

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

THERMAL ENERGY STUDIES. III. THE OCTANOLS¹

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A most interesting series of compounds in which to study the distribution of thermal energy may be found among the isomeric derivatives of a long-chain compound such as octane. The possibility of long wave-like vibrations in such a chain provides a variety of frequency values not found in more compact molecules and offers an unusual means of approach to the problem of molecular structure. A remarkable series of compounds of this sort has recently been assembled by E. E. Reid and his associates, who have carefully prepared in unusually large amounts all the possible octanols. As part of a general study of their physical properties the measurement of the heat capacities was undertaken and included in the program of thermal energy studies² previously described.

At first glance one might think this series peculiarly unfitted for heat capacity measurements because of the difficulty of making the compounds crystallize. On the other hand, for that very reason this appeared to be a good opportunity to get further knowledge of the forces involved in crystallization and of the nature of glasses. This has been a subject of interest for a great many years and as Gibson and Giauque,³ and Parks, Huffman and Cattoir⁴ have shown, the study of heat capacities yields information of great value in this field.

Results

The preparation of the materials will be described in papers by E. E. Reid and co-workers to appear shortly. The octanols, as received from them, were measured calorimetrically by the method of calibrated heat conduction as previously described.² The results are presented in Table I and Fig. 1.

It is immediately evident from an inspection of the figure that we have a related series of curves going from octanol-1, where the extra methyl group and hydroxyl group are at the maximum of separation, to the compounds where both groups are located near the middle of the molecule. This variation however is limited almost entirely to the temperature range in which melting or softening takes place, 120 to 240°K. It is very striking that below and above this range the heat capacities of all the compounds

¹ From a dissertation submitted in partial fulfilment of the requirements for the degree of Master of Arts.

² Richard H. Smith and Donald H. Andrews, *THIS JOURNAL*, **53**, 3644, 3661 (1931).

³ G. E. Gibson and W. F. Giauque, *ibid.*, **45**, 93 (1923).

⁴ G. S. Parks and H. M. Huffman, *J. Phys. Chem.*, **31**, 1842 (1927); G. S. Parks, H. M. Huffman and F. R. Cattoir, *ibid.*, **32**, 1366 (1928).

have about the same value, though there is a tendency for the curves to spread apart again above 250°K.

In looking for an explanation of this behavior we might divide the factors influencing heat capacity into two groups, the differences in internal energy due to changes in molecular structure, and the differences in the motion of the molecule as a whole in the crystal lattice.

With regard to the internal energy, we may expect the influence of changes in the position of the methyl and hydroxyl groups to be rather small in the region of temperature below 250°K. In an analysis of the vibrations

TABLE I
DATA FOR THE OCTANOLS

(1) Octanol-1	(6) 2-Methylheptanol-2	(11) 5-Methylheptanol-2			
(2) Octanol-2	(7) 4-Methylheptanol-2	(12) 3-Methylheptanol-2			
(3) Octanol-3	(8) 4-Methylheptanol-3	(13) 2-Methylheptanol-4			
(4) Octanol-4	(9) 4-Methylheptanol-4	(14) 2-Methylheptanol-1			
(5) 6-Methylheptanol-3	(10) 5-Methylheptanol-1	(15) 6-Methylheptanol-2			
T, °K.	(1)	(2)	(3)	(4)	(5)
101.9	25.0	25.2	25.5	26.6	27.3
126.1	28.0	29.0	30.1	32.8	31.5
147.4	31.9	32.5	35.1	36.1	36.2
166.7	35.0	36.3	38.8	39.8	41.3
184.4	37.9	40.5	41.3	44.0	47.8 ^a
201.1	40.5	44.6	51.5 ^a	50.8 ^a	..
216.9	43.0	56.2 ^a	64.5	66.1	..
231.7	47.0 ^a	..	66.6	64.5	61.3
246.0	58.3	64.2	69.5	66.5	63.6
259.8	63.4	67.5	72.4	69.5	66.4
273.1	66.9	71.4	75.0	73.1	69.2
286.0	68.0	74.9	78.0	76.7	71.5
298.5	..	78.9	80.9	80.7	74.2
310.7	84.1	75.6
322.6	79.4

^a Temperature at which melting begins.

