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A SIMPLE CALORIMETER FOR HEATS OF FUSION. DATA ON THE FUSION OF PSEUDOCUMENE, MESITYLENE (α AND β), HEMIMELLITENE, *o*- AND *m*-XYLENE, AND ON TWO TRANSITIONS OF HEMIMELLITENE

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ABSTRACT

A vacuum flask with a thermoelement serves as a simple calorimeter for measuring heats of fusion quickly and economically, with an accuracy of a few percent. The following heats of fusion (with estimated uncertainties), in k-cal. per mole, were obtained: pseudocumene, $-44.1°$ C., 2.75 ± 0.06; hemimellitene, $-25.5°$ C., 2.00 ± 0.05; mesitylene (α), $-44.8°$ C., 2.28 ± 0.06; mesitylene (β), $-51.7°$ C., 1.91 ± 0.05; *o*-xylene, $-25.3°$ C., 3.33 ± 0.07; *m*-xylene, $-47.9°$ C., 2.76 ± 0.05. Hemimellitene was found to have two transitions below the freezing point, with the following heats of transition, in *k*-cal. per mole: hemimellitene ($\gamma \rightarrow \beta$), $-58 \pm 2°$ C., 0.28 ± 0.04; hemimellitene ($\beta \rightarrow \alpha$), $-46 \pm 1°$ C., 0.36 ± 0.04.

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I. INTRODUCTION

The simple calorimeter described here was assembled in order to provide a means for measuring as quickly and economically as practicable, and with an accuracy of a few percent, the heats of fusion of certain hydrocarbons for which there are no data. Values for the heats of fusion of these substances are required in order to compute the purity of various samples of them from their freezing curves.

II. APPARATUS AND METHOD

The apparatus is shown in figure 1. *A* is an unsilvered vacuum jacketed, pyrex glass flask, the bulb of which has a capacity of about 30 cm^3; *B* is a 2-junction copper-constantan thermoelement sealed with deKhotinsky wax through the rubber stopper *C; D* is a cork support.

The principle of the method is to determine the time required to melt a given mass of the substance contained in the flask, when the latter is surrounded by dry air whose temperature is nearly that of the room. The temperature of the air bath is Δt degrees above that of the melting substance. The time rate of flow of heat energy into the flask for any given temperature head, Δt, is determined from experiments with "standard" substances whose heats of fusion are known.

The experimental procedure was as follows: The empty vacuum flask with solid rubber stopper was weighed; the bulb of the flask was filled with the substance under investigation; the flask, with stopper and contents, was weighed; the solid stopper was replaced by one carrying the thermoelement; the bulb of the flask was immersed in liquid air and allowed to remain there until a temperature well below (30 to 60° C.) the freezing point was reached; the flask was then dried and placed in the dry air bath (a glass jar, 12 by 13 by 14 inches, with a close fitting aluminum plate as cover) with the bottom tip of the flask resting on a large cork stopper and the rubber stopper at the top touching a rubber covered lateral support; the emf of the thermoelement was read to 0.01 millivolt at intervals of 2 to 5 minutes except during the melting period, when the intervals were longer.

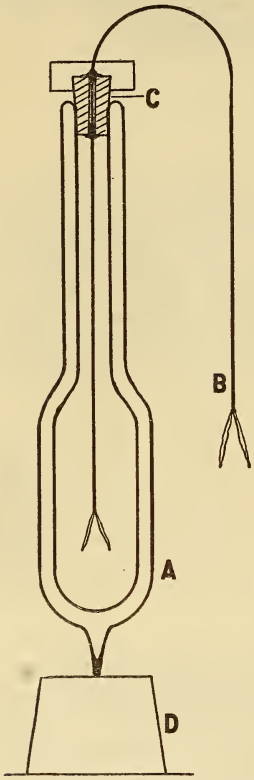

FIGURE 1.—*Sketch of the apparatus*

A, vacuum flask; *B*, 2-junction thermoelement; *C*, rubber stopper; *D*, cork support; length of flask, 8 inches, over all.

