

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

## THE HEAT CAPACITIES AND HEAT OF CRYSTALLIZATION OF SOME ISOMERIC AROMATIC COMPOUNDS

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RECEIVED FEBRUARY 17, 1926

PUBLISHED MAY 5, 1926

In the course of investigations of the mutual solubility of some sets of *ortho*, *meta* and *para* isomers,<sup>2</sup> which yield solutions substantially ideal, we observed that the heat of crystallization, as derived from the slope of the solubility curve, in some cases agreed passably with the calorimetric value found in the literature, whereas in other cases the discrepancy was as much as 1000 calories. This, and the further fact that calorimetric data on many of the compounds were lacking, led us to undertake a series of calorimetric determinations, the results of which are here presented and discussed. The new results agree satisfactorily with the solubility data,<sup>2</sup> a fact which leads to the belief that the previous low values resulted from lack of the necessary purity of the material. Another reason for the work was to secure a series of heats of fusion which could be used as standards in ascertaining the possible accuracy of a method of "radiation calorimetry,"<sup>3</sup> applicable to the determination of heat of transition, which in many cases cannot be readily determined by present methods.

The principle of the method used is to compare the amount of heat transferred to the calorimeter by the substance in dropping from a temperature ranging through its freezing temperature, with that given up by a silver bar under identical conditions; in other words, the use, as a transfer instrument, of a simple type of calorimeter calibrated by identical experiments with silver. The specific heats of some 28 substances, both as crystals and as liquid, and the heats of crystallization were determined; we used only substances which melt well above ordinary temperature, for substances ordinarily liquid would have required a modification of method and would have been more troublesome to purify adequately. Our object was to secure values of moderate accuracy (of the order of 1%) for a

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<sup>2</sup> Johnston, Andrews and Kohman, (a) *J. Phys. Chem.*, **29**, 882; (b) 914; (c) 1041; (d) 1048; (e) 1317 (1925).

<sup>3</sup> Essentially a comparison of heating, or cooling, curves observed under carefully controlled conditions. Ruff and Plato, *Ber.*, **36**, 2357 (1903); **58**, 350 (1908). Hüttner and Tammann, *Z. anorg. Chem.*, **43**, 215 (1905). Plato, *Z. physik. Chem.*, **55**, 721 (1906); **63**, 453 (1908). White, *Am. J. Sci.*, **28**, 485 (1909). Schwarz and Sturm, *Ber.*, **47**, 1730 (1914). Roos [*Z. anorg. Chem.*, **94**, 329 (1916)] has used it to obtain values of heat of melting of some metals.

considerable number of related substances, rather than to restrict ourselves to a small number of substances in an endeavor to secure results of higher accuracy; any marked increase in accuracy could be obtained only by a disproportionate expenditure of time and trouble in securing the requisite purity of material.

In this type of work, purity of material is of the utmost importance, for a small percentage of admixture may cause a very large percentage error in specific heat just below the melting temperature and in heat of freezing. Indeed, to obtain the substances sufficiently pure proved to be the most difficult part of the problem, and necessitated repeated crystallizations and sublimations; the criterion of purity was either the form of the time-temperature (cooling or heating) curve,<sup>4</sup> or that of the heat-content curve itself.

The substances investigated are the three (*o*, *m* and *p*) dinitrobenzenes, nitro-anilines, dihydroxybenzenes, toluic acids, amino-, chloro- and nitrobenzoic acids, benzene, benzoic acid, quinone, naphthalene,  $\alpha$ - and  $\beta$ -naphthol and hydroxy-acetanilide.

### Experimental Part

**Materials.**—The first step is to provide material of the requisite purity in sufficient quantity; this was accomplished either by a process of fractional crystallization<sup>5</sup> or by sublimation in a vacuum.<sup>6</sup> The necessary details are given later under the several substances. The next step is to make up specimens of the material which satisfy the calorimetric requirements. The specimens were sealed in numbered,<sup>7</sup> thin-walled glass tubes about 7 mm. in diameter and 80 mm. long, the volume of the material being about 3 cc. The diameter of the tubes was purposely made small in order to ensure that the temperature should be uniform throughout the specimen within five minutes after the tube was dropped into the calorimeter; calculations based on the heat diffusivity of naphthalene indicated that this would be so in a tube of this diameter, and this was confirmed by direct measurement of temperature by means of a thermo-element in an open tube, of the same size, containing naphthalene, which was plunged into a bath at a different temperature. Inattention to this detail—that is, the use of specimens too large to yield all of their heat to the calorimeter in a few minutes—has been one cause of low results in the past.

<sup>4</sup> White, *J. Phys. Chem.*, **24**, 392 (1920). Ref. 2 b.

<sup>5</sup> As, for example, by Richards and Hall, *THIS JOURNAL*, **39**, 531 (1917).

<sup>6</sup> By means of an apparatus essentially the same as that described by R. Kempf, *J. prakt. Chem.*, **78**, 201 (1908).

<sup>7</sup> The numbers were applied by the litharge process, as follows: add glycerol to an ordinary pad for a rubber stamp, stamp the required number on to the glass and dust litharge onto the wet ink; blow off the excess, and burn what adheres into the glass by heating it to its softening temperature.

In preparing a specimen, the empty tube, previously closed at one end, was weighed; the material was melted into the tube, the latter sealed off, and weighed with its contents; the end-portion was burned clean and weighed; by this means, as was corroborated by special experiments, the precise weight of glass and of material in the specimen was ascertained. Some of the substances darkened or showed other evidence of decomposition when heated in the presence of air; in these cases the tube containing the unmelted material was alternately evacuated and filled with dry hydrogen, nitrogen or carbon dioxide, the process being repeated several times before the tube was sealed off, whereupon the substance was melted down. Finally this method was replaced by a better, namely, to attach the specimen tubes directly to the vacuum sublimation apparatus, to run in the melted charge and seal off in a vacuum; in these cases, it was necessary, in order to ascertain the weight of the material to open and clean the tube and to weigh the glass, after the series of determinations.

The silver standard was a bar of pure silver of approximately the same size as a specimen. It was compared directly with silver turnings sealed in a glass specimen tube, and also with water similarly enclosed; the results were consistent within  $\pm 0.2\%$  and, therefore, the silver bar was used in practice by reason of its greater convenience.

