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

IRREGULARITIES IN THE SPECIFIC HEATS OF CERTAIN ORGANIC LIQUIDS

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The specific heats of most liquids increase regularly with the temperature, either as straight line functions, or as curves which become steeper as the temperature rises. Irregularities in the temperature–specific heat curves are of special interest for they show that more than one species of molecule is present in the liquid, and the recent work of Baker[1] has added new significance to the study of such liquids. Water[2] and sulfur[3] exhibit irregularities, and it was thought that other examples might be found with the help of a sufficiently improved experimental technique. An adiabatic calorimeter was developed, which successfully eliminated heat losses and permitted accurate differential measurements of the specific heats of liquids nearly to their boiling points.[4] Of the fifteen organic liquids examined thus far, benzene, ethyl benzene, and carbon tetrachloride exhibited distinct irregularities. Satisfactory results could not be obtained with benzene and ethyl benzene in spite of the fact that eight complete sets of determinations over the same range of temperature were made. The agreement of four similar experiments with carbon tetrachloride was somewhat better. This irregularity in the case of the specific heat of benzene was apparently encountered by Mills and MacRae[5] who, on failing to check duplicate experiments, state "The results of the check experiment show that the series of experiments 6 to 11 are correct, though we could never locate the exact trouble with series 1 to 5." The two curves described by these authors show a difference of almost 1% in the specific heat of benzene.

The object of this paper is to present the results of further exploration of these irregularities. The details of the experimental procedure are given in a preceding paper,[4] the only difference being in the fact that the temperature interval was decreased from 5° or 6° to 2°. The smaller interval magnified the experimental error but permitted a closer examination of the nature of the irregularities.

Purification of Materials

The benzene, obtained from Barrett and Company, was treated in the usual manner to remove thiophene, after which it gave no test for this substance. It was purified by

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[1] Baker, *J. Chem. Soc.*, **121**, 508 (1922).

[2] Bousfield, *Phil. Trans.*, **211A**, 199 (1911).

[3] Lewis and Randall, THIS JOURNAL, **33**, 476 (1911).

[4] Williams and Daniels, *ibid.*, **46**, 903 (1924).

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

repeated distillations and fractional crystallizations until the liquid gave practically the same physical constants that are given by Richards and Shipley.[6] The fraction used boiled between 80.16° and 80.21° (760 mm.), as determined with the help of a barostat; n_D^{25}, 1.49819. After three specific heat determinations, the liquid froze at 5.44°, which corresponds to a total impurity of less than 0.1 mole-per cent. of water, as shown by these authors.

Carbon tetrachloride, from Merck and Company, was refluxed over mercury and washed with concd. sulfuric acid to remove sulfides. It was then washed with dil. sodium hydroxide and water, dried over fused calcium chloride and fractionated. The fraction used boiled between 76.45° and 76.52° (760 mm.); n_D^{25}, 1.45930.

Ethyl benzene from two sources was used. No. 1 was prepared by Professor G. S. Skinner of this Department. No. 2 was obtained from Kahlbaum. The treatment in each case was the same. After removal of the sulfur with mercury and with sulfuric acid each sample was dried with phosphorus pentoxide and fractionated. No. 1 boiled at 136.0–136.1°; n_D^{25}, 1.49390. No. 2 boiled at 136.0–136.2°; n_D^{25}, 1.49386.

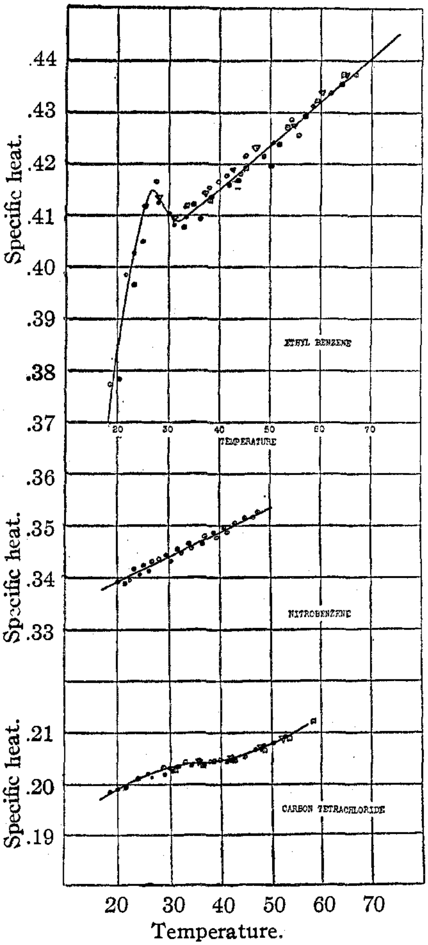

Fig. 1.

