In the determinations of octavalent and quadrivalent osmium the agreement between the results obtained by this method and those obtained by other methods is somewhat better than 0.2%.

Summary

Potentiometric methods are described (1) for the determination of bromine in hydrobromic acid solutions of octavalent and quadrivalent osmium, (2) for the determination of octavalent osmium by titration of the bromine liberated when it is reduced by concentrated hydrobromic acid and (3) for the determination of quadrivalent osmium by determining the bromine required to oxidize it to the octavalent form when the reaction takes place in dilute hydrobromic acid. The reagent used is hydrazine sulfate. The accuracy of the method is about 0.2%.

LOS ANGELES, CALIFORNIA

THERMAL CONDUCTIVITY OF THE NORMAL PRIMARY SATURATED ALCOHOLS

BY M. DANILOFF

Accurate quantitative information as to the variation of thermal conductivity of successive members of homologous series with molecular weight and with temperature is essential for the formulation of a defensible molecular theory of liquids. At the present time systematic data available on the subject under comparable conditions are scattered and incomplete.[1]

To supply this deficiency the thermal conductivity of seven normal primary saturated alcohols at 30, 75 and 100° and at atmospheric pressure have been determined by the writer by means of a special form of radial heat flow calorimeter comprising a thin cylindrical sheath of liquid.

The alcohols were obtained from the Eastman Kodak Chemical Company, Rochester, N. Y., and were of a very high order of purity as is shown by their range of boiling temperatures given in the summary of the results (Table I). Shipped in sealed bottles with ground-glass stoppers the samples were and remained perfectly colorless.

The apparatus used consisted chiefly of Bridgman's cylindrical calorimeter and is fully described elsewhere.[2]

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[1] "International Critical Tables," 1929, Vol. V, p. 227, Table VI and p. 228, Tables X–XI; Landolt–Börnstein, "Physikalisch-Chemische Tabellen," 1931, Table 271, p. 1278; II Erg. Bd.; also ed. of 1927, I Erg. Bd.; Table 271, p. 715; Glazebrook's "Dictionary of Applied Physics," Article on "Thermal Conductivity," Vol. I, p. 429.

[2] P. W. Bridgman, "The Thermal Conductivity of Liquids under Pressure," *Proc. Am. Acad. Arts Sciences*, **59**, 7 (1923); J. F. Downie–Smith. "Thermal Conductivity of Liquids," *Ind. Eng. Chem.*, **22**, 1246 (1930).

Certain improvements were introduced by the writer, as, for example, the replacement of the manganin heating element by one of chromel of much higher resistance and of the same dimensions as previously. A special apparatus was constructed to ensure complete evacuation of the liquids from the calorimeter. This consisted essentially of a thick-walled cylinder into which the calorimeter could be inserted with a push fit. The whole was then immersed in an oil-bath and heated to approximately 120°, after which the cylinder with the calorimeter was placed under high vacuum (initial pressure less than 0.01 mm.) for eighteen hours in a thermally insulated flask. To ensure complete filling of the calorimeter by the more viscous alcohols, both the calorimeter and the liquids were preheated to approximately 80°. The calorimeter was then filled under high vacuum.

To prevent violent deflections of the galvanometer caused by Hertzian waves emanating from the contact of the thermostat, the latter was shunted by a condenser of high capacity. Close temperature regulation of the constant temperature bath at 100° proved difficult with the simple form of mercury-in-glass thermostat used in the original apparatus, but this difficulty was successfully overcome through the use of a toluene-mercury-in-glass thermostat.

In order to eliminate systematic errors due to possible electrical leaks each run consisted of four tests made with each of the four possible combinations of polarity of the thermocouple and heating element circuits.

Each value determined by the writer is a mean of a number of runs sufficiently large to reduce the probable error of the mean to 0.5% of the value of the mean of the means. The number of runs necessary to achieve this end varied from 8 to 15, but was in general in the neighborhood of 10. The standard deviation and the probable error of the mean were computed by the classical methods of statistics.

The results obtained are summarized in Table I and are also shown graphically in Figs. 1 and 2.

