Table VIII

	$\Delta H_f°(XO_3)(g)$	$\Delta H_f°(XO_3^-)$ (g)	E
ClO_3	17.7 ± 0.1	−47	65 ± 0.5
BrO_3	39.8 ± 0.2	−34	74 ± 0.5
IO_3	78 ± 15	−49	127 ± 16

general formula M^IX^I or $M^{II}X^I_2$, for this is the form of the template graphs used for interpolation. Extension of the method to cover systems of the type $M^I_2X^{II}$ and $M^{II}X^{II}$ is discussed in a further publication.

Acknowledgments. It is a pleasure to thank the American Chemical Society (Petroleum Research Fund) for partial financial support.

Effect of Hydrostatic Pressure on Gases Dissolved in Water

by T. Enns, P. F. Scholander, and E. D. Bradstreet

University of California, San Diego, La Jolla, California[1a,b] *(Received May 1, 1964)*

The effect of hydrostatic pressure on equilibrium pressures of a gas dissolved in water has been determined by direct measurement. At approximately 100 atm. hydrostatic pressure the equilibrium pressure increase was approximately 13% for helium, 16% for carbon dioxide, and 14% for nitrogen, oxygen, and argon. Extrapolation of the data indicates that when dissolved surface gases are carried to a depth of 10,000 m., their equilibrium partial pressure increases by a factor of 4.

Several species of deep water fish have swim bladders in which partial pressures of nitrogen gas up to 10 atm. have been observed. As the apparent source of this gas is the atmosphere, the gas pressure must have increased correspondingly. Before determining the role played by the fish in inflating its swim bladder at high pressures, it is necessary to determine the equilibrium pressure for dissolved gases at various depths.

The literature gives no direct data on such gas equilibrium pressures. An attempt to calculate the pressures from the partial molal volume data of Kritchevsky and Iliinskaya[2] has been made by Klotz,[3] but, contrary to existing information, the implication in the equations is that gas diffusion equilibrium exists between surface and ocean deeps. Considerable information is available on the solubility of gases at high pressures applied to both gas and liquid. The data of Wiebe, Gady, and Heins[4] for nitrogen at 75 and 100 atm. when inserted in eq. 4 below give a partial molal volume of 32.1 cm.^{3} which agrees with the values in Table I.

Water equilibrated with gas at or near atmospheric pressure has been subjected to hydrostatic pressures up to approximately 100 atm., and the resultant gas equilibrium pressure has been determined directly. In nitrogen, oxygen, and argon the gas equilibrium pressure increase was approximately 14%/100 atm. Helium showed a slightly smaller and carbon dioxide a slightly greater equilibrium pressure increase.

Simple thermodynamic calculations extrapolate the data to give equilibrium pressures of gases dissolved at the surface and carried to ocean depths. The same calculations yield new values of partial molal volumes

(1) (a) Contribution from the Scripps Institution of Oceanography, University of California, San Diego; (b) this work was supported by Research Grants RG 5979 and GM 10521 from the U. S. Public Health Service.

(2) I. Kritchevsky and A. Iliinskaya, *Acta Physiochim. URSS*, **20**, 327 (1945).

(3) I. M. Klotz, *Limnol. Oceanog.*, **8**, 149 (1963).

(4) R. Wiebe, V. L. Gady, and J. Heins, *J. Am. Chem. Soc.*, **55**, 947 (1933).

Table I[a]

Gas	p in mm. at $P \approx 102$ atm.	p in mm. at $P = 68$ atm.	p in mm. at $P = 34$ atm.	p in mm. at $P = 0$	ln (p_{102}/p_0)	β, cm.^{3}/mole
O_2	839.5	805	771	734.5	0.133	31.9
	892	855	819	781	.133	31.9
	410.5	390	373	359	.1345	32.2
	508	484	464	443	.135	32.3
O_2 at 0.5°	789			682	.1457	32.0
O_2 in sea water	842	806	775	737	.131	31.7
N_2	843	803	773	733	.1385	33.2
	811	777	744	705	.1385	33.2
	844	806.5	769	732	.140	33.5
N_2 in detergent	811	774	742	712	.133	31.9
Ar	849	814	779	741	.135	32.3
	839	803	771	734	.134	32.1
He	815[b]	779	748	719	.124	29.7
	828.5	797.5	765	732	.124	29.7
CO_2	817	779	742	705	.1475	35.3
	849.5	811.5	774	737	.143	34.3

[a] P = Hydrostatic pressure; p = gas equilibrium pressure. [b] P = 102.7 atm.