Results

The specific heat determinations are shown in Figs. 1, 2 and 3, where the various characters represent continuous experiments performed on different days. The results check well with the results designated by squares and triangles which were obtained previously,[4] using larger temperature intervals. It is easy to understand why determinations over wide temperature intervals should be erratic if a "hump" exists in the curve, for the quantity of heat absorbed in one experiment may include the energy of "transformation" corresponding to the "hump," whereas the check determination may come at a slightly higher or lower temperature and include less of this extra energy. The fact that the experimental points do not appear to lie close to the smooth line may be explained in part by the large scale of plotting, each square corresponding to 0.01 on the specific heat ordinate

[6] Richards and Shipley, **This Journal, 41,** 2022 (1919).

To show that experimental errors cannot account for the irregularities, determinations over 2° intervals were made on nitrobenzene, a liquid that

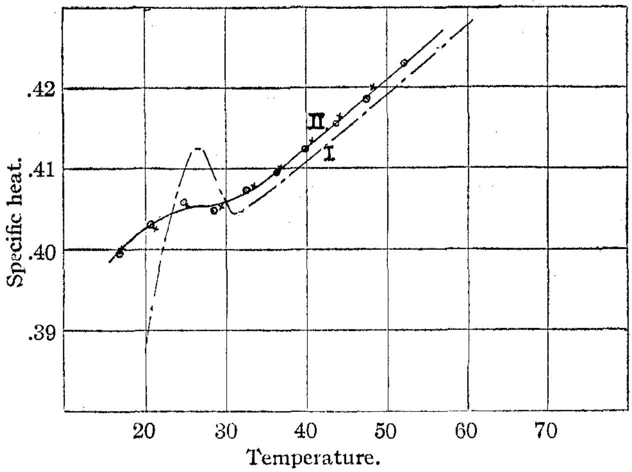

Fig. 2.—I. Ethyl benzene. II. Ethyl benzene saturated with water (6°).

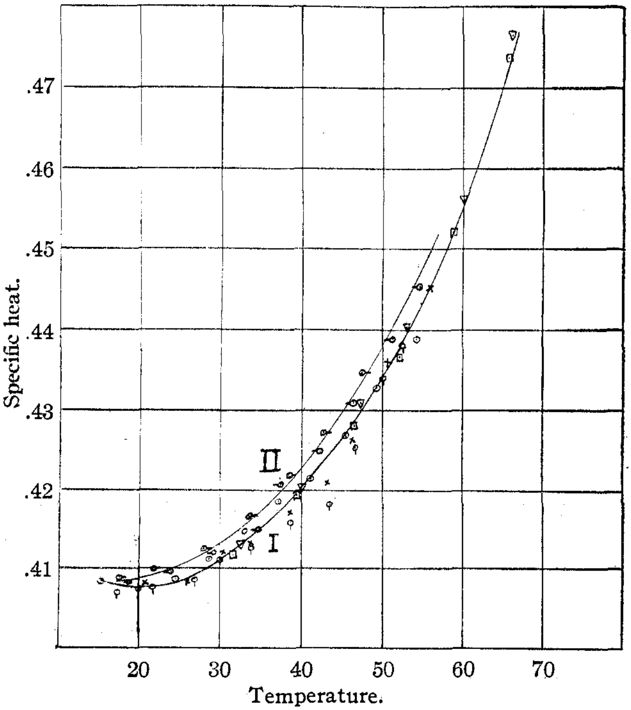

Fig. 3.—I. Benzene. II. Benzene (0.035% of water).

behaves normally, and possesses a specific heat between that of benzene and ethyl benzene on the one hand, and that of carbon tetrachloride on the other. As shown in Fig. 1, the points fall satisfactorily on a straight line and there is no evidence of the irregularities observed with the other three liquids in question.

It was thought that other physical properties should exhibit irregularities corresponding to the irregularities in the specific heat curves. The vapor pressure of carbon tetrachloride was determined by the method of Ramsay and Young[7] at frequent intervals in the region of the expected irregularity. The logarithms of the vapor pressures were plotted against the reciprocals of the absolute temperatures as shown in Fig. 4. The results check closely with those of Young[8] and no indication of irregularity is evident. In Fig. 5 the vapor pressures of ethyl benzene, as determined by Woringer,[9] are plotted in the same way, and here again there is no evidence of irregularity in the temperature coefficient of vapor pressure.

