LXXVII.—*The Melting-point Curves of the Monobasic Fatty Acids.*

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THE melting points of the monobasic fatty acids lie on two curves, one for the even and the other for the odd acids. Both curves show a minimum in the neighbourhood of 4 or 5 carbon atoms. The law governing the shape of these curves has not yet been completely elucidated, and this is very largely due to the fact that the melting point is a property which concerns both the liquid and the solid state. *X*-Ray measurements by Müller, Piper, and others have made clear the nature of the structure of long-chain compounds in the solid state, but very little is known about the molecular structure in the liquid state. Until the properties of liquids are better understood, it is doubtful if any comprehensive theory can be advanced to explain the melting-point curves.

It is, however, possible from a study of the heats of crystallisation of long-chain compounds to make a step forward in the study of their melting points. For the monobasic fatty acids, the heats of crystallisation are known up to the acid with 26 carbon atoms in the chain (Garner and King, J., 1929, 1849). The curve of the heat of crystallisation plotted against the number of carbon atoms gives a minimum at about the same point as that on the melting-point curves (Garner, Madden, and Rushbrooke, J., 1926, 2491). There is thus some relationship between the heat of crystallisation and the melting points.

In an earlier paper (*ibid.*), a theory of the melting points was put forward which was based on the view that the melting point was that temperature at which the probability of the attachment of a molecule to the crystal surface was equal to the probability of its detachment. These probabilities depend on the critical increments of attachment and detachment of the various groups in the molecule, and also on the length of the molecule. If, as is reasonably certain, the attachment is by means of the methylene and terminal groups, then the number of methylene groups in the molecule is obviously an important factor. This is particularly the case for the probability of attachment of the molecule in its right place on the surface. Consider a molecule of a monobasic acid which is attached by four methylene groups to the surface. Number these 1, 2, 3, and 4 from the carboxyl group upwards. Any one of these methylene groups on collision with the surface can be held by a group already forming part of the solid. There are four types of methylene groups with which it can combine, and only one of these types of combination can result in the building up of a crystal lattice. The chance of a molecule being attached in the correct place is therefore 1/4, or for an acid with n carbon atoms, $1/\frac{1}{2}(n-2)$. Thus, the probability of attachment to the surface in the correct configuration increases as the carbon chain shortens. This factor accounts for the minimum in the melting-point curves for the monobasic fatty acids. It enters into the equation for the relationship between the heat of crystallisation and temperature in the following fashion (see previous paper for details) :

$$Q_{n+2}/4{\cdot}57T_{n+2} - Q_n/4{\cdot}57T_n = \log_{10}k'_1/k''_1 + \log_{10}n/(n-2), \quad . \quad (1)$$

where Q_{n+2} and Q_n are the molar heats of crystallisation for the acids with $n+2$ and n carbon atoms, T_{n+2} and T_n are the respective melting points, k'_1 is a constant depending on the rate of activation of a methylene group on the surface, and k''_1 is a similar factor for the process occurring on crystallisation.

It follows from (1) that

$$\Delta(Q/4{\cdot}57T) - \log_{10} n/(n-2) = \log_{10} k'_1/k''_1 \quad . \quad (2)$$

$\mathrm{Log}_{10}\, n/(n-2)$ becomes negligibly small as compared with

$\Delta(Q/4{\cdot}57T)$ when the carbon chain is 24—30 atoms long; therefore, on integrating the above equation, we obtain

$$\Delta Q/T - 0{\cdot}00475\Sigma_{24}^{n} \log_{10} n/(n-2) = \text{constant} \times n + \text{a constant} \quad . \quad (3)$$

The term on the left when plotted against n should give a straight line. This is found to be the case from $n = 4$ to $n = 24$ for the even members of the homologous series. The term on the left in equation (3) is found to be equal to $0{\cdot}002698n - 0{\cdot}0061$. The degree of correspondence between the values for Q/T from this equation and the observed values of Q/T can be seen from the table, in cols. 3 and 4. The magnitude of the correction factor is seen from col. 2. Col. 5 contains values of Q given by the product of Q/T (calc.) and T (obs.), and col. 6 gives the observed values of Q. The agreement is such as might be expected from the experimental error in the determination of Q. The figures for acetic acid cannot be given because it contains no methylene groups.

No. of C atoms.	$\Sigma_{24}^{n} \log_{10} n/n-2$ $\times 0{\cdot}00475$.	Q/T, calc.	Q/T, obs.	Q (calc.). (Cals./g.-mol.).	Q (obs.).
24	0·000000	0·05866	0·05927	20·88	21·10
22	0·000173	0·05343	0·05325	18·81	18·75
20	0·000382	0·04824	0·04882	16·75	16·95
18	0·000661	0·04313			
16	0·000880	0·03795	0·03873	12·73	12·98
14	0·001185	0·03287	0·03289	10·74	10·74
12	0·001547	0·02783	0·02762	8·82	8·75
10	0·001990	0·02287	0·02199	6·96	6·69
8	0·002561	0·01805	0·01766	5·22	5·11
6	0·003366	0·01346	0·01336	3·63	3·60
4	0·004732	0·00942	0·009872	2·52	2·64

It will be seen that the entropy change on crystallisation can therefore be accurately represented by the equation

$$Q/T = 0{\cdot}002698n - 0{\cdot}0061 + 0{\cdot}00475\Sigma_{24}^{n} \log_{10} n/(n-2).$$

In order to make a calculation of the temperature of melting of an unknown acid, it is necessary to be able to derive a value for Q. The manner in which the heat of crystallisation varies with the number of atoms in the carbon chain has not been interpreted theoretically, so that it is only possible to employ an empirical relationship similar to that given previously. For acids having more than 12 carbon atoms, Q increases at the rate of 2·060 Cals./g.-mol. for every two methylene groups added to the chain.

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