4. The values of the equilibrium constants obtained in this paper, together with those discussed in a previous paper for the reaction $FeO + CO = Fe + CO_2$, have been combined in two independent sets to calculate the constant of the water gas reaction. The values of this constant so calculated are in good agreement with one another at all temperatures, and the values of I in the free-energy equation calculated from them show a satisfactory constancy.

5. The values of the water: gas equilibrium constant and free-energy integration constant calculated from the iron oxide equilibria, while consistent among themselves, are not in agreement with the values directly determined. Reasons have been given for the belief that the latter values are less reliable than the former. Corrections to the free-energy data relating to carbon monoxide and carbon dioxide have been made on the basis of the new results.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE SPECIFIC HEATS OF CERTAIN ORGANIC LIQUIDS AT ELEVATED TEMPERATURES

BY JOHN W. WILLIAMS AND FARRINGTON DANIELS

RECEIVED JANUARY 22, 1924

It is an interesting fact that the specific heats of gases and solids and their temperature coefficients have been studied much more carefully than those of liquids, although the latter can be measured with greater precision. The reason for this situation is obvious; for solids, and particularly gases, are simpler systems than liquids and their specific heats have been treated mathematically with considerable success. The specific heats of liquids, however, are less amenable to theoretical analysis, for they are complicated by association. When the liquid is heated the complex molecules are broken up and heat is absorbed. This heat is included in many cases as a considerable part of the observed specific heat and prevents the treatment of specific heat as a simple function of the atom.

Before progress can be made in the interpretation of the specific heats of liquids it is necessary to obtain accurate, differential measurements of many liquids over a wide temperature range. Since the heat required to raise the temperature of a liquid includes the energy used in changing from one molecular form to another, irregularities in the specific heat—temperature curves are of particular interest. The whole problem has received new significance since the work of H. B. Baker[1] on dry liquids

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[1] (a) Baker, *J. Chem. Soc.*, **101**, 2339 (1912); **121**, 568 (1922). (b) Lewis, THIS JOURNAL, **45**, 2836 (1923).

has indicated that it should be possible to study the separate properties of the different molecular species in a liquid by removing every trace of water and thus "freezing" the equilibrium for one temperature.

The data on the specific heats of organic liquids are at present rather meager. There is practically no information on the change of the specific heat over small temperature intervals and the agreement between existing values is unsatisfactory. Among the important contributions in this field are those of Regnault,[2] Louguinine,[3] Schiff,[4] and Mills and MacRae.[5]

Method

Since it was desired to determine the temperature coefficient of specific heat, it was necessary to use a method capable of measuring the absorption of heat over comparatively small temperature ranges. Many of the specific-heat data in the literature have been determined by the method of cooling or the method of mixtures to give an average specific heat over a considerable range of temperature and the irregularities in the specific heats at different temperatures, which are of particular interest, are wiped out.

The adiabatic method of Richards[6] is the best for most calorimetric measurements and in the present investigation it is particularly essential. Any method which permits the outer bath to be cooler than the calorimeter, allows evaporation of the liquid and when, as in the present investigation the liquid is close to its boiling point, this evaporation introduces a correction too large to be made with accuracy. The distillation in a non-adiabatic calorimeter may readily become so great in such cases as to introduce an appreciable error even from the loss of weight of the liquid.

It is necessary then to use a strictly adiabatic method and to prevent all transference of heat to the cold room. In a previous research it had been found that the transference of heat along a platinum resistance thermometer of the calorimetric type, from the inner calorimeter to the room amounted to as much as 0.35 calorie per minute when the calorimeter was 15° above the temperature of the room, even though the whole upper part of the thermometer was immersed in the outer bath which was kept at the same temperature as the inner calorimeter. This difficulty is eliminated in the present case by placing the platinum resistance thermometer in the *outer* bath where conduction of heat along the thermometer to the room can introduce no measured heat losses. Since the outer bath is

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[2] Regnault, *Ann. chim. phys.*, [2] **73**, 1 (1840) through [3] **67**, 427 (1863).

[3] Louguinine, *ibid.*, [5] **27**, 398 (1882) through [7] **27**, 105 (1902).

[4] Schiff, *Z. physik. Chem.*, 1, 376 (1887).

[5] Mills and MacRae, *J. Phys. Chem.*, **14**, 797 (1910); **15**, 54 (1911).

[6] Richards, *Proc. Am. Acad. Arts Sci.*, **41**, 3 (1905); THIS JOURNAL, **31**, 1275 (1909), and later papers.

kept at the temperature of the inner liquid it is just as satisfactory to measure the temperature rise of the former. The readings on the bridge of the calorimetric thermometer are taken only when the thermel galvanometer registers zero. The thermel is completely immersed, so that heat cannot be lost by conduction along its wires to the colder room.

Apparatus

The apparatus used in the determination of the specific heats of organic liquids and suitable for use at elevated temperatures is shown diagrammatically in Fig. 1.

