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THE SPECIFIC HEATS AND LATENT HEATS OF FUSION OF ICE AND OF SEVERAL ORGANIC COMPOUNDS

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Introduction

In the case of compounds containing elements which form exceptions to Dulong and Petit's law, Kopp's law has been applied by making use of the abnormal values, on the assumption that, over the same temperature range, this abnormal value is approximately constant. Nernst and others have pointed out that this procedure is not justified, inasmuch as the constitution of the molecule plays a part in governing the molecular heat. One would expect the effect of constitution to be most pronounced over the range of temperature where a large variation of atomic heat with the temperature takes place. From this point of view, an investigation was started to determine the specific heats of compounds containing oxygen, hydrogen and carbon, over the temperature range —180° to 0°.

The method, which incidentally enables one to determine the latent heats of fusion of low-melting compounds, may be briefly outlined as follows.

Fifteen to twenty g. of the compound to be investigated was sealed into a platinum vessel (the container). Temperature baths, which could be kept constant at any temperature in the range —180° to 0°, were used to bring the container and its contents to any desired temperature within the above range. The container was then transferred into an adiabatic calorimeter, and the total heat taken up from the initial temperature to the

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[1] This article is an abstract of a thesis presented by L. J. Waldbauer to the Faculty of Graduate Studies and Research of McGill University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy in May, 1923.

final temperature, 16.5°, measured. The empty container was put through the same procedure, and by a subtraction, the heat content over this temperature range, per gram of substance, was calculated. The initial temperature was varied, and the results were plotted in a curve, the first derivative of which gives the specific heats. If the compound melts below 16.5°, the latent heat of fusion is obtained directly from the heat-content curve. The compounds investigated so far are water, benzene, methyl alcohol, acetone, phenol, *p*-xylene, naphthalene and benzophenone.

Experimental Method

A platinum crucible was spun into the form of a cylinder having a capacity of 20 cc. and the cover affixed with gold solder. A small, threaded platinum tube of 4mm. diameter formed the sole opening of the vessel; this could be closed by a tight-fitting screw plug, also made of platinum. Two platinum vanes, forming a cross, were placed in the vessel to aid in heat conduction. The container was dried in a vacuum each time before it was filled. To insure a perfectly gas-tight seal, the bottom of the container was brought into contact with solid carbon dioxide and at the same time the top of the filling tube was warmed and a few milligrams of de Khotinsky cement applied to the top of the screw thread.

The container, attached to a silk thread with a cork at the other end, was placed in a tightly-fitting brass tube closed at one end. Immediately above the container were placed two copper disks with wool between them. The temperature baths which were employed have been described in detail elsewhere.[2] Ether and solid carbon dioxide were used in the range 0° to —78.2°; the lowest-boiling fraction of petroleum ether, and liquid air were used for the range below —78.2°. For the lowest temperature liquid air was employed as the bath liquid.[3] A platinum thermometer, calibrated by the United States Bureau of Standards, was used to measure the temperature of the bath.

An adiabatic calorimeter was used, the copper calorimeter vessel having a capacity of 1300 cc. The calorimeter liquid was stirred by the up- and-down motion of a disk. The outer bath contained 10 liters of water. Considerable attention was paid to the stirring of the latter. Four stirrers, each with two pairs of propeller blades, were arranged so that two neighboring stirrers rotated in one direction and two in the other. A multiple thermel was placed in the bath and calorimeter and the usual precautions[4] were taken to ensure its proper working. It was used throughout as a null instrument. By the addition of hot or cold water, the outer bath was kept at the same temperature as the inner within 0.0005°. During the

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[2] Maass and Wright, This Journal, **43**, 1099 (1921).

[3] The liquid air was obtained from L'Air Liquid Cie., and contained a large excess of oxygen, its boiling point varying between —182.9° and —183.7°.

[4] White, This Journal, **36**, 2292 (1914).

short periods when large temperature changes were taking place in the calorimeter, it was possible to keep the temperature difference within 0.01°. The temperature was measured by means of a Beckmann thermometer (calibrated by the Bureau of Standards) placed in the outer bath.

