

FIG. 2 SOLUBILITY OF OXYGEN IN WATER

DISCUSSION

Oxygen shows unusually high solubility at 32 F. The solubility decreases with increasing temperature in the range from 32 to 233 F and then increases with increasing temperature as shown in Figs. 3 and 4.

At room temperature where the gas solubility is small the fugacity of the water in the liquid phase may be calculated from Raoult's law. If the pressure change is small then Henry's law applies to the dissolved gas. When the solubilities of gases are measured at high pressures then the influence of pressure cannot be disregarded; consequently, the usual expression for Henry's law must be corrected. A knowledge of the partial molal volume of the dissolved gas is needed in order to make this correction (2). These data for oxygen are not available.

Fig. 4 shows that Henry's law cannot be used to predict the solubility over a wide pressure range. Actually, the solubility would increase to a maximum value and then decrease with increasing partial pressure of oxygen (3, 4).

At the present time we must depend completely upon experimental investigations for our solubility information.

ACKNOWLEDGMENTS

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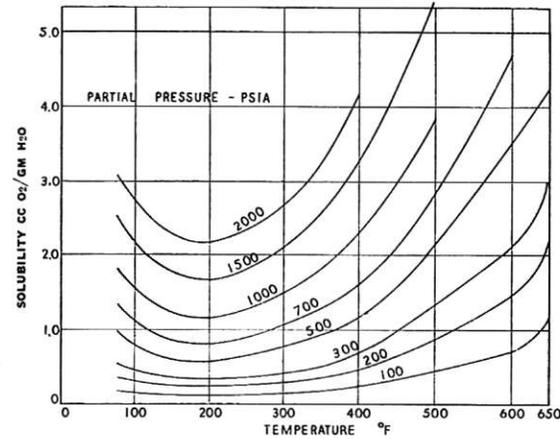


FIG. 3 SOLUBILITY OF OXYGEN IN WATER AS A FUNCTION OF TEMPERATURE

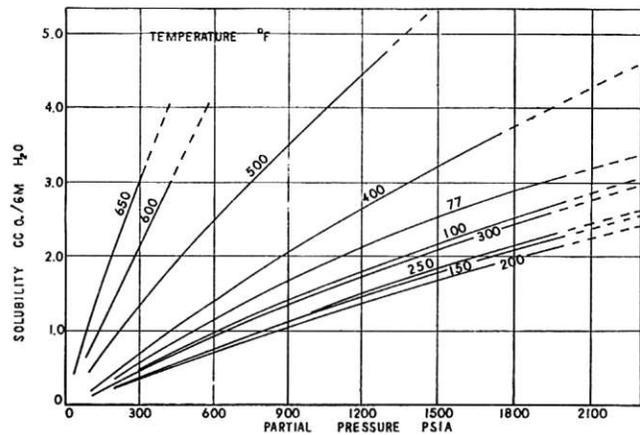


FIG. 4 SOLUBILITY OF OXYGEN IN WATER AS A FUNCTION OF PRESSURE

7 "Solubilities of Gases in Liquids at High Pressure," by K. Frolich, E. J. Tauch, J. J. Hogan, and A. A. Peer, *Industrial and Engineering Chemistry*, vol. 23, 1931, pp. 548-550.

8 "The Solubility of Hydrogen, Oxygen, Nitrogen and Helium in Water at Elevated Temperatures," by H. A. Pray, C. E. Schweichert, and B. H. Minnich, Battelle Memorial Institute, BMI-T-25, May 15, 1950, and *Industrial and Engineering Chemistry*, vol. 44, 1952, pp. 1146-1151.

Discussion

A. WATSON.⁶ It is encouraging to see the authors' results—additional data to fill in the largely uncharted regions of high temperature and pressure. The writer is wondering about the details of the analytical procedures used. Even though they may appear elsewhere, a brief discussion should prove helpful. Along the same lines, what measures were taken to assure that at any one time only liquid or vapor phase was removed from the equilibrium chamber in sampling?

The authors speak of corrosion of the equipment with the use of oxygen under high pressure. Undoubtedly, some hydrogen was produced and this would affect the solubility of oxygen to some extent. Was the effect of hydrogen considered in finally evaluating the oxygen solubility? Perhaps this is what the authors had in mind when they state, "The errors involved in the vapor-sample analysis were due partly to the corrosive nature of oxygen gas in the presence of water vapor."

⁶ Hall Laboratories, Inc., Pittsburgh, Pa.

The authors state, "The pressures shown in Fig. 2 are the total pressures of the system as measured with a gage." With a carbon-steel bomb, this would be a measure of water vapor, oxygen, and hydrogen. The writer believes different results would be secured in a noncorrosive environment, for example, with the stainless-steel chamber. Were the results obtained primarily with the stainless-steel saturation vessel?

The writer does not understand the statement, "At room temperature where the gas solubility is small the fugacity of the water in the liquid phase may be calculated from Raoult's law." At room temperature the gas solubility is relatively large.

The applicability of the authors' data and those of other investigators to many practical problems is undoubtedly great. However, it should be remembered that the values obtained represent equilibrium conditions with rather large partial pressures of oxygen. In a field with which the writer is familiar—boiler operation—only very small amounts of oxygen ordinarily can be present in the feedwater going to high-pressure, high-temperature units. Therefore, in the operating boiler proper, the partial pressure of oxygen in the steam must be quite low, and the solubility of oxygen in the water is, for all practical purposes, zero. This behavior is, of course, advantageous since corrosion is thereby minimized.

AUTHORS' CLOSURE

When the period of agitation was terminated (5 to 20 hr period) and the vessel fastened in a vertical position, a representa-

tive liquid sample could be obtained immediately. Consecutive liquid samples were duplicates.

A considerable period of time (10 to 20 min) was required for the liquid phase to drain from the wall of the vapor sample chamber. Usually a period of one to two hours was allowed for complete drainage.

The liquid-phase analysis apparatus consisted of a water-cooled burette, leveling bulbs, and a drying train. The sample was collected over mercury. The last traces of water vapor were obtained by passing dry gas through the sample chamber, the tubing, and through the drying train.

All of the high-pressure equipment was stainless steel. The type 347 steel was satisfactory but the 304 was severely corroded by the oxygen. The initial corrosion was very rapid. Hydrogen could not be detected after a few hours of operation at high temperatures.

The large errors involved in the vapor sample analysis resulted from leakage past corroded valve stems and seats. Drops of condensate were lost as a result of this leakage.

The relative solubility of oxygen in water is not small at room temperature; however, the mole fraction of oxygen in the water is very small. Therefore the liquid phase may be treated as a dilute solution. Thus, since the concentration of the solute is small, the fugacity of the solvent can be calculated by means of Raoult's law and the relationship of the fugacities of the components obtained from the Gibbs-Duhem equation.