The liquid to be measured is contained in a cylindrical copper vessel 8 cm. high and 6 cm. in diameter, supported in an enclosing vessel with an air gap of 7 mm. between the two. It rests on three glass points and is centered by asbestos supports.

The enclosing vessel is of copper 12 cm. high and 8 cm. in diameter, fitted with a threaded cover of bronze. The cover is provided with an upright tube for the stirrer and with conical stuffing boxes, for the admission of the heater and thermocouple. A tight joint is conveniently made by filling the stuffing boxes with asbestos and tightening the nuts. The cover, with all of the parts supported by it, is screwed into a ring brazed to the copper cylinder. White lead in the threads keeps the joint tight and acts as a lubricant.

The leads pass out through small copper tubing which runs through the bath for a distance of 20 cm. in order to prevent thermal leakage from the inner liquid along the wires to the cold air of the room. The sheath is insulated, thermally, from the cover and the copper tubing by a small section of glass tubing held by cement. The inner stirrer is a single brass propeller, brazed to a brass shaft and attached to the main shaft by asbestos board to prevent thermal contact between the liquid and the outer bath. A cap attached to the upper shaft rotates in the liquid of the outer bath so as to make a seal and prevent the movement of air. Such a precaution is absolutely necessary in work of this kind where there is a large temperature difference and where, owing to the high vapor pressure of the inner liquid, a current of air will evaporate an appreciable amount of liquid and cause the absorption of a considerable quantity of heat. The heat generated by the stirrer is negligible, for all bearings with their attendant friction are placed so that they cannot conduct heat to the inner calorimeter and the rate of stirring is too slow to generate appreciable heat in the liquid.

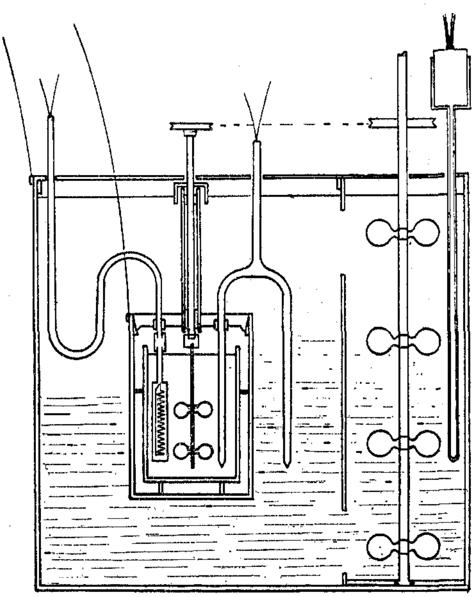
Fig. 1.—Adiabatic calorimeter.

The multiple thermel of five copper-constantan thermocouples is enclosed in a thin glass tube, and connected to a sensitive galvanometer. A little oil in the tubes gives quicker response to temperature changes in the bath. One division on the scale corresponds to 0.001° and the temperature of the outer bath is adjusted so as to keep the galvanometer beam as closely as possible on zero—within 0.01° or 0.02° except for an occasional, momentary fluctuation caused by changes in the line voltage.

The temperatures are measured with a platinum resistance thermometer[7] and a special bridge of the highest precision.[7] The temperature differences are accurate to less than 0.001°.

The tank for the outer bath is constructed of sheet copper, brazed along the seams. It is packed in asbestos contained in a still larger can. The bath consists of 9 liters of glycerol in which is dissolved 20 g. of ferric chloride to make it an electrolytic conductor.[8] It is heated externally with resistance wire wound around the tank, and internally by passage of the alternating current directly through the liquid bath,[9] from the insulated calorimeter to the tank. A rheostat in the external heating circuit and a rheostat and switch in series with the electrolytic circuit allow efficient temperature control.

Purification of Materials

Benzene.—The benzene, obtained from Barrett and Company, was shaken with concd. sulfuric acid, washed with dil. sodium hydroxide solution, and with distilled water. It was frozen out twice and fractionated and showed no blackening with mercury. A fraction boiling between 80.15° and 80.25° was obtained; n_D^{25}, 1.50060. All the liquids were distilled with a barostat[10] at exactly 760 mm.; and standardized thermometers were used.

Toluene.—This material was obtained from the Mallinckrodt Chemical Company. It was shaken with concd. sulfuric acid, washed with dil. sodium hydroxide and distilled water. After standing over mercury for a week it was dried with phosphorus pentoxide and fractionated, a fraction boiling between 110.5° and 110.6° being used; n_D^{25}, 1.49746.

Ethyl Benzene.—The liquid was prepared by Professor G. S. Skinner of this Department. It was dehydrated with phosphorus pentoxide and fractionated. The fraction used distilled over between 136.0° and 136.1°; n_D^{25}, 1.49386.

***o*-, *m*- and *p*-Xylenes.**—These liquids were obtained from Kahlbaum. For purification the *ortho* and *meta* products were subjected to the same treatment. They were shaken with concd. sulfuric acid, treated with dil. sodium hydroxide solution and washed with water. They were refluxed over mercury and dried with phosphorus pentoxide. After repeated fractionations, a sufficient amount of *o*-xylene was obtained which boiled between 142.3° and 142.5°; n_D^{25}, 1.50027. The *m*-xylene boiled between 139.3° and 139.4°; n_D^{25}, 1.49566. *p*-Xylene received the same treatment and in addition was fractionally crystallized six times. The final fraction boiled between 138.3° and 138.4°; n_D^{25}, 1.49396.