T, °K.	(6)	(7)	(8)	(9)	(10)
101.9	24.0	25.7	25.3	24.3	29.1
126.1	32.6	31.0	36.7	29.9	33.6
147.4	35.9	42.7	53.8	34.2	51.4
166.7	39.9	53.4	55.7	49.8	53.8
184.4	46.1	55.0	57.3	55.5	55.8
201.1	54.8 ^a	57.4	58.6	57.2	56.9
216.9	..	59.2	59.2	58.8	57.3
231.7	62.5	61.2	60.3	61.2	58.7
246.0	65.2	63.7	62.7	64.8	61.3
259.8	69.1	66.9	65.9	69.7	64.0
273.1	73.3	70.3	68.6	74.6	66.9
286.0	76.9	72.3	70.7	81.8	69.8
298.5	80.7	74.7	73.9	87.8	72.7
310.7	84.1

TABLE I (Concluded)

T, °K.	(11)	(12)	(13)	(14)	(15)
101.9	28.5	32.8	26.1	27.1	26.0
126.1	32.6	55.3	30.7	31.6	31.3
147.4	52.0	57.1	34.6	40.1	40.1
166.7	54.6	58.7	49.5	47.7	53.4
184.4	56.2	59.5	56.0	54.3	54.4
201.1	57.2	59.8	58.1	62.7 ^a	53.9
216.8	57.5	60.9	59.3
231.7	58.8	63.4	61.4	..	62.1
246.0	60.9	65.7	64.3	..	63.3
259.8	63.7	68.3	67.4	67.0	66.6
273.1	66.6	69.9	71.1	68.1	70.1
286.0	69.3	70.9	75.0	70.5	72.9
298.5	70.8	71.1	79.3	74.8	75.3
310.7	80.1	..

in a long-chain molecule Lewis⁵ has shown that, in general, we will have a series of frequencies in which the slowest corresponds to the longest possible wave in the chain and the fastest to the vibrations of the atoms in pairs.

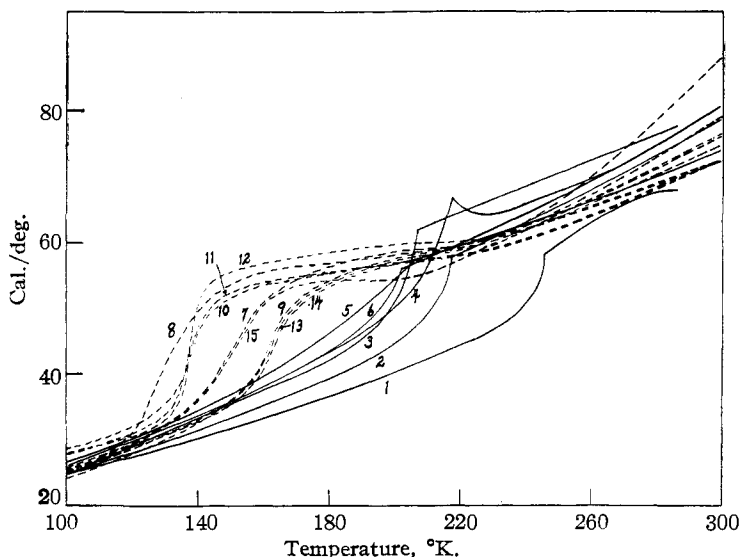


Fig. 1.—Heat capacity per mole for the octanols. See Table I for key to numbers. Crystalline compounds shown with solid lines, glasses with dotted lines.

The Raman spectrum of heptane,⁶ for example, has its lowest frequency in the neighborhood of 150 cm.^{-1} and a group of frequencies fairly evenly spaced extending from there up to 1100 cm.^{-1} , which appears to be the

⁵ A. B. Lewis, *Phys. Rev.*, **36**, 568 (1930).

⁶ D. H. Andrews, *ibid.*, **36**, 544 (1930).

fastest possible value, excepting those due to hydrogen. In consequence of these values one finds that at 100°K. only about a third of the internal vibrations will be contributing appreciably to the heat capacity, as may be seen readily by consulting tables⁷ of the value of the heat capacity from Einstein's formula for various frequencies. We might expect the shifting of the methyl or hydroxyl group to change the frequencies on the average by the order of a few per cent. or less. It is easy to see, therefore, why all the compounds have about the same heat capacity at 100°K.

At 300°K., however, all the frequencies are contributing and the heat capacity due to internal vibration makes up by far the greater part of the total observed value. It is, therefore, not surprising to find evidence of a variation in heat capacity with change in structure.

With regard to the energy of the molecule vibrating as a whole in the crystal lattice it is evident that changes in the shape of the molecule will have a much greater effect. This appears to be closely related to the ease with which the molecule can fit itself into a crystal lattice, a property largely dependent on the symmetry of the molecule. Thus the curves show a transition from octanol-1, which is the most symmetrical of the compounds and crystallizes readily, through octanols 2, 3, 4 and two of the methylheptanols, which crystallize much less readily, to the compounds which presumably are much less symmetrical and which cannot be made to crystallize at all.

If we regard the forces which hold the molecules in the crystal lattice, as emanating from the individual atoms and as extending only over distances of the order of magnitude of the diameters of the atoms,⁸ we can understand more clearly the significance of the above facts. Let us consider the action between liquid and crystal in the case of a symmetrical compound such as octanol-1 at a temperature slightly below the freezing point. A molecule from the liquid might attach itself to the crystal surface in two different ways. In the first place it might fit into a place in the crystal lattice with proper orientation so that it becomes a regular unit of the lattice. In this case it is presumably attracted to the crystal lattice at the maximum possible number of points and the drop in potential energy is so great that its thermal energy of motion is not on the average sufficient to shake it loose and send it back into the liquid.

