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, α- and β-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° lie within a narrow range of values; this is particularly true for the triads of *ortho*, *meta* and *para* isomers.

NEW HAVEN, CONNECTICUT

THE SPECIFIC HEATS OF SOME ISOMERS OF THE TYPE ORTHO, META AND PARA C₆H₄XY FROM 110° to 340°K.

BY DONALD H. ANDREWS[1]

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°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.[2,3] It seemed important to secure enough data so

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[2] 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).

[3] Andrews, Lynn and Johnston, THIS JOURNAL, **48**, 1274 (1926).

that eventually a number of comparisons of specific heat could be made between compounds of different structure; and for this reason, measurements of easily attainable accuracy on a fairly large number of compounds were sought rather than measurements of extreme accuracy on only one or two compounds. For this purpose a new type of calorimeter has been constructed, designed for speed of operation and large range of temperature with an accuracy of one or two per cent. With this calorimeter the specific heats of eleven compounds of the type C_6H_4XY have been measured from 110° to 340°K.

Apparatus and Procedure

The calorimeter differs from those previously employed in that the quantity of heat which goes to raise the temperature of the substance under investigation is measured by "calibrated heat conduction." The procedure is briefly as follows. The substance is placed inside a copper ball, surrounded by a layer of glass wool, through which heat is slowly conducted to it from the outside, while its temperature and the temperature gradient across the glass wool are measured at frequent intervals. By comparison of this gradient with that observed with a standard substance, the quantity of heat which in a given interval has flowed into the ball can be calculated, and from this and the rise in temperature of the substance during that interval, its heat capacity can be derived.
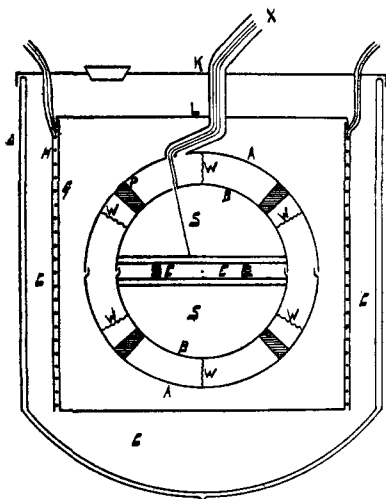

Fig. 1.—Diagram of calorimeter.

The Calorimeter.—The calorimeter is shown diagrammatically in Fig. 1. The inner copper ball B, in which the substance is placed, is made of two hemispheres (diameter 57 mm., wall thickness 0.3 mm.) which fit together at a snug slip joint at the "equator." In the space S in each hemisphere are soldered thirty vanes of thin copper radiating from the polar axis, to promote conduction and, therefore, temperature uniformity, throughout the sample. These vanes extend to a plane parallel to the equatorial plane, as indicated by the outer pair of parallel lines in the figure. The substance is packed in the cells between these vanes which are so close together that no portion of it is more than 3 mm. from a vane. Two circular covers E of thin copper fit tightly over the vanes to hold the substance in place; when the two hemispheres are in position, two springs hold these covers against the vanes. Each of the hemispheres B is rigidly supported by wooden pegs P inside a larger copper hemisphere A (diameter 77 mm.) so that when the inner ones are fitted together the outer ones also fit in a slip joint. Between the inner and outer spheres the space is loosely packed with glass wool, constituting a region of low heat conductivity, both uniform and constant. When in position for measurement the two halves of this double-walled ball are bound together with adhesive

tape and copper wire and packed inside the can C with copper wool. The can is a cylinder of copper sheeting, fitted with a bottom and a loose cover L; a 100-ohm heating coil of constantan is wound on it. It also is packed with copper wool in a Dewar jar D which has a loose cover K with a hole through which liquid air can be poured into the copper wool between C and D, to cool the whole system.

The Temperature Measuring System.—To measure the temperature difference between the inner and outer copper shells, there are six constantan wires W forming six parallel circuits between A and B which are connected by the copper wires X to a White double potentiometer. The temperature inside the inner shell is observed by means of a pair of constantan wires, soldered to the axis of the vanes and coming out to the customary ice junctions, thus forming with the copper wire from the inner shell a pair of thermocouples. These wires are brought out in rubber tubes for mechanical protection. The whole system is shielded against electrical leaks. The constantan wire for the thermocouples, which was taken from a spool of No. 30 Ideal wire, found to be of exceptionally good quality,[4] was tested for uniformity by passing through liquid air; its temperature scale is based on a calibration against the Eastman-Rodebush standard thermocouple[5] and is considered correct to 0.1°.