Methanol and n-butanol have not been tested by the writer since reliable values of their thermal conductivities at the desired temperatures had already been published by a previous investigator.[2]

Figure 1 in which the thermal conductivities of the alcohols at different temperatures have been plotted against molecular weight shows the existence of a marked minimum of thermal conductivity for n-hexyl alcohol. This is not an isolated instance; in fact, maxima and minima of physical properties in homologous series for the member containing six carbon atoms (or for members closely adjacent to the latter) are of not infrequent occurrence. The following examples may be cited: the melting points at atmospheric pressure of saturated alcohols, o-toluidines, p-bromo-anilines and p-bromonaphthalenes; the ionization constants of the carboxylic acids have a minimum around the six carbon atom member. The molecular

TABLE I

THERMAL CONDUCTIVITIES IN GRAM-CAL. PER SEC. PER SQ. CM. PER °C. PER CM. $\times 10^6$
OF NORMAL PRIMARY SATURATED ALCOHOLS AT 30, 75 AND 100 °C. AND AT
ATMOSPHERIC PRESSURE

Alcohol	Range of boiling temp., °C.	Number of carbon atoms	Molecular weight	Thermal conductivity $\times 10^6$ at		
				30°	75°	100°
Methyl		1	32.04	503[a]	492[b]	...
Ethyl[c]		2	46.05	433	416[b]	...
n-Propyl	96–98[d]	3	60.08	409	393	...
n-Butyl		4	74.10	394[a]	382[a]	...
n-Amyl	136–139[d]	5	88.11	388	375	368
n-Hexyl	155–157[d]	6	102.15	386	374	368
n-Heptyl	154–156[d]	7	116.17	389	376	372
n-Octyl	191–194[d]	8	130.18	398	387	375
n-Nonyl	97–99 (14 mm.)	9	144.21	401	391·	382

[a] Value obtained by P. W. Bridgman.[2]   [b] Extrapolated value obtained from P. W. Bridgman.[2]   [c] The sample of ethyl alcohol used contained 99.8% of absolute ethanol, the impurities consisting chiefly of water.   [d] At atmospheric pressure.

optical rotation of the methyl esters of dibasic fatty acids shows three relative maxima for the members containing 3, 6 and 9 carbon atoms.
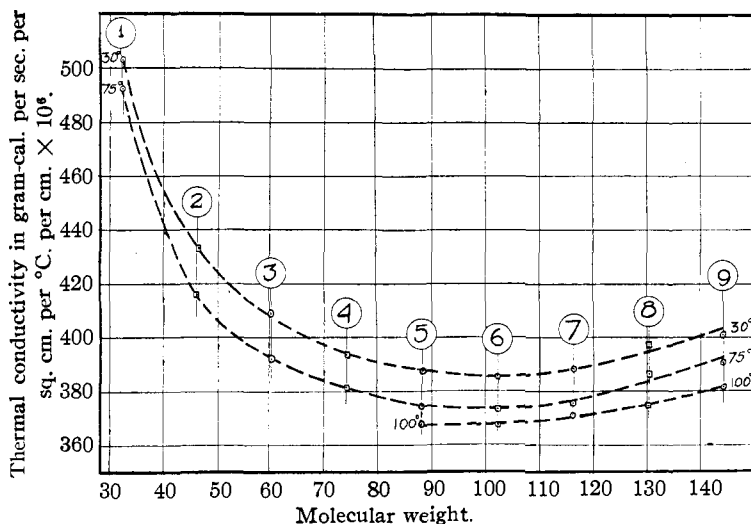

Fig. 1.—Variation of thermal conductivity of normal primary saturated alcohols with molecular weight at 30, 75 and 100° and at atmospheric pressure. The figures in the circles indicate the number of carbon atoms in the alcohol.

It has been suggested that a possible explanation of this behavior lies in the known fact that the angles between the bonds of the carbon atoms are equal to 120°, and, therefore, that the spirals formed by the open-chain hydrocarbons could be expected to exhibit singular spatial relations when

the number of carbon atoms present in the chain is a multiple of three. Recent x-ray studies seem to point in the same direction.

An examination of the curves of Fig. 1 as well as a comparison between the thermal conductivities of isomeric alcohols leads to the conclusion that the thermal conductivities of saturated alcohols do not possess the property of additivity.

