our determinations have been made, de Kock[1] has shown, in an exhaustive study of the subject, that such is the case, and that a small difference in the solubility coëfficients of the solutes in the two modifications of the solvent may produce variations in the depression constant. It appears then from the fairly uniform values in Table I that these substances have solubility coëfficients which do not differ widely, and for such substances azoxyanisol might be used in cryoscopic work, but it also appears from the results of the experiments with ketones, as given in Table II, that there are compounds which have large variations in the solubility coëfficients, and that it is these variations which are responsible for the differences in the molecular depression constant, and hence render cryoscopic work with azoxyanisol unreliable.

SYRACUSE UNIVERSITY,
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A CRITICISM OF CLARKE'S NEW LAW IN THERMOCHEMISTRY.[2]

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A discussion of F. W. Clarke's paper, "A New Law in Thermochemistry," by W. v. Löben, appeared some time ago in the *Zeitschrift für anorganischen Chemie* (34, 175 (1903)), and in a later article Julius Thomsen stated his opinion that Clarke's results have no significance.

v. Löben maintains, and rightly, that Clarke has reasoned in a circle and that his constant is not a constant, since in the equation

$$\frac{4K}{12a + 6b - c - 8n} = \text{const.},$$

the different heats of combustion of isomers will change the value of K, while the denominator of that term takes no account of isomerism.

The authors of this paper look upon the work of Clarke as a painstaking and commendable attempt to reduce the data of ther-

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[1] *Ztschr. phys. Chem.*, 48, 151.

[2] A. A. Noyes, in his abstract of Clarke's paper (This Journal, 25, R 256), suggests that possibly the choice of even integral numbers of henotherms to represent the various elementary heat effects may have brought about the agreement between the calculated and the observed heat effects as given by Clarke.

mal chemistry to an orderly system. It is true the method applied is that of assuming the constant first and working back from the above equation to a more exact value of the constant; it is true, too, that for derivatives of the hydrocarbons Clarke finds it necessary to introduce modifications into his formula to keep his constant constant. Further, it is evident that in choosing this constant upon which to build his equation Clarke took 13,700, because it is the value in thermal units attributed to the chemical affinity (or electrical strain) between hydrogen ions and hydroxyl ions. This arbitrary choice of the constant, 13,700, seems to us fortunate in that it enables one to test, along thermal lines, the validity of the conception that the affinity of elements and radicals for each other is the same and is independent of the individual element, dependent solely upon the number of valencies or atomic linkings involved; or, in terms of the ionic conception, dependent upon the number of electrical charges upon the ions in the reaction. Such a simplification would be welcome, if it accorded with the facts. It is evident that Clarke has neglected to consider the intensity factor which, of course, enters into the 13,700. On his basis the capacity factor is the same for all atoms or radicals, and this equivalence of the capacity factors of energy (coulombs) for different elements or radicals is the essence of Faraday's law of electrolysis. The fact that different voltages are required to decompose substances which take the same current is good evidence that all atomic linkings are not of the same thermal value.

A critical discussion of Clarke's mathematical work is given by v. Löben, as stated above. In addition we have represented graphically the deviations of Clarke's constant from a steady value and compared the heats of combustion as calculated by Clarke from his corrected constant "henotherm," with those obtained experimentally by Julius Thomsen.

The general type of the curves is shown in Plates I and II, the data for which were taken from Clarke's paper, "A New Law in Thermochemistry," pages 26 to 28. In general, the ordinates for the series of curves plotted by us are in per cent. variation of the calculated heat of combustion from the experimentally determined value; abscissae are usually CH_2 increments for the members of the ascending homologous series. Clarke's error is sometimes negative and sometimes positive, consequently we have plotted positive and negative values for his results. Thomsen's error being a true experimental error

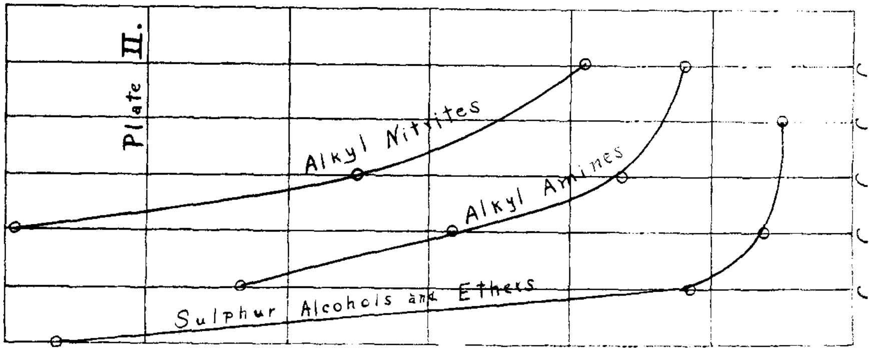
Plate II.
Alkyl Nitrites
Alkyl Amines
Sulphur Alcohols and Ethers