The dry air bath was in temperature equilibrium with the air of the laboratory and its temperature stayed about 1° C. below that of the room air. The temperature of the dry air in the bath changed about 0.2 to 0.8° C. during the course of an experiment.

Figure 2 shows a plot of log Δt, where Δt is the difference in temperature between the substance in the flask and the surrounding air, against the time for experiments 23 and 24, with *n*-decane and *n*-octane, respectively. The data required from these plots are (1) the average ordinate during the melting period, the antilogarithm of which is Δt_f, and (2) the length of the abscissa (through this average ordinate) intercepted by the two straight lines, which is z_f, the time of melting.

If m is the mass of the substance in the flask, and l_f is its heat of fusion in cal. per g, then, at the given temperature head of Δt_f, the rate of flow of heat energy into the flask from its surrounding air, during the melting period, is

$$A = ml_f/z_f \text{ cal. min.}^{-1}$$

Having determined the value of A for various values of Δt_f from experiments with "standard" substances, then for the "unknown" substance

$$l_f = z_f A/m \qquad \text{cal. g}^{-1}$$

III. MATERIALS

The hydrocarbons employed in the present investigation were as follows: *n*-octane (F.P. −56.8° C.) and *n*-dodecane (F.P. −9.8° C.) prepared synthetically by Mair [1]; *n*-decane (F.P. −29.8° C.) pre-

[1] Mair, B. J., B.S.Jour. Research, vol. 9, p. 457, 1932.

pared from petroleum by Bruun and Hicks-Bruun [2]; benzene prepared by the Bureau des Étalons Physico-Chimiques, University of Brussels; *o*-xylene (F.P. −25.3° C.) and *m*-xylene (F.P. −47.9° C.) prepared from petroleum by White and Rose [3]; pseudocumene (1, 2, 4-trimethylbenzene, F.P. −44.1°C.), mesitylene (1, 3, 5-trimethylbenzene, F.P. −44.8° C.), and hemimellitene (1, 2, 3-trimethyl-

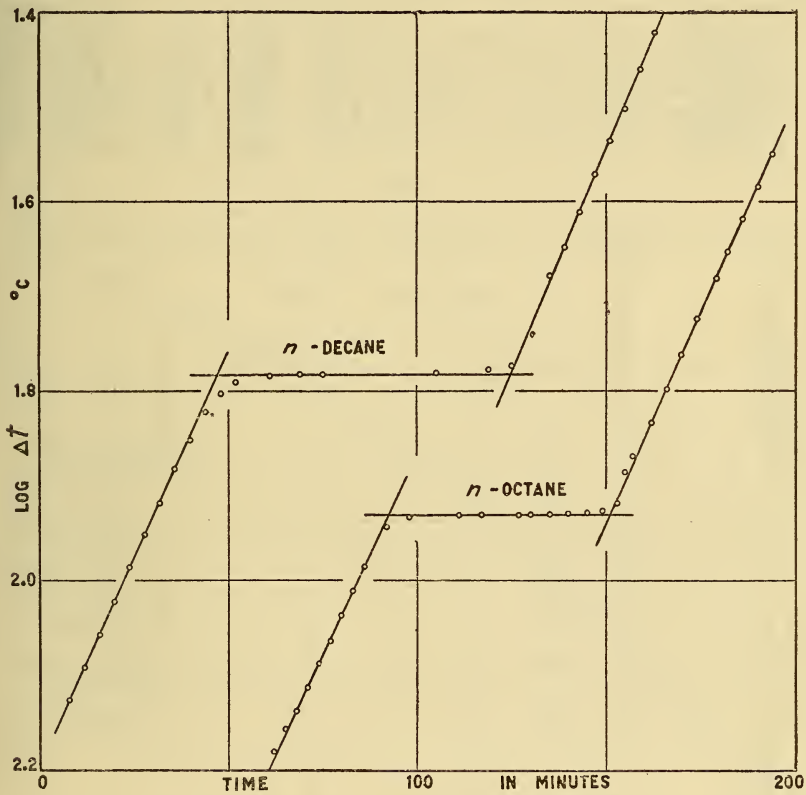

FIGURE 2.—*Curves for n-octane and n-decane.*
The scale of ordinates gives log Δt in °C. The scale of abscissae gives the time in minutes.