Procedure.—The accuracy of the measurements depends largely on the proper manipulation of the calorimeter. The two hemispheres, loaded with a weighed quantity (35 to 50 g.) of the organic compound, are wrapped together and packed in place. Liquid air is slowly poured in through the hole in the cover until the Dewar jar and contents are at about 80°K. A current of one ampere is then passed through the heating coil and finally adjusted so that the temperature difference between the inner and outer shells is 500 microvolts; by careful regulation it proved to be possible to keep this difference constant to within 0.3 microvolt (roughly, 0.01°) for the entire run. The thermocouple at the center of the ball is now connected to the potentiometer and the latter regulated so that the cross hair of the galvanometer telescope starts at one end of the scale, and gradually moves toward the center as the temperature rises. At the instant the cross hair passes the center of the scale, a stopwatch is started; then at one-minute intervals for ten minutes the temperature difference across the glass wool between the two shells is read. Before the eleventh minute the system is switched back to the thermocouple at the center with appropriate change in the potentiometer dials, and the stopwatch stopped when the cross hair again crosses the center. Finally, readings against a "check" coil are made to correct for change of zero point.

The temperature rose on the average 250 microvolts (roughly, 10°) in ten minutes, so that a complete run over the whole temperature range took about five hours. The lower limit of the range depends on the time necessary to attain a "steady state" of constant temperature gradient after the rise from 80°K. begins; this steady state seemed to be reached at about 110°K. The upper limit depends only on the melting point of the material investigated; for this series of compounds 340° seemed high

[4] Randall and Vanselow, THIS JOURNAL, 46, 2425 (1924).

[5] Eastman and Rodebush, ibid., 40, 489 (1918).

enough, but there is no reason why the calorimeter cannot be used up to temperatures at which the condition of some of the materials of which it is composed (for example, solder or glass wool) begins to be permanently affected.

Calculation and Calibration.—The actual experimental data are in the form of the rise in temperature, Δ microvolts (for instance, 259.90), which takes place in the time interval, t (626.0) seconds, during which the temperature difference (head) between the outer and inner copper shells is φ (498.82) microvolts; θ (3400 microvolts below 0°C.) is the mean temperature of the substance during the observation and w (50.042) the weight of the substance in grams. Consequently, for the figures given, $\varphi t/\Delta$ $= Q = 120.07$, this quantity Q being proportional to the total heat capacity of the inner shell and its contents; for if k be the number of calories per second per microvolt of head that pass through the glass wool layer at the temperature θ, then $kt\varphi$ is the number of calories that have passed into the inner shell during the measurement.[6] If, at θ, $1/E$ is the number of degrees per microvolt, then kEQ is the total heat capacity of the inner shell and contents. But this may also be expressed as $a + wc_p$, where a is the effective heat capacity of the calorimeter shell and c_p the specific heat of the substance. Thus

$$kEQ = a + wc_p \tag{1}$$

Now the variation of k and $1/E$ with temperature is regular enough so that our experimental values of Q plotted against θ give a smooth curve from which by interpolation we can find Q at any desired temperature; examples of such curves for p-nitro-aniline and for lead are given in Fig. 2. We may write Equation 1 in the form

$$Q = \frac{a}{kE} + \frac{c_p}{kE}w \tag{2}$$

and see that at constant temperature, k, E, a and c_p being, therefore, constant, Q should be a linear function of w, the weight of the substance taken.

This relation was shown to be true experimentally by making a series of runs with weights of nitro-aniline ranging from 25 to 50 g., interpolating from the smooth curves, for a given θ, values of Q and plotting these against the corresponding values of w. Such graphs, made for values of θ at 500-microvolt intervals from 5000 below to 3000 microvolts above 0°C., proved to be a series of straight lines; from these the number of grams of nitroaniline corresponding to any value of Q at any temperature can be read. Identical experiments with a substance of known specific heat (lead,[7] in this instance, in quantity ranging from 250 to 450 g.) yielded an analo-

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[6] This is not strictly true because the glass wool has an appreciable heat capacity which, however, is small enough to make the relation sufficiently accurate for the range in which we require it. The change of k and E with the temperature in the range of an observation is so small that it may be neglected.

