The average deviation is seen to be a little less than one part in a thousand, which is somewhat better than the agreement between the values of Verschoyle, and Holborn and Otto, and Van Urk.

Verschoyle's inference that the gas used in our measurements was not pure is thus seen to be unfounded. In fact, the method of purification employed would preclude the possibility of "the presence of a gas of comparatively high boiling point."

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## NOTE

**The Calculation of Activities from Freezing Points.**—In the calculation of activities from freezing points by the method of Lewis and Randall,[1] the drawing of the A graph ($j/m$ against $m$) in dilute solution, and its extrapolation to infinite dilution, present some difficulty, since the quantity $j/m$ is particularly susceptible to experimental errors which increase in magnitude as the solution becomes dilute. Lewis and Randall point out that inaccuracy in the drawing of the curve causes very little error in the final results. It is, nevertheless, desirable that the curve should be drawn as accurately as possible. As guidance in the drawing of the curve at great dilutions, they remark that the curve has a horizontal tangent at zero concentration; while this seems to be true for aqueous solutions of non-electrolytes, it does not appear to be true for those non-aqueous solutions whose deviation from the ideal is usually attributed to association. It is the object of this note to point out another aid in the drawing of the, A plot—more generally applicable than that of Lewis and Randall, although still, unfortunately, inapplicable in all cases: it is usually possible to deduce the limiting value of $j/m$ from the B graph ($\theta/m$ against $\theta$), and a knowledge of this limiting value is a great aid in the drawing of the A graph.

If the relation between the depression ($\theta$) and the molality ($m$) can be expressed by an empirical equation of the type

$$\theta/m = \lambda + \alpha\theta + \beta\theta^2 + \gamma\theta^3 + \dots \qquad (1)$$

where $\lambda$, $\alpha$, $\beta$, $\gamma$ are constants, then

$$\frac{\partial\, \theta/m}{\partial\, \theta} = \alpha + 2\beta\theta + 3\gamma\theta^2 + \dots \qquad (2)$$

and

$$j/m = \frac{1 - \dfrac{\theta}{\lambda m}}{m} = -\frac{\alpha\theta}{\lambda m} - \frac{\beta\theta^2}{\lambda m} - \frac{\gamma\theta^3}{\lambda m} - \dots \qquad (3)$$

In the limiting case ($\theta = 0$), since $\theta/m = \lambda$,

$$-j/m = \alpha = \frac{\partial\, \theta/m}{\partial\, \theta} \qquad (4)$$

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[1] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**, Chap. 23.

that is to say, when $\theta = 0$, $j/m$ is numerically equal, but opposite in sign to the slope of the tangent to the B plot.

It is not necessary, or even desirable, to evaluate Equation 1. It is, however, necessary for the applicability of the method to any particular case that this equation should be capable of evaluation—a fact that can easily be ascertained by inspection of the B graph.

The slope of the tangent to the B plot can usually be estimated with fair accuracy; $\theta/m$ is not so susceptible to experimental errors as $j/m$; the B plot can be drawn to infinite dilution without the uncertainty of extrapolation since $\lambda$ is known; and lastly, when the method can be employed at all, the B plot is an almost straight line in dilute solution, so that little error is involved in drawing its tangent.

The method is generally applicable to aqueous solutions of non-electrolytes, but not of electrolytes, for here an equation of Type 1 cannot be made to fit the experimental facts; consequently, the B graph is markedly curved in dilute solution and it is impossible to draw its tangent at infinite dilution. I have recently been engaged in the calculation of activities of so-called associated substances in nitrobenzene solution.[2] Here, alcohols and phenols are so fundamentally different in their behavior from carboxylic acids that it suggests that the abnormalities of the two classes are due to different causes. With carboxylic acids this method is inapplicable for the same reasons as with aqueous solutions of electrolytes. With alcohols and phenols the method is applicable, and is particularly valuable, for with these substances the A curve has no horizontal tangent at zero concentration.

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[2] Bury, *J. Phys. Chem.*, **30**, 694 (1926).