The pre-cooled container was kept for an hour or longer at the desired temperature in a constant-temperature bath. It was then transferred into the calorimeter vessel. This transfer could be carried out within a few seconds. As soon as the container was pulled out of its brass jacket, the disks and wool fell off. The cork attached to the silk thread was thicker at the top, to fit the tube which led to the calorimeter and which was considerably wider than the container. The length of silk thread had been so chosen that the container was suspended in the center of the calorimeter liquid. The heat gain of the container during transfer is negligible; moreover, the empty container underwent the same treatment and any such gain would be compensated for, as shown in the following sample calculation.

Calorimeter temperature	initial 4.450°; final 2.294°
Correction for standard	—0.002°; —0.005°
Temperature change of calorimeter	2.159°
Setting factor for Beckmann	0.9985
Weight of water	840.0 g.
Heat equivalent of calorimeter vessel, stirrer and thermel	2453 cal. per deg.
Calorimeter heat change	1863.7 cal.
Temperature of container	initial —183.6°; final 17.489°
Heat change of empty container	186.4 cal.
Heat taken up by container contents	1677.3 cal.
Weight of acetone	15.747 g.
Heat taken up per g. of acetone between —183.6° and 17.5°	106.58 cal.
Specific heat of liquid acetone	0.53 cal. per degree
Heat taken up per g. of acetone between —183.6° and 16.5°	106.05 cal.

The calculation is self-explanatory and it will be seen from it how the heat change is always calculated to the same end temperature. The values for the total heat change, given in Table I, are the mean of three or four determinations which agreed with one another to within 0.2% and, in the case of water, where the temperature change in the calorimeter was much larger, to within 0.1%. The range in temperature in the calorimeter lay between 21° and 16°. The specific heat of water was taken as unity in this range.

Experimental Results

In Table I, the first column gives the initial temperature of the container; the other columns represent the heat (*H*) which must be added in order to heat 1 g. of substance from the initial temperature to 16.5°.

Water.—In the case of water, these values are plotted in Curve I, Fig. 1. It was found that, starting with the value —41.8°, this and the

TABLE I

HEAT CONTENT PER GRAM OF SUBSTANCE, IN CALORIES

Initial temp. °C.	Water	Methyl alcohol	Benzene	Acetone
6			4.30	
0			36.74	
− 3.18	97.50			
− 10.0			40.37	
− 28.6	109.37			
− 38.0			50.02	
− 58.2	122.06			
− 60.0			56.06	
− 78.2	129.86	52.18	61.49	46.07
− 90.0		59.33		53.35
−104.0		85.79		82.26
−110.0	141.25			
−135.5		106.26		93.44
−138.7	149.46			
−182.7	158.16			
−183.3			81.46	
−183.4		121.48		
−183.6				106.06

lower values can be represented by the empirical expression: $H = 95.84 - 0.485t - 0.000457t^2 + 0.00000182t^3$. Obviously, the specific heat, c, is given by $-dH/dT$, so that $c = 0.485 + 0.000914t - 0.00000546t^2$. Table II, Col. 2, gives the specific heats calculated for various temperatures from this expression, with the exception of the first few values, which were found

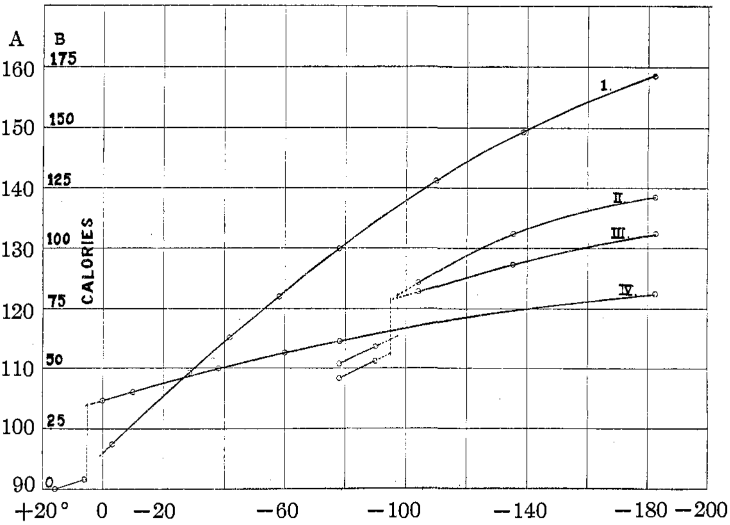

Fig. 1.

by drawing the tangents to the heat-absorption curve, plotted on a very large scale.