benzene, F.P. −25.5° C.) prepared from petroleum by Mair and Schicktanz [4].

IV. STANDARDIZATION EXPERIMENTS

Table 1 gives the data obtained in the experiments with the "standard" substances, values for whose heats of fusion were taken from the data of Parks and coworkers.[5]

[2] Bruun, J. H., and Hicks-Bruun, M. M., B.S.Jour. Research, vol. 8, p. 583, 1932.
[3] White, J. D., and Rose, F. W., Jr., B.S.Jour. Research, vol. 9, p. 711, 1932.
[4] Mair, B. J., and Schicktanz, S. T., B.S.Jour. Research, vol. 11, 1933.
[5] (*a*) Huffmann, H. M., Parks, G. S., and Barmore, M., J.Am.Chem.Soc., vol. 53, p. 3876, 1931; (*b*) Huffmann, H. M., Parks, G. S., and Daniels, A. C., J.Am.Chem.Soc., vol. 52, p. 1547, 1930.

TABLE 1.—*Data from the Standardizing Experiments*

Experiment no.	Substance	Mass	Value for the heat of fusion (from Parks et al.)	Δt_f	z_f	A
		g	*cal. g*$^{-1}$	°*C.*	*min.*	*cal. min.*$^{-1}$
1	*n*-decane	24.99	48.34	57.7	85.4	14.14
2	*n*-decane	24.99	48.34	58.1	85.3	14.16
3	*n*-octane	23.19	43.21	85.7	57.0	17.58
4	*n*-octane	23.19	43.21	85.7	56.2	17.83
11	*n*-dodecane	25.57	51.33	36.3	129.4	10.14
12	benzene	29.53	30.09	22.5	138.5	6.42
13	*n*-nonane	24.80	41.21	85.7	56.5	18.09
23	*n*-octane	24.19	43.21	85.1	58.9	17.74
24	*n*-decane	24.13	48.34	61.0	77.9	14.97