**The High-Temperature Bath.**—The specimen (or the silver bar) was heated to a definite temperature in a small air-bath, which consisted essentially of a hollow brass cylinder, of internal diameter slightly larger than the specimen tubes, wound externally with Nichrome ribbon over a layer of mica, and wrapped with several layers of asbestos. This bath was mounted so that it could be swung into position directly over the calorimeter when the specimen was to be dropped; it was closed at the bottom by a sliding trap door and at the top by a plug of asbestos. By hand regulation the temperature variation could be kept within  $0.05^\circ$  per minute, the temperature being measured by a thermo-element ( $T_1$ ) soldered into a long vertical hole in the brass cylinder. The thermo-element was of silk-covered copper-constantan (each No. 30 B. and S. gage); it was duly calibrated, and its readings were converted to degrees, in the usual way.<sup>8</sup>

**The Calorimeter.**—The calorimetric arrangement consisted essentially of a pair of similar, wide-mouthed, silvered, pint-size vacuum bottles, containing kerosene, each closed by a cork (through which passed the thermo-elements, etc.) and surrounded by appropriate insulating material. One of these (*C*) served as the calorimeter proper, the other (*B*) as the reference temperature, the pair of bottles being selected by trial on the basis that their rates of cooling should be equal; they were in fact so nearly alike that the small difference in temperature between them was not affected

<sup>8</sup> See, for instance, Adams and Johnston, *Am. J. Sci.*, 33, 534 (1912).

appreciably by the changes in temperature of the room. The calorimeter was provided with a small trap door, opened only at the instant when the specimen was dropped in from the high-temperature bath. The specimen was caught in a small basket of light copper wire, suspended, below the liquid level, by three threads which passed out over pulleys and thence to a motor-driven crank mechanism; this served as a stirrer, which moved the specimen up and down in the liquid and ensured uniformity of temperature in the calorimeter within five minutes after the hot specimen had been introduced.

In our mode of experiment, the actual heat capacity of the calorimeter liquid need not be known; this enabled us to use kerosene which, as compared to water, possesses several advantages. The lower specific heat of kerosene results in a larger temperature rise for a given volume of liquid, and lessens errors caused by splashing; its lower heat of vaporization cuts down errors due to evaporation; and in particular, its very low electrical conductivity permits of the direct exposure of the bare thermoelement junctions to the liquid. The amount of oil in the calorimeter was maintained constant, so as to lessen the number of calibrations, its level being indicated by a glass needle attached to a small glass float. Since the kerosene expands appreciably with temperature, the level was always adjusted at our basis temperature  $22^{\circ}$ . The heat added by the specimens to the calorimeter was allowed to accumulate until the temperature of the oil was about  $3^{\circ}$  higher than in the reference bath *B*; thereupon the oil was cooled by inserting a long test-tube containing ice.

The temperature of the reference bath *B*—which, as noted above, did not change appreciably during the determination—was read on a thermometer to  $0.01^{\circ}$ ; in any case, any change, provided that it is regular (as it was), is automatically taken care of in the method of computation of the actual drop in temperature. The *difference* in temperature between *B* and the calorimeter—with which alone, therefore, we were concerned during the determination—was measured by a 20-junction, copper-constantan thermo-element  $T_2$ .<sup>9</sup> Its bare junctions in the calorimeter were distributed in two horizontal circles, one near the top of the liquid, the other near the bottom, and were supported on a copper cylinder which fitted into the Dewar vessel. With this arrangement of the junctions one has a very sensitive criterion of uniformity of temperature within the calorimeter—

<sup>9</sup> This multiple thermo-element is similar to those previously described [W. P. White, *Phys. Rev.*, **23**, 449 (1909); *THIS JOURNAL*, **36**, 2292 (1914). L. H. Adams, *ibid.*, **37**, 481 (1915)], except that each junction is covered only with an open capillary glass tube. In the construction of such thermo-elements it is advantageous to pair all of the wires at one end, then at the other end to pair *any* two unlike wires which by electrical test are found to be unpaired at the first end. A piece of heavy tungsten wire continuously heated in a blast lamp, is a convenient "soldering-iron" in silver soldering the pairs of wires.

namely, when the rate of change of electromotive force with time becomes constant. This thermocouple was tested in the usual way, but a precise calibration was not necessary, as we were using it in effect merely as a transfer instrument.

**Experimental Method.**—When the specimen (or silver bar) had been brought to the desired temperature, readings of the thermo-element  $T_1$  in the oven and of  $T_2$  in the calorimeter were made on alternate minutes, by aid of a White double potentiometer, for several minutes; the specimen was dropped, and after three or four minutes, regular readings of  $T_2$  were resumed and continued for several minutes. From these data, by extrapolation, the precise temperature drop of the specimen and the temperature rise (in terms of microvolts) of the calorimeter were computed. The latter was converted into calories yielded by the specimen to the calorimeter, by means of identical experiments, through similar temperature ranges, with the silver bar, on the basis that the heat capacity<sup>10</sup> of 1 gram of silver at  $t^\circ\text{C}$ . is  $0.05566 + 0.00001337t$  calories; these calibrations proved to be so closely concordant that one for every six or eight runs was ample.

The heat capacity of the glass used (a soda glass from the Kimble Glass Company) was determined in an identical manner at temperatures ranging up to  $155^\circ$ ; its mean specific heat per gram, from  $t^\circ$  to  $22^\circ$  proved to be  $0.192 + 0.000122t$  and this formula was used in allowing for the heat contributed by the glass inclosing the specimen.

**Accuracy.**—On the high-temperature element  $T_1$ , the accuracy of reading was 1 microvolt, or  $0.02^\circ$ ; but allowing for calibration errors and for temperature differences between bath and specimen, we may estimate that the constant temperature of the specimen was accurate to about  $0.1^\circ$ . The accuracy of the final temperature of the specimen was about the same, and corresponds to  $\pm 5$  cal. per mole. The error in the extrapolated readings of the calorimeter element was not more than  $\pm 2$  microvolts on a mean total rise of about 650 microvolts, or 0.3%, equivalent to 20 cal. per mole. Thus the total error should be  $\pm 5 \pm 5 \pm 20 = \pm 30$  calories per mole. This appears to be about the accuracy of the later determinations, if one may judge from the correspondence of the individual results with a smooth curve; but the earlier determinations, made before the thermo-junctions were distributed in the calorimeter, are less accurate.