***iso*-Propyl Alcohol.**—This was obtained from Professor G. S. Skinner of this Department. It was digested with fused calcium oxide, distilled and digested with barium oxide. It was fractionated from the dehydrating agent and the liquid used boiled between 81.95° and 82.05°; n_D^{25}, 1.37709.

Ethyl Alcohol.—A 99% alcohol was dehydrated over metallic sodium. The purified alcohol was then fractionated, the final fraction which was used boiling to within 0.1°.

***iso*-Amyl Alcohol.**—This was a Kahlbaum product. It was digested over unslaked lime and then distilled, the first and last portions being discarded. It was digested over

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[7] Manufactured by the Leeds and Northrup Co.

[8] It was first planned to carry the specific-heat measurements to 500° and fused zinc chloride was found to be a suitable liquid for electrolytic heating of the outer bath.

[9] Daniels, This Journal, **38**, 1473 (1916).

[10] Mathews and Fayville, *J. Phys. Chem.*, **22**, 1 (1918).

barium oxide, treated with sodium and fractionated. The sample used boiled between 131.1° and 131.3°; n_D^{25}, 1.40611.

n-**Butyl Alcohol.**—The method of purification of this liquid (obtained from Kahlbaum) was similar to that used for *iso*-amyl alcohol. The fraction used boiled between 117.6° and 117.7°; n_D^{25}, 1.39753.

iso-**Butyl Alcohol.**—The refined reagent was obtained from the U. S. Industrial Chemical Company. It was dehydrated over anhydrous barium oxide. The alcohol used boiled between 107.7° and 107.8°; n_D^{25}, 1.39411.

Nitrobenzene.—This substance was obtained in a purified condition from the Eastman Kodak Company. It was carefully fractionated, the sample used boiling between 209.4° and 209.6°.

Chloroform.—The material was obtained from the Mallinckrodt Chemical Company. It was treated with concd. sulfuric acid to remove alcohol, washed with dil. sodium hydroxide solution and water. It was dried over fused calcium chloride, and further dried over phosphorus pentoxide. A fraction boiling between 61.05° and 61.10° was obtained for use; n_D^{25}, 1.44660.

Carbon Tetrachloride.—The preparation (obtained from Merck and Company) was refluxed over mercury and washed with concd. sulfuric acid to remove sulfides. It was washed with dil. sodium hydroxide solution and water. It was dried over fused calcium chloride and fractionated. The fraction boiled between 76.45° and 76.5°; n_D^{25}, 1.45930.

n-**Heptane.**—The material, from the distillation of *Pinus Jeffreyi* obtained through the kindness of Professor E. Kremers of this University, was cooled with ice water, saturated with hydrogen chloride and allowed to stand. After the resinous deposit had separated, the gas was removed by washing with water. The heptane was then dried with sodium wire and fractionated. The final product boiled between 98.25° and 98.37°; n_D^{25}, 1.38635.

Acknowledgment is due Mr. G. B. Ramsdell of this Laboratory who purified, in part, a few of these liquids during an investigation with Dr. J. H. Mathews on latent heats of vaporization.

Procedure

A given volume (160 cc.) of the purified liquid is accurately weighed and introduced into the calorimeter. Measured amounts of electrical energy are passed through the heater for definite time intervals. The heating of the outer bath is regulated so as to keep the thermel always on zero, thus insuring adiabatic control. The final temperature of one determination is made the initial temperature of the succeeding determination and a whole series of results from about 30° up to about 80° or above can be obtained with a single sample.

The diagram of the apparatus used in measuring the input of energy is shown in Fig. 2.

An isolated storage battery supplies the current and a rheostat composed of resistance wire dipping into a deep tube of mercury makes possible its regulation. The voltage drop across the heating unit, H, is determined by means of a volt-box, V, and a potentiometer, P. The current is determined by measuring with the potentiometer the voltage drop across a one ohm standard coil, O. The "dummy heater" D, equal in resistance to the heating coil, keeps the batteries at the desired voltage previous to an experiment. The energy input is kept constant throughout the whole experiment by adjusting the rheostat in the storage battery circuit so as to keep the galvanometer of the potentiometer circuit always on zero. The energy input is obtained by multiplying the voltage drop across the heating coil by the current in amperes and the time in seconds as measured by two stop watches.