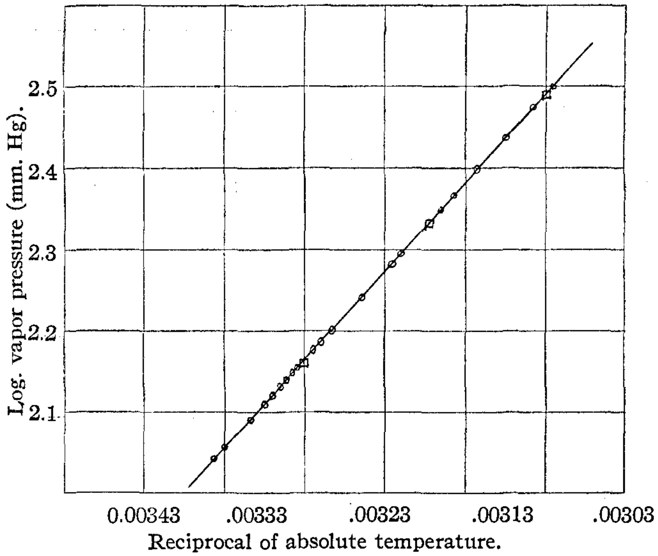

Fig. 4.—Carbon tetrachloride.

The densities of ethyl benzene and carbon tetrachloride were determined carefully at frequent temperature intervals with a large pycnometer, holding 60 cc. of the liquid. The results are shown in Figs. 6 and 7 and the agreement with other investigators is entirely satisfactory. Again, there is no indication of irregularities in the temperature coefficient cor-

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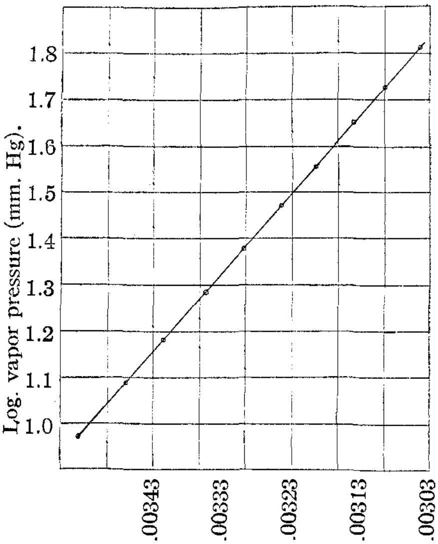
[7] Ramsay and Young, *J. Chem. Soc.*, **59**, 911 (1891).

[8] Young, *Proc. Roy. Soc. Dublin*, **12**, 374 (1910).

[9] Woringer, *Z. physik. Chem.*, **34**, 257 (1900).

responding to the irregularities in the temperature coefficients of specific heat.

Vapor pressure and density determinations on benzene were not carried out. The constants given in the literature have been frequently checked and show no irregularities corresponding to those in the specific heat–temperature curve.



Reciprocal of absolute temperature.
Fig. 5.—Ethyl benzene (Woringer).

It will be noticed in Figs. 2 and 3 that two curves are given. In each case the lower curve gives the specific heat of the pure liquid (ethyl benzene and benzene) while the upper curve gives the specific heat of these liquids after they had been saturated with water at 6°. There is a considerable variation in the position of the points which determine the curves for the pure liquid, while those which determine the upper curves are very regular and almost perfectly reproducible. It is evident that these curves do not show the same pronounced irregularity of slope which is characteristic of those for the pure liquid. In the case of ethyl benzene the curve still shows a negative slope, but for benzene this change in direction was not obtained, probably because it was impossible to carry out the determinations at a sufficiently low temperature.

Theoretical

It has been stated that the increase in specific heat with temperature proceeds regularly in the case of liquids of the normal type which are composed of a single molecular species. It is natural, then, to suppose that irregular changes are caused by the presence of two or more molecular species, the change from one form to another causing an absorption of heat. The curves show that the transformation occurs at a more or less definite and reproducible temperature.

In the case of carbon tetrachloride the slope before and after the transformation is nearly the same. In the case of ethyl benzene it appears to be steeper before the transformation, although the curve may flatten out at temperatures below the range of the present data. The determinations could not be carried out below 15°, so there is no indication as to the direction of the slope of the benzene curve below the transformation temperature.