The largest single source of error in determinations on crystalline material, is the presence of impurities, which results in a fractional melting through a considerable range below its proper melting temperature. This does not appreciably affect the determinations on the liquid, since the heat

<sup>10</sup> This is the value, in terms of calories (1 cal. = 4.182 joules), selected provisionally for International Critical Tables. Initially the computations were all made on the basis of a slightly different curve, which coincided with the above at  $250^\circ$ , but diverged by about 1% at  $120^\circ$  and 1.7% at  $20^\circ$ ; for this reason the values cited in the previous papers (Refs. 1 c and 1 d) differ somewhat from those now presented.

of melting and heat capacity of the impurity are of the same magnitude as for the liquid itself; the largest source of error here is, probably, incomplete crystallization<sup>11</sup> owing to the sudden quenching of the material.

The experimental results were plotted in terms of molal heat content,  $H$ , against temperature as abscissa, on the basis that at 22° the heat content is zero; in other words, the actual heat yielded to the calorimeter at 22° by the substance at  $t$  was plotted against  $t$ , the only calculation involved being to bring this to a molal basis. As the calorimeter was usually not precisely at 22°, this necessitated a small correction, for which an approximate value of the specific heat of the substance sufficed. What was judged to be the best curve was drawn through the set of points for (l) the liquid, (s) the crystals; these were extended<sup>12</sup> to the melting temperature, the difference in ordinate then representing the heat of freezing. From the pair of curves so drawn—which do not diverge far from linearity—a pair of empirical expressions of the form  $H = a + bt + ct^2$  were derived,  $H$  being in terms of gram-calories per mole at  $t^\circ$  referred to the heat content of the substance in its stable state at 22° as zero. The difference between the pair of values of  $H$ , calculated at the melting temperature, is the heat of freezing ( $\Delta H_f$ ) given; the value so obtained is, we venture to believe, accurate within about 50–100 cal., equivalent to about  $\pm 1\%$ . From each empirical formula, moreover, the true molal heat capacity, within the temperature range, is easily derived by differentiation; namely,  $dH_s/dt = b + 2ct$ ; and  $dH_l/dt = b' + 2c't$ .

The results are presented in the form of tables, which give for each substance, both as solid and as liquid: the number of separate observations, the experimental temperature range, the three coefficients in each empirical  $H-t$  equation, the maximum ( $\Delta_m$ ), and average ( $\Delta_a$ , taken without regard to sign) difference between the experimental values of  $H$  and the curve, and the heat of freezing ( $\Delta H_f$ ). The source and method of purification of each substance are given, also the melting temperature of the purified sample, as determined from a cooling curve taken under controlled conditions, the temperature being measured by means of a calibrated thermocouple of fine wire.<sup>13</sup> The shape of the cooling curve was used as a criterion of purity. For comparison, the results of recent direct calorimetric determinations as given in the literature are included.

<sup>11</sup> For instance, Massol and Faucon [*Compt. rend.*, **153**, 268 (1911)] found the heat of fusion and of solidification to be 46.7 and 37.4 cal. per g., respectively, in the case of lauric acid which, however, undoubtedly crystallizes less readily than do the compounds discussed here. Compare also Griffiths, *J. Chem. Soc.*, [II] **106**, 245 (1914).

<sup>12</sup> In a few cases, by reason of supercooling, a point was observed on the liquid curve at a temperature somewhat below the true freezing temperature.

<sup>13</sup> Ref. 1 b. The melting temperature as given in Stelzner, "Literatur Register der Organischen Chemie," 1923, or in Beilstein-Prager-Jacobson, "Organische Chemie," is included in parentheses; these are referred to as *S* and *B*, respectively.

In only one case, that of *m*-dinitrobenzene, do we tabulate and plot the experimental data; this is done, in Table I and in Fig. 1, to emphasize the pronounced effect caused by lack of purity of the material. The upturn in the curve for the solid begins at the eutectic temperature with the impurity<sup>14</sup> and results in a much too small apparent heat of melting. Indeed,

TABLE I  
EXPERIMENTAL DATA ON *m*-DINITROBENZENE

| Temp., °C. | Impure<br><i>H</i> obs. | $\Delta$ | Temp., °C. | Purified<br><i>H</i> obs. | $\Delta$ |
|------------|-------------------------|----------|------------|---------------------------|----------|
| 53.63      | 1495                    | -39      | 52.54      | 1402                      | +1       |
| 70.63      | 2387                    | -103     | 59.44      | 1636                      | +99      |
| 70.67      | 2401                    | -115     | 68.03      | 2146                      | +9       |
| 72.20      | 2527                    | -65      | 69.24      | 2185                      | +30      |
| 72.38      | 2630                    | -259     | 79.33      | 2720                      | +1       |
| 73.00      | 2435                    | -33      | 83.67      | 2903                      | +39      |
| 73.40      | 2530                    | -108     | 85.48      | 3112                      | -78      |
| 73.81      | 2886                    | -443     |            |                           |          |
| 74.01      | 2922                    | -470     | 90.08      | melts                     |          |
| 74.08      | 2879                    | -423     |            |                           |          |
| 74.12      | 2903                    | -345     | 97.98      | 7948                      | +14      |
| 75.59      | 2615                    | -83      | 98.22      | 7788                      | +191     |
| 75.59      | 2666                    | -134     | 121.78     | 9600                      | -15      |
| 76.71      | 2682                    | -94      | 133.61     | 10397                     | -5       |
| 78.06      | 3097                    | -441     | 166.04     | 12607                     | -3       |
| 84.61      | 4159                    | -1170    | 211.26     | 15682                     | +6       |
| 89.81      | melts                   |          | 245.92     | 18038                     | +14      |
| 97.19      | 8135                    | -229     |            |                           |          |
| 149.26     | 11318                   | +142     |            |                           |          |
| 158.96     | 12083                   | +38      |            |                           |          |

TABLE II  
DINITROBENZENES

|                           | No. of<br>obs. | Temp.<br>range, °C. | <i>a</i> | <i>b</i> | <i>c</i> | $\Delta_m$ | $\Delta_a$ | $\Delta H_f$ |
|---------------------------|----------------|---------------------|----------|----------|----------|------------|------------|--------------|
| <i>ortho</i> <sup>a</sup> | 11             | 55                  | -989     | 42.86    | 0.074    | 281        | 69         | 5460         |
| 1                         | 9              | 240                 | 3256     | 58.67    | .028     | 265        | 83         |              |
| <i>meta</i> <sup>b</sup>  | 7              | 53                  | -944     | 41.71    | .0565    | 99         | 37         | 4150         |
| 1                         | 7              | 245                 | 1280     | 68.20    | ...      | 191        | 35         |              |
| <i>para</i> <sup>c</sup>  | 13             | 55                  | -980     | 43.53    | .0478    | 226        | 94         | 6720         |
| 1                         | 3              | 210                 | 4913     | 46.94    | .0555    | 175        | 99         |              |

<sup>a</sup> Prepared by Dr. G. T. Kohman; recrystallized four times from 95% ethyl alcohol; m. p., 116.93° (*B.*, 116.5–118.5°).

