3. The oxalic and malonic acid reactions seem to be similar although they show a marked difference in their temperature coefficients and quantum efficiencies.

4. Two mechanisms are discussed. The reaction may be due to the decomposition of an intermediate uranyl ion–acid complex, or it may be explained by collisions of the second kind between activated uranyl ions and acid molecules.

CHICAGO, ILLINOIS

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

THE HEAT CAPACITY OF TOLUENE FROM 14°K. TO 298°K. THE ENTROPY AND THE FREE ENERGY OF FORMATION

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Very few low temperature thermal measurements on aromatic hydrocarbons have been made. The only true specific heats which have been published are those of Nernst[2] for benzene but even these data are very scanty and do not agree well among themselves.

This paper presents specific heat, heat of fusion and temperature of fusion data for toluene. The specific heat measurements were carried down to 14°K. The methods and apparatus and the accuracy of measurement have been discussed elsewhere.[3]

One change in the apparatus was made before starting this work. Due to an unfortunate explosion the portable hydrogen liquefier, previously used, was demolished. A new liquefier, similar to that described by Latimer and Greensfelder,[4] was built in as a permanent unit. Both of these liquefiers were designed by Mr. G. F. Nelson of this Laboratory and built under his supervision.

Material.—The toluene was the best product of the Eastman Kodak Company (sulfur free). Treatment of a sample with concd. sulfuric acid gave no coloration in ten minutes. The material was dried for several days with fused calcium chloride, decanted off, and carefully fractionated three times. The middle portion used had a volume of 200 cc. and a boiling range of 0.03°. The density, d_4^0, 0.88456, compares favorably with the Leiden measurement,[5] d_4^0, 0.88445, and with that of Biron,[6] d_4^0, 0.88450. The fusion curves indicated exceptional purity.

The Measurements.—The specific heat results are given in Table I and shown graphically in Figure 1. No abnormal behavior was noted in either the crystals or liquid.

[1] National Research Fellow in Chemistry.

[2] Nernst, *Ann. Physik*, (4) **36**, 395 (1911).

[3] Kelley, THIS JOURNAL, **51**, 180 (1929).

[4] Latimer and Greensfelder, *ibid.*, **50**, 2209 (1928).

[5] *Comm. Phys. Lab. Univ. Leiden*, No. 157.

[6] Biron, *Chem. Zentr.*, I, 1910 (1913).

TABLE I

SPECIFIC HEAT OF TOLUENE (IN 15°-GRAM CALORIES)

T, °K.	C_p, cal./mole	T, °K.	C_p, cal./mole	T, °K.	C_p, cal./mole
		Crystals			
16.72	2.202	50.86	10.33	120.45	16.39
20.50	3.298	60.48	11.73	128.52	17.16
23.97	4.268	69.16	12.64	135.77	17.53
27.74	5.346	75.23	13.19	144.07	17.94
32.31	6.532	84.44	13.89	152.41	18.46
37.22	7.776	93.29	14.29	162.33	19.29
41.68	8.676	102.73	15.00	166.60	19.24
45.80	9.483	112.25	15.80		
		Liquid			
183.83	32.02	222.77	33.41	262.76	34.67
192.60	32.38	232.68	33.50	273.17	35.37
203.05	32.58	242.52	33.64	284.44	36.59
213.23	32.74	252.48	34.57		

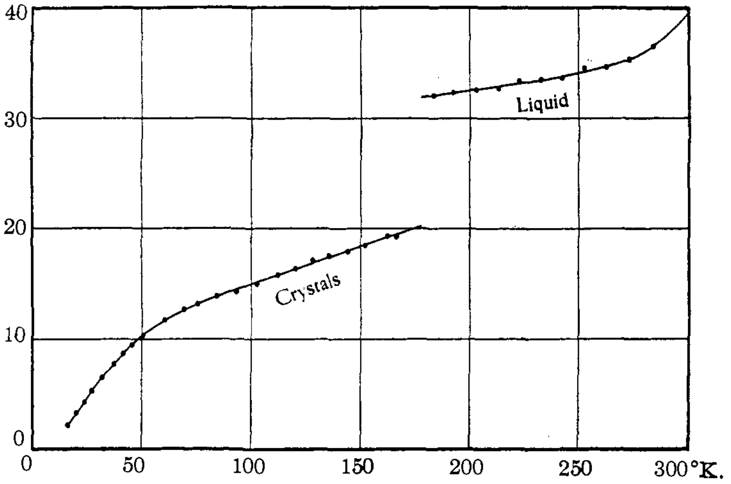

Fig. 1.—The heat capacity of toluene in calories per mole.