[7] As given by Eucken, *Ber. physik. Ges.*, **15**, 503 (1913).

gous series of straight lines. These lines serve to calibrate the calorimetric set-up; for if, at a given temperature, w_b g. of nitro-aniline of specific heat c_b give the same value of Q as w_a g. of lead of specific heat c_a, it follows from Equation 1 that

$$w_b c_b = w_a c_a \qquad (3)$$

since k, a and E are identical in both cases. Thus, the calculation of c_b at θ' consists in reading from the appropriate $Q-w_b$ line that value of w_b which would give the same value of Q as was observed when the calorimeter was loaded with w_a g. of the standard substance. This process was repeated for each of the charges w_a and the resulting values of c_a at θ' were averaged.
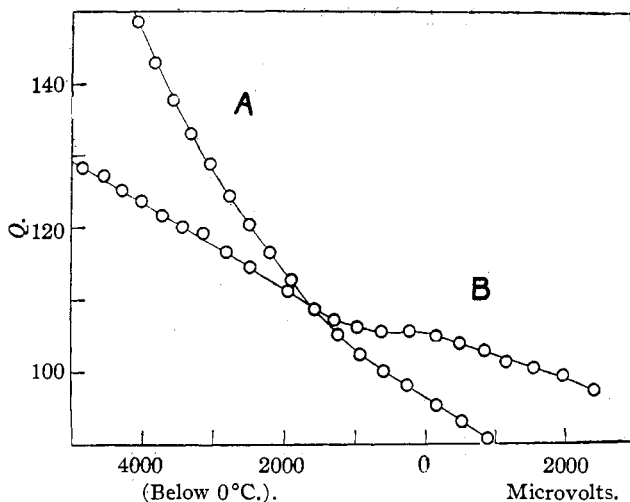

Fig. 2.—The circles represent experimentally secured values of Q for (A) lead and (B) p-nitro-aniline.

Perhaps the most obvious source of uncertainty in the method is lack of uniformity of temperature of the substance owing to its poor thermal conductivity. There is no direct and sure way to ascertain how large this is; but a calculation[8] from the data available indicates that it can be

[8] Substances of the type C₆H₄XY generally have a thermal conductivity of 0.0003 cal./cm. deg. sec. Assuming the value for the packed mass of crystals to be one-tenth of this, the difference in temperature between the center and the outside of one of the cells would be 3° at the constant rate of heating employed, namely 1° per minute. This rate of heating never changes by more than 0.01% during an observation so that the temperature gradient is extremely constant and can scarcely affect measurement of rise in temperature of the mass as a whole. For example, if the outside of the shell changes from 200.00° to 210.00° in ten minutes, the inside must have changed from 197.00° to 207.00°. The rise in temperature, 10.00°, is unchanged but the mean temperature is about 204° instead of 205°, the exact difference depending on the shape of the cell. This introduces an error of 0.1 cal. per degree in the molal heat capacity, which is negligible.

neglected, and the way in which the results agree among themselves and with the results secured by other calorimetric methods confirms this view. Errors due to changes in the constants of the apparatus were guarded against by frequent calibration; the value of k showed a regular increase of about 2% in a month.

Another common source of error in specific-heat work is impurity in the materials. The error introduced because the specific heat of the impurity is different from that of the pure substance is quite negligible when, as is the case here, the impurity is of the same nature as the substance in which it occurs; but, on the other hand, above the eutectic temperature of the impurity and the compound, partial melting takes place and the inclusion of part of the heat of fusion in the specific heat produces a very large error.[3] Consequently, it is extremely difficult to secure isomers pure enough to give reliable results near the melting point, though at lower temperatures even 1% or more of impurity is permissible. For these reasons Kahlbaum products, without purification, were judged satisfactory for this research. Melting curves indicated the impurity to be less than 0.5% and the specific-heat curves confirm this.