<sup>b</sup> Source unknown; initially melted at 89.8° but when fractionally crystallized to the tenth row from redistilled benzene, it melted at 90.08° (*B.*, 88–89.8°). The purified material gave the continuous line in Fig. 1; the impure, the dotted line.  $\Delta H_f = 4870$  according to Robertson [*J. Chem. Soc.*, 81, 1237 (1902)]. He proposes the relation  $\Delta H/T_m V^{1/3} = \text{constant}$ ,  $T_m$  being the melting temperature and  $V$  the molal volume.

<sup>c</sup> Prepared by Dr. D. H. Andrews; recrystallized from 95% alcohol; m. p., 173.5° (*B.*, 171–174°).

<sup>14</sup> This is possibly the *ortho*, the *o-m* eutectic temperature being 63.0°.

on the basis that the impurity forms an ideal solution with the compound, from this divergence one can, by application of the equation of the ideal solution,<sup>2</sup> calculate the molecular proportion of impurity. In the present case this proved to be 2.7%, in full agreement with the value derived from the difference in melting temperature. This example makes it clear that one need make use of the most accurate calorimetric methods only if one can be sure of obtaining and maintaining during the determination the corresponding degree of purity.

TABLE III  
TOLUIC ACIDS

|                           | No. of | Temp.  |          |          |          |            |            |              |      |
|---------------------------|--------|--------|----------|----------|----------|------------|------------|--------------|------|
|                           | obs.   | range, | <i>a</i> | <i>b</i> | <i>c</i> | $\Delta_m$ | $\Delta_a$ | $\Delta H_f$ |      |
|                           |        | °C.    |          |          |          |            |            |              |      |
| <i>ortho</i> <sup>a</sup> | s      | 9      | 50       | -870     | 37.75    | 0.082      | 67         | 20           | 4820 |
|                           | 1      | 14     | 200      | 2250     | 57.50    | .050       | 330        | 155          |      |
| <i>meta</i> <sup>b</sup>  | s      | 5      | 55       | -799     | 32.49    | .133       | 142        | 62           | 3760 |
|                           | 1      | 6      | 170      | 281      | 68.56    | .028       | 200        | 70           |      |
| <i>para</i> <sup>c</sup>  | s      | 15     | 50       | -846     | 36.85    | .072       | 116        | 41           | 5430 |
|                           | 1      | 18     | 225      | 2757     | 43.04    | .094       | 115        | 60           |      |

<sup>a</sup> From Kahlbaum, used as received. Colorless; melted to a colorless liquid at 103.7° (*S.*, 101°).

<sup>b</sup> As *ortho*; m. p., 108.75° (*B.*, 110.5°).

<sup>c</sup> As *ortho*; m. p., 179.6° (*S.*, 178-179°).

TABLE IV  
NITROBENZOIC ACIDS

|                           | No. of | Temp.  |          |          |          |            |            |              |      |
|---------------------------|--------|--------|----------|----------|----------|------------|------------|--------------|------|
|                           | obs.   | range, | <i>a</i> | <i>b</i> | <i>c</i> | $\Delta_m$ | $\Delta_a$ | $\Delta H_f$ |      |
|                           |        | °C.    |          |          |          |            |            |              |      |
| <i>ortho</i> <sup>a</sup> | s      | 14     | 60       | -959     | 41.88    | 0.079      | 106        | 43           | 6690 |
|                           | 1      | 5      | 240      | 4800     | 52.50    | .050       | 192        | 75           |      |
| <i>meta</i> <sup>b</sup>  | s      | 15     | 75       | -848     | 36.28    | .103       | 166        | 58           | 4620 |
|                           | 1      | 8      | 225      | 428      | 67.72    | .048       | 104        | 54           |      |
| <i>para</i> <sup>c</sup>  | s      | 12     | 75       | -905     | 39.61    | .069       | 147        | 69           | 8820 |
|                           | 1      | 2      | 245      | 3600     | 75.00    | ..         | 105        | 90           |      |

<sup>a</sup> Source unknown; initially quite impure. Fractionally crystallized to the tenth row from 95% alcohol; contents of two middle flasks heated for seven hours at 90° in a stream of dry air; m. p., 145.8° (*S.*, 147°).

<sup>b</sup> Source unknown; purification similar to *ortho*. This substance always cracked the thin glass tube on solidification, necessitating the use of thicker glass; m. p., 141.1° (*S.*, 140-141°).

<sup>c</sup> Purified by sublimation by Dr. A. W. Francis; m. p., 239.2° (*S.*, 238°).