When the temperature corresponding to the maximum in the curve has been passed, most of the molecules stable at the lower temperature have been changed and the corresponding absorption of heat is less. With ethyl benzene this decrease in heat absorption per degree is greater than the natural increase in specific heat with temperature and a negative slope is observed between 26° and 31°. In other words the curve given in Fig. 1 is produced by adding two curves. The first is a regular specific heat curve, slightly convex to the abscissa. The second is an inverted "U" the area of which represents the heat of transformation, the ordinates giving the heat absorbed while the temperature is increased 1°. The maximum ordinate of this second curve, indicates the temperature

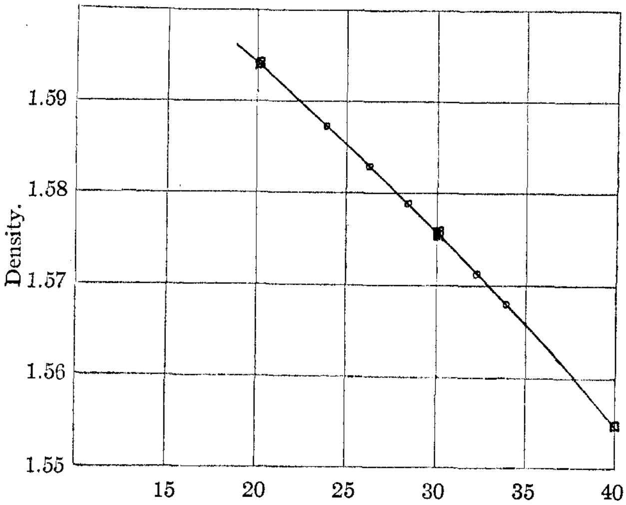


Fig. 6.—Carbon tetrachloride.

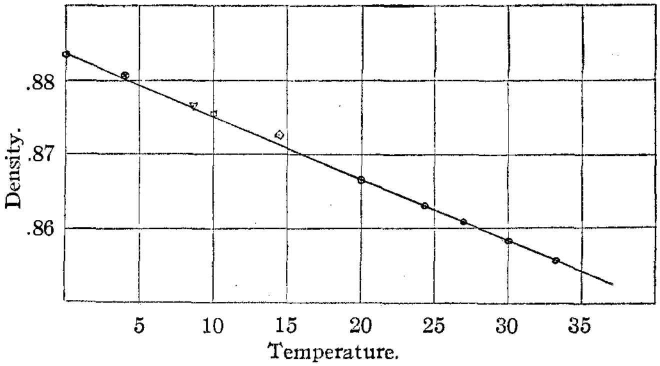


Fig. 7.—Ethyl benzene.

at which the largest number of molecules is changing. At lower temperatures the transformation is only started and at higher temperatures it is nearly over.

With carbon tetrachloride the decrease in heat absorption, caused by the transformation, is just equal to the natural increase in specific heat and the curve for the liquid is nearly horizontal from 33° to 42°.

The amount of heat absorbed in the transformation of one molecular species of carbon tetrachloride to the other was estimated graphically. A straight line was extrapolated down from the upper part of the curve (Fig. 1) until it met the extrapolation of the lower part of the curve. The area enclosed was taken as a measure of the heat required for the molecular change. It was approximately 0.056 calorie per g., or 8.6 calories per g. molecule.

Impurities in a liquid might possibly cause an irregularity in the temperature-specific heat curve, although it would be necessary to assume that the liquid and the impurity form a chemical compound which is unstable above the transformation temperature. The other liquids, examined so far, exhibit no irregularities in the specific heat curves, although their purification was no more extensive than that of the carbon tetrachloride, ethyl benzene and benzene. The physical constants of these three liquids agree well with those obtained by other investigators and it is safe to say that the material used in these specific heat investigations was fully as pure as that of other investigators. There is no reason why the explanation of a change from one molecular species to another in a pure liquid should not be acceptable, especially as the phenomenon has been established already in the case of water and sulfur. To remove the suspicion that the irregularity in the specific heat was due to an impurity, the ethyl benzene was redistilled and physical constants were determined for the first half and the last half. The densities agreed within 1 part in 5000 and the refractive indices were identical within the limits of experimental error. Furthermore, ethyl benzene from two different sources gave the same specific heat values.

In the specific heat measurements of benzene and ethyl benzene the deviations of single determinations from the smooth curve are larger than the experimental error and larger than the deviations in the measurements of other liquids. These facts indicate, possibly, that the transformation from one molecular species to another is a slow process which is influenced by accidental circumstances.

