

THE CONCENTRATION AT WHICH HEATS OF DILUTION ARE MEASURED IN
THE CALORIMETRIC METHOD

Sir:

In a series of excellent experimental papers, E. Lange and A. L. Robinson and their collaborators [for a summary of their work to 1931, see E. Lange and A. L. Robinson, *Chem. Rev.*, **9**, 89 (1931)] have greatly improved the precision with which heats of dilution can be measured and have recorded results at much higher dilution than previous investigators. Unfortunately, their method of standardizing their data to the reference state of infinite dilution is open to a misunderstanding in respect to the concentration for which the heat of dilution has been actually measured which appears to be quite widespread.

They dilute a volume of solution at a given initial concentration with a measured amount of water to a readily computed final concentration and measure the heat evolved in the process. Thus

$$\frac{\text{NaCl} + n_1 \text{H}_2\text{O}}{0.01 \text{ } m} + x \text{H}_2\text{O} = \frac{\text{NaCl} + (n_1 + x) \text{H}_2\text{O}}{0.0005 \text{ } m}$$

$$\Delta H = \bar{L}_2(0.0005 \text{ } m) + (n_1 + x) \bar{L}_1 - \bar{L}_2(0.01 \text{ } m) - n_1 \bar{L}_1(0.01)$$

These so called intermediate changes in heat content when calculated to one mole of salt are designated in Lange's notation as $V_{(c \text{ initial } c \text{ final})}$. Each dilution experiment thus gives two points on a curve, the initial and final concentrations. When a region of concentration is reached where these ΔH values become proportional to \sqrt{c} (c = moles/liter), an extrapolation is made to $c = 0$ whereby these intermediate heats of dilution are interpreted as integral heats of dilution by addition of the quantity of V_c obtained by graphical extrapolation.

$$\frac{\text{NaCl} + n_1 \text{H}_2\text{O}}{0.0005 \text{ } m} + (\infty - n_1) \text{H}_2\text{O} = \frac{\text{NaCl} + \infty \text{H}_2\text{O}}{m = 0}$$

$$\Delta H = -\bar{L}_2(0.0005 \text{ } m) - n_1 \bar{L}_1(0.0005) = V_c(\text{Lange's notation})$$

Lange and Robinson represent their results by curves in which the values for both the initial and final concentrations are plotted, thereby giving the impression that measurements of the heat of dilution have actually been made for the lower concentration. In fact, in their conclusions they state that the integral heats of dilution have been measured over a range which includes the lower concentration limits. [See, for example E. Lange and A. L. Robinson, *THIS JOURNAL*, **52**, 4218 (1930); H. Hammerschmid and A. L. Robinson, *ibid.*, **54**, 3120 (1932)]. That the measured values should refer only to the initial concentration and not to the final or any intermediate concentration is obvious when we recognize that, had the authors been able to measure the heat evolved by the addition of an infinite volume of water, all of the plotted points corresponding to the final concentrations would have vanished. All the data recorded in

their final tables, in the two papers referred to, below 0.0125 *m* (0.00625 *m* in the case of sodium bromide) should be designated as extrapolated and not as interpolated values. Although the values which they record for the final concentrations are very likely correct, it is, nevertheless, desirable to point out that they do not constitute measured values, but involve the acceptance of the validity of the Debye-Hückel theory. This theory is without doubt the best to employ at the present time, yet there have been examples in which specific individual characteristics have been obscured by its use at concentrations which, at the time, were thought to be sufficiently dilute for application.

DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
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V. K. LA MER
I. A. COWPERTHWAIT

THE OXYGEN VALENCE ANGLE AND THE STRUCTURE OF GLUCOSE AND RELATED COMPOUNDS

Sir:

During the last ten years an extensive series of investigations has been carried out on the synthesis and structure of various oxygen-bridged ring compounds from the point of view of elucidating the structure and properties of glucose and polysaccharides. During the progress of this work, it has become more and more evident that the assignment of the same tetrahedral angle to both the oxygen and carbon atoms is incorrect and that many of the anomalies found in the study of carbohydrate chemistry are due to the lack of recognition of this factor.

In the case of furanose and pyranose ring forms of the sugars this point has also been stressed by Haworth, Cox and other workers.

During the last three years a careful study has been made on the electric moments of ethylene oxide, propylene oxide, trimethylene oxide, tetrahydrofuran (tetramethylene oxide) and tetrahydropyran (pentamethylene oxide), and the oxygen valence angles calculated in each case. These have been determined as follows.

OXYGEN VALENCE ANGLES IN CYCLIC ETHERS		
Compound	Moment ($\times 10^{18}$)	Oxygen valence angle
Ethylene oxide	1.88	77°
Propylene oxide	1.88	65 ^{ca}
		77°
Trimethylene oxide	2.01	102°
Tetrahydrofuran	1.71 ^a	105°
		ca. 100 ^{ca}
Tetrahydropyran	1.87	88°

^a Smyth and Walls, THIS JOURNAL, 54, 3230 (1932).