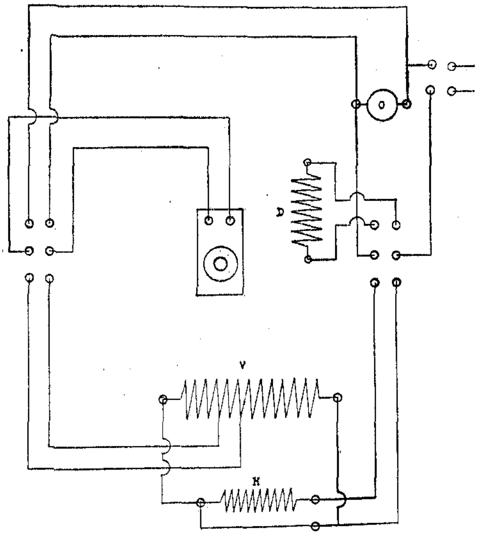

Fig. 2.—Potentiometer circuits.

The accurate determination of the water equivalent of the calorimeter presented some difficulties. The total heat capacities of the substances which absorb part of the measured heat are given in Table I.

The water equivalent used in the calculations is taken as 64 joules per degree at 30°, with an increase of 0.3 joule for every 10° rise in temperature.

This value was checked using the values of the specific heats of benzene, carbon tetrachloride and chloroform obtained by Mills and MacRae,[5] as follows.

Water equivalent at 30° using chloroform as a standard, 64.1 joules per degree; using carbon tetrachloride, 63.0 joules per degree; using benzene, 65.7 joules per degree.

Although the agreement is satisfactory at low temperatures there are wide discrepancies at the higher temperatures. The results of Mills and MacRae at the higher temperatures are considerably lower than those of any other investigator.

Table I

Water Equivalent for Calorimetric System at 30°

Material	Wt. G.	Sp. ht.	Ht. capacity in Joules per degree
Copper	132	0.092	50.77
Solder	15	.041	2.59
Glass	5.5	.165	3.81
Mica	2	.208	1.77
Oil	2.5	.50	5.23
		Total	64.2

Using water as a standard and taking the data of Callender and Barnes, the value of 68.8 joules per degree was obtained. This value is considered less reliable because the heating units of this particular calorimeter were not designed for the use of liquids of as high a specific heat as that of water, and the adiabatic control was not efficient.

In an investigation of this kind in which liquids are heated nearly to their boiling points it is very important to guard against including in the specific heat any absorption of heat due to the latent heat of vaporization. This error was proved negligible in each case by an experiment. After the temperature was carried as close to the boiling point as was considered safe the specific-heat determinations were finished, the heating coil was disconnected, and the temperature of the outer bath was kept equal to that of the inner liquid for 20 minutes or more by passing current through the outer bath as needed to keep the thermel on zero. Whenever vaporization or conduction of heat to the colder room was taking place the temperature of the inner liquid fell. In no case was the fall of temperature over a 20-minute period greater than 0.003°; usually it was nearer 0.001°, showing that the error introduced by evaporation was negligible. These tests showed further that the adiabatic control was entirely satisfactory.

Although the evaporation of large quantities of liquid due to condensation of the vapor on cold surfaces was eliminated, there must have been some vaporization, as the vapor pressure increased during the heating. The air space around the inner can was therefore made as small as possible. The actual volume was 200 cc., but when the partial pressure of the vapor increased some of the vapor was carried out with the displaced air. It was proved by an experiment that the evaporation from this source was less than half of that required to saturate the air space. A bulb of benzene with an air space was heated at a rate equal to that used in the calorimetric experiments. The quantity of benzene vapor forced out through a capillary tube was determined by surrounding the capillary with a freezing mixture, cutting it off and weighing the condensed benzene. Even at temperatures near the boiling point, where the vapor-pressure curve is steepest, the total corrections did not amount to as much as 0.1% of the specific heat and they were not included in the calculations.

The data for one of the liquids (ethyl alcohol) are shown in detail in the following table to illustrate the calculations.

TABLE II

DATA FOR ETHYL ALCOHOL

Weight of sample (corrected to a vacuum) 123.2 g. Voltage drop across heating unit 5.782 v. Current through heating unit, 0.2814 amp.

Mean temp. °C.	Temp. rise °C.	Time Seconds	Calorimeter input	Total input	Alcohol input	Sp. ht.[a]
27.49	4.923	1112	314.6	1809.3	1495	0.5894
32.47	4.985	1134	319.3	1845.0	1526	.5940
37.45	4.950	1165	317.8	1895.5	1578	.6185
42.39	4.980	1201	320.6	1954.5	1634	.6368
47.36	4.965	1227	320.4	1996.0	1676	.6552
52.34	4.972	1264	321.5	2056.5	1735	.6770
57.33	4.980	1312	322.7	2134.5	1812	.7062

[a] Specific heat = [joules per degree per gram] ÷ 4.182.