TABLE I

MOLAL HEAT CAPACITIES OF THE NITRO-ANILINES

Temp., ° K.	Cal. per degree			
	ortho	meta	para[a]	Calcd.[b]
110.3	17.1	17.5	17.2	17.0
131.6	19.5	19.8	19.6	19.6
151.3	21.9	22.1	22.0	22.1
169.6	23.9	24.3	24.3	24.3
186.6	25.9	26.3	26.2	26.4
202.7	27.7	28.1	28.3	28.4
218.0	29.9	30.0	30.3	30.2
232.6	31.7	32.1	32.1	32.0
246.6	33.5	34.0	33.8	33.8
260.1	35.5	35.8	35.6	35.4
273.1	37.0	37.3	37.0	37.0
285.7	38.6	38.6	38.3	38.6
297.9	40.2	40.0	39.6	40.1
L	39.3	40.1	40.4	
309.7	42.0	41.7	41.9	41.5
321.2	45.2	43.6	43.1	42.9
L	43.1	45.1	44.4	
332.5	53.4	46.0	44.6	44.3
L	44.9	47.5	46.3	
343.7		48.5	46.3	45.7
L		49.8	48.3	

[a] An average of the values calculated from seven runs with p-nitro-aniline calibrated against five runs with lead.

[b] Calculated from the equation obtained from a "least-squares" solution of the p-nitro-aniline values from 110.3° to 321.2°K.

$$C_p = 3.5 + 0.1229 \, T$$

The experimental results, in terms of molal heat capacity, are presented in Tables I, II, III and IV.   The graph of these series is surprisingly linear, as is shown by comparison of the values computed from a least-squares linear solution with the experimental and by Figs. 3 and 4.   For instance, for p-nitro-aniline the average difference between the calculated and observed values is 0.5%, the largest being 1.2%.

TABLE II

MOLAL HEAT CAPACITIES OF THE NITROBENZOIC ACIDS

| | Calories per degree | | | | | |
| Temp., °K. | ortho | | meta | | para | |
	Obs.	Calcd.[a]	Obs.	Calcd.[a]	Obs	Calcd.[a]
110.3	20.2	19.9	19.7	19.7	20.5	20.2
131.6	23.0	22.8	22.4	22.3	22.9	22.9
151.3	25.7	25.5	25.0	24.8	25.5	25.4
169.6	28.1	28.0	27.4	27.2	27.9	27.7
186.6	30.2	30.4	29.3	29.3	29.7	29.8
202.7	32.1	32.6	30.9	31.4	31.6	31.9
218.0	34.3	34.7	33.3	33.3	33.6	33.8
232.6	36.1	36.7	35.0	35.1	35.4	35.7
246.6	38.3	38.7	36.4	36.9	36.7	37.4
260.1	41.6	40.5	38.8	38.6	39.1	39.1
273.1	42.9	42.3	40.4	40.2	40.9	40.8
285.7	44.2	44.0	41.8	41.8	42.5	42.4
297.9	45.4	45.7	43.0	43.4	43.7	43.9
L	45.9		41.4		43.1	
309.7	47.7	47.4	45.3	44.9	45.8	45.4
321.2	48.7	48.9	46.5	46.3	47.3	46.9
L	49.5		46.2		46.3	
332.5	50.0	50.5	48.0	47.8	49.2	48.3
L	51.3		48.5		47.8	
343.7	51.5	52.0	50.0	49.2	51.3	49.7
L	53.0		50.8		49.4	

[a] The calculated values were secured with the help of the following equations derived from "least-squares" solutions of the observed values 110.3° to 321.2°K. $ortho$: $C_p = 4.7 + 0.1377T$; $meta$: $C_p = 5.7 + 0.1265T$; $para$: $C_p = 6.2 + 0.1266T$.

TABLE III

MOLAL HEAT CAPACITIES OF THE DIHYDROXYBENZENES[a]

| | Calories per degree | | | | | |
| Temp., °K. | ortho | | meta | | para | |
	Obs.	Calcd.[b]	Obs.	Calcd.[b]	Obs.	Calcd.[b]
110.3	13.3	13.1	12.7	13.0	12.5	12.2
Lange[c]					12.9	
131.6	15.4	15.4	14.6	15.0	14.5	14.4
151.3	17.6	17.5	16.6	16.9	16.6	16.6
169.6	19.5	19.5	18.3	18.7	18.7	18.5
186.6	21.2	21.3	20.0	20.3	20.1	20.3
202.7	22.9	23.1	21.6	21.9	21.8	22.0
218.0	24.7	24.7	23.2	23.4	23.4	23.6
232.6	26.2	26.3	24.5	24.8	24.8	25.2

TABLE III (*Concluded*)