Table II

Specific Heats of Ice

Temperature °C.	Calculated (this Lab.)	Dickinson and Osborne	Nernst	Nernst: calculated
0	0.485	0.5057	...	0.622
− 10	.475	.4871	0.533	.532
− 20	.465	.4684	.478	.475
− 30	.453	.4498	.451	.440
− 40	.440	.4312	..	..
− 50	.426	...	.410	.404
− 60	.411	...	..	..
− 70	.394	...	.374	.378
− 80	.377	...	.367	.349
−100	.339	...	..	..
−110	.319	...	.309	.302
−120	.297	...	..	..
−140	.250	...	.277	.260
−160	.199	...	..	..
−170	.172	...	.214	.217
−180	.144	...	.199	.201

Col. 3 gives the values found by Dickinson and Osborne,[5] Col. 4 the values found by Nernst,[6] and Col. 5, the values calculated by Nernst. In Fig. 2, the curve represents the values given in Col. 2. Dickinson and Osborne's values are represented by the dotted line. The values obtained by Nernst are represented by circles.

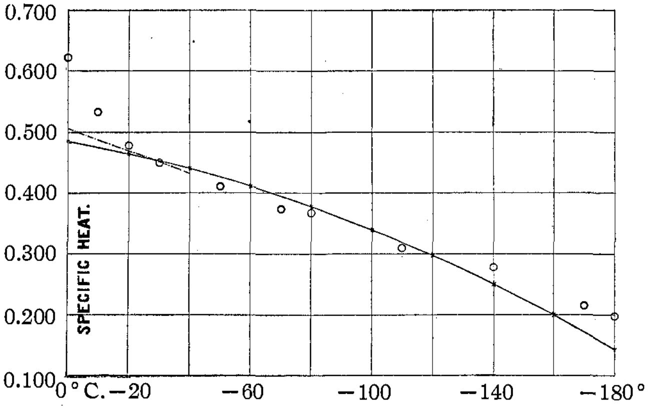

Fig. 2.

In comparing the values in Table II, it may be advisable to point out

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[5] U. S. Bur. Standards, *Sci. Paper,* **248** (1915).

[6] Nernst, "Theory of the Solid State," University of London, **1914**, p. 90.

first of all what the authors consider to be an essential feature of the experimental method. It is difficult to obtain a substance absolutely pure, and the slightest amount of impurity will involve a large error in the specific-heat determination, where the method used is such that the final temperature lies at, or a little below, the melting point. The presence of a slight amount of impurity will cause some of the solid to melt before the melting point is reached. This will cause a negligible error, from the point of view of the change of the specific heat of the material, provided that the amount is very small, but on account of the latent heat of fusion (which is large) the apparent value of the specific heat will be greatly affected near the melting point. This source of error disappears in the method described above, since the latent heat of fusion of all the ice enters into each determination, and cancels out, provided no ice is molten at the initial temperature.

Dickinson and Osborne, who laid great stress on the purification of the water, obtained values agreeing within less than 2% with those obtained by the present authors. Their values are slightly higher near the melting point. Their investigation covered only a small temperature range.