Results

The final results are shown in the accompanying graphs (Figs. 3 to 7) where specific heat is plotted against temperature (Centigrade) for all the fifteen liquids studied. The crosses represent one continuous set of determinations and the circles another set, made with a new weight of liquid

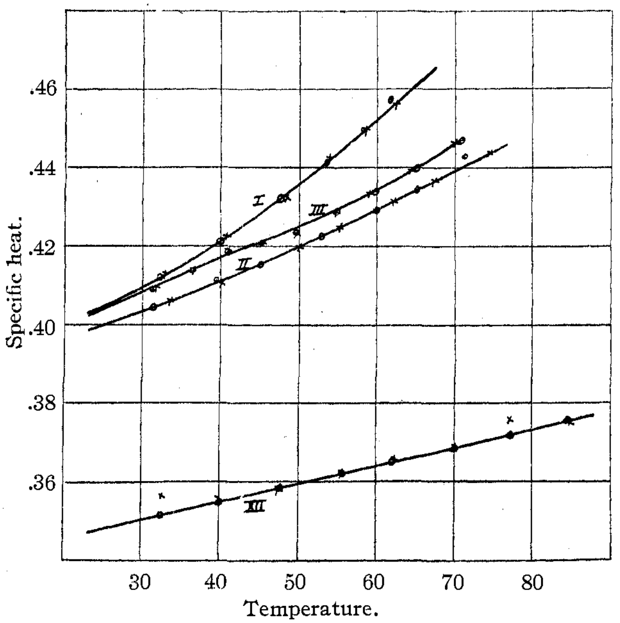

Fig. 3.—(I) Benzene. (II) Toluene. (III) Ethyl benzene. (XII) Nitrobenzene.

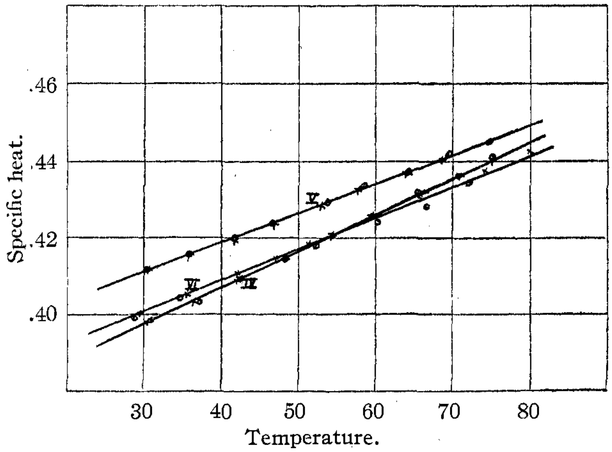

Fig. 4.—(IV) *p*-Xylene. (V) *o*-Xylene. (VI) *m*-Xylene.

on a different day. In nearly every case the two independent determinations check closely and fall on a smooth curve within 0.001 calorie per degree. Departure from a smooth curve does not *necessarily* imply experimental error and the significance of such irregularities will be discussed later.

The empirical equations which give the specific heat at constant pressure (C_p) as a function of the temperature (Centigrade) are given in Table III.

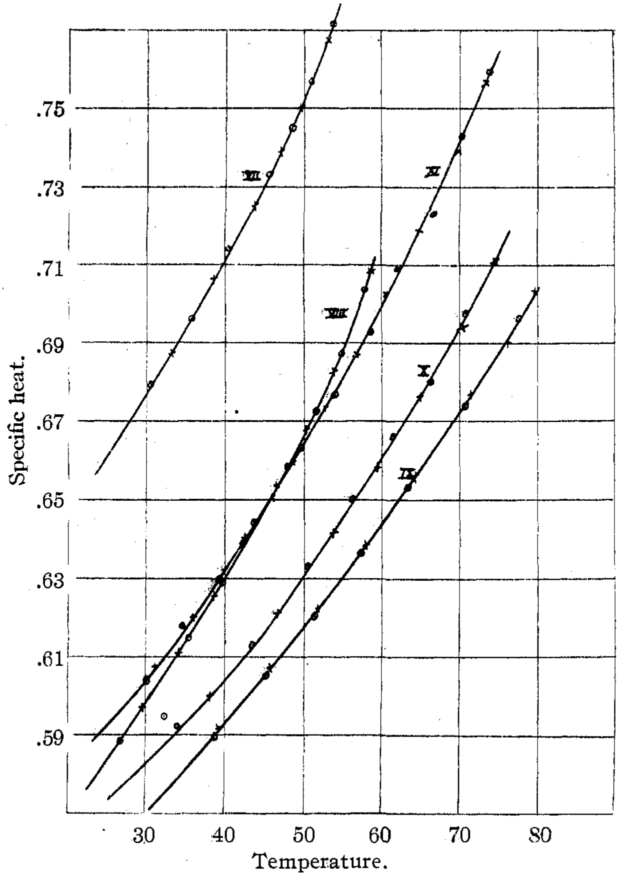

Fig. 5.—(VII) *iso*-Propyl alcohol. (VIII) Ethyl alcohol. (IX) *iso*-Amyl alcohol. (X) *n*-Butyl alcohol. (XI) *iso*-Butyl alcohol.

