[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE JOHNS HOPKINS UNIVERSITY]

AN APPLICATION OF THE RULE OF DULONG AND PETIT TO MOLECULES[1,2]

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A little over one hundred years ago Dulong and Petit[3] announced the empirical rule that the heat capacity per gram atom is about the same for all solid elements. Since that time the theoretical significance of this rule has been made apparent and the exceptions to it explained by the development of classical kinetic theory and quantum theory. For solids other than the elements, however, very little progress has been made in accounting for the heat capacities. With the hope of throwing some light on this latter problem, particularly for the compounds of carbon, the senior author and his associates have been measuring the heat capacities of a number of compounds. The results for the series of halogen derivatives of benzene presented here seem to show that the principles, of which the rule of Dulong and Petit is a part, can be applied to complicated molecules when the nature of the molecule is sufficiently understood.

The Calorimetric Measurements

The measurements of heat capacity were made in a calorimeter which operates on the principle of calibrated heat conduction, described in a paper by Andrews[4] where a general description of the method may be found.

The Calorimeter used for these observations embodies a number of improvements over the one previously described. As shown in Fig. 1 the inner vessel, which contains the substance to be studied, is a gold-plated copper can equipped with vanes to facilitate the conduction of heat throughout the material. This can is supported by four adjustable wooden pegs inside a heavy copper cylinder, also gold-plated. Both inner and outer can are equipped with covers not shown in the figure.

Temperature is measured by means of thermocouples of No. 30 constantan wire attached to the inner and outer cans.[5] There is a heating coil of the same wire wound on the outside of the outer can.

The Method.—The calorimeter is placed in a gallon Dewar and liquid air is poured on it until the whole apparatus is at constant temperature at about 90°K. Then a current is passed through the heating coil of such strength that the whole apparatus is

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[1] In memory of Ira Remsen.

[2] From the dissertation submitted by E. Haworth in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[3] Dulong and Petit, *Ann. chim. phys.*, **10**, 395 (1819).

[4] Andrews, THIS JOURNAL, **48**, 1287 (1926).

[5] The calibration of the thermocouples is described in a paper by Andrews, *J. Franklin Inst.*, **206**, 285 (1928). Measurements made with the thermocouple junction directly in the material studied as compared with those where the junction was soldered to the walls of the container indicate that errors of temperature measurements due to poor thermal conductivity of the material are not appreciable.

warmed at the rate of about half a degree a minute until 50° is reached. The heat capacity at different temperatures is calculated from the rate of heating of the inner can and the temperature head between the two cans, the constants for heat conduction of this particular apparatus being determined by calibration with hydroquinone.[6]

The Materials.—The substances which were studied were secured from the Eastman Kodak Co. The freezing point curves[7] indicate less than 1% impurity in every case.

The Results

The values of the heat capacity for mono-, di-, tetra- and hexachlorobenzene and for mono- and dibromobenzene are given in Table I. The relative accuracy seems to be about 1 or 2%. The absolute accuracy may not be quite as good as this in certain measurements because of uncertainties in the temperature scale. Comparison with the very limited data available from other sources indicates that at any rate the errors are not large enough to affect appreciably the conclusions drawn from the data.

Conclusions

The principal interest in these two groups of compounds centers in the values we may secure for the heat capacity of the halogen atoms attached to the benzene ring. The rather complicated factors entering into the heat capacity of the ring itself have been discussed by Andrews.[8]

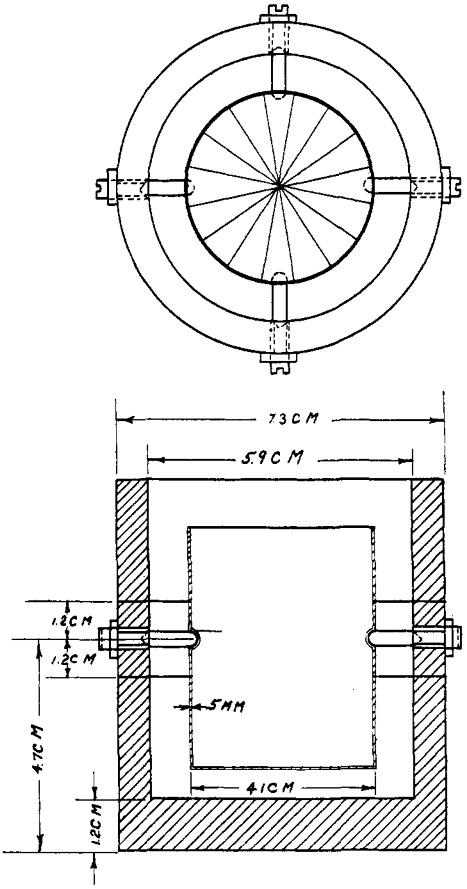

Fig. 1.—The calorimeter.