Temp., °K.	ortho		meta		para	
	Obs.	Calcd.b	Obs.	Calcd.b	Obs.	Calcd.b
Lange					25.8	
246.6	27.6	27.8	25.7	26.1	26.2	26.6
260.1	29.3	29.2	27.7	27.4	28.2	28.1
273.1	30.7	30.6	29.1	28.7	29.8	29.5
Lange					30.2	
285.7	32.0	32.0	30.3	29.9	31.0	30.8
297.9	33.1	33.3	31.4	31.1	31.9	32.1
L	31.5		31.3		33.4	
309.7	34.9	34.6	33.1	32.2	33.6	33.3
321.2	35.7	35.8	34.1	33.3	34.7	34.5
L	35.4		35.8		35.4	
332.5	36.7	37.0	35.7	34.4	35.3	35.7
L	37.3		37.9		36.4	
343.7	37.5	38.2	37.8	35.5	36.2	36.9
L	39.1		40.1		37.4	

[a] ortho = catechol, meta = resorcinol, para = hydroquinol.

[b] Calculated from "least-squares" solutions of the observed values from 110.3° to 321.2°K. ortho: $C_p = 1.3 + 0.1074T$; meta: $C_p = 2.3 + 0.0966T$; para: $C_p = 0.6 + 0.1058T$.

[c] Derived by graphical interpolation from Lange's values.[11]

TABLE IV

MOLAL HEAT CAPACITIES OF o- AND m-DINITROBENZENES

Temp., °K.	ortho		meta	
	Obs.	Calcd.a	Obs.	Calcd.a
110.3	20.6	20.7	21.0	21.3
131.6	23.3	23.4	23.9	24.0
151.3	26.2	25.9	26.7	26.6
169.6	28.6	28.3	29.2	28.9
186.6	30.6	30.4	31.3	31.1
202.7	32.3	32.5	33.3	33.2
218.0	34.1	34.4	35.4	35.2
232.6	36.8	36.3	37.2	37.1
246.6	37.5	38.1	38.5	38.8
260.1	39.5	39.8	40.5	40.6
273.1	41.5	41.5	42.3	42.0
285.7	43.2	43.1	43.9	43.9
297.9	44.5	44.6	45.0	45.5
L	46.6		44.7	
309.7	46.1	46.1	47.2	47.0
321.2	47.9	47.6	48.7	48.5
L	50.0		47.2	
332.5	48.9	49.0		49.9
L	51.7		48.4	
343.7	51.4	50.4		51.4
L	53.3		49.7	

[a] Calculated from "least-squares" solutions of the observed values from 110.3° to 321.2°K. ortho: $C_p = 6.7 + 0.1274T$; meta: $C_p = 7.1 + 0.1289T$.

The reliability of these measurements is corroborated by comparison of the results with those obtained by the method of mixtures, presented in the preceding paper;[3] values calculated from the expressions given there are included in the tables, being designated L. The present values are somewhat smaller than the previous data;[9] this difference may be due, largely or entirely, to a lack of consistency between the specific heat of the lead and silver used as standards, and in any case is no greater than
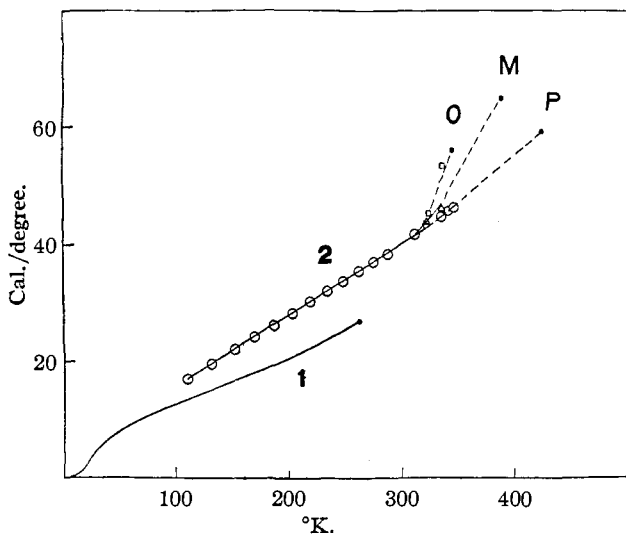

