[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

A RELATION BETWEEN THE MOLECULAR WEIGHTS AND MELTING POINTS OF ORGANIC COMPOUNDS

BY J. B. AUSTIN

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The recent paper of Hildebrand and Wachter[1] focuses attention once more on the need for some expression which will aid in a critical selection of the best values for the melting points of organic compounds. Longinescu has given the following formula[2]

$$\left(\frac{T}{10\,D}\right)^2 = n \qquad (1)$$

where n is the number of atoms in the molecule, D is the density and T is the melting point on the absolute scale. This relation is only partially satisfactory, however, for it does not involve the molecular weight directly, and is not sufficiently sensitive for critical use; hence it was decided to attempt to derive an equation involving the molecular weight and melting point directly and possessing considerable sensitivity.

In considering relations with which to start, the well-known formula of Lindemann[3] for determining the characteristic vibrations of the atoms in a monatomic solid suggested itself as a plausible beginning. This equation is of the form

$$\nu = \text{const.}\sqrt{\frac{T}{MV^{2/3}}} \qquad (2)$$

where ν is the frequency of the vibration, T is the absolute melting point, M is the atomic weight and V is the atomic volume. In the derivation of this expression several simplifying assumptions are introduced: it is assumed that the atoms of the solid are arranged in cubes, that their vibrations are simple harmonic and that the Law of Dulong and Petit is valid. In spite of these rather limiting assumptions the result as given above is in agreement with experimental evidence as Grüneisen has shown.[4] The vibrators postulated by Lindemann are merely spherical bodies and might with equal validity be considered as polyatomic molecules. In this case ν would be the molecular vibration frequency, V the molecular volume and M the molecular weight. Solving for M we obtain

$$M = \text{const.}\,\frac{1}{\nu^2}\,\frac{T}{V^{2/3}} \qquad (3)$$

At this point we may hazard a guess that for most organic substances ν is of the same order of magnitude, while for substances of related struc-

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[1] Hildebrand and Wachter, THIS JOURNAL, **51,** 2487 (1929).

[2] Longinescu, *J. chim. phys.*, **1,** 296, 391 (1903).

[3] Lindemann, *Physik. Z.*, **11,** 609 (1910).

[4] Grüneisen, *Ann. Physik*, **39,** 296 (1912).

ture it should be almost the same. Aside from expecting such an assumption to hold as a result of general experience in the similarity of physical properties of related organic molecules, we have an indication of its existence in the so-called "Crompton–Walden Rule" which relates the heat of fusion and the absolute melting point, as follows

$$\frac{\Delta H_F}{T_F} = \text{const.} \tag{4}$$

The heat of fusion, being roughly a measure of the work required to separate the molecules, must be, in some measure, a criterion of the magnitude of the molecular vibrations, and especially is this true near the melting point. The constancy of this ratio indicates, therefore, that in corresponding states most organic materials have nearly equal molecular vibrations. The ν in Equation 3 may, therefore, be included in the constant term. Moreover, V may be expressed in terms of M, D_m, the density at the melting point, and Avogadro's number. Making these changes in Equation 3, we obtain

$$M^5 = C'\, D_m^2\, T^3 \tag{5}$$

or

$$\log M = C + \frac{3}{5}\log T + \frac{2}{5}\log D_m \tag{6}$$

where C is a new constant.

However, the density as usually measured is not the density at the melting point but the density at room temperature. These densities are related by the expression

$$D = D_m\,(1 + \alpha t) \tag{7}$$

where α is the coefficient of cubical expansion and t is the difference between the melting point and room temperature. For organic solids not many data are available but α seems to have a value of about 0.00025. Since t is usually not very large, this correction is, in general, negligible. For liquids we may take α as 0.0011 without introducing considerable error. Here again t is small, so that the correction term will be insignificant, especially as compared with errors introduced by other approximations. Thus, for the present purpose, D and D_m may be taken as equal. Hence our desired expression is

$$\log M = \text{const.} + \frac{3}{5}\log T + \frac{2}{5}\log D \tag{8}$$

We may now proceed to test our equation: first in a case where the density term is negligible and second in a case where it must be considered.

It will be observed that the constants for benzene and toluene are lower than the others; this abnormality seems to be typical of the first members of a series and has been discussed by Smyth in connection with electric moments.[5]

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[5] Smyth, This Journal, **51**, 2380 (1929).

Table I

Aromatic Hydrocarbons

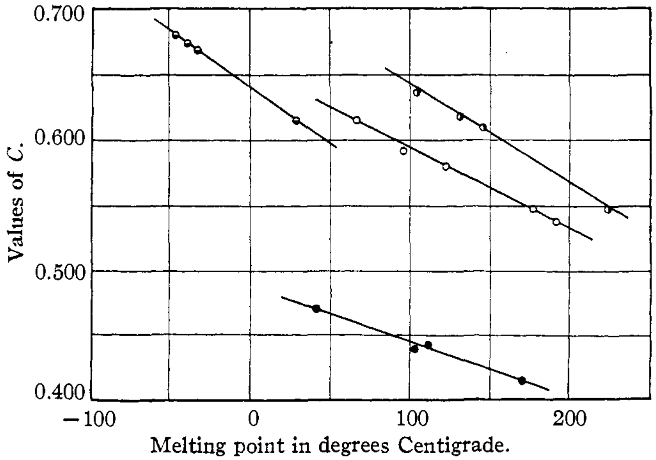
Substance	T_m	D	M	Const.
p-Xylene	286	0.861	106	0.551
Benzene	278	.878	78	.432
o-Xylene	246	.879	106	.580
m-Xylene	215	.865	106	.625
Ethylbenzene	180	.868	106	.672
Toluene	178	.866	92	.642

