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CORRECTION TO THE EQUATION OF STATE FOR NITROGEN[1]

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The recalculation of certain quantities from the equation of state for nitrogen has disclosed an error in determining the mass of nitrogen employed in the equation of state measurements. The mass of nitrogen actually present was 0.51185 g. instead of 0.51451 g. as originally computed.

The pressures and temperatures measured remain as given in the original article while the volumes are increased in the ratio of 0.51451 to 0.51185 (1.005197). The change in specific volumes modifies somewhat the constants of the equation of state for nitrogen. The equation as now determined is as follows: $p = [2.9286/(v - \delta)]\,T - 1650.5/(v + 0.313)^2$, where $\log_{10} \delta = 0.2174 - (0.4307/v)$, $\beta = 1.6497$ and $\alpha = 0.9918$. The pressures calculated from this equation are in substantially as good agreement with the observed pressures as those calculated from the old equation.

Van Urk[2] and more recently Verschoyle[3] have pointed out the fact that the pv products for nitrogen at 0.0° as first reported are not in agreement with those of European observers.

Verschoyle, on the other hand, gives the following equation for his own 0.0° isotherm for nitrogen: $pv = (1.00049 - 0.000496\,p + 0.000003334\,p^2)$, where pressures are in international atmospheres and volumes are referred to the volume of nitrogen at 0.0° and one atmosphere as unity. Verschoyle shows that this equation gives pv values agreeing reasonably well with those of Holborn and Otto[4] and Van Urk.

For purposes of comparison with our corrected pv products, Verschoyle's equation has been converted to units of cc. per g. The weight of a liter of nitrogen at 0.0° and one atmosphere being taken as 1.2507 g., the volume of 1 g. becomes 799.55 cc. and the Verschoyle equation becomes $pv = 799.55\,(1.00049 - 0.0004961\,p + 0.000003334\,p^2)$.

Our observed pv products and those calculated from the above equation of Verschoyle are listed in Table I.

TABLE I

COMPARISON OF pv PRODUCTS AT 0.0° VERSCHOYLE AND SMITH AND TAYLOR

p, atm.	34.175	39.251	46.054	55.835	70.979	86.707	111.962	160.224
pv, obs.	790.10	789.09	786.98	785.74	784.81	784.41	787.80	805.29
pv, calcd.	789.50	788.48	787.32	786.66	785.22	785.59	788.95	804.82
(Obs.-calcd.)	+0.60	+0.61	−0.34	−0.92	−0.41	−1.18	−1.15	+0.47

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[1] Smith and Taylor, "Equation of State for Pure Nitrogen, Gas Phase," THIS JOURNAL, **45**, 2107 (1923).

[2] Van Urk, *Thesis*, Leiden, 1924.

[3] Verschoyle, *Proc. Roy. Soc.*, **IIIA**, 552 (1926).

[4] Holborn and Otto, *Z. Physik*, **23**, 77 (1924).

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 (θ/m against θ), and a knowledge of this limiting value is a great aid in the drawing of the A graph.

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

$$\theta/m = \lambda + \alpha\theta + \beta\theta^2 + \gamma\theta^3 + \dots \tag{1}$$

where λ, α, β, γ are constants, then

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

and

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

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

$$-j/m = \alpha = \frac{\partial\,\theta/m}{\partial\,\theta} \tag{4}$$

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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.