TABLE V  
DIHYDROXYBENZENES

|                           | No. of | Temp.  |          |          |          |            |            |              |      |
|---------------------------|--------|--------|----------|----------|----------|------------|------------|--------------|------|
|                           | obs.   | range, | <i>a</i> | <i>b</i> | <i>c</i> | $\Delta_m$ | $\Delta_a$ | $\Delta H_f$ |      |
|                           |        | °C.    |          |          |          |            |            |              |      |
| <i>ortho</i> <sup>a</sup> | s      | 5      | 60       | -643     | 27.41    | 0.083      | 43         | 20           | 5440 |
|                           | 1      | 6      | 200      | 2920     | 50.90    | .030       | 24         | 17           |      |
| <i>meta</i> <sup>b</sup>  | s      | 6      | 60       | -630     | 26.53    | .096       | 57         | 29           | 5090 |
|                           | 1      | 6      | 200      | 2542     | 49.78    | .035       | 107        | 41           |      |



TABLE V (Concluded)

|                          |   | No. of<br>obs. | Temp.<br>range, °C. | a    | b     | c    | $\Delta_m$ | $\Delta_a$ | $\Delta H_f$ |
|--------------------------|---|----------------|---------------------|------|-------|------|------------|------------|--------------|
| <i>para</i> <sup>c</sup> | s | 7              | 60                  | -707 | 31.20 | .044 | 48         | 21         | 6480         |
|                          | 1 | 5              | 200                 | 2460 | 54.20 | .022 | 71         | 30         |              |

<sup>a</sup> Catechol from the Eastman Kodak Company; sublimed in a vacuum; samples sealed up in an atmosphere of carbon dioxide. For the melting-point determination, a tube with a reëntrant capillary was attached directly to the sublimation apparatus and filled in a vacuum; the thermo-element was inserted into the capillary tube and a cooling curve taken, the substance thus being always under its own vapor pressure; m. p., 104.3° (*B.*, 104-105°).

<sup>b</sup> Resorcinol; same as *ortho* in every particular; m. p., 109.6-109.7° (*B.*, 110-110.7°);  $\Delta H_f$ , 2300, according to Schükarew [*Z. physik. Chem.*, 71, 97 (1910)].

<sup>c</sup> Quinol; same as *ortho* in every particular; m. p., 172.3° (*B.*, 169-172°). For the mean molal specific heat of these three substances between 14° and 26° Magie [*Phys. Rev.*, 16, 381 (1903)] gives 35.7, 30.3 and 28.4 cal., respectively.

TABLE VI  
CHLOROBENZOIC ACIDS

|                           |   | No. of<br>obs. | Temp.<br>range, °C. | a     | b     | c     | $\Delta_m$ | $\Delta_a$ | $\Delta H_f$ |
|---------------------------|---|----------------|---------------------|-------|-------|-------|------------|------------|--------------|
| <i>ortho</i> <sup>a</sup> | s | 8              | 60                  | -813  | 35.65 | 0.066 | 66         | 17         | 6150         |
|                           | 1 | 7              | 200                 | 2490  | 61.31 | .028  | 121        | 35         |              |
| <i>meta</i> <sup>b</sup>  | s | 10             | 60                  | -826  | 36.29 | .057  | 190        | 48         | 5700         |
|                           | 1 | 5              | 205                 | 3605  | 41.75 | .075  | 63         | 40         |              |
| <i>para</i> <sup>c</sup>  | s | 12             | 60                  | -896  | 37.90 | .0435 | 99         | 31         | 7710         |
|                           | 1 | 3              | 265                 | -2142 | 85.71 | ..    | 70         | 55         |              |

<sup>a</sup> From the Eastman Kodak Company; sublimed in a vacuum once; m. p., 140.2° (*S.*, 140.65°).

<sup>b</sup> As *ortho*, but sublimed thrice; m. p., 154.25° (*S.*, 154°).

<sup>c</sup> As *ortho*; m. p., 239.7° (*S.*, 235-236°).

TABLE VII  
AMINO BENZOIC ACIDS<sup>a</sup>

|                           |   | No. of<br>obs. | Temp.<br>range, °C. | a    | b     | c      | $\Delta_m$ | $\Delta_a$ | $\Delta H_f$ |
|---------------------------|---|----------------|---------------------|------|-------|--------|------------|------------|--------------|
| <i>ortho</i> <sup>b</sup> | s | 8              | 60                  | -812 | 34.87 | 0.0934 | 91         | 54         | 4870         |
|                           | 1 | 3              | 160                 | 2380 | 60    | ...    | 55         | 40         |              |
| <i>meta</i> <sup>c</sup>  | s | 6              | 60                  | -804 | 34.71 | .084   | 63         | 33         | 5220         |
|                           | 1 | 3              | 180                 | 2585 | 60    | ...    | 68         | 42         |              |
| <i>para</i> <sup>a</sup>  | s | 6              | 60                  | -897 | 39.44 | .0603  | 58         | 21         | 5000         |
|                           | 1 | 2              | 190                 | 2185 | 61    | ...    | 1          | 1          |              |

<sup>a</sup> Investigation of these substances was unsatisfactory on account of partial decomposition into carbon dioxide and aniline [for rates of decomposition with hot water, see McMaster and Shriner, *THIS JOURNAL*, 45, 751 (1923)]; this induced premature melting and also caused the samples to explode. For this reason a new specimen was required for each determination on the liquid and it was not feasible to go far beyond the melting temperature. Moreover, it accounts for the fact that some of the liquid points lie below the true melting temperature.

<sup>b</sup> From the Eastman Kodak Company; sublimed twice in a vacuum with slight decomposition; m. p. (heating curve), 144.6°; (Thiele tube) 144.5-145°; (*S.*, 144°).

<sup>c</sup> As *ortho*; m. p. (Thiele tube), 179.5-180° (*B.*, 174°).

<sup>d</sup> As *ortho*, but also recrystallized once from boiled water in absence of air; m. p. (Thiele tube), 188–188.5° (*S.*, 186°).

TABLE VIII  
NITRO-ANILINES

|                           |          | No. of obs. | Temp. range, °C. | <i>a</i> | <i>b</i> | <i>c</i> | $\Delta_m$ | $\Delta_a$ | $\Delta H_f$ |
|---------------------------|----------|-------------|------------------|----------|----------|----------|------------|------------|--------------|
| <i>ortho</i> <sup>a</sup> | <i>s</i> | 4           | 50               | −813     | 35.16    | 0.082    | 63         | 34         | 3850         |
|                           | 1        | 6           | 150              | 1960     | 55.36    | .0438    | 107        | 31         |              |
| <i>meta</i> <sup>b</sup>  | <i>s</i> | 5           | 70               | −820     | 35.00    | .105     | 119        | 60         | 5660         |
|                           | 1        | 7           | 210              | 3404     | 54.20    | .040     | 143        | 75         |              |
| <i>para</i> <sup>c</sup>  | <i>s</i> | 16          | 80               | −875     | 36.00    | .087     | 124        | 39         | 5040         |
|                           | 1        | 9           | 195              | 2140     | 59.00    | .024     | 150        | 52         |              |

<sup>a</sup> From the Eastman Kodak Company, used as received; m. p., 69.3° (*S.*, 71.5°).

