Prof. C. Boswell, Dr. G. E. Francis, Miss M. Blundell and Miss M. Jeremy for help in various ways.

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Solubility of Oxygen in Water

THE rate at which self-purification can occur in waters polluted by oxidizable organic matter may depend largely on the rate at which oxygen from the air is dissolved by the water. In natural water the rate of solution is influenced by many variable factors; but Adeney and Becker[1] have stated that for constant conditions, and for a uniformly mixed body of water, it is proportional to the difference between the concentration of oxygen in solution and the saturation or equilibrium concentration. Unfortunately, the absolute saturation values are not known with great precision; indeed, some of the values published by several independent investigators differ by as much as 0·4 part of oxygen per million at temperatures in the range 0°–35° C. The most generally accepted values are, however, those quoted by the American Public Health Association in "Standard Methods for Examination of Water and Sewage"[2]; these are based on gasometric determinations by C. J. J. Fox[3].

In an investigation to provide information about the effect of natural variable factors on surface aeration, we have made many measurements of rates of aeration of pure water, the concentration of dissolved oxygen being determined by the Winkler[4] titration method using an amperometric end-point[5] in the final titration of iodine. We have consistently found that over a range of temperature 0°–35° C. the Adeney and Becker law of aeration is not satisfied when rates of solution of atmospheric oxygen are evaluated from the difference between the accepted saturation values and the dissolved oxygen concentration of the solution determined by the Winkler method. This discrepancy arises because the accepted saturation values are higher than the values obtained when the concentration of oxygen in water in equilibrium with atmospheric oxygen is determined by the Winkler method. This is a matter of some importance since it is the Winkler method which is most commonly used for the determination of dissolved oxygen and hence of rates of solution both in the laboratory and in field investigations.

In our experiments, the concentration of oxygen in deionized distilled water was either reduced or increased to a value well below or above the saturation value at a given temperature; the water was then slowly stirred to bring it into equilibrium with an atmosphere of air which had been saturated with water vapour and from which carbon dioxide had been removed. Measurements of dissolved oxygen were made at intervals until several successive samples, taken over a period of days, gave a constant value when corrected for changes in atmospheric pressure. This value was assumed to be the saturation concentration at the temperature of the experiment. The results obtained by this procedure are related by the empirical equation $C_S = 14{\cdot}16 - 0{\cdot}3943T + 0{\cdot}007714T^2 - 0{\cdot}0000646T^3$, where C_S equals saturation concentration in parts of oxygen per million and T equals temperature in degrees C. The standard error of the curve is 0·05 part of oxygen per million. A comparison between these values and those determined gasometrically by Fox are shown in Fig. 1. It is noteworthy that much better agreement with Adeney and Becker's law of aeration may be obtained with these saturation values than with the generally accepted ones. Moreover, for the purpose of determining rates of solution in natural waters, these saturation values are less 'artificial' than the accepted values in that they were obtained in waters in equilibrium with atmospheric oxygen rather than with pure oxygen in a sealed apparatus. It is of interest in this connexion that Holroyd and Parker[6] in their work on the dynamics of aeration have reported that they were unable to approach the accepted saturation values, though they attributed this to a thermometric error.

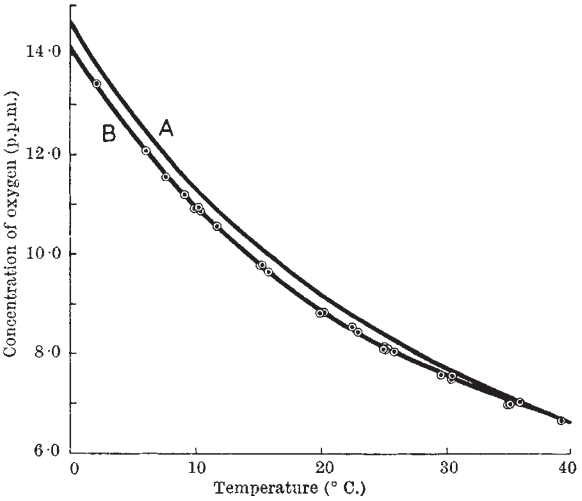

Fig. 1. Curve *A*, saturation values taken from "Standard Methods" calculated by Whipple and Whipple on measurements made by C. J. J. Fox (atmosphere assumed to contain 20·9 per cent oxygen); curve *B*, saturation values determined by the Winkler method

The discrepancy between the saturation values we have obtained and the standard values has stimulated interest in the determination of absolute saturation values. A number of gasometric determinations of the saturation value of oxygen at 25° C. have been made in this laboratory, and the results so far obtained are in close agreement with the value calculated from the above equation at this temperature. These investigations are being continued, and a full account will be published elsewhere.

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