Fig. 3.—Molal heat capacity of benzene (1) and the nitro-anilines (2) Experimental points: ○ *para*
△ *meta* ⎱ (points below 310°
□ *ortho* ⎰ coincide with *para*)
● melting temperatures
The solid line through the circles represents the equation secured by the "least-squares" solution of the values for *p*-nitro-aniline. The values for *o*- and *m*-nitro-aniline are also represented by this line.   The broken lines represent the equations of Andrews, Lynn and Johnston, based on experiments from 320°K. to the melting points shown as large dots.

the differences observed by different investigators using the same method.[10] A check on the accuracy of the work at low temperatures is provided by measurements of Lange[11] on hydroquinone, secured by means of a calorimeter, of the Nernst-Eucken type, suspended in a vacuum and heated with a measured quantity of electrical energy; his results, as shown by Fig. 4,

[9] The main exception is *o*-nitro-aniline which is near its melting point and may not have been pure.
[10] Ref. 3, p. 1280. and also p. 1278 with reference to silver.
[11] Lange, Z. *physik. Chem.*, 110, 351 (1924).

average about 0.5 cal. higher than the author's, both at 110° and 273°K. These comparisons indicate that the accuracy of the method is of the order of 0.5 cal. per degree.
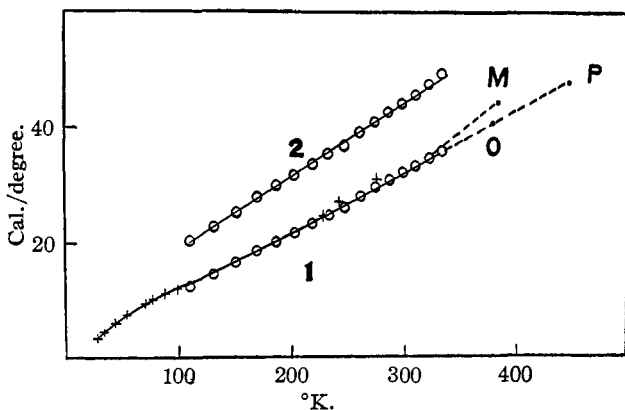

Fig. 4.—The heat capacities of the dihydroxybenzenes (1) and the nitrobenzoic acids (2). Experimental points for *para:* O—Author. +—F. Lange. ●—Melting temperatures. Dotted lines represent the equations of Andrews, Lynn and Johnston. For both substances the values for the *ortho* and *meta* forms are very nearly coincident with the above curves below 320°K.

Conclusions

According to the results, there is very little difference between the heat capacities of the *ortho, meta* and *para* isomers of a given compound from a point 30° below the melting point of the lowest melting isomer, to the lower limit of the investigation, 110°K. If future work shows, as is quite probable, that the heat-capacity curves are similarly coincident from 110° to 10°K. we may conclude that the entropies of the *ortho, meta* and *para* isomers are very nearly equal. The heats of combustion[12] do not differ by more than 1% in the *ortho, meta* and *para* groups investigated, so there is presumably little difference in the heats of formation. Consequently, it seems unlikely that the difference in structure between the *ortho, meta* and *para* isomers causes appreciable difference in the free energy of formation.

The small difference between the heat capacities of the nitrobenzoic acids and dinitrobenzenes is also worth noting. The agreement of the curve for *p*-nitrobenzoic acid[13] with the curve for *o*-dinitrobenzene is

[12] Landolt-Börnstein-Roth, "Tabellen," heats of combustion for the dihydroxybenzenes, dinitrobenzenes and nitrobenzoic acids.

[13] The upper part of the curve for *o*-nitrobenzoic acid shows a break at 260°K. and values above that temperature lie about 3% above the *para* and *meta* curves. *p*-Dinitrobenzene was not available in quantity sufficient for measurements of heat capacity.

strikingly close. The equations are $c_p = 6.2 + 0.1266T$ and $c_p = 6.7 + 0.1274T$, respectively. The slopes of the corresponding *meta* curves have about the same value, 0.1265 and 0.1289, respectively and the intercepts are 5.7 and 7.1. This resemblance is not surprising because the two sets of compounds are quite alike in many ways; the carboxyl group has about the same electrical character and molecular weight as the nitro group. The curve which represents the three nitro-anilines has a slightly smaller slope and intercept, $0.1229T + 3.5$, as might be expected.

The curve for the *p*-dihydroxybenzene, extended by Lange's measurements, covers the largest range of temperature; it shows a close resemblance to benzene as may be seen in Table V, which contains values of the differences between the molal heat capacities of the two substances. For these compounds the molal heat capacity is apparently not the sum of the heat capacities of the individual atoms.

TABLE V

THE DIFFERENCE BETWEEN THE MOLAL HEAT CAPACITY OF *p*-DIHYDROXYBENZENE,[a]
C_1 AND OF BENZENE, C_2

Temp., °K.	30	40	60	80	100	120	140
$C_1 - C_2$, cal./degree	−0.9	−1.2	−0.8	−0.7	−0.8	−0.5	−0.3

°K.	160	180	200	220	240	260
$C_1 - C_2$	+0.3	+0.7	+1.3	+1.2	−0.1	−0.9

[a] Interpolated from Lange's values[11] from 30° to 100° and the author's values from 120° to 260°. The values for benzene are Nernst's (Ref. 14).

With regard to the distribution of energy within the molecule, there are as yet hardly sufficient data to make possible a thorough study of the number of degrees of freedom in a molecule or of the temperatures at which the degrees of freedom absorb energy. In a general way the fact that the melting points of a group of isomers differ by 100° while the specific heats are essentially the same implies that the forces binding the molecules together are not affecting the mechanism which is absorbing energy. The relation which appears to be true for the isomers, namely that the specific heat is a linear function of the temperature over a fairly large range, seems to be true also for the few organic compounds which have been measured by other investigators.[14] It appears to be a characteristic of the carbon to carbon bond. These relations are now being studied in the light of the quantum theory and in a later paper it will be shown that the general

[14] Benzene (see Fig. 3), reported by Nernst, *Ann. Physik*, **36**, 395 (1911). Acetone, Maass and Waldbauer (Ref. 2). (Their graphs for benzene and methyl alcohol are not straight lines for any very large range.) Formic acid and urea, Gibson, Latimer and Parks, THIS JOURNAL, **42**, 1533 (1920). Glycerol, Gibson and Giauque, *ibid.*, **45**, 93 (1923). Ethyl alcohol, Gibson, Parks and Latimer, *ibid.*, **42**, 1542 (1920). Methyl, ethyl and butyl alcohol, Parks, *ibid.*, **47**, 338 (1925). Grape sugar, Simon, *Ann. Physik*, [4] **68**, 241 (1922). Dihalogen compounds of benzene, Narbutt.[2] Quinone and quinhydrone, Fritz Lange, *Z. physik. Chem.*, **110**, 351 (1924).

course of the specific-heat curve for nearly all the organic solids ever measured, can be predicted from the degrees of freedom and the frequencies of vibration of the different atoms, as calculated from band spectra and melting points.

These are some of the questions on which it is hoped further measurements will throw more light. At present the specific heats of the nitroanilines are being measured from 110° to 2°K. in order to get more complete knowledge of the typical curve; it is hoped that when this is done the work with the conduction calorimeter may be extended to a larger number of compounds.

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Summary

1. A new type of calorimeter has been constructed employing the method of calibrated heat conduction, which in simplicity, speed of manipulation and range of temperature appears to be an improvement over previous methods where an accuracy within one or two per cent. suffices.

2. The specific heats of eleven isomers of the type ortho, meta and para C_6H_4XY have been measured from 110° to 340°K.

3. The specific heat seems to be a linear function of the temperature from 110° to about 320°K. and is but slightly changed by the difference in structure between the ortho, meta and para isomers.

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NOTES

The Mechanism of Ammonia Synthesis in Low-Voltage Arcs.— The formation of ammonia from gaseous mixtures of nitrogen and hydrogen by means of slowly moving electrons was studied by Storch and Olson.[1] They determined the rate of the reaction by pressure methods and the products of the reaction by chemical indicators. From their experiments ammonia forms when the applied potential is 17 volts, the rate of formation then remains constant until the potential reaches 23 volts, at which point an abrupt increase in ammonia synthesis occurs.

Recently Kwei[2] published a spectroscopic study of low-voltage arcs in nitrogen-hydrogen mixtures. He detected the ammonia bands at 23 volts, thus confirming Storch and Olson's second point, but failed to notice these bands at the 17-volt stage. Kwei advances the following two explanations of the discrepancy: (1) associated molecules are formed as the

[1] Storch and Olson, THIS JOURNAL, **45**, 1605 (1923).

[2] Kwei, Phys. Rev., **26**, 537 (1925).