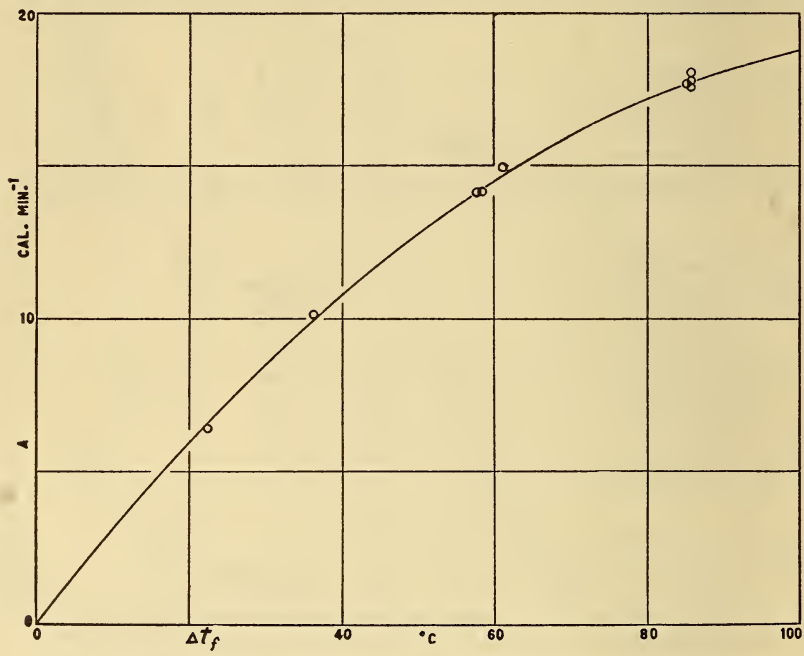

FIGURE 3.—*Plot of the data from the standardizing experiments.*

The scale of ordinates gives A, the heat flow into the flask, in cal. per min. The scale of abscissae gives Δt_f, the difference between the temperature of the substance at its melting point and that of the air surrounding the flask, in °C.

The experiments with the "standard" substances were run both before and after the experiments with the "unknowns", and the thermal conductance of the flask was apparently unchanged during the course of the experiments, which extended over a period of 4 weeks.

The data from the standardizing experiments are plotted in figure 3, where A, the heat flow in cal. per minute, is plotted againsy Δt_f, the difference in temperature between the substance at its melting point and the air surrounding the flask. The equation of the curve is given by

$$A = 0.323\ \Delta t_f - 0.00135\ (\Delta t_f)^2$$

The flask used in the present investigation served very well for substances freezing in the range 0° to −70° C. For lower temperatures a flask with a smaller heat leak would be better. For substances melting above room temperature, the reverse process of starting the experiment with the flask containing the liquid substance at a temperature of 30° to 60° above the melting point and letting it cool down to the room temperature should be feasible. With a silvered flask the heat flow would more nearly approach Newton's law of cooling, that is, $A/\Delta t_f$ would be more nearly constant. To secure a sufficiently large heat flow with a silvered flask, it could, instead of being evacuated, be filled with hydrogen or with nitrogen. Elimination of the vacuum would be expected to improve the constancy of the thermal conductance of the flask over a long period of time.

V.

The experimental data and determinations are given in table 2.

TABLE 2.—*Experimental Data*

Exp. no.	Substance	Mass	Δt_f	z_f	Heat of fusion
		g	°*C.*	*min.*	*cal. g*$^{-1}$
5	Hemimellitene (α)	29.70	56.6	34.9	16.40
6	Hemimellitene (α)	29.70	53.5	38.3	17.30
7	Hemimellitene (α)	29.70	49.8	38.6	16.56
10	*o*-Xylene	30.70	50.1	75.3	31.39
22	*o*-Xylene	27.02	52.5	65.5	32.09
25	*o*-Xylene	30.43	53.0	70.3	30.77
14	*m*-Xylene	29.92	75.3	46.3	25.78
15	*m*-Xylene	29.92	75.3	47.0	26.17
16	Mesitylene (β)	29.50	77.1	27.6	15.79
17	Mesitylene (β)	29.50	77.4	28.0	16.05
18	Pseudocumene	28.62	72.4	40.7	23.19
19	Pseudocumene	28.62	74.8	39.1	22.69
20	Mesitylene (α)	28.75	72.1	33.4	18.90
21	Mesitylene (α)	28.38	72.8	33.7	19.42
					Heat of transition
7	Hemimellitene (γ→β)	29.70	78.9	4.0	2.30
7	Hemimellitene (β→α)	29.70	66.5	5.8	3.03

In figure 4 are plotted the data from experiments 7 and 15, with hemimellitene and *m*-xylene, respectively. As indicated by the curve in figure 4, hemimellitene has three stable solid forms. Values for the two heats of transition were computed from this curve. From these and other experiments the transition temperatures for hemimellitene were determined to be −46 ± 1 and −58 ± 2° C. In the case of mesitylene, Mair and Schicktanz [6] found both a stable (F.P. −44.8° C.) and a metastable crystalline form (F.P. −51.7° C.). The heats of fusion of both of these crystalline forms of mesitylene were determined.

[6] See footnote 4, p. 555.

