

saturation solubility<sup>2-9</sup>. Many other determinations of this quantity have been made by equilibrating the liquid phase with air and subsequently determining the dissolved oxygen by chemical means<sup>5,7,10-13</sup>. The solubility coefficients for oxygen in distilled water obtained over the past eighty years by these two methods show no significant difference<sup>7</sup> (range about 2.5% at 25° C for all studies quoted). Morris, Stumm and Galal<sup>5</sup> used both approaches in a single investigation.

Murray and Riley (ref. 7, Table 3) compared their own smooth curve data, obtained by an air saturation method, with solubility coefficients determined by pure oxygen saturation. The maximum difference between the two methods, at any of nine temperatures between 5.90° C and 28.31° C, was 0.02 ml. litre<sup>-1</sup> (0.4%).

All these results are in conflict with the approximately 25% difference predicted for such comparisons by Maharajh and Walkley (ref. 1, Fig. 1).

Because no experimental details are given on the saturation method used, and only the briefest description of the analytical procedure is available, it is not possible to speculate on possible reasons for the disagreement between some of their results and the considerable body of literature evidence cited above. I wish here to point out this disagreement, and to urge that the results of Maharajh and Walkley should be treated with caution until substantiated further.

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## Applicability of Henry's Law: An Analysis of the Data of Maharajh and Walkley

THE recent report of Maharajh and Walkley<sup>1</sup> claims that the solubility of oxygen in water is lowered by the presence of a second gas such as nitrogen. This observation conflicts with Henry's law. They base their claim upon measured solubility data which appear to show a significant interaction between the dissolved gases (each present at concentrations less than 50 p.p.m.). The purpose of this note is to demonstrate that a thermodynamic analysis of these data yields an unreasonable value for the nonideality of the aqueous solution of dissolved gases. We therefore question the validity of their data and reiterate the applicability of Henry's law to slightly soluble gases, both pure and mixed.

Their solubility diagram<sup>1</sup> for oxygen + nitrogen gas dissolved in water contains an error: the solubilities are too high by a factor of 10<sup>3</sup>. We assume that this is a typographical error. The Gibbs-Duhem equation may be applied to this diagram; at constant temperature and pressure<sup>2</sup>

$$x_1 d\mu_1 + x_2 d\mu_2 + x_3 d\mu_3 = 0$$

where 1 refers to oxygen, 2 to nitrogen and 3 to water.  $\mu$  is the chemical potential; for this system

$$x_1 d \ln K_1 + x_2 d \ln K_2 + x_3 d \ln \gamma_3 = 0$$

$K$  is the Henry's law "constant" and  $\gamma_3$  is the activity coefficient of water. Integration ( $x_3 \approx 1$ ) gives

$$\Delta \ln \gamma_3 = - \int_{x_1=0}^{2.2 \times 10^{-5}} x_1 d \ln K_1 - \int_{x_2=0}^{2.2 \times 10^{-5}} x_2 d \ln K_2$$

According to the data

$$\Delta \ln \gamma_3 = 3.73 \times 10^{-6} - 2.14 \times 10^{-6} = 1.59 \times 10^{-6}$$

For concentrations of dissolved gas less than a few mol %, the activity coefficient of the solvent is accurately described by the equation<sup>3</sup>

$$\ln \gamma_3 = A(1 - x_3)^2$$

For pure dissolved oxygen the mol fraction of oxygen is  $(1 - x_3) = 2.2 \times 10^{-5}$  and for pure dissolved nitrogen  $(1 - x_3) = 1.3 \times 10^{-5}$ . Using the experimental value of  $\Delta \ln \gamma$  we get  $A = 4,700$ . This value of  $A$  is absurdly high. For example at mol fraction dissolved gas equal to 0.005 (which occurs at about 1,000 atmosphere for nitrogen) this value of  $A$  predicts that the Henry's "constant" ( $K$ ) is reduced by a factor of 10<sup>20</sup> from its value at infinite dilution!

These calculations confirm some obvious physical considerations. Henry's law (the Krichevsky-Kasarnovsky equation<sup>3</sup>) is obeyed for the pure gases up to at least 0.5 mol % dissolved gas. At one atmosphere the mol % dissolved gas is about 0.001, or 500 times less. Therefore one would expect Henry's law to work to a very high accuracy under the conditions studied by Maharajh and Walkley.

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