The specific heats as determined at 30°, and as extrapolated to 20° and to the boiling points are included in Table IV. The extrapolation to the boiling point is not very reliable because the course of the curve may change, and the extrapolation was not even attempted in cases where an interval greater than 20° was involved. It is interesting to note that the

TABLE III

EMPIRICAL EQUATIONS

	$C_p =$
Benzene	$0.3824 + 0.000655t + 0.0_584t^2$
Toluene	$.3726 + .000846t$
Ethyl benzene	$.3821 + .000886t$
o-Xylene	$.3874 + .000775t$
m-Xylene	$.3764 + .000812t$
p-Xylene	$.3695 + .00093t$
*iso*Propyl alcohol	$.5675 + .00359t + .0_516t^2$
Ethyl alcohol	$.5068 + .00286t + .0_554t^2$
iso-Amyl alcohol	$.4895 + .00255t + .0_692t^2$
n-Butyl alcohol	$.4992 + .00263t + .0_518t^2$
iso-Butyl alcohol	$.4988 + .00327t + .0_525t^2$
Nitrobenzene	$.3306 + .000452t$
Chloroform	$.2250 + .000304t$
Carbon tetrachloride	$.1854 + .00047t$
Heptane	$.4755 + .00142t$

higher-boiling alcohols have very high specific heats—greater than unity, at temperatures in the neighborhood of 100°.

TABLE IV

SPECIFIC HEATS AND RELATED CONSTANTS

Liquid	Sp. ht. 30°	Molal ht. B. p.	B. p. °C.	λ	Mol. vol. B. p.	$\alpha \times 10^5$	Internal pressure (atm.)	Mol. ht. 20°	Mol. vol. 20°	Mol. ht./Mol. vol. 20°	Mol. ht./Mol. vol. 50°	Mol. ht./Mol. vol. B. p.
Benzene	0.4095	38.75	80.2	735	96	124	2815	31.35	89.5	0.353	0.368	0.390
Toluene	.3980	42.90	110.7	800	118.3	110	3120	35.8	104.0[a]	.354	.357	.362
Ethyl benzene	.4088	58.35	135.8	812	139.5	96	3645	42.5	121.3	.347	.362	.416
o-Xylene	.4112	52.90	141.0	876	138	97	3580	42.85	123.0	.348	.360	.384
m-Xylene	.4010	52.30	139.2	876	140	100	3395	41.8	122.9	.340	.352	.374
p-Xylene	.3973	52.40	137.5	860	140.3	101	3310	41.3	123.4	.335	.350	.367
iso-Propyl alcohol	.6765	...	82.1	949	80.9	109	(4655)	38.8	76.2	.507	...	...
Ethyl alcohol	.5978	40.35	78.4	990	62.1	103	(4400)	26.1	57.4	.447	.522	...
iso-Amyl alcohol	.5698	...	137.8	1100	...	...	...	48.3	108.8	.444	...	...
n-Butyl alcohol	.5820	...	116.0	1063	...	...	...	41.5	91.5	.453	...	...
iso-Butyl alcohol	.6034	...	106.4	996	...	...	...	43.1	92.0	.466	...	...
Nitrobenzene	.3442	...	210.9	...	122.1	84	4810	42.0	103.7	.405	.410	...
Chloroform	.2340	29.08	61.2	705	84.5	127	2735	27.6	79.3[a]	.343	.342	.346
Carbon tetrachloride	.2000	34.60	76.8	707	103.7	124	2590	30.1	94.0[a]	.313	.322	.334
Heptane	.5180	61.5	98.4	755	162.6	128	2745	50.4	143.0[a]	.353	.370	.378

[a] These values are taken from a research by Mathews and Ramsdell which has not yet been published.

Theoretical

In order to compare the specific heats with other related properties Table IV is given. The table is self explanatory except perhaps that in the fifth column, λ, stands for latent heat of vaporization per mole, and α is defined as $1/v \left(\frac{dv}{dt}\right)$ where v is the volume in cubic centimeters of 1 g.

The liquids with high boiling points, and hence high molar heats of vaporization, by Trouton's law usually possess high molar-heat capacities. These properties are related in that they all involve the absorption of energy to pull the molecules apart.

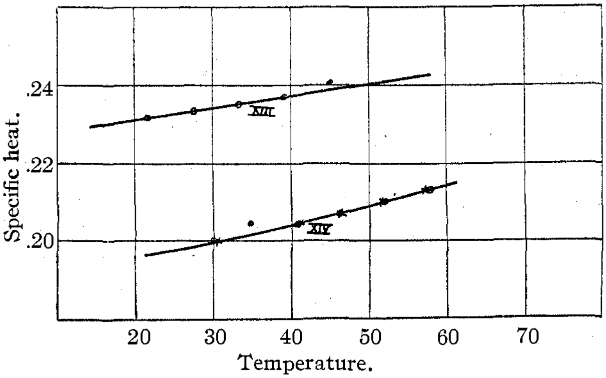

Fig. 6.—(XIII) Chloroform. (XIV) Carbon tetrachloride.