It seems very likely that since the heat capacity of the hydrogen atoms is practically negligible, the ring itself always has about the same heat capacity regardless of the groups attached to it. This conclusion is substantiated by the data in Table II, where the difference between the heat

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[6] Values taken from Andrews, ref. 4, in which paper the details of calibration may be found.

[7] Andrews, Kohman and Johnston, *J. Phys. Chem.*, **29**, 914 (1925).

[8] Andrews, *Verslag. Kgl. Akad. Wetenschappen Amsterdam*, **29**, 744 (1926).

TABLE I

C_p PER GRAM MOLE IN CALORIES PER DEGREE[a]

Temp., °K.	C_6H_6, calcd.	$C_6H_4Cl_2$	*p*-$C_6H_2Cl_4$	1,2,4,5-$C_6H_2Cl_4$	C_6Cl_6	C_6H_5Br	*p*-C_6H_4Br
101.2	11.6	13.3	15.6	20.8	20.5	14.2	17.5
125.7	13.4	15.4	17.6	22.9	30.3	16.1	19.9
147.1	15.1	17.4	19.9	25.6	33.9	18.1	21.9
166.4	16.7	19.3	22.0	27.8	36.3	19.7	23.8
184.3	18.2	21.1	24.1	30.1	39.2	21.2	25.6
201.0	19.5	23.1	26.4	32.2	41.5	23.0	27.5
216.8	20.8	25.4	28.9	34.3	44.3	25.5	29.6
231.7	22.1		28.1	37.1	47.8	30.5	32.1
246.1	23.5		30.0	39.5	50.9		34.4
259.8	24.9		34.9	41.3	53.3		36.4
273.1	26.2		37.5	43.3	56.1		38.0
286.3	27.5		39.2	45.8	58.9		39.8
299.8	28.7		41.1	48.4	61.6		41.7
311.7	30.0		44.7	50.5	64.5		43.6
323.9	31.4		51.0	52.7	68.0		46.0
335.8	32.8			55.4	71.8		48.7

[a] J. Narbutt, *Z. Electrochem.*, **24**, 339 (1918), has measured the mean heat capacity of *p*-$C_6H_4Cl_2$ and *p*-$C_6H_4Br_2$ between various temperatures (−78 to 80°) and 0° by the method of mixtures. He finds, for example, the heat capacity at 217°K. to be 26.8 for $C_6H_4Cl_2$ and 27.8 for $C_6H_4Br_2$, and at 273°K., 32.4 and 33.0. The difference between these values and the authors' is probably due to the different methods employed, Narbutt's being below and the authors' above the true values. It is believed, however, that the accuracy of the authors' measurements, especially relative to one another, is amply sufficient to justify the conclusions drawn from the data.

capacity of the ring[9] and the heat capacity of each compound is shown divided by the number of substituent groups in the compound. The result is thus the apparent heat capacity per halogen atom in each of the compounds.

This table seems to indicate that the heat capacity per halogen atom is relatively independent of the *number* of halogen atoms attached to the ring. The apparent lack of effect on the heat capacity of *position*, that is, *m*-, *p*-, etc., has been pointed out before.[4]

The fact that the values approach 6 cal. per degree at about room temperature suggests that Dulong and Petit's rule may be applicable. The plausibility of this may be shown in the following way. We believe that

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[9] The values of the heat capacity of the ring are those calculated from the infrared frequencies as explained in the paper by Andrews, ref. 8. These differ slightly from the observed values for benzene, but were used instead of the latter because of the uncertainty of the observed values in the neighborhood of the melting point and the obvious lack of observed values for the solid above the melting point. For a somewhat similar reason the term for the work of expansion (see reference above) is taken for hydroquinone rather than for benzene. The accuracy of the heat capacity of the ring so calculated should suffice, however, for the present purpose.

