Reports

Partial Pressure of Gases Dissolved at Great Depth

Abstract. *Thermodynamic considerations have been applied to data showing that the solubilities of oxygen, carbon dioxide, and helium in water decrease with increasing pressure and depth. When water is saturated with a given gas at 1 atmosphere absolute, the equilibrium partial pressure of the gas at any depth is equal to the partial pressure of that gas if it were contained in a gas column extending from the surface to that particular depth.*

The effect of high hydrostatic pressures on the partial pressure of O_2 (P_{O_2}) in water was measured by Enns *et al.* (*1*). They reported an increase of 13.4 percent in the P_{O_2} when water, saturated with 100 percent O_2 at 1 atm absolute, was exposed to a hydrostatic pressure of 100 atm. The method was very ingenious, and the apparatus consisted of a Teflon tube closed at one end full of 100 percent O_2 at 1 atm and immersed in water enclosed in a syringe, saturated with the same gas at 1 atm. This syringe in turn was enclosed in a pressure chamber filled with liquid so that 100 atm of pressure could easily be applied. The Teflon tube was attached to a steel tube carried out through the wall of the pressure chamber to a capillary tube containing a kerosene index drop and then to a manometer to measure the pressure required to keep the index drop from moving. When pressure was applied to the chamber, and thus to the barrel of the syringe, O_2 began to diffuse through the wall of the Teflon tube and to displace the kerosene index drop. It was noted that a bucking pressure of 13.4 percent of an atmosphere above atmospheric pressure was sufficient to keep the index drop stationary. The same was true with other gases tried (N_2, Ar, CO_2, and He), although a slightly higher pressure (14.53 percent) was needed for CO_2 and a slightly lower pressure (12.4 percent) was needed for He. From these data Enns *et al.* predicted by a long extrapolation that, at 1000 atm or about 10,000 m of depth, P_{O_2} would be about 4 atm, although the actual molar concentration of O_2 was the same as that at the surface.

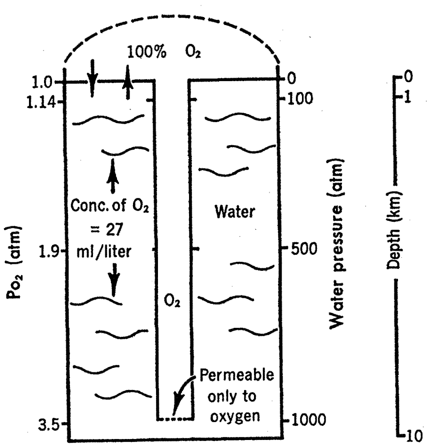

Fig. 1. Diagram of a "theoretical" Teflon tube containing O_2 and immersed to a depth of 10 km in water. For explanation, see text.

To explore the consequences of this fact I imagined a Teflon tube (Fig. 1) open at the top and closed at the bottom, extending from the surface to a depth of 10,000 m and filled with 100 percent O_2. In theory it is assumed that the Teflon is permeable only to O_2. With a P_{O_2} of 4 atm in the water I thought at first that O_2 would diffuse from the water into the Teflon tube. Since the tube was open to 100 percent O_2 at the surface, a perpetual motion machine would be realized. But I calculated the barometric pressure that would obtain at a depth of 10,000 m of O_2 (Fig. 2) and discovered that it would also be about 4 atm, actually closer to 3.5 atm.

Enns (*2*) pointed out, however, that with He in the tube in place of O_2 the pressure at the bottom of the Teflon tube would be only 1.17 atm, and with CO_2 the pressure would be 5.7 atm, so perhaps the agreement between the barometric pressure and P_{O_2} was only a coincidence. Coincidence or not, perpetual motion is impossible, so there had to be some equilibrium. I noted that He should have considerable buoyancy in water since 1 mole weighs only 4 g, but the partial molal volume is 29.7 ml/mole. Carbon dioxide, on the other hand, has a molecular weight M of 44 and a partial molal volume of 34.8 ml/mole and, therefore, has some negative buoyancy in water.

I used the following equation [equation 16 of Klotz (*3*)] to calculate the concentration of various gases in water at different depths

$$\log \frac{m_d}{m_s} = 1.71 \times 10^{-8}\, M[1 - (\bar{v}\rho/M)]d \qquad (1)$$

Here m is the amount of the gas in a unit volume of water at depth d or at the surface s, $\bar{v}$ is the volume occupied by 1 g of the gas, ρ is the density of the medium (1.023 g/cm³ for seawater), and d is the depth in centimeters. For O_2 the term $[1 - (\bar{v}\rho/M)]$ is close to zero so that $(m_d/m_s) \cong 1.0$. For He, however, $[1 - (\bar{v}\rho/M)]$ has a value of -6.5 and the value of (m_d/m_s) is 0.35. Thus, because of the buoyancy of He, its concentration, after complete equilibrium has been achieved at 10,000 m, would be only about one-third of that at the surface. For CO_2 the reverse is true, and the concentration at 10,000 m would be 1.39 times as great as that at the surface because of the tendency of CO_2 to settle in water.