The alcohols, benzene and a few other liquids give curves which become steeper continuously—while the majority of the liquids have specific heats which increase regularly, apparently as a straight line function of the temperature over the range studied. Those which do not give straight lines require a considerable quantity of energy to break up the associated molecules and this energy increases as the temperature rises because at

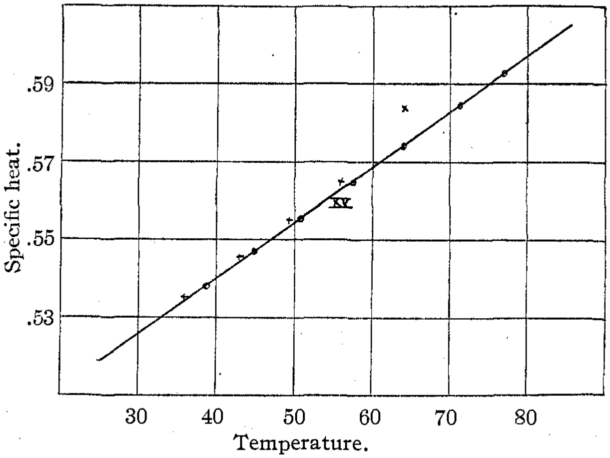

Fig. 7.—(XV) Heptane.

the higher temperatures more of the depolymerization is taking place. Obviously this cannot continue indefinitely, and if the other factors increased uniformly the curve should go through a point of inflection and flatten out as the depolymerization becomes more complete. This inflection point may not be reached until the boiling point is passed. These liquids are the ones which give abnormal heats of vaporization and are otherwise characterized as "associated."

The internal pressures of liquids have been calculated in a number of different ways and used by Hildebrand[11] in studies of solubility. Internal pressure is defined as the force which, together with the external pressure, opposes the thermal pressure which is due to the kinetic energy of the molecules. It is the "a/v^2" in the familiar van der Waals' equation. It was thought possible to calculate internal pressures of the liquids from the specific-heat data, and indeed an equation relating specific heat and internal pressure has been proposed by Kleeman,[12] $P = \frac{C-(3R/2)}{V\alpha}$ where P is the internal pressure in atmospheres, V is the volume of a gram molecule in liters (Table IV), α is the coefficient of expansion (Table IV) and C is the internal molal heat capacity, which is defined by Kleeman as the difference between the observed molal heat capacity and the energy necessary to overcome external pressure. This relation would not be expected to hold for liquids in which an appreciable fraction of the energy is used in breaking up associated molecules. The internal pressures as calculated with this formula are shown in the eighth column of Table IV and they agree roughly with the internal pressures as calculated by other methods.

The entropy increases involved in heating the liquids from 25° (standard temperature) to their boiling points may be calculated from the empirical equations for the specific heats at different temperatures. These entropy increases per mole are as follows: heptane, 11.6 entropy units; carbon tetrachloride, 4.9; chloroform, 3.2; toluene, 9.4. The calculations for the other liquids were not made because the extrapolations are not considered sufficiently reliable. These values together with the measurements of heats of vaporization at the boiling points are useful in thermodynamical calculations involving the vapor state.

Perhaps the most striking relationship is shown in the last columns of Table IV; from which it is evident that the molal heat capacity divided by the molal volume gives a ratio which is nearly the same for many liquids. This relationship was noticed early in the experimental work, for the calorimeter was always filled with the same volume of liquid and the time required for a specific-heat determination was about the same for all the liquids except the alcohols and water.

[11] Hildebrand, THIS JOURNAL, **38**, 1459 (1916); **41**, 1071 (1919).

[12] Kleeman, "Kinetic Theory of Gases," John Wiley and Sons, New York, **1920**, p. 104.

It is obvious that the same ratio is obtained by dividing the specific heat by the specific volume or by multiplying the specific heat by the density. It may be said that *the heat capacity per cubic centimeter of unassociated liquids is a constant,* approximately 0.35 calorie per degree at room temperature and slightly more than this at higher temperatures.

Schiff[13] called attention to this relationship in 1886 but he restricted it unnecessarily to esters of the formula $C_nH_{2n}O_2$ at equal fractions of their critical temperatures.

This rule, though only approximate, is useful in estimating the specific heats of the liquids at various temperatures when their densities are known. It seems to hold over a wide range of temperatures and for a large number of liquids. The hydrocarbons give the value 0.35 to 0.37 quite regularly, and a great many liquids, including even some of the inorganic liquids, have values between 0.3 and 0.4. Most of the liquids which have a heat capacity greater than 0.4 cal. per degree per cubic centimeter contain oxygen, or are known to be associated. If it is permissible to add one more criterion to the already large number of unsatisfactory criteria for molecular association in a liquid, it may be said that *if the product of the specific heat of a liquid and its density is much greater than 0.4 the liquid probably contains associated molecules* which are broken down as the temperature is raised. This relation is similar to the one according to which a liquid is said to be associated if its heat of vaporization is greater than that given by Trouton's rule.