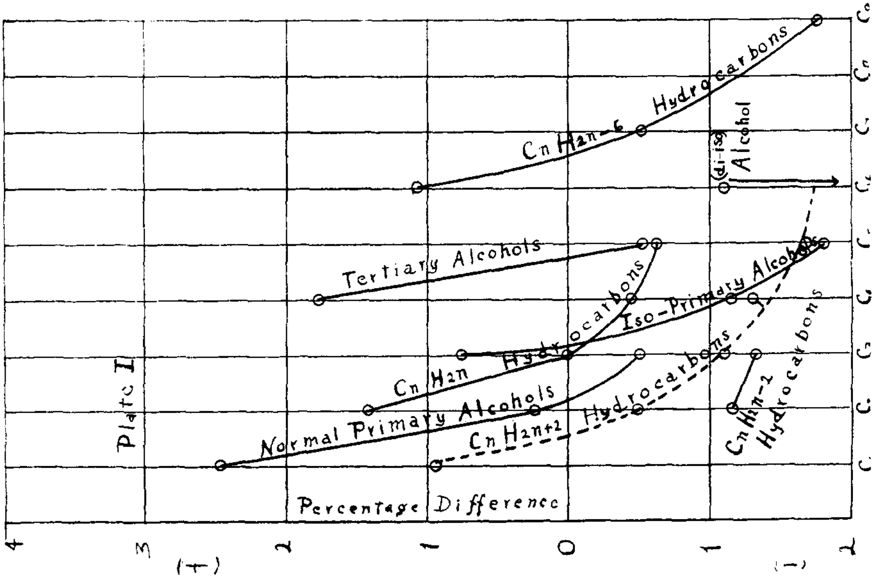
Plate I
Cn H2n-6 Hydrocarbons
(di-iso) Alcohol
Tertiary Alcohols
Iso-Primary Alcohols
Cn H2n Hydrocarbons
Normal Primary Alcohols
Cn H2n+2 Hydrocarbons
Cn H2n-2 Hydrocarbons
Percentage Difference
4
3
(+)
2
1
0
1
(−)
2

is likely to fall either positive or negative, and naturally becomes less and less as we ascend the series, since the total heat measured is greater on a gram-molecule of substance; therefore, we have plotted his curves in duplicate, using both the positive and negative ordinate with the same abscissae. In general, these curves show that Clarke's error starts well up on the positive ordinate for lower members of the homologous series where the carbon content is small and passes by a regular gradation, as we ascend the homologous series, through zero into the field of negative ordinates and becomes asymptotic to the axis of abscissa. This regularity of the curve of Clarke's error is observed in the paraffin, benzene and ethylene series for hydrocarbons, in the paraffin halides, alcohols, acids, amines, sulphur alcohols and sulphur ethers, and nitrites. The acetylene series, so far as studied, shows the same regularity for Clarke's error, although the curve lies entirely in the region of negative ordinates. The exceptional deviation of carbon tetrachloride from Clarke's law appears upon plotting the curve of his deviations for methane, methyl chloride, chloroform and carbon tetrachloride to be no exception at all, but rather exactly what is to be expected of a compound robbed of all four hydrogen atoms. A curve was roughly plotted by us from purely theoretical considerations, which shows that the diminution in the heat of combustion for members of an homologous series due to arbitrarily imagining one hydrogen atom to be removed from each member of the series forms a less and less per cent. of the total heat of combustion as we ascend the series. This is precisely the sort of regularity shown by the curves for Clarke's error. Such a regularity going through all classes of compounds considered by him shows, beyond question, that the deviations are not accidental or of the true experimental order of those of Thomsen, but are due to the CH_2 increment running throughout the series. Consequently, allowing Clarke all latitude as to his mathematical processes, he has not secured a constant thermal value for different atomic linkings. His so-called constant retains, mathematically concealed, the chemical differences in different organic compounds, and is really no more than recognizing that variation in physical properties in homologous series keeps pace with the CH_2 increment, a consideration not new.

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