<sup>b</sup> As *ortho*; m. p., 111.8° (*S.*, 112°).

<sup>c</sup> As *ortho*; m. p., 147.5° (*S.*, 147°).

TABLE IX

NAPHTHALENE,  $\alpha$ - AND  $\beta$ -NAPHTHOL

|                                 |          | No. of obs. | Temp. range, °C. | <i>a</i> | <i>b</i> | <i>c</i> | $\Delta_m$ | $\Delta_a$ | $\Delta H_f$ |
|---------------------------------|----------|-------------|------------------|----------|----------|----------|------------|------------|--------------|
| Naphthalene <sup>a</sup>        | <i>s</i> | 7           | 55               | −764     | 32.07    | 0.120    | 115        | 45         | 4540         |
|                                 | 1        | 13          | 200              | 3278     | 43.26    | .058     | 83         | 39         |              |
| $\alpha$ -Naphthol <sup>b</sup> | <i>s</i> | 5           | 45               | −812     | 34.60    | .106     | 49         | 24         | 5610         |
|                                 | 1        | 9           | 180              | 3209     | 56.16    | .055     | 158        | 45         |              |
| $\beta$ -Naphthol <sup>c</sup>  | <i>s</i> | 4           | 60               | −853     | 36.73    | .092     | 159        | 57         | 4490         |
|                                 | 1        | 5           | 205              | 1743     | 58.16    | .045     | 89         | 47         |              |

<sup>a</sup> Kahlbaum, used as received; m. p., 79.98° (*B.*, 79.6–80.98°);  $\Delta H_f$ , 4550–4570 in the literature [Alluard, *Ann. chim. phys.*, **57**, 476 (1859). Battelli, *Rend. accad. Lincei*, **1**, 621 (1885). Pickering, *Proc. Roy. Soc. (London)*, **49**, 18 (1890). Auwers, *Z. physik. Chem.*, **18**, 595 (1895). Mathews, *THIS JOURNAL*, **39**, 1125 (1917)]. Battelli [*Atti ist. Veneto*, [6] **3**, 1781 (1884–1885)] gives as mean molal specific heat 42.8 from 60–70° and 50.7 from 80–85°.

<sup>b</sup> From the Eastman Kodak Company, vacuum-distilled twice and sealed in an atmosphere of nitrogen; m. p. (under its own vapor pressure—compare catechol); 95.0° (*B.*, 94.0°).

<sup>c</sup> As  $\alpha$ -naphthol, except that it was sublimed thrice; m. p., 120.6° (*B.*, 122–123°).

TABLE X

BENZENE, BENZOIC ACID, QUINONE AND HYDROXY-ACETANILIDE

|                                  |          | No. of obs. | Temp. range, °C. | <i>a</i> | <i>b</i> | <i>c</i> | $\Delta_m$ | $\Delta_a$ | $\Delta H_f$ |
|----------------------------------|----------|-------------|------------------|----------|----------|----------|------------|------------|--------------|
| Benzene <sup>a</sup>             | <i>s</i> | 4           | −18              | −3012    | 26.64    | ...      | 18         | 17         | 2360         |
|                                  | 1        | 11          | 110              | −671     | 29.64    | 0.040    | 27         | 15         |              |
| Benzoic acid <sup>b</sup>        | <i>s</i> | 6           | 55               | −727     | 35.60    | .030     | 131        | 54         | 4140         |
|                                  | 1        | 5           | 200              | 1191     | 51.77    | .047     | 70         | 27         |              |
| Quinone <sup>c</sup>             | <i>s</i> | 12          | 60               | −656     | 28.40    | .065     | 47         | 21         | 4410         |
|                                  | 1        | 10          | 160              | 3280     | 35.00    | .044     | 49         | 18         |              |
| Hydroxy-acetanilide <sup>d</sup> | <i>s</i> | 10          | 50               | −812     | 37.78    | .117     | 209        | 68         | 5080         |
|                                  | 1        | 7           | 140              | 2740     | 59.70    | .060     | 350        | 142        |              |

<sup>a</sup> Kahlbaum, thiophene free, recrystallized twice, then distilled. The determinations on the solid were made by suspending a thermometer, and the specimen on a

linen thread, in a dry test-tube immersed in an ice-salt mixture or in ice. After an hour, the specimen was quickly transferred to the calorimeter; m. p.,  $5.40^{\circ}$  (S.,  $4.0$ – $5.7^{\circ}$ ). The most recent data for  $\Delta H_f$  are 2371 [Meyer, *Z. physik. Chem.*, **72**, 225 (1910)], 2370 [Padoa, *Atti. accad. Lincei*, [2] **28**, 239 (1919)], 2348 [Stratton and Partington, *Phil. Mag.*, **48**, 1085 (1924)] and 2384 [Maass and Waldbauer, *THIS JOURNAL*, **47**, 1 (1925)]. There are seven older values, all but two of which range from 2348 to 2394. The value provisionally selected for *Inter. Crit. Tables* (private communication from the editor, Dr. E. W. Washburn) is  $2370 \pm 26$ .

Maass and Waldbauer give values of the specific heat of solid benzene from  $-183^{\circ}$  to  $0^{\circ}$ . Equations for  $dH/dT$  recomputed to a molal basis, as given in recent papers [(a) Mills and Macrae, *J. Phys. Chem.*, **14**, 797 (1910). (b) Tréhin, *Ann. phys.*, [9] **15**, 246 (1921). (c) Williams and Daniels, *THIS JOURNAL*, **46**, 912 (1924). (d) Present paper. (e) Provisionally selected for *Inter. Crit. Tables* (private communication from the editor, Dr. E. W. Washburn)] follow.

$$\begin{array}{ll} \text{(a)} & 31.00 + 0.045t \quad (5-70^{\circ}) \\ \text{(b)} & 30.53 + .073t \quad (16-58^{\circ}) \\ \text{(c)} & 29.86 + .0511t + 0.00066t^2 \quad (30-80^{\circ}) \\ \text{(d)} & 29.64 + .080t \quad (20-110^{\circ}) \\ \text{(e)} & 31.85 - .049t + 0.0017t^2 \quad (5-90^{\circ}) \end{array}$$

The stated accuracy of (a) is about 0.5%, of (b) about 1%, of (c) about 0.2%; yet the agreement between the several formulas is less satisfactory than is desirable, as is obvious from the following table.

| $t$ | a    | b    | c    | d    | e    |
|-----|------|------|------|------|------|
| 10  | 31.4 | 31.2 | 30.4 | 30.4 | 31.5 |
| 30  | 32.3 | 32.7 | 32.0 | 32.0 | 31.9 |
| 50  | 33.2 | 34.1 | 34.1 | 33.6 | 33.7 |
| 70  | 34.1 | 35.6 | 36.7 | 35.2 | 36.6 |

We venture to believe that, if all of the several authors had published the values of  $H$ , which they actually measured, instead of merely the specific heats derived from these measurements, one would find that all of the series of values of  $H$  would be tolerably concordant; that together these would permit of a better estimate of the specific heat curve; and therefore that the original measured values of heat content should, wherever possible, be published.