The fact that the molal heat capacity divided by the molal volume is nearly constant for many liquids, leads to the suggestion that molal heat capacities are both additive and constitutive but that the constitutive factors in heat capacity are the same as the constitutive factors in volume. In other words, the heat required to raise the temperature of a mole of liquid depends chiefly on the number of atoms, and although different arrangements of atoms in the molecule cause differences in the molal heat capacities, they cause proportionally the same differences in the molal volumes. The part of the heat capacity which is a function of molecular constitution may be eliminated by dividing by an experimentally determined quantity—volume, which depends on molecular constitution in the same way as does the heat capacity. However, if associated molecules are broken down as the temperature is raised, an additional quantity of heat is absorbed, and the heat capacity becomes larger, but the volume is not increased proportionally. In such cases the ratio of specific heat to specific volume may be considerably greater than 0.4 and in fact the difference between this ratio and 0.4 may be taken as a rough measure of the "de-association" taking place. For water the ratio is practically unity. It is interesting that molecules containing oxygen usually give

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[13] Schiff, *Ann.*, **234**, 300 (1886).

an abnormally high ratio of heat capacity to volume, that is, they have a tendency to form complexes which are broken down at the higher temperatures.

The application of Kopp's law to liquids is not satisfactory, the sum of the atomic heat capacities being usually greater than that of the molar heat capacities. This is to be expected, because the atomic heats of the solids have been used and the heat capacities of crystals consist of two factors, the kinetic energy of the atoms ($3/2\ R$), and the potential energy of displacement from fixed points in the crystal lattice. The latter is often as great as the former in crystals, but it must be smaller in the case of liquids, for the lattice is less rigid if it exists at all.

Irregularities in specific heat—temperature curves for liquids are particularly interesting, for they signify a change from one form of molecule to another, corresponding to the transition temperatures of crystalline solids. In crystals all the atoms are in the same condition and there is a sharp transition temperature, but in liquids, as in gases, a definite equilibrium is set up which changes as the temperature rises, and the "transition" is spread out over a considerable temperature range. Over these temperature intervals, then, more heat is required to raise the temperature 1° because some of it is used in breaking up the associated molecules, and the specific-heat curves change their slope.

In past researches, except in the case of water and a few other liquids, the measurements have not been sufficiently accurate to determine these changes in slope, or they have been carried out over such wide temperature ranges that the irregularities have been lost. Of the 15 liquids studied in the present investigation, all appear to give straight lines or smooth, regular, concave curves except two—ethyl benzene and carbon tetrachloride. Although the curves for these two liquids have been drawn straight in Figs. 3 and 6 and given empirical equations of the first order for practical purposes of recording the data, the curves are distinctly irregular.[14] The temperatures at which these curves become steeper must indicate the temperature at which a "transition" from one species of molecule to another is taking place. These liquids are being subjected to extreme drying in an attempt to "freeze" the equilibrium at one temperature as has been done by H. B. Baker[1a] for certain other liquids. In the light of Baker's work it is likely that the liquids whose specific heat—temperature graphs are curved, or those for which the ratio of heat capacity to volume is greater than 0.4 will show abnormal properties on treatment with phosphorus pentoxide, whereas those which give a ratio of about 0.35 and a straight line for a specific heat—temperature graph, probably cannot be made to show these abnormalities.

Acknowledgment is made of a grant from the Rumford Fund of the

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[14] They will be discussed more fully in a later paper.

American Academy of Arts and Sciences, with which some of the instruments used in this investigation were purchased.

Summary

1. An adiabatic calorimeter for measuring the specific heats of liquids accurately at elevated temperatures has been described.
2. The specific heats of 15 liquids have been determined over small temperature intervals from 30° to nearly 80°. The liquids are benzene, toluene, ethyl benzene, *o*-xylene, *m*-xylene, *p*-xylene, *iso*-propyl alcohol, ethyl alcohol, *iso*-amyl alcohol, *n*-butyl alcohol, *iso*-butyl alcohol, nitrobenzene, chloroform, carbon tetrachloride and heptane. The results have been recorded as graphs and as empirical equations.
3. Other physical properties of these liquids, related to heat capacity, have been tabulated.
4. The product of specific heat and density is approximately constant (about 0.35 calorie per cc.) for unassociated liquids. This relation is useful in predicting unknown specific heats and in studying the association of liquids.
5. Irregularities in specific heat-temperature curves indicate a change in equilibrium between different kinds of molecules in a liquid.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

X-RAY DIFFRACTION PATTERNS FROM CRYSTALLINE AND LIQUID BENZENE

BY E. D. EASTMAN

RECEIVED JANUARY 23, 1924

Broomé[1] has recently published X-ray diffraction data from powder photographs of crystalline benzene. Shortly before the appearance of his paper similar observations had been completed by the present writer. The more extended study of the crystal structure of benzene of which the latter measurements were to have been a part has been discontinued because its primary object, the determination of the molecular structure of benzene, now appears unlikely to be achieved by this method. The powder data are nevertheless of some interest and value. It is therefore deemed desirable to record here those obtained, especially since the experimental methods by which they were obtained differ considerably from Broomé's, and since certain minor differences in interpretation are indicated, although the two sets of results are in general in good agreement. In addition to the data concerning the crystals, a few observations on liquid benzene have been made and will be discussed.

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[1] Broomé, *Physik. Z.*, **24**, 124 (1923).