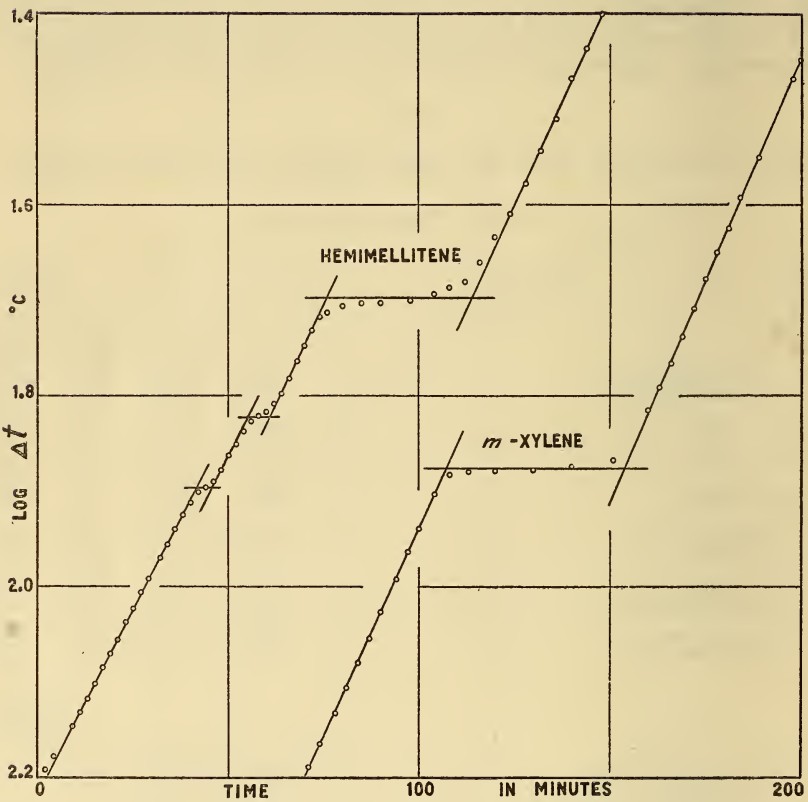

FIGURE 4.—*Curves for hemimellitene and m-xylene.*

The scale of ordinates gives log Δt in °C. The scale of abscissas gives the time in minutes.

TABLE 3.—*Heats of Fusion*

Substance	Molecular weight	F.P.	Heat of fusion (with estimated uncertainty)
	g	° *C.*	*k-cal. mole*$^{-1}$
Pseudocumene	120.09	−44.1	2.75±0.06
Hemimellitene (α)	120.09	−25.5	2.00±0.05
Mesitylene (α)	120.09	−44.8	2.28±0.06
Mesitylene (β)	120.09	−51.7	1.91±0.05
o-Xylene	106.08	−25.3	3.33±0.07
m-Xylene	106.08	−47.9	2.76±0.05

TABLE 4.—*Heats of Transition*

Substance	Transition temperature	Heat of transition (with estimated uncertainty)
	° *C.*	*k-ca'. mole*$^{-1}$
Hemimellitene (γ→β)	−58±2	0.28±0.04
Hemimellitene (β→α)	−46±1	0.36±0.04

VI. CONCLUSION

The values obtained from the present investigation, together with the estimated uncertainties, are given in tables 3 and 4. No other data exist for hemimellitene and mesitylene. Parks and coworkers [7] found for *m*-xylene [8] (F.P. −53.5° C.) 2.73, for *o*-xylene (F.P. −25.3° C.) 3.11, for pseudocumene (F.P. −44.5° C.) 3.02, k-cal. per mole.

WASHINGTON, July 28, 1933.

[7] See footnote 5, p. 555.
[8] Huffman, Parks, and Daniels (see footnotes 5b, p. 555) state that their *m*-xylene was not very pure. Their sample froze 5.6° C. below the freezing point of the sample used in the present investigation.