On the other hand, a molecule might become attached to the crystal surface in an irregular sort of way, with only a few of its attractive forces operating. In this case if it is only a few degrees below the melting point, its thermal energy will probably be enough to shake it loose almost immediately. However, if the temperature drops too far below the melting point,

⁷ W. Nernst, "The New Heat Theorem," E. P. Dutton and Co., New York, 1926.

⁸ D. H. Andrews, "Some Evidence on the Nature of Extra Molecular Forces," "Colloid Symposium Annual," 1930, Vol. VII, p. 119.

the molecule may stick permanently in this irregular position and we begin to get the formation of a glass.

Now in an unsymmetrical compound the tendency for the molecule to attach itself to other molecules in the latter fashion becomes almost as large as the tendency to fit into the crystal lattice in a regular way. There may be very little difference in the number of points of attachment or in the potential energies of the two states. We can, therefore, imagine that the temperature range may become negligibly small in which the rate of crystal formation is greater than the rate of glass formation. This appears to be true for a number of the octanols. Since in this picture of the formation of a glass we believe the molecule to be less firmly bound than in the crystal, it is to be expected that the heat capacity will be larger than in the crystal.

As we approach the temperature of the liquid state these points of attachment or, as we might call them, inter-molecular bonds are frequently broken and reformed due to the piling up of thermal energy at particular points. As temperature increases the frequency of breaking becomes greater, and the number of bonds holding at any one time becomes less. In the case of glasses there is a gradual transition to the liquid state where the frequency of the breaking of the bonds is great enough to permit movement throughout the liquid. In the case of crystals, a point is reached, melting temperature, at which the number of bonds holding at any time is insufficient to preserve complete orientation and we get formation of the liquid. With fairly chaotic arrangement of the molecules, however, we might expect about the same number of bonds holding for any of the compounds with which we are dealing, whether symmetrical or unsymmetrical, so that it is not surprising to find the heat capacities very much the same for both cases in the liquid state. In this fashion, by assuming attraction between the molecules operating at rather definite points, we can see quite clearly why the heat capacities vary with the temperature in the manner which has been observed. It is hoped that when data from the Raman spectra are available with which to calculate frequencies of internal vibration, a more exact analysis of the meaning of the curves can be made.

Although with some compounds such as the silicates there appears to be a relation between glass formation and viscosity, the straight-chain octanols crystallize most easily and are at the same time most viscous.⁹ This seems to imply that the factors mentioned above are the important ones in the case of the octanols.

Summary

1. The heat capacities of fifteen of the octanols have been measured between 100 and 300°K.

⁹ E. C. Bingham and L. B. Darrel, *J. Rheology*, 1, 174 (1930).

2. The shape of the curve depends both on the internal energy and on the tendency of the compound to form a glass. There is a gradual change in shape from the straight chain which readily forms crystals to the unsymmetrical molecules which will only form glasses.

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THERMAL ENERGY STUDIES. IV. COMPARISON OF CONTINUOUS AND DISCONTINUOUS METHODS OF MEASURING HEAT CAPACITIES. HEAT CAPACITIES OF SOME ALIPHATIC BROMIDES¹

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One of the major experimental difficulties in the measurement of the heat capacities of organic compounds is the slowness with which thermal equilibrium is established following a change in temperature. Organic compounds in any form are as a rule very poor heat conductors and when occasionally a compound crystallizes in long fine needles or some other state that is hard to pack solidly, it becomes an almost perfect heat insulator. The standard method of heat capacity measurement has always involved bringing the substance to uniform temperature, passing in a known quantity of energy electrically, and waiting for thermal equilibrium to be established at some higher temperature. With a substance of very low heat conductivity this period of waiting frequently becomes so long that heat leaks to the surroundings of the calorimeter practically invalidate the measurement.

To overcome these difficulties a new method based on calibrated heat conduction was developed by Andrews,² Haworth³ and Smith⁴ which proved very successful with a number of compounds. This method, however, is a comparative and not an absolute one. It therefore seemed worth while to make a study of an absolute method of heat capacity measurement in which some of these sources of error might be eliminated.

The principle of continuous heating which was used by the authors mentioned above seemed to offer the most favorable possibility of avoiding delays and errors due to poor heat conduction. In the older methods it was generally customary to produce the heat either in a coil wound on the

¹ From a thesis submitted by Robert F. Deese, Jr., to the Graduate School of the Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

² D. H. Andrews, *THIS JOURNAL*, **48**, 1287 (1926).

³ D. H. Andrews and E. Haworth, *ibid.*, **50**, 2998 (1928).

⁴ R. H. Smith and D. H. Andrews, *ibid.*, **53**, 3644 (1931).