Table II

Monosaccharoses

Substance	T_m	D	M	Const., neglecting D	Const., corrected for D
Levulose	377	1.669	180	0.705	0.637
d-Mannose	405	1.540	180	.695	.620
d-Glucose	419	1.544	180	.685	.610
Dambose	497	1.752	180	.645	.548

It will be seen at once that while the constants for each class of material are of the same order of magnitude, they vary considerably within the class. This variation, which probably arises from the assumption that ν is constant, is emphasized by the logarithmic form of the function. If, however, C is plotted against T for each class, the points fall on a straight line as shown in Fig. 1, in which the lines shown are picked at random from a number of such lines used in testing the equation.



◑, Monosaccharoses; ○, aromatic acids; ◒, aromatic chlorides; ●, aromatic alcohols.

Fig. 1.

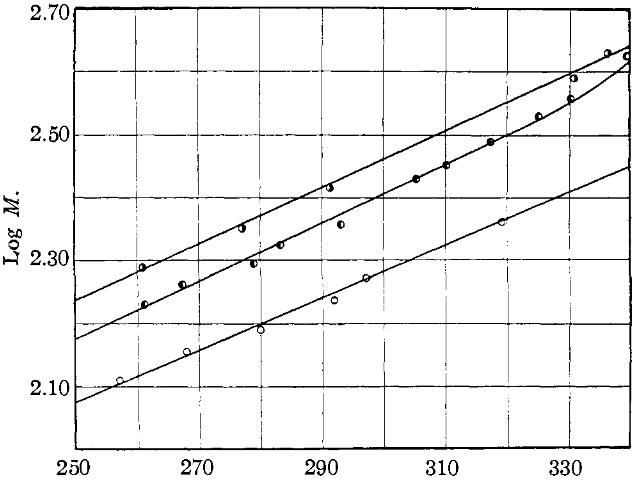
This linear variation of the "constant" with temperature means that Equation 8 should read

$$\log M = A' + BT_m + \frac{3}{5}\log T_m + \frac{2}{5}\log D \qquad (9)$$

The introduction of the term in T seems to add to the complexity of the expression but by making a few approximations we may greatly simplify it. Thus D is nearly unity for a great many organic substances, hence log D approaches zero and the term involving it may be neglected. Moreover, a variation in T from 100 to 600 on the absolute scale causes the term in log T to vary from 1.2 to 1.6; since this extreme variation in T produces such a small effect we may, as a first approximation, combine the first and third terms on the left side of (9) to obtain

$$\log M = A + BT_m \qquad (10)$$

This equation is found to represent the observed data with considerable accuracy, as the curves in Fig. 2 show. The line for the normal paraffins shows the greatest curvature but even this is small enough so that the linear relation may be assumed to hold over a limited range.



○, Aliphatic alcohols; ◑, olefins; ◐, normal paraffins.

Fig. 2.

Curves of this sort are chiefly useful in a critical examination of recorded data. For example, in the case of dicetyl, discussed by Hildebrand and Wachter, the use of the value of 75°, given as the melting point in the "International Critical Tables," throws the point for dicetyl considerably off the curve, whereas the value of 70° selected by them gives a point which falls nicely on the curve. Another application is the calculation of melting points which have not been experimentally determined. There are numerous series of homologs for which the melting points of but 3 or 4 members have been determined. These 3 or 4 points are, however, sufficient to allow the construction of a curve from which the melting point of any compound of the series may be easily read off.

From a study of a number of such curves it would appear that the lines for straight-chain paraffins and their simple derivatives, such as the alcohols, have the same, or very nearly the same slope; hence a common value of B may be given which defines a family of lines. This value of B is 0.0040 and the family of lines may be represented by the equation

$$\log M = A + 0.0040\,T \tag{11}$$

For such a family, data for a single member of a given series will serve to determine A and fix the line for that series. With branched chain and cyclic compounds the slopes are in general different. In many cases the slope has a negative sign; this is true of the series given in Fig. 1, since the "constant" lines have a negative slope and the slope of Equation 10 is the same as for the "constant" lines.

It should be mentioned in conclusion that Equation 10 applies only to true homologs; a series such as the normal paraffins has one curve, the secondary paraffins another. Complete failure results if an attempt is made to include isomers of the ortho–meta–para type in one curve.

Summary

A relation between the melting points and molecular weights of organic homologs has been derived. It is particularly useful in a critical examination of melting point data.

New Haven, Connecticut

[Contribution from the Department of Physical Chemistry, McGill University]

THE ADSORPTION OF WATER BY WOOD

By Lloyd M. Pidgeon and O. Maass

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Variation in the amount of adsorbed water in wood has a definite effect on many of its physical properties, such as swelling, strength, etc. In spite of the practical importance of these properties few determinations have been made of the adsorption of water by wood and cellulose throughout an extended range of vapor pressure and temperature. Even fewer determinations have been conducted by methods free from inherent error.

In this paper a method is detailed whereby the adsorption of water by various samples of coniferous woods and pure cellulose has been examined throughout the complete range of vapor pressures and between the temperatures of 12 and 42°. The corresponding adsorption isothermals are of particular interest from the point of view of the modern theory of gel structure.

While a considerable number of investigations on the fiber saturation point of wood have been made, the complete adsorption has rarely been