative data concerning the energy of activation and collision frequency factor in a reaction leading to the direct synthesis of the pyridine nucleus. A constant pressure-continuous flow method seemed to offer the best means for this experimental study, for by restricting the reaction to small conversions the complications due to side reactions can be avoided. In consequence of the possible complexity of this system, and the small conversions thus necessary, the rate of reaction was measured by the formation of cyanopyridine rather than by disappearance of either of the reactants.

Experimental

Description of Flow Apparatus.—Three capillary type flowmeters were used to measure and control the rates of flow of the three gases, cyanogen and butadiene and nitrogen. The former two gases met in a mixing tube fitted with glass beads and were passed through a calcium chloride tube before reaching the reaction vessel in the hot zone. The nitrogen, when used, was passed through a phosphorus pentoxide tube before entering the system. The reaction vessel was all Pyrex, with capillary inlet and outlet tubes to the constant temperature reaction volume, and a thermocouple well extending the length of the reaction zone. The products of the reaction and unchanged reagents were collected in three receivers, the first being cooled to -80° and the latter two, -192°. The pressure immediately before the reaction was measured by a manometer, and the tem-

(1) Abstracted in part from the thesis submitted by P. J. Hawkins in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry at University College, London.

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(3) P. J. Hawkins and G. J. Janz, *J. Chem. Soc.*, 1479, 1485 (1949).

(4) G. J. Janz, R. G. Asch and A. G. Keenan, *Can. J. Research*, **B25**, 272 (1947); G. J. Janz and A. G. Keenan, *ibid.*, **B25**, 283 (1947); G. J. Janz and P. J. Hawkins, *Nature*, **162**, 28 (1948).

(5) K. Alder, "Newer Methods of Preparative Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1948, p. 503.