In many homologous series the physical properties of the member of lowest molecular weight are often exceptional, but in the series under consideration this cannot be said to be true, for the value for methyl alcohol, although relatively high, fits the general curves well. Also the members with odd and even numbers of carbon atoms are seen to possess values of thermal conductivity lying on a common curve.
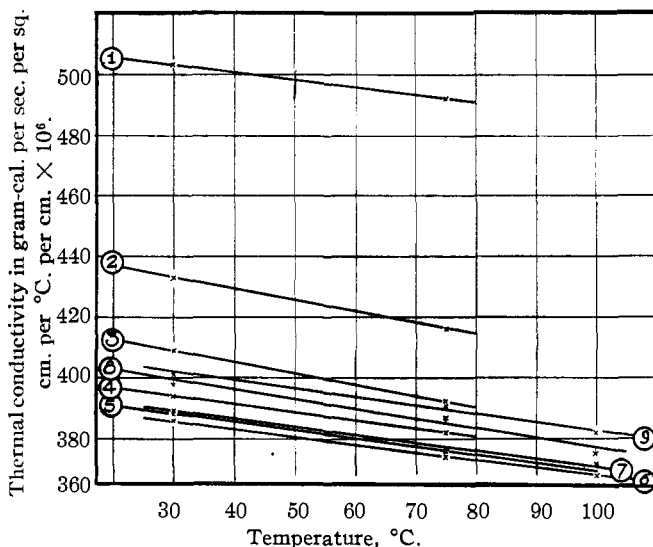

Fig. 2.—Variation with temperature at atmospheric pressure of the thermal conductivity of saturated normal primary alcohols. The figures in the circles indicate the number of carbon atoms in the alcohols.

Figure 2 in which the thermal conductivities of the different alcohols have been plotted against temperature shows that normal saturated alcohols have a negative temperature coefficient of thermal conductivity and that the variation of thermal conductivity with temperature is very nearly linear. The temperature coefficient has substantially the same value for all the alcohols investigated. The curve for normal butanol was fitted to values taken from P. W. Bridgman[2] and agrees well with the writer's own curves. This is the more significant because an error in a value of thermal conductivity may cause a very much larger error in the temperature coefficient of thermal conductivity.

The writer is indebted to Professor P. W. Bridgman of Harvard College for the loan of his cylindrical calorimeter and to Mr. J. F. Downie-Smith, Assistant in draughting at the Harvard Engineering School, for the use of his equipment.

CAMBRIDGE, MASSACHUSETTS

CONCERNING THE ACIDITY OF SOLUTIONS OF SODIUM METAPHOSPHATES. APPROXIMATE STRENGTH OF MONOMETAPHOSPHORIC ACID. VI

BY SAMUEL J. KIEHL AND THOMAS M. HILL

The acidity of solutions of sodium monometaphosphate, which was prepared by the method of Beans and one of us,[1] was found to diminish when it was recrystallized several times from water. This feeble acid reaction of such solutions of the fused product obtained by heating monosodium orthophosphate has been known since Graham's[2] memorable work. In his report this statement is found concerning the "fused insoluble variety:" "When the preceding insoluble variety, or the biphosphate in any condition, is heated in a platinum crucible to low redness, it undergoes fusion, and on cooling presents itself as a transparent glass, which deliquesces in a damp atmosphere and is highly soluble in water. *But the fused salt has undergone a most extraordinary and permanent change of properties.* The solution has a very feeble acid reaction when compared with crystallized biphosphate." This salt referred to by Graham is classed by J. W. Mellor[3] in a summary as a hexametaphosphate, under which he gives the property of acidity referred to above. G. Tammann[4] believed that Graham's salt was a mixture of three isomeric hexametaphosphates.

The significant fact that the salt prepared by us diminished in acidity when it was recrystallized several times from water indicated that the substance responsible for the acidity was capable of separation and that it existed as an impurity. The source and identity of the acid impurity was therefore sought.

Graham[2] also prepared disodium dihydrogen pyrophosphate by carefully heating monosodium orthophosphate and under properties stated that the solution was acid when no monosodium orthophosphate, detectable by silver nitrate, remained. He found also that the solutions became

[1] Beans and Kiehl, THIS JOURNAL, 49, 1878 (1927).

[2] Graham, *Phil. Trans.*, 123, 253 (1833).

[3] Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. II, 1922, p. 870.

[4] Tammann, *J. prakt. Chem.*, [2] 45, 463 (1892).