Evidently, a temperature-specific heat curve which can show clearly an absorption of heat of 0.056 calorie per g. is a more sensitive test for molecular complexity than are other tests. A calculation of the heat of vaporization of carbon tetrachloride with the Clausius-Clapeyron equation gives 7180 calories per mole. The addition of 8.6 calories to this makes an increase of about one part in 830, and d $ln\ P/dT$ should then be steeper by 0.12% below 32° than above 41°. In order to detect the predicted irregularity, the experimental measurements would have to be made with an accuracy such that vapor pressures separated by an interval of 1° could be determined to 0.07 mm. The irregularity in the vapor pressure of ethyl benzene should be larger than those just described, but the present data are insufficient to permit even an estimate of its magnitude. The data obtained for benzene are also insufficient for such a calculation. It seems probable, however, that the heat absorbed in the change is of the same order of magnitude as that for carbon tetrachloride.[10]

In view of the very small changes in the vapor pressures which are to be expected, it is doubtful whether molecular-weight determinations or surface-tension measurements would be sufficiently sensitive to detect the presence of different molecular species.

Perhaps of even greater significance than the actual irregularities in the specific heat curves for these liquids is the effect of the addition of water. As has been stated, the curves obtained after the liquids were saturated with water are distinctly more regular and more easily reproduced. It may be inferred from this fact that the water, although present in an amount not exceeding 0.04%, catalyzes the change from one molecular species to the other. It is proposed to continue this study by determining the effects of various catalysts on the liquids which show irregular specific heat–temperature curves.

The small magnitude of the heat of transformation furnishes an interesting field for speculation. It shows either that the transformation from one form to the other is accompanied by a very slight energy change, or that only a small fraction of the total number of molecules is involved in the change. If the change is one in which associated molecules are broken up, a larger absorption of heat might be expected. According to the familiar van't Hoff isochor equation, a small heat of reaction shows that the equilibrium changes but slightly with temperature. In the present case the whole change occurs within a few degrees. Although further experimental facts are necessary before a complete interpretation of the phenomena can be given, it seems possible that the liquids may possess a mobile type of crystal lattice and that the transformations observed in the case of benzene, ethyl benzene and carbon tetrachloride are similar to transitions occurring in crystals.

[10] The slight changes in vapor pressure show that the transformations in this investigation cannot account for the large increases in boiling points observed by Baker.[1] Furthermore, there are grounds for expecting these transformations to lead to an actual decrease in boiling point when the liquids are dried at low temperatures. It is planned to discuss the matter more fully in a later communication from this Laboratory, after further experimental information is available.

Acknowledgment is made of a grant from the Rumford Fund of the American Academy of Arts and Sciences, with which some of the instruments used in this investigation were purchased.

Summary

1. Distinct irregularities occur in the temperature–specific heat curves of benzene, ethyl benzene and carbon tetrachloride, which indicate molecular changes in the liquid.

2. Measurements of vapor pressure and density fail to show corresponding irregularities.

3. Water catalyzes the change from one molecular species to the other in the case of benzene and ethyl benzene.

4. Differential specific heat measurements of liquids offer an excellent method for the study of association.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF ILLINOIS]

THE USE OF BROMATE IN VOLUMETRIC ANALYSIS. IV. THE PREPARATION AND PROPERTIES OF NORMAL AND BASIC MERCURIC BROMATE[1a]

BY G. FREDERICK SMITH

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In former papers of this series[1b] it has been demonstrated that the presence of the mercuric ion advantageously alters the usual course of oxidation reactions involving bromate. The oxidation value of bromates in certain reactions was shown to be increased from five equivalents to six, new reactions were indicated, and a general increase in flexibility was obtained.

For these reactions the mercuric ion must be present in amount equivalent to the bromide ion resulting from the reduction of the bromate. This condition would be automatically adjusted in the reduction of the mercuric bromates. If their preparation and properties were satisfactory their value for use as oxidation reagents would be proved.

The following paper describes the preparation of normal and basic mercuric bromates, their stability, solubilities and general theoretical relationships.

Previous Studies

The preparation and properties of normal and basic mercuric bromate are described in Gmelin-Kraut.[2] Groth[3] describes the preparation of hydroxy-mercuric bromate from freshly precipitated mercuric oxide and excess of bromic acid and gives crystal

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[1a] Read before the Division of Physical and Inorganic Chemistry, 67th Meeting of the American Chemical Society, Washington, D. C.

[1b] Smith, THIS JOURNAL, **45**, 1115, 1417, 1666 (1923).

[2] Gmelin-Kraut, **5**, part 2, p. 752 (1914).

[3] Groth, "Chem. Kryst.," **1908** [II] p. 126.