<sup>b</sup> Kahlbaum, used as received; m. p.,  $121.8^{\circ}$  (S.,  $119.5$ – $121^{\circ}$ ).

<sup>c</sup> Eastman Kodak Company; steam distilled thrice, then sublimed in a vacuum once; m. p.,  $112.8$ – $112.9^{\circ}$  (B.,  $115.7^{\circ}$ ). Kurbatov [*Ann. Inst. techn. Petrograd*, **24**, 1 (1917)] gives as the mean molal specific heat between  $113^{\circ}$  and  $180^{\circ}$ ,  $57.3$  cal.

<sup>d</sup> Prepared by Miss Ruth Watts, as will be described in a forthcoming publication by R. Watts and A. J. Hill. This substance was investigated incidentally; it occurs in two crystal habits, prisms and needles, which however are identical in behavior on melting and in heat content; m. p.,  $91.3^{\circ}$ .

### Discussion of Results

The  $H-t$  graphs for the several substances are like that for pure *m*-dinitrobenzene, as illustrated in Fig. 1; but they indicate little regularity except in the curves for the solids, which in their slight upward curvature are very similar. In some cases this may be due in part to impurity which was not entirely removed; in part it is no doubt real, in accordance with the general rule that the specific heat of crystals increases with increasing temperature.

In Table XI we have brought together our values, for the several compounds investigated, of (1) the melting temperature,  $t_m$ ; (2) the molal heat of melting ( $\Delta H_f$ ) at  $t_m$ , the molal heat capacity (specific heat) as calculated from the several empirical equations previously given, (3)  $C_1$  of the liquid at  $t_m$ , (4)  $C_s$  of the solid at  $t_m$ , (5)  $C'_s$  of the solid at  $25^\circ$ .

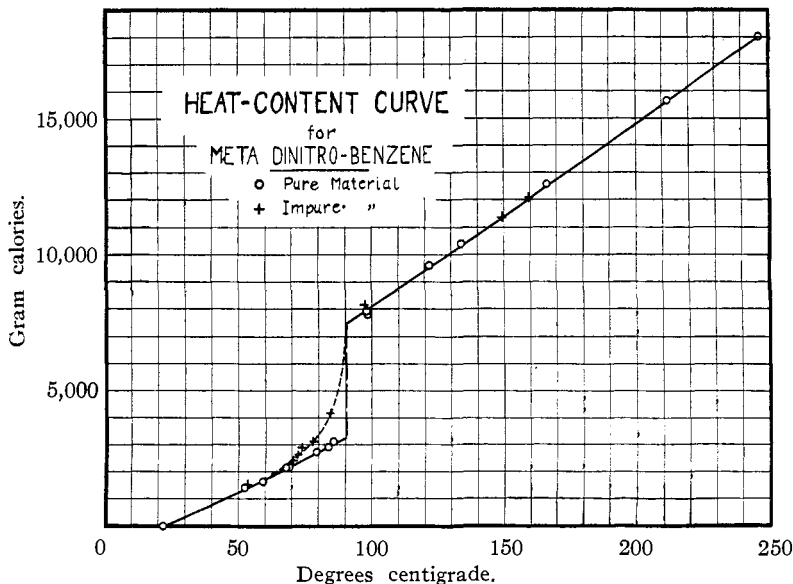


Fig. 1.

In comparing the heats of melting of the seven triads of isomeric disubstituted benzenes, we observed that: (1) for the *para* it is always higher than for the *ortho*;<sup>15</sup> (2) for the *meta* it is either lower (in the first five cases), or higher (in the two containing an  $\text{NH}_2$  group) than for both *ortho* and *para*. But there is no marked regularity between heat of melting and melting temperature, or other property measured hitherto; there may well be, however, between heat content and volume, but data on the latter are lacking.

In comparing the heat capacities at the melting temperature, we find again that both  $C_1$  and  $C_s$  for the *para* are always higher than for the *ortho*; no regularity with respect to either for the *meta*, however, is apparent. The ratio  $C_1/C_s$  for the several compounds ranges from about 1 to 1.4, the mean being about 1.2; the difference  $C_1 - C_s$  is very variable. One would expect that  $C_1$  and  $C_s$  would be most nearly alike for non-polar compounds, on the basis that the energy supplied goes to increase the distance between adjacent molecules in the liquid as in the solid; whereas with polar liquids additional heat would be required to break down the

<sup>15</sup> This is true likewise of their melting temperatures.