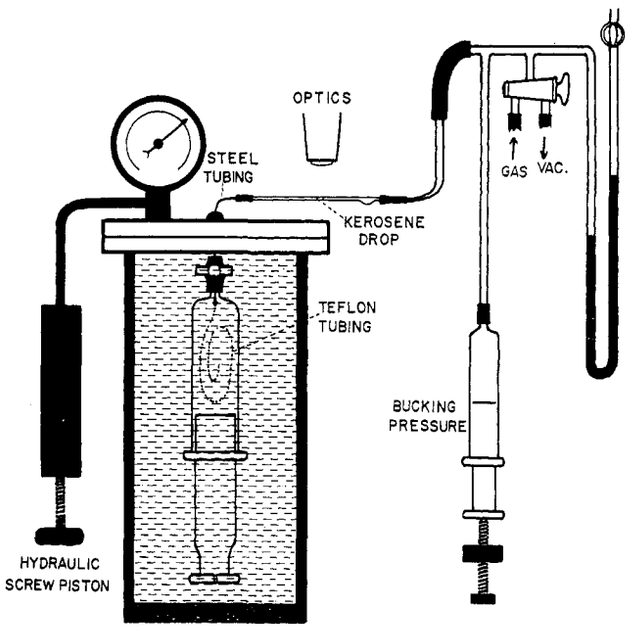

Figure 1. Pressure chamber and gas pressure measurement apparatus.

for the dissolved gases comparable to those reported by Kritchevsky and Iliinskaya.[2]

The gas equilibrium pressures were determined by a null point measurement of gas pressure developed inside a Teflon tube inserted in a pressure chamber containing the desired gas solutions. The nominal dimensions of the Teflon were 0.3 mm. i.d. and 0.23 mm. wall thickness. The length of the tube varied from 10 cm. for relatively insoluble gases to 30 cm. for more soluble gases. The Teflon tube will withstand external pressure of at least 150 atm. without collapsing.

Procedure

Water was gas extracted repeatedly. Gas at the desired pressure was dissolved in it at controlled temperature. Distilled water was used except as noted. The equilibration vessel was shaken during the gas uptake, and the process was complete after 0.5 to 1 hr. The solution was then transferred anaerobically to a 100-cc. syringe through a short section of 0.32-cm. i.d. vacuum tubing. This tubing remained attached to the syringe after filling and was sealed with a screw clamp.

One end of the gas-sensing Teflon tube was closed with a slightly tapered glass rod. The other end was forced over the end of a stainless steel tube (no. 26 needle tubing) about 12 cm. long. This tubing passed through a seal in the lid of the pressure tank near the middle of its length.

The apparatus (Figure 1) was assembled by loosening the clamp on the syringe, inserting the Teflon in the syringe until the stainless steel tube was inside the rubber tube, and then clamping the rubber tightly. This seal was checked by pushing on the syringe plunger. The syringe was then taped to a support on the pressure chamber lid, and the lid was placed on the water-filled pressure chamber so that the syringe was inside the chamber and all air was expelled from the chamber. The external end of the stainless steel tube was immediately connected to the gas-handling system; the Teflon tube was evacuated and then filled with the appropriate gas at atmospheric pressure.

Measurements were made in the following manner. The end of the stainless steel tube was connected to the gas-handling system by a glass tube about 5 cm. long with a 0.5 mm. i.d. A kerosene drop was introduced into this tube and observed on the scale of a microscope. The movement of this drop was timed, and the bucking pressure was adjusted until the drop did not move. Pressures were read on a mercury manometer (Figure 1). Stirring of the solution was found unnecessary because the null measurements moved only negligible amounts of gas in or out of the solutions.

In each experiment, gas equilibrium pressure determinations were made consecutively at 1500 (102 atm.), 1000, 500, and 0 p.s.i.g. pressure, in that order. Checks gave the same values when the sequence was reversed. The gauge used in these experiments was calibrated against a dead weight gauge.

In all experiments except one, the water temperature

was 25°. One experiment was conducted with a detergent solution having a surface tension equal to 30% of that of water.

Results

For all gases examined, the equilibrium pressure inside the Teflon tube was increased by about 14% when the hydrostatic pressure increased from 0 to 1500 p.s.i. (gauge). Water vapor readily crosses the Teflon tube walls; hence, the vapor pressure corresponding to the water temperatures was subtracted from all gas pressure values.