This does not tell us, however, from a theoretical point of view, what the partial pressures of the gases would be in the water at 10,000 m. If, however, for O_2 with no significant buoyancy factor the pressure is 3.5 atm, then for He the pressure would be 0.35×3.33 or 1.17 atm, and for CO_2 it would be 1.39×4.10 or 5.68 atm (*1*). These rough values come close to the values of 1.17 for He and 5.65 for CO_2 calculated from the following atmospheric pressure equation

$$p = p_0\, e^{\frac{Mx}{RT}} \qquad (2)$$

where p_0 is the pressure at the surface, p is the pressure at an altitude or depth x (in centimeters), R is the universal gas constant (8.5×10^4 g-cm), and T is the temperature in degrees Kelvin.

At equilibrium, a gas in water ad-

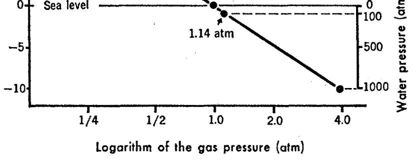

Fig. 2. Partial pressure of O_2 which can be calculated for an O_2-filled Teflon tube, as a function of altitude or depth, by means of Eq. 2.

Table 1. Values for gases in water calculated for conditions at the surface and for a depth of 10 km, on the assumption that both the concentration and partial pressure are affected by depth.

Gas	Partial pressure of gas (atm)		M/partial molal volume (mole/ml)	Relative concentration of gas		Partial pressure of gas in water at a depth of 10 km (atm)
	At surface	At 10 km		At surface	At 10 km	
He	1.0	1.17	4/29.7	1.0	0.35	1.4
O_2	1.0	3.55	32/32	1.0	1.0	4.0
CO_2	1.0	5.7	44/34.8	1.0	1.39	5.7

justs until the force of diffusion tending to equalize the chemical potential (but not the partial pressure) is just balanced by the force of gravity. In water, the partial pressure is a function not only of the concentration but also of the buoyancy of the gas. For He the diffusion is downward, but the gravity factor is upward, whereas the reverse is true of CO_2. For O_2 there is no buoyancy factor because M is 32 and the partial molal volume is 32 ml/mole. In thermodynamics the molar free energy or the chemical potential for any gas is constant at complete equilibrium at all depths, but the total chemical potential becomes the sum of two terms, one of which is the work done against gravity (as by He) and the other is the work done on the gas by gravity (as on CO_2). Thus the total chemical potential is

$$\mu = \mu' + M\psi \qquad (3)$$

where μ' is the chemical potential and $M\psi$ is the potential of the gravitational field.

These considerations lead one to the conclusion that the theoretical Teflon tube experiment permits one to calculate the partial pressure of any gas in water at any depth (Table 1). If so, then the chemical potential must also be the same at depth in the Teflon tube and in the water. Likewise, this relation ought to be true for any fluid. In every field there will be a certain solubility, partial molal volume of the gas, and density of the fluid for a given temperature, but somehow all these varying factors must balance out to give the same partial pressure of the gas that one calculates for a gas-filled tube with a membrane permeable only to that one gas. Such a tube is approximated by a Teflon tube when only one gas is present. Permeability to water might be a complicating factor, and for this reason it is assumed in theory that the membrane is permeable only to the single gas in question. It seems a rather large order to expect that such a "theoretical" Teflon tube could reach equilibrium with the same gas in any other fluid in much less than 10^6 years and a depth of 10^6 cm, but otherwise it would seem possible to use this experiment for a perpetual motion machine.

What is needed is a rigid thermodynamic proof that the partial pressure in the water at a given depth is actually equal to the partial pressure in the gas-filled Teflon tube. If this were not true, there could be diffusion of the gas either into the water or out and this would constitute perpetual motion. I have seen a proof of this kind provided by thermodynamicists whom I have consulted, and there have been many, including Klotz, whose equation was used above.

I would like to know what happens outside the Teflon tube to "tell" the water molecules how much harder they will have to "squeeze" the O_2 to prevent the O_2 in the tube from diffusing into that long fanciful reservoir of oxygenated water. Actually, the water would have to act on the few O_2 molecules so that their partial pressure increases exponentially from its sea-level value (without any change in O_2 molarity). In the O_2 tube the process is well known, and the pressure increases because there is an increasingly higher pressure of O_2 pushing down from above. The O_2 in the O_2 tube is compressed but the O_2 in the main tube outside the Teflon tube is in a nearly incompressible watery medium, and I do not clearly understand the mechanism required to bring about the necessary rise in the partial pressure of the O_2. Nor do I clearly understand why the effect of pressure is exponential and not linear.

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Lunar Crust: Structure and Composition

Abstract. *Lunar seismic data from artificial impacts recorded at three Apollo seismometers are interpreted to determine the structure of the moon's interior to a depth of about 100 kilometers. In the Fra Mauro region of Oceanus Procellarum, the moon has a layered crust 65 kilometers thick. The seismic velocities in the upper 25 kilometers are consistent with those in lunar basalts. Between 25 and 65 kilometers, the nearly constant velocity (6.8 kilometers per second) corresponds to velocities in gabbroic and anorthositic rocks. The apparent velocity is high (about 9 kilometers per second) in the lunar mantle immediately below the crust.*

With the successful recording of impacts of the lunar module (LM) ascent stage and Saturn (S-IV B) rocket by the Apollo 12, Apollo 14, and Apollo 15 seismometers, discrete seismic phases that can be interpreted in terms of a velocity structure inside the moon have become available. Travel times, amplitudes, and wave shapes of compressional (P) waves have been obtained for distances from source to receiver between $\Delta = 67$ km and $\Delta = 357$ km. These data are inverted to determine