TABLE II

Cpd.	100°K.	140°K.	180°K.	220°K.	260°K.	300°K.
			C_p PER CHLORINE ATOM			
C_6Cl_6	2.5	3.0	3.5	4.0	4.7	5.5
$C_6H_2Cl_4$	2.2	2.5	2.9	3.5	4.2	5.0
$C_6H_4Cl_2$	1.9	2.4	3.0	3.9	5.2	
C_6H_5Cl	1.5	2.6	3.0			
Calcd. from infra-red	1.6	2.7	3.4	3.9	4.3	4.6
			C_p PER BROMINE ATOM			
$C_6H_4Br_2$	3.0	3.2	3.7	4.5	5.7	6.1
C_6H_5Br	2.5	2.6	3.1			
Calcd. from infra-red	1.8	2.8	3.5	4.1	4.4	4.7

the halogen atom is attached to the ring by a normal non-polar or so-called homopolar bond. There is considerable evidence[10] that all bonds of this type are of almost identical nature and strength even when in such apparently different circumstances as joining H—H, C—C, or C—Cl. Now one of

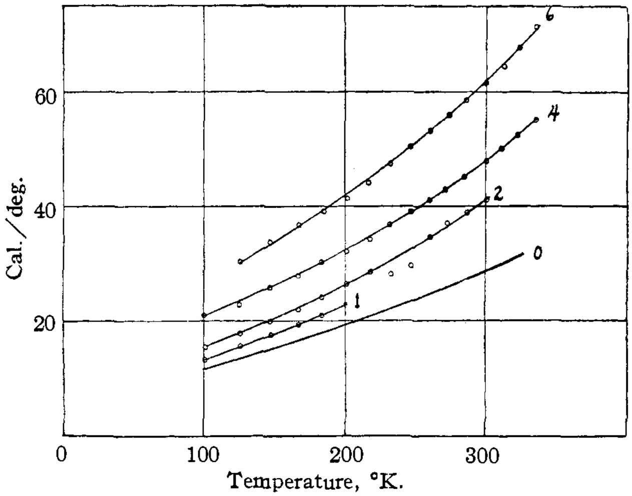

Fig. 2.—C_p for (0) C_6H_6, (1) C_6H_5Cl, (2) $C_6H_4Cl_2$, (4) $C_6H_2Cl_4$, (6) C_6Cl_6.

the characteristics of this type of bond is its spring-like nature. We may indeed think of the chlorine atom as joined to a carbon atom of the ring by a short spiral spring. In this case there should be two characteristic frequencies of vibration; one for motion parallel to the direction of the bond, which stretches the bond directly; the other perpendicular to this, which bends the bond without directly stretching it. This latter type of motion should involve a smaller restoring force than the first type and should have a lower frequency.

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[10] Bates and Andrews, *Proc. Nat. Acad. Sci.*, **14**, 124 (1928).

The values of frequencies such as these can be secured from absorption spectra, as both Salant[11] and Andrews[8] have shown. Thus Ellis[12] has found characteristic absorption in the infra-red corresponding to fundamental frequencies of 1.79×10^{13} sec. for C—Cl and 1.74×10^{13} sec.^{-1} for C—Br. Now it seems quite likely by analogy with other compounds that this is the frequency of motion parallel to the bond. If we assume as a very rough first approximation that the ratio of parallel frequency to perpendicular frequency is the same for C—Cl, or C—Br as for C—C, namely,[8] 1470/568, we get values for the frequency perpendicular which are $\theta = 334$ and $\theta = 325$ for C—Cl and C—Br, respectively, expressed in the notation for use in the Einstein specific heat equation for harmonic oscillation. The values for the frequency parallel are $\theta = 856$ and $\theta = 845$. Using these values we can calculate with the help of the Einstein equation what the heat capacity of the halogen atom is if these conditions are all fulfilled. The results of this calculation are given in the last rows of Table II. The agreement is certainly as good as can be expected and shows that atoms attached to a heavy group like the benzene ring do approach the Dulong and Petit value in a manner similar to the elements.

It is a little venturesome to draw conclusions as to what this picture of the molecule will tell about chemical activity, but it seems worth pointing out that since the effective masses are about the same for all the C—Cl vibrating systems, the values of the frequency and consequently of the heat capacity must depend only on the strength of the bond in each case. Since the heat capacities are so nearly the same in all cases we must conclude that the strengths of the bonds are also about the same. Thus, though changes occur in the molecule as we increase the number of substituent groups, such as changes in directive influence to produce different chemical activity, there is no evidence that these changes have any marked effect on the actual mechanical strength of the bonds.

Summary

Measurements have been made of the heat capacities of mono-, di-, tetra- and hexachlorobenzene and of mono- and dibromobenzene. The heat capacity per halogen atom in these compounds seems to approach the Dulong and Petit value of 6 cal. per degree at room temperature in a way predictable from optically observed frequencies in the infra-red. The strength of the carbon–halogen bond in every case seems to be about the same, there being no evidence of directive influence upon it.

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[11] Salant, *Proc. Nat. Acad. Sci.*, **12**, 334, 370 (1926).

[12] Ellis, *Phys. Rev.*, **28**, 25 (1926).