The extraordinarily high values obtained by Nernst near the melting point are probably due to the error pointed out above. If this is so, the calculated values for the specific heat given in the last column are obviously not in agreement with the experimental facts, although the hypothesis of the structure of crystalline water, upon which it has been based, has been substantiated by X-ray analysis.[7]

The values given in the literature, for the latent heat of fusion of ice, vary from 80.03 to 79.24 calories per gram. Using the values obtained by Barnes,[8] for the specific heat of water, 16.58 calories are required to heat 1 g. of water from 0° to 16.5°. As has already been mentioned, the empirical equation does not represent the heat-content curve accurately, at the higher temperatures. The value at —3.18°, for instance, which was determined with particular accuracy, since the Beckmann thermometer could be used for the initial temperature, has a value of 97.50 calories, whereas the equation gives 97.37 calories. Hence the graph was used to determine the ordinate at 0°, and from this a value of 96.00 calories was obtained. It follows that the latent heat of fusion, calculated from these determinations, is 79.42 calories. This is 0.4% lower than that obtained by Dickinson and Osborne.

Methyl Alcohol, free from formaldehyde and acetone, melting at —97°, was examined. In this case, the container held 15 g. of substance. The values given in Table I, are plotted in graphic form in Fig. 1, Curve

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[7] St. John, *Proc. Nat. Acad. Sci.*, **4**, 193 (1919). Bragg, *Proc. Phys. Soc. London*, **34**, 98 (1922).

[8] Barnes, *Phil. Trans.*, **199**, 110 (1902).

II, and the latent heat of fusion can be read directly from the curve. The value thus found is 16.40 cals. The specific heat of the solid was measured by drawing tangents to the heat-capacity curve, plotted on a large scale. These values are tabulated in Table III, Col. 2.

TABLE III

SPECIFIC HEATS OF METHYL ALCOHOL, BENZENE AND ACETONE

Temperature °C.	Methyl alcohol	Benzene	Acetone
0	..	0.362	..
− 20	..	.356	..
− 40	..	.336	..
− 60	..	.298	..
− 80	..	.261	..
−100	0.79	.225	0.40
−120	.65	.192	.36
−140	.49	.170	.31
−160	.30	.155	.28
−180	.17	.133	.21

To estimate the average heat capacity over the range —78.2° to —183.6°, the heat-capacity curve was extrapolated to —78.2° and the difference in the ordinates calculated. The extrapolated curve gave a reading of 71.7 calories at this temperature.

Benzene.—Thiophene-free benzene was recrystallized by freezing out about seven-eighths by weight, pouring off the supernatant liquid, melting and repeating the operation. After six such recrystallizations, the melting point was found to be 5.49° and the benzene was then dried over metallic sodium for several days; 15.5 g. was used in filling the container. The heat capacities are given in Table I, and shown graphically in Fig. 1, Curve IV.

From the curve, the latent heat of fusion is found to be 30.56 calories. According to Nernst,[9] the freezing-point constant for benzene is 4900, as determined from molecular weights. From previously determined values of the latent heat, the freezing-point constant for benzene is 5100. Using the value found in this investigation, the calculated freezing-point constant is found to be 5025.5, a closer agreement with the value obtained from molecular-weight determinations.

The specific heats of the solid benzene are tabulated in Table III, Col. 3.

Acetone.—Approximately 15.5 g. of Kahlbaum acetone, purified by means of the sodium bisulfite compound and melting at —94.6°, was used in these measurements. The heat capacity per gram at various temperatures is tabulated in Table I, and is shown graphically in Fig. 1, Curve III.

From the curve, the latent heat of fusion was found to be 19.60 calories. The specific heats of the solid acetone at various temperatures are given

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[9] Nernst, "Theoretische Chemie," Enke, **1913**, p. 149.

in Table III, Col. 4. The heat-capacity curve was extrapolated to —78.2°, and the heat capacity at this temperature found to be 63.3 calories.

Other Substances.—A number of organic compounds that were readily obtainable in a pure state were examined for their heat capacities over the temperature ranges, —183.6° to 16.5° and —78.2° to 16.5°. The results are given in Table IV, together with the heat capacities over these temperature ranges of the compounds previously mentioned.

TABLE IV

HEAT CONTENTS OVER THE RANGE —183.6° TO —78.2°

Compound	Mol. wt.	Heat from −183.6° to 16.5°	Heat from −78.2° to 16.5°	Heat capacity per g. from −183.6° to −78.2°	Average specific heat	Molecular heat from −183.6° to −78.2°
Water	18.016	158.40	129.90	28.50	...	513.50
Methyl alcohol	32.037	121.5	71.70	49.8	...	1594.80
Acetone	58.063	106.1	63.30	42.8	...	2482.60
Benzene	78.048	81.45	61.49	20.0	...	1559.07
p-Xylene	106.120	89.4	68.14	21.2	0.201	2252.58
Phenol	94.078	42.2	24.60	17.6	.167	1654.27
Benzophenone	182.145	38.15	23.32	14.8	.140	2701.24
Naphthalene	128.114	38.2	23.5	14.7	.140	1887.65

The various columns of this table are self-explanatory. The last one represents the number of calories required to heat one gram molecule from —183.6° to —78.2°. It is easy to show, by the values in this column, that the atomic heats of carbon, hydrogen and oxygen when combined, depend largely on the constitution of the molecule. Thus, taking benzene and *p*-xylene, the heat required to heat a gram-atom of hydrogen and a gram-atom of carbon through the temperature range indicated above, is found to be 87 calories and 173 calories, respectively, by assuming the validity of Kopp's law. Using these values, the heat required to warm a mole of naphthalene would be 2426 calories, about 25% higher than the observed value. Similar calculations with the other compounds show that where, in accordance with the quantum theory, the molecular heats are in what might be called an "incomplete" state, the effect of an element over the same temperature range varies from compound to compound. It follows, therefore, that over a range of temperature in which the specific heat varies greatly, the atomic heat of an element depends, to a large extent, on the manner in which it is combined. It may be possible to establish the relationship between atomic heat and chemical constitution. For instance, it follows from the above calculation, that carbon in an aromatic compound has quite a different value from the carbon in a methyl group. To establish this, a systematic study of related compounds is necessary, and it is the intention of the authors to undertake this in the future.

According to Crompton's hypothesis,[10] alcohol and acetone should have practically the same latent heats of fusion, as their melting points lie so close together. Actually, that of acetone is 20% higher. In the equilibrium, liquid-solid, energy is also required to overcome molecular cohesive force when the solid changes into a liquid and the molecular surface energy of acetone is considerably greater than that of methyl alcohol.

Acknowledgment is hereby made of a Sterry Hunt Scholarship which has made possible the continuation of this work.

Summary

1. A method for the measurement of specific heats and latent heats of fusion at low temperatures, has been described.

2. The specific heats of ice, benzene, methyl alcohol and acetone were determined from —183.6° to their respective melting points.

3. The specific heat of ice was determined with particular care and the empirical formula, $c = 0.485 + 0.000914t - 0.00000546t^2$ found to express the relation between specific heat and temperature.

4. The average specific heats of phenol, *p*-xylene, naphthalene and benzophenone were determined over the range —183.6° to —78.2°.

5. The latent heats of fusion of water, benzene, acetone and methyl alcohol were determined.

6. Further evidence has been advanced to prove that atomic heat is a highly constitutive property, where the specific heat of a compound varies greatly with the temperature.

MONTREAL, CANADA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE BEHAVIOR OF ELECTRODES OF PLATINUM AND PLATINUM ALLOYS IN ELECTROMETRIC ANALYSIS. I

DISSIMILAR ELECTRODES

BY R. G. VAN NAME AND F. FENWICK[1]

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It has recently been shown[2] that the end-point in certain reactions may be determined with sufficient accuracy for analytical purposes by observing the accompanying sudden change in the difference in potential between two inert electrodes of different metals or alloys immersed directly in the solution. Even better results were obtained when the electrodes were both of the same material (pure platinum) and their dissimilarity was arti-

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[10] Crompton, *Proc. Chem. Soc.*, **65**, 240 (1895).

[1] National Research Fellow in Chemistry.

[2] Willard and Fenwick, THIS JOURNAL, **44**, 2504 (1922).