TABLE XI  
COMPARISON OF RESULTS ON HEAT OF MELTING AND SPECIFIC HEAT

| Substance           |          | 1      | 2            | 3              | 4              | 5             |
|---------------------|----------|--------|--------------|----------------|----------------|---------------|
|                     |          | $t_m$  | $\Delta H_f$ | $t_m$<br>$C_1$ | $t_m$<br>$C_s$ | 25°<br>$C_s'$ |
| $C_6H_4CH_3COOH$    | <i>o</i> | 103.7  | 4820         | 67.9           | 54.8           | 41.9          |
|                     | <i>m</i> | 108.75 | 3760         | 74.6           | 57.1           | 39.7          |
|                     | <i>p</i> | 179.6  | 5430         | 76.8           | 62.7           | 39.3          |
| $C_6H_4(NO_2)_2$    | <i>o</i> | 116.93 | 5460         | 65.2           | 60.2           | 46.6          |
|                     | <i>m</i> | 90.08  | 4150         | 68.2           | 51.9           | 44.7          |
|                     | <i>p</i> | 173.5  | 6720         | 66.2           | 60.1           | 45.9          |
| $C_6H_4NO_2COOH$    | <i>o</i> | 145.8  | 6690         | 67.0           | 64.9           | 45.9          |
|                     | <i>m</i> | 141.1  | 4620         | 81.3           | 65.3           | 41.4          |
|                     | <i>p</i> | 239.2  | 8820         | 75.0           | 72.6           | 43.1          |
| $C_6H_4(OH)_2$      | <i>o</i> | 104.3  | 5440         | 57.2           | 44.7           | 31.6          |
|                     | <i>m</i> | 109.7  | 5090         | 57.5           | 47.6           | 31.3          |
|                     | <i>p</i> | 172.3  | 6480         | 61.8           | 46.4           | 33.4          |
| $C_6H_4ClCOOH$      | <i>o</i> | 140.2  | 6150         | 69.2           | 54.2           | 39.0          |
|                     | <i>m</i> | 154.25 | 5700         | 64.9           | 53.9           | 39.1          |
|                     | <i>p</i> | 239.7  | 7710         | 85.7           | 58.8           | 40.1          |
| $C_6H_4NH_2COOH$    | <i>o</i> | 145.0  | 4870         | ..             | 62.0           | 39.6          |
|                     | <i>m</i> | 180.0  | 5220         | ..             | 64.9           | 38.9          |
|                     | <i>p</i> | 188.5  | 5000         | ..             | 62.2           | 42.5          |
| $C_6H_4NO_2NH_2$    | <i>o</i> | 69.3   | 3850         | 59.4           | 46.5           | 39.3          |
|                     | <i>m</i> | 111.8  | 5660         | 63.1           | 58.5           | 40.2          |
|                     | <i>p</i> | 147.5  | 5040         | 66.1           | 61.7           | 40.4          |
| Naphthalene         |          | 79.98  | 4540         | 52.5           | 51.3           | 38.1          |
| $\alpha$ -Naphthol  |          | 95.0   | 5610         | 66.6           | 54.7           | 39.9          |
| $\beta$ -Naphthol   |          | 120.6  | 4490         | 69.0           | 58.9           | 41.3          |
| Benzene             |          | 5.40   | 2360         | 30.1           | 26.6           | ..            |
| Benzoic acid        |          | 121.8  | 4140         | 63.2           | 42.9           | 37.1          |
| Quinone             |          | 112.9  | 4410         | 44.9           | 43.1           | 31.7          |
| Hydroxy-acetanilide |          | 91.3   | 5080         | 70.7           | 59.2           | 43.6          |

“associated” molecules—and consequently the disparity between  $C_1$  and  $C_s$  would be still greater—unless either the diminution of degree of association with increase of temperature, or the heat of association, is very small. For naphthalene, benzene and quinone,  $C_1/C_s$  is nearly unity, as it is likewise for *o*- and *p*-nitrobenzoic acid; whereas it is 1.4 for benzoic acid and for *p*-chlorobenzoic acid.

The heat capacities ( $C_s'$ ) of the solids at 25°, which temperature was chosen as being low enough to obviate abnormalities due to impurity, are nearly alike within the triads; moreover, the differences from one substance to another are much smaller than at the respective melting temperatures. The increase in heat capacity between 25° and the melting temperature ranges from about 5 to 29 with a mean of about 17. Some of this increase may be due to the presence of impurity, and hence be only apparent, but we believe that it cannot altogether be ascribed to this cause.

We had hoped that the data would show greater regularity than has

proved to be the case. Some further regularities might be apparent if a longer series of closely related compounds were studied and if the measurements were extended to other properties such, for instance, as the volume changes associated with change of temperature.

### Summary

Experimental results are presented on the heat of crystallization and specific heats, both as solid and as liquid, of the following substances: the *ortho*, *meta* and *para* toluic acids, dinitrobenzenes, nitrobenzoic acids, dihydroxybenzenes, chlorobenzoic acids, aminobenzoic acids, nitroanilines; naphthalene,  $\alpha$ - and  $\beta$ -naphthol, benzene, benzoic acid, quinone and hydroxy-acetanilide. The heat of melting and specific heat proved to be greater for the *para* than for the corresponding *ortho* isomer; the values for the *meta* isomer show no apparent regularity. The molal heat capacities of the several substances as solids at  $25^\circ$  lie within a narrow range of values; this is particularly true for the triads of *ortho*, *meta* and *para* isomers.

NEW HAVEN, CONNECTICUT

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

## THE SPECIFIC HEATS OF SOME ISOMERS OF THE TYPE ORTHO, META AND PARA $C_6H_4XY$ FROM $110^\circ$ to $340^\circ K.$

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RECEIVED FEBRUARY 17, 1926

PUBLISHED MAY 5, 1926

The specific heats discussed in this paper were measured primarily because they promised to be of interest in the study of the properties and reactions of the simpler derivatives of benzene from the standpoint of physical chemistry. For example, a knowledge of the values of the specific heat from room temperature down to  $100^\circ K.$ , or preferably lower, together with the heat of formation, makes possible a calculation of the free energy of formation. We may also expect the variation of the specific heat with temperature to throw light on the distribution of energy within the molecule and on the "structure," especially in the ranges where this variation represents the change of rate of energy absorption as the molecule passes from a state of little energy to the state in which we generally deal with it at room temperature. With such relations in mind some of the disubstituted derivatives of benzene have been selected for investigation, these compounds being of special interest because they have recently been studied by others.<sup>2,3</sup> It seemed important to secure enough data so

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<sup>2</sup> Narbutt, *Z. Elektrochem.*, **25**, 57 (1919). Francis and Hill, *THIS JOURNAL*, **46**, 2498 (1924). Francis, Hill and Johnston, *ibid.*, **47**, 2211 (1925). Maass and Waldbauer, *ibid.*, **47**, 7 (1925). Johnston, Andrews and Kohman, *J. Phys. Chem.*, **29**, 882, 914, 1041, 1048, 1317 (1925). Johnston and Collett, *ibid.*, **30**, 70 (1926).

<sup>3</sup> Andrews, Lynn and Johnston, *THIS JOURNAL*, **48**, 1274 (1926).