The heat of fusion and temperature of fusion data appear in Table II. The fusion temperature of toluene recorded here is almost exactly (to 0.01°) the same as that obtained at Leiden.[5]

TABLE II

FUSION DATA

T, °K.	Heat of fusion in cal. per mole		
	1st result	2nd result	Mean
177.95	1584	1579	1582

The Entropy.—The entropy was calculated in the usual manner. The extrapolation below the initial temperature of the lowest measurement was made by means of the Debye function with $\Theta = 91$. Table III contains the results of the entropy calculation.

TABLE III

ENTROPY OF TOLUENE

0–14 °K. (extrap.)	crystals	= 0.52
14–177.95	crystals	= 25.50
1582/177.95	fusion	= 8.89
177.95–298.1	liquid	= 17.46
$S_{298.1}$ for 1 mole of liquid toluene =		52.4 ± 0.3 E. U.

Preliminary Measurements on *m*-Xylene.—Similar measurements were carried out on *m*-xylene. However, the fusion curves revealed a considerable amount of impurity and for that reason the specific heat data are not worthy of publication. The entropy value obtained, namely 60.3 E. U. per mole, is probably not in serious error and has been checked by Parks and Huffman,[7] who also unfortunately did not have a pure sample.

Free Energy Calculations and Discussion.—The free energy of formation from the elements was calculated by means of the equation, $\Delta F = \Delta H - T\Delta S$. The heat of combustion data of Richards and co-workers[8] were used, corrections being made to 15° calories and to the standard of temperature used here, 298.1 °K. The heats of formation of carbon dioxide and water and the values for the entropies of the elements were those adopted in previous work.[3] For the purpose of comparison the free energy of benzene has also been calculated, using the value of 42.4 E. U. for its entropy at 298.1 °K.[9] Table IV contains the resulting thermal data, the 15° calorie being used throughout.

TABLE IV

THERMAL DATA

Substance	Heat of combustion	$\Delta H_{298.1}$	$\Delta S_{298.1}$	$\Delta F_{298.1}$
Benzene	781,700	11,120	−54.2	27,300
Toluene	935,100	1,930	−75.1	24,300
m-Xylene	1,090,500	−5,260	−98.1	24,000

From the entropy of benzene and the values given for toluene and *m*-xylene in this paper it may be seen that the entropy difference between benzene and toluene is 10.0 units and between toluene and *m*-xylene 7.9 units. These differences are of the same order of magnitude as the value associated with a CH_2 increment in the homologous series of primary

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[7] Parks and Huffman, personal communication.

[8] Richards and Barry, THIS JOURNAL, **37**, 993 (1915); Richards and Davis, *ibid.*, **42**, 1599 (1920).

[9] This value was obtained by Parks and Huffman of Stanford University from their unpublished measurements. From Nernst's data a value of 42.2 E. U. may be calculated.

saturated aliphatic alcohols,[10] which has been shown to be 7.7 E. U. In the case of the alcohol series the free energy of formation changed by about 500 cal. per CH_2 group added. No similar definite statement can be made in the present case partly because the heats of combustion utilized in spite of their high percentage accuracy may be in error by a few hundred calories due to their magnitude.

Summary

1. Specific heat measurements on toluene covering the temperature range from 14 to 298°K. have been made.
2. The heat of fusion and temperature of fusion were measured.
3. The entropy and free energy of toluene at 298°K. have been calculated. Preliminary values on *m*-xylene are also included.

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[CONTRIBUTION NO. 16 FROM THE EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY]

THE MOVEMENT OF GASES AROUND ELECTRICALLY HEATED WIRES

BY SAM LENHER AND GUY B. TAYLOR

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In conducting some experiments on the kinetics of the catalytic oxidation of sulfur dioxide by the hot wire method in which the pressure change was being followed on a mercury manometer, it was observed that the mercury meniscus oscillated slightly, indicating a periodic pressure change. Further investigation showed that this periodic effect was not a catalytic phenomenon since it occurred in air and other gases where no chemical reaction was possible.

Platinum wires, 0.25 mm. in diameter and 10 cm. or more in length, were sealed in glass cylinders 3 to 6 cm. in diameter. When the wire was heated electrically to any temperature from about 300° to a white heat, a small periodic pressure change could be detected on a sensitive manometer. The fluctuations occurred from 50 to 100 times per minute and were synchronized with a minute change in the heating current. The current fluctuation was detected by putting the secondary of a small transformer in series with the storage battery used for heating the wire and connecting the primary with a high sensitivity galvanometer. The same effects were observed with wires sealed in spherical glass vessels.

The magnitude of the pressure change at a pressure of one atmosphere when the wire was either nearly vertical or horizontal was a fraction of a centimeter of water. As the tilt of the vessel was increased the periodic

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[10] Kelley, THIS JOURNAL, **51**, 779 (1929).