In each experiment natural logarithms of gas pressures were plotted as abscissas, and water gauge pressures, as ordinates. Straight lines were drawn to best fit the points, and the differences between their intercepts on the abscissa and at 102 atm. were recorded under $\ln (p_{102}/p_0)$ in Table I. Figure 2 shows plots of all data obtained at 25° and approximately atmospheric pressure. For each gas, data from different runs are superimposed for best agreement by arbitrary displacement of abscissas.

The effect of reduced surface tension of water was probably not significant. Hence, it must be concluded that surface tension plays no major role in the observed hydrostatic effect on gas equilibrium.

From eq. 3 derived below the partial molal volumes of the gases were calculated and are shown in the last column of Table I.

Discussion

If the dissolved gas is considered an ideal gas within the accuracy of this experiment, the measured equilibrium pressure is proportional to the activity and to the fugacity of the gas. The effect of pressure on the latter is given by[5]

$$\left(\frac{\partial \ln f}{\partial P}\right)_{T,x} = \frac{\bar{v}}{RT} \tag{1}$$

where f = fugacity, P = hydrostatic pressure, $\bar{v}$ = partial molal volume, R = gas constant (82.06 atm./°K.), T = absolute temperature, and x = dissolved gas concentration.

If $\bar{v}$ is assumed constant over the range of the experiment, integration between hydrostatic pressures P_1 and P_2 gives

$$\ln (f_1/f_2) = \bar{v}\frac{(P_1 - P_2)}{RT} \tag{2}$$

where f_1 and f_2 are the fugacities corresponding to P_1 and P_2.

Substituting the ratio of the equilibrium partial pressures p_1 and p_2 for the ratio of the fugacities

$$\ln (p_1/p_2) = \frac{\bar{v}(P_1 - P_2)}{RT} \tag{3}$$

It may be added that, since these experiments were conducted at constant x, the pressure dependence of the Henry's law constant, $k = p/x$, is given by

$$\ln (k_1/k_2) = \frac{\bar{v}(P_1 - P_2)}{RT} \tag{4}$$

The data indicate that the effect of hydrostatic pressure on the activity of dissolved gases is essentially the same for oxygen, argon, and nitrogen. Helium and carbon dioxide show a slight difference. The same conclusion applies to the partial molal volumes which average approximately 33 cc. for nitrogen, 32 cc. for oxygen and argon, 29.7 cc. for helium, and 35 cc. for carbon dioxide.

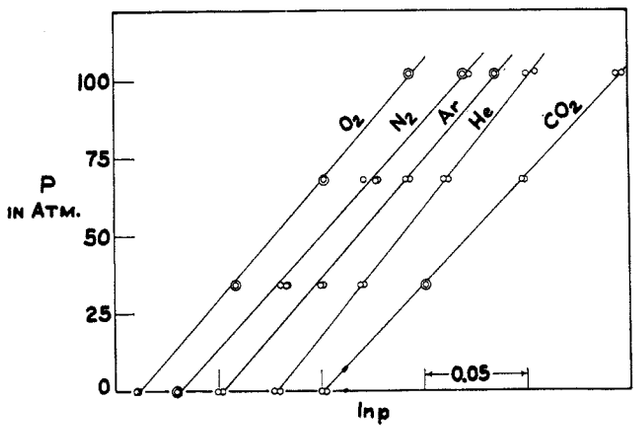

Figure 2. Effect of hydrostatic pressure on equilibrium pressure of dissolved gases. Abscissas arbitrarily displaced.

The values of partial molal volumes reported here are average values based on straight lines drawn as in Figure 2. Actually, all gases except helium give slightly curved plots indicating a decrease in partial molal volume with increase in hydrostatic pressure.

The data may be extended to calculate equilibrium partial pressure of gas at ocean depths. For dissolved gases which have their origin in water equilibrated with the atmosphere at the surface, eq. 3 gives the gas pressures at depths. At 10,000 m. depth the pressures so calculated are approximately four times as great as at the surface. It may be noted that marine organisms living at this depth may be exposed to an oxygen activity four times that of the atmosphere.

(5) G. N. Lewis and M. Randall, "Thermodynamics," revised by K. S. Pitzer and L. Brewer, McGraw-Hill Book Co., Inc., New York, N. Y., 1961, p. 204.