The Effect of Foreign Molecules on the Absorption Coefficient of Oxygen in the Schumann Region

Edwin G. Schneider

The Effect of Foreign Molecules on the Absorption Coefficient of Oxygen in the Schumann Region

EDWIN G. SCHNEIDER

Research Laboratory of Physics, Harvard University, Cambridge, Massachusetts

(Received November 18, 1936)

The absorption coefficient of oxygen in the continuous band having a maximum at 1450A is not altered by the addition of 80 percent nitrogen at pressures less than 15 mm of mercury, the range covered by these experiments. The conclusion is drawn that, at least at low pressures, the absorption of oxygen in the Schumann region is not effected by collisions with foreign molecules.

ABSORPTION of ultraviolet light by oxygen in a band having a maximum near 1450A has been used as a means of inducing photochemical reactions involving oxygen. According to Herzberg,[1] the absorption of a light quantum of wave-length shorter than about 1800A results in the production of a neutral and an excited oxygen atom. Since the interpretation of some of these photochemical studies depends on the assumption that the absorption of oxygen in this band is not altered by the presence of foreign molecules, an investigation of the validity of this assumption seemed advisable.

The apparatus for measuring the absorption of oxygen consisted of a hydrogen discharge tube, a vacuum spectrograph and two cells of length 2.27 and 4.75 cm equipped with lithium fluoride windows. The cells were introduced, one at a time, between the light source and the slit of the spectrograph. The absorption of the gas was measured quantitatively by comparing the intensity of the light passing through the tube when evacuated to a pressure less than 5×10^{-5} mm of mercury with the intensity when gas was introduced at a known pressure. Further details of the method of photographic photometry used in these experiments have been given in a previous publication.[2]

A mixture of 20 percent oxygen and 80 percent nitrogen was selected for investigation because this combination was used as a standard by G. B. Kistiakowsky[3] in studying the reaction of oxygen and hydrogen induced by absorption of extreme ultraviolet light. Tank nitrogen when purified by passing over hot copper and dried with phos-

phorous pentoxide was completely transparent in the wave-length region covered in this investigation provided the pressure was lower than 10 cm in the longer cell. Since the pressure was kept below this value for all of the measurements, the absorption of the nitrogen may be neglected. Furthermore, since Warburg[4] has found that the yield of ozone per quantum of absorbed ultraviolet light is not changed by the addition of nitrogen, the nitrogen may be considered as an inert gas.

Because the oxygen disappeared slowly during prolonged exposure to ultraviolet light, it was necessary to keep the gas flowing through the cell. The flow was sufficient to completely change the gas in the absorption tube five times a minute.

Since there is negligible change in reflection of the light at the surface of the absorption tube when the pressure of the gas is altered a few millimeters, the intensity of the light, I, transmitted by the gas column may be expressed in the following form:

$$I = I_0 e^{-apd},$$

where I_0 is the intensity through the cell when highly evacuated, a is the absorption coefficient per unit length per unit pressure, p is the pressure, and d is the length of the gas column.

This equation shows that a plot of $\log_e I_0/I$ against pd should be a straight line if the absorption coefficient of oxygen is not altered by an increase in pressure of the gas. Fig. 1 shows such a plot for three wave-lengths within the continuous absorption band of oxygen. The points may be seen to lie along a straight line to within experimental error for total gas pressures ranging

[1] Herzberg, Zeits. f. physik. Chemie **4B**, 223 (1929).
[2] Schneider, Phys. Rev. **45**, 152 (1934).
[3] Kistiakowsky, J. Am. Chem. Soc. **52**, 1868 (1930).
[4] Warburg, Sitz. Akad. Wiss. Wien. 216 (1912); 872 (1914).

from 2.3 mm to 15.0 mm. Because of the high absorption at greater pressures, it was impossible to make accurate measurements beyond 15 mm of mercury. Since an increase in pressure increases the number of collisions between molecules, these experiments show that at low pressures an increase in the number of collisions has no effect on the absorption of oxygen in the Schumann region.

The slopes of the lines in Fig. 1 give the absorption coefficient for the nitrogen-oxygen mixture. When expressed in terms of the partial pressure of oxygen, the absorption coefficient for the maximum of the band, 1450A, is 0.55/cm/mm of mercury. Since the measurements were made at a temperature of 25° centigrade, the absorption coefficient reduced to normal temperature and pressure is 460 as compared with the value of 490 per cm at N.T.P. obtained by Ladenburg
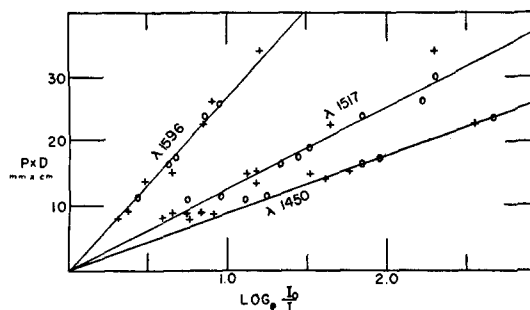

Fig. 1. The logarithm of the opacity of a mixture of 20 percent oxygen and 80 percent nitrogen as a function of the pressure in mm of mercury times the thickness. (0) represents a layer of gas 4.75 cm thick and (+) 2.27 cm.

and Van Voorhis[5] for pure oxygen. The fact that these two values agree to within the experimental error shows that the addition of nitrogen had no influence on the absorption of the oxygen.

[5] Ladenburg and Van Voorhis, Phys. Rev. 43, 315 (1933).

A Thermodynamic Treatment of Systems, in Particular of Solutions, from the Point of View of Activity and Related Functions

Roy W. Goranson

Geophysical Laboratory, Carnegie Institution of Washington, Washington, D. C.

(Received August 26, 1936)

The purpose of this paper is to present a consistent thermodynamic treatment of solutions based on activity and activity coefficient. On the basis of the argument presented interrelations of these quantities are obtained for dissociated and undissociated components. Expressions are also derived for the fugacity and activity of a component in a gas mixture.

IN 1878 Gibbs deduced an equation for dilute solutions. If this equation were to be redefined in terms of molar units, one of Gibbs' constants identified with the gas constant, and the resulting equation be assumed applicable over the whole range of concentration we would have the ordinary ideal solution definition. In application it was found in general that some solutions approximated very closely to this equation, others only when very dilute, and still others not at all. The latter type, namely solutions of electrolytes, were classified separately and a limiting law obtained by formally patching the existing one.

To extend the usefulness of this type of equation so that it might be applicable to all solutions and reduce to it when "infinitely" dilute and when "ideal," Lewis and Randall replaced the molar concentration factor by a function of the independent variables and named it activity, which was a truly inspired idea. The ratio of the activity to the molar concentration of the species, which they named activity coefficient, thus automatically cataloged all solutions in terms of deviations from the "ideal solution." This general pattern has, however, been partially concealed by their phraseology and some apparent ambiguity in defining their functions; as a result there have appeared in text books a variety of interpretations some of which are justifiable whereas others lead to mutually inconsistent interrelations of the ac-