[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS]

The Enthalpy, Entropy and Specific Heat of Liquid *p*-Xylene from 0 to 300°. The Heat of Fusion

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It has been found possible to obtain reasonably accurate values for the enthalpy referred to 0° of saturated liquids at temperatures approaching the critical using an ice calorimeter. (The term "saturated," as applied here to a liquid, has the meaning, "in equilibrium with its own vapor.") Only small samples, amounting to a few ml. are required. The technique and theory of the measurements are described here and results of measurements upon *p*-xylene are given.

Experimental

The apparatus with the exception of the capsule has been described recently.[1,1a] The determination of enthalpy is accomplished by heating the sample, enclosed in a capsule, to a desired temperature in a furnace, followed by dropping it into an ice calorimeter and measuring the heat evolved in cooling the sample and container to 0°. A small part of this heat results from condensation of vapor and must be corrected for. The heat content of the empty capsule together with the small heat loss during the drop are accounted for in separate "blank" experiments.

Sample.—The *p*-xylene was from NBS standard sample no. 215 and contained 0.07 ± 0.03 mole per cent. of impurity as estimated from freezing point measurement.[2]

Capsule.—During the measurements the sample was contained in a cylindrical monel capsule with hemispherical ends. The capsule had an over-all length of 2.5 in., the cylindrical portion having $^5/_8$ in. o. d. and 0.015 in. wall thickness. Its weight was 12 g. and its internal volume 10 ml. A short length of 1 mm. i. d. monel filling-tube was silver-soldered to the bottom of the capsule. After filling the capsule and boiling its contents for a time to expel air, the filling-tube was sealed with silver solder. The capsule had been previously tested with water at 290° and 75 atm. pressure. The highest pressure attained by the *p*-xylene during these measurements was 20 atm.

Method.—According to Osborne[3] the heat evolved in cooling a capsule containing a liquid in equilibrium with its vapor from temperature 2 to temperature 1 is given by

$$Q]_1^2 = [q - PV + mH_{\text{sat}} + (V - mv)L/(v' - v)]_1^2 \quad (1)$$

(q = effective enthalpy of capsule, shields and suspension wire; P = vapor pressure; V = internal volume of the capsule; m = total mass of fluid; H_{sat} = enthalpy per unit mass of saturated liquid; v' and v are the specific volumes of saturated vapor and liquid, respectively; L = heat of vaporization per unit mass). The last term, which represents the major part of the heat evolved in condensing vapor as the sample cools, may be written, $(V - mv)T\,\mathrm{d}P/\mathrm{d}T]_1^2$, where T denotes absolute temperature. With the ice calorimeter, temperature 1 is necessarily 0°, while temperature 2 is the temperature of the furnace, t°.

First experimental method: if V, v, P and $\mathrm{d}P/\mathrm{d}T$ are known, the second and fourth terms on the right in eqn. 1 may be calculated and H_{sat} determined as a function of temperature from a series of measurements of $Q]_0^t$ and a series of measurements of $q]_0^t$ at various values of t. Obviously, it will be advantageous to adjust the amount of fluid in the capsule so that the vapor space will be as small as possible, thereby reducing the magnitude of the last term in equation 1.

Second experimental method: where one of the quantities v, P or $\mathrm{d}P/\mathrm{d}T$ cannot be approximated with desired accuracy, it may be evaluated by making a third series of experiments with a small amount of fluid in the capsule. When this is done, equation 1 may be written twice for a given pair of temperatures, once for the high filling of the capsule—hereafter referred to as HF—and once for the low filling (LF). The equations may then be solved for the unknowns $H_{\text{sat}}]_0^t$ and either $v]_0^t$, $P]_0^t$ or $\mathrm{d}P/\mathrm{d}T]_0^t$. (Since $P]_0^t$ and $\mathrm{d}P/\mathrm{d}T]_0^t$ are dependent quantities, they may be evaluated simultaneously if desired—say by a method of successive approximations—together with the enthalpy.) The values of v, P or $\mathrm{d}P/\mathrm{d}T$ obtained in this way are not highly accurate. However, $H_{\text{sat.}}]_0^t$ can be determined with about the same accuracy as by the first method.

As a test both methods have been employed. Eighteen HF experiments and eighteen blank experiments were made at six temperatures between 50.3 and 300.9°. As a check on the extrapolated values of $\mathrm{d}P/\mathrm{d}T$ which were felt to be a potentially greater source of error than the other extrapolated quantities, ten LF experiments were made at four temperatures between 154.5 and 300.9°. No LF experiments were made at lower temperatures where $\mathrm{d}P/\mathrm{d}T$ was accurately known.

The mass of *p*-xylene was 4.8778 g. for HF and 0.8833 g. for LF. All weights were corrected for buoyancy. Values of P and $\mathrm{d}P/\mathrm{d}T$ were taken from recent measurements[4] extending up to 139°. Liquid densities up to 155° have been measured by Massart.[5] In order to obtain liquid densities up to 300°, the equation given by Massart for the mean density of saturated liquid and vapor *p*-xylene was extrapolated and combined with saturated

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[1] D. C. Ginnings and R. J. Corruccini, *J. Research Nat. Bur. Standards*, **38**, 583 (1947).

[1a] D. C. Ginnings and R. J. Corruccini, *ibid.*, **38**, 593 (1947).

[2] B. J. Mair, D. J. Termini, C. B. Willingham and F. D. Rossini, *ibid.*, **37**, 229 (1946).

[3] N. S. Osborne, *Bur. Standards J. Research*, **4**, 609 (1930).

[4] C. B. Willingham, W. J. Taylor, J. M. Pignocco and F. D. Rossini, *J. Research Nat. Bur. Standards*, **35**, 219 (1945).

[5] L. Massart, *Bull. soc. chim. Belg.*, **45**, 87 (1936).

vapor densities calculated from an equation of Meyers.[6] The critical data of Altschul[7] were employed.

The volume of the capsule at room temperature was measured by determining the weight of water which it would hold. Using the coefficient of thermal expansion of monel, the volume was calculated to be 10.13 cc. at 0° and 10.26 cc. at 300°. Expansion due to pressure within the capsule was shown to be negligible.

The time during which the capsule was held in the furnace before dropping was at least twenty minutes when empty, thirty minutes with LF and fifty minutes with HF. Occasional longer experiments which were interspersed gave no consistent differences in the results.

The time required for the capsule and calorimeter to reach effective thermal equilibrium after a drop was on the average thirty-one minutes for the empty capsule, fifty-seven minutes for LF and seventy-eight minutes for HF with two exceptions which will be noted later. These times, as well as the time required by the capsule in the furnace, could have been shortened had there been systems of heat-diffusing vanes in both the capsule and calorimeter.

In order to determine whether the results varied with time, as might result from chemical change of the *p*-xylene, both the HF and LF series were begun and finished with experiments at the same temperature of 300.9°. The mean of the initial experiments of a series was within 0.06% of the mean of the final experiments.

Enthalpies, Entropies and Specific Heats.—The calculation of enthalpy is summarized in Table I. Each value of Q or q shown is the mean of two to four experiments.

TABLE I

THE ENTHALPY OF SATURATED LIQUID *p*-XYLENE

(1 cal. = 4.1833 int. j.)

t, °C.	$Q_{HF}]_0^t$ cal.	$Q_{LF}]_0^t$ cal.	$q]_0^t$ cal.	PV cal.	v cc. g.$^{-1}$	$(V - mv)_{HF}$ TdP/dT cal.	$H_{sat}]_0^t$ cal.g.$^{-1}$
0	0	0	0	0.0	1.138	0.0	0
50.3	162.3		61.7	.0	1.198	.1	20.62
110.5	369.6		136.6	.1	1.281	.5	47.70
154.5	534.1	256.8	192.5	.4	1.353	(1.4)[a]	69.84
200.7	716.2	342.8	252.0	1.0	1.452	(2.9)[a]	94.79
254.0	940.4	448.6	321.9	2.6	1.601	(5.0)[a]	126.33
300.9	1151.8	549.8	384.0	5.1	1.837	(4.9)[a]	157.45

[a] These values are included in order to indicate the magnitude of this term had the first experimental method been used throughout.

Before the experimental work had been completed, an extrapolation of the vapor pressure to the critical temperature had been carried out by comparison of the available data on *p*-xylene[4,7] with existing data on benzene[8] and toluene[9] which have been reported up to the respective critical points of those compounds. It is interesting to note that values of dP/dT obtained in this way were within a few per cent. of the experimental values and that their use according to the first experimental method would not have altered the values of enthalpy by more than 0.05%.

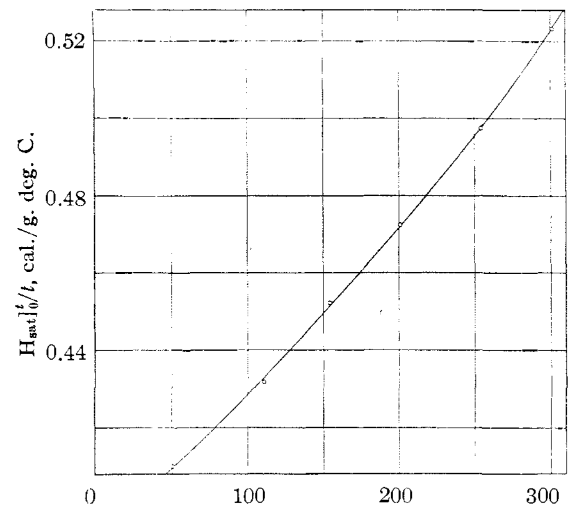

Fig. 1.—$H_{sat}]_0^t/t$ *vs.* t for liquid *p*-xylene. Radius of the circles corresponds to about 0.1%.

In order to obtain smoothed values of enthalpy it was found useful to construct a graph of $H_{sat}]_0^t/t$ *vs.* t since irregularities in the enthalpy–temperature function are greatly magnified. This graph is shown in Fig. 1. Figure 2 shows values of enthalpy corresponding to the smooth curve of Fig. 1. The experimental values are not shown in Fig. 2 since the deviations of the smooth curve from them are indistinguishable on the scale employed.

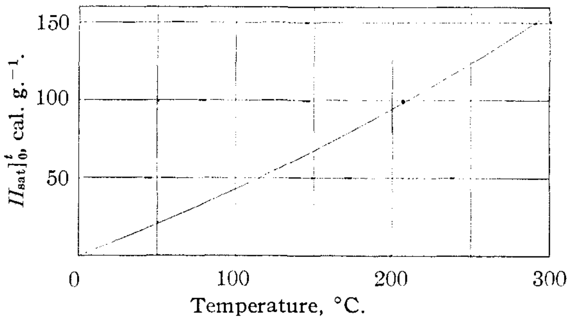

Fig. 2.—The enthalpy of saturated liquid *p*-xylene.

The specific heat along the saturation path, C_{sat}, was obtained using the relation

$$C_{sat} = dH_{sat}/dT - v\,dP/dT \qquad (2)$$

The term, $v\,dP/dT$, amounted to 2% of C_{sat} at 300°, diminishing to $^1/_2$% at 200° and 0.1% at 100°. Values of dH_{sat}/dT were obtained graphically from Fig. 1 using the relation

$$dH_{sat}/dT = H_{sat}]_0^t/t + t\,d(H_{sat}]_0^t/t)/dT \qquad (3)$$

and were checked by the method of Rutledge[10] and by recovering the values of enthalpy by integration. The saturation entropy referred to 0°, $S_{sat}]_0^t = \int_0^t (C_{sat}/T)dt$, was obtained using Simpson's rule. The relative error in deriving the specific heats and entropies was less than experi-

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[6] C. H. Meyers, *Bur. Standards J. Research*, **11**, 691 (1933). Equation 1 was used taking $A = 0.70$ and employing extrapolated vapor pressures.

[7] M. Altschul, *Z. physik. Chem.*, **11**, 590 (1893).

[8] "International Critical Tables," Vol. III, 244 (1928).

[9] N. W. Krase and J. B. Goodman, *Ind. Eng. Chem.*, **22**, 13 (1930).

[10] G. Rutledge, *Phys. Rev.*, **40**, 262 (1932).

mental error except possibly for terminal portions of the temperature range.

Smoothed values of enthalpy, specific heat and entropy are given in Table II. The smoothed values of enthalpy are within 0.1% of the observed values in Table I with the exception of the observed value at 110.5° which is low by 0.2%.

TABLE II

THE ENTHALPY, SPECIFIC HEAT AND ENTROPY OF SATURATED LIQUID *p*-XYLENE AT ROUNDED TEMPERATURES

1 cal. = 4.1833 int. j.; 0 °C. = 273.16 °K.

t, °C.	$H_{sat}]_0^t$ cal. g.$^{-1}$	C_{sat}, cal.g.$^{-1}$deg.$^{-1}$C.	$S_{sat}]_0^t$ cal.g.$^{-1}$ deg.$^{-1}$ K.
0	0[a]	0.3934[a]	0[a]
(13.2[b]	5.25	.4013	0.01875)
20	7.99	.4057	.02823
40	16.24	.4198	.05546
60	24.78	.4350	.08191
80	33.64	.4513	.10774
100	42.84	.4686	.13307
120	52.40	.4864	.15799
140	62.32	.5043	.18256
160	72.61	.5223	.20681
180	83.27	.5406	.23078
200	94.32	.5596	.25452
220	105.78	.5801	.27810
240	117.70	.6029	.30161
260	130.14	.6285	.32514
280	143.16	.6573	.34879
300	156.82	.6893	.37267

[a] Undercooled. [b] Melting point.

The specific heats are compared in Fig. 3 with values of C_P from previous investigations[11,12,13] and are found to be different by as much as 4%. (The specific heat at a constant pressure of one atmosphere is calculated to be about 0.1% higher than C_{sat} at the boiling point, the difference diminishing rapidly at lower temperatures.) Of the previous data, those of Pitzer and Scott appear to deserve the greatest weight. The comparison with them is not decisive, since it is made in a region of temperature in which both methods used were at a disadvantage. Pitzer and Scott employed a low-temperature calorimeter and have stated that the accuracy of their results diminishes above room temperature and that "the uncertainty in the results may well exceed 1%." On the other hand, the results of the present investigation are least accurate below 100° due to use of the noble metal thermocouple in a region to which it is ill-suited, together with the uncertainty attached to determining the slope of the enthalpy-temperature function at the end of the curve.

Heat of Fusion.—The measurements of enthalpy were complicated by the fact that *p*-xylene is a solid over part of the experimental range employed (m. p. = 13.2°). However, out of twenty-eight experiments, freezing occurred on only two, as evidenced by a much higher experimental result and a prolonged evolution of heat from the sample, lasting two hours in one case and three and one-half hours in the other. The freezing occurred on HF experiments made at 300.9°. Comparison of these experiments with four others at the same temperature on which undercooling occurred, resulted in a value of 37.83 cal.g.$^{-1}$ for the heat of fusion at 0°. Taking the mean specific heat in the interval, 0–13.2°, to be 0.3975 cal.g.$^{-1}$ for the liquid (Table II) and 0.3467 for the solid,[11] the heat of fusion at the melting point was calculated to be 38.50 cal.g.$^{-1}$. This result may be compared with the value 38.5 ± 0.2 obtained by Pitzer and Scott[11] by direct measurement.

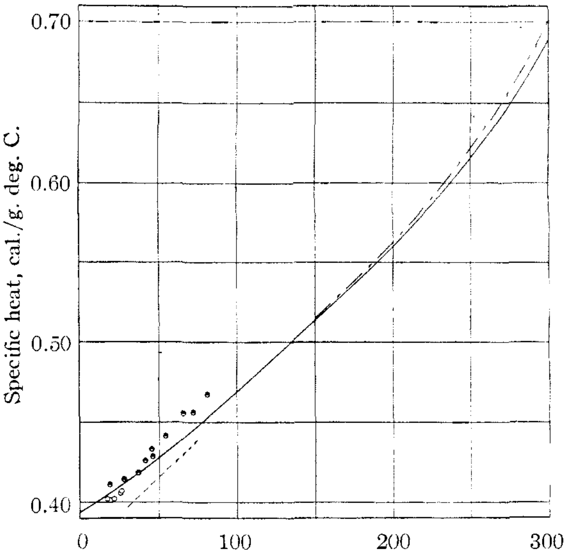

Fig. 3.—The specific heat of liquid *p*-xylene: ——— C_{sat}, this investigation; – – – – – dH_{sat}/dT, this investigation; ● C_P, Pitzer and Scott; ○ C_P, Huffman, Parks and Daniels; - - - - C_P from equation by Williams and Daniels who did not give their original data.

Reproducibility of Results.—Grouping together the forty-six experiments which were made in the three series, the average deviation from the mean was found to be 0.10 cal. or 0.025%. The maximum deviation from the mean was 0.08%. ("Deviation from the mean" is the difference between an experimental result in a given series and the mean of the experimental results in that series at the same temperature.) Experiments ranged in magnitude from 60 to 1400 cal. These figures are intended to indicate reproducibility or "precision" and not over-all accuracy.

An indication of the accuracy is given by a measurement upon water, made using the same apparatus and capsule. Two HF and two LF experiments were made at 254.0°. (Vapor pressure = 42.0 atm.) The value of $H_{sat}]_0^{254}$ obtained by the first experimental method (without the use

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(11) K. S. Pitzer and D. W. Scott, THIS JOURNAL, **65**, 803 (1943).

(12) H. M. Huffman, G. S. Parks and A. C. Daniels, *ibid.*, **52**, 1547 (1930).

(13) J. W. Williams and F. Daniels, *ibid.*, **46**, 903 (1924).

of LF data) taking values of v and $T\,\mathrm{d}P/\mathrm{d}T$ from ref. 14 was 0.05% greater than that obtained using both HF and LF data (second experimental method). Between these two results falls a value determined with considerable care by Osborne, Stimson and Ginnings[14] using calorimeters of a different type. This agreement was undoubtedly somewhat fortuitous since the probable error of the enthalpy measurement is estimated as being 0.2%, except at temperatures below 100° in which range it is greater. This estimate is based upon suspected systematic errors of which the largest is the error involved in measuring the temperature of the sample in the furnace.

Summary

1. There has been described the experimental technique of measuring the enthalpy of saturated liquids from 0° to near the critical point utilizing an ice calorimeter.
2. The enthalpy, entropy and specific heat of saturated liquid p-xylene have been determined in the range, 0° to 300°.
3. The heat of fusion of p-xylene at 0° has been determined.

WASHINGTON, D. C. RECEIVED MAY 5, 1947

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[14] N. S. Osborne, H. F. Stimson and D. C. Ginnings, *J. Research Natl. Bur. Standards*, **23**, 261 (1939).

[CONTRIBUTION FROM THE MOORE LABORATORY OF CHEMISTRY, AMHERST COLLEGE, AND THE RESEARCH LABORATORY OF GODFREY L. CABOT, INC.]

Heats of Adsorption on Carbon Black. II

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The results of an experimental investigation of the heats of low temperature van der Waals adsorption of nitrogen, oxygen and argon on a series of carbon blacks of varying rubber reinforcing ability have been reported in a recent publication.[3] In addition to their relation to the problem of rubber reinforcement, these results have some significance from a fundamental point of view. The carbon blacks used in the present study are well defined, highly reproducible, non-porous materials of high surface area. There is a considerable body of information[4] available concerning the structure of the underlying solid and the extent of adsorbent surface based on X-ray diffraction and electron microscope studies. The heat measurements with the elementary gas adsorbates have revealed interesting differences in the state of surface of the various blacks, differences which permit some degree of correlation with rubber reinforcing abilities of the blacks. Obviously any such correlation would give promise of greater significance with adsorbates more nearly like rubber in chemical composition. For that reason we have undertaken a study of the heats of adsorption at 0° of several saturated and unsaturated hydrocarbons of low molecular weight which can be handled conveniently in the vapor state.[5]

Experimental

Materials.—The five samples of carbon black, previously studied,[3] were used also in the present experiments. They include three commercial blacks, Spheron Grade 6 (MPC), Sterling S (SRF), and Sterling L (HMF).[3] The first of these is a reinforcing channel black and the other two are typical furnace blacks.[6] The list is completed by a sample of Spheron Grade 6 heated to 927° to remove most of the chemisorbed surface oxides ("devolatilized" Grade 6), and a sample of Grade 6 heated to "graphitizing" temperatures 2800–3300° and designated as Graphon. Prior to each adsorption run, the black under investigation was outgassed at 200°, a temperature sufficient to remove physically occluded air and moisture without desorption of the chemisorbed gases normally present on the carbon surface.

The butane and 1-butene were research-grade hydrocarbons purchased from the Phillips Petroleum Company. All other hydrocarbons used in the investigation were kindly supplied by the Esso Laboratories, Standard Oil Development Company, and were of warranted purity of at least 99%. Any air introduced during transfer was removed by evacuation of the system while the hydrocarbon was frozen out in a side trap immersed in liquid nitrogen, followed by several bulb to bulb distillations.

Apparatus.—The calorimeter used in this work was essentially the same as that already described,[3] although a somewhat more convenient method was devised for inserting the electrical calibration unit. The adsorption apparatus used in conjunction with the calorimeter was redesigned with mercury "cut-offs" to prevent contact of the hydrocarbons with stopcock grease. This modified apparatus has been described in a separate publication.[7] An ice-bath served to produce a uniform constant temperature around the calorimeter.

Results and Discussion

The experimental results are presented in Figs. 1–7 and Table I. Figures 1 and 2 give the B.E.T.[8]

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[1] Amherst College, Amherst, Mass.

[2] Godfrey L. Cabot, Inc., Boston, Mass.

[3] Beebe, Biscoe, Smith and Wendell, THIS JOURNAL, **69**, 95 (1947).

[4] (a) Emmett and DeWitt, *Ind. Eng. Chem., Anal. Ed.*, **13**, 28 (1941); (b) Smith, Thornhill and Bray, *Ind. Eng. Chem.*, **33**, 1303 (1941); (c) Wiegand and Ladd, *Rubber Age*, **50**, 431 (1942); (d) Warren, *J. Chem. Phys.*, **2**, 551 (1934); (e) Biscoe and Warren, *J. Appl. Phys.*, **13**, 364 (1942).

[5] The simple mono- and di-olefins selected for study are, of course, far removed from the complex, unsaturated high polymer, rubber. The danger of drawing analogies between the two has been amply discussed by Farmer [for example, see Farmer, "Advances in Colloid Science II," Interscience Publishers, Inc., New York, N. Y., 1946, pp. 301-302]. On the other hand, rubber is hardly suitable as an adsorbate in the present calorimetric procedure. Accordingly, simple hydrocarbons of chemical, if not structural, similarity to rubber were chosen for initial study, the possible use of more complex systems being reserved for future investigation.

[6] Cohan, *Chem. Eng. News*, **23**, 2078 (1945).

[7] Wendell, *Ind. Eng. Chem.*, **18**, 454 (1946).

[8] B.E.T. has reference to the method of Brunauer, Emmett and Teller based on the theory of multilayer adsorption due to these authors [THIS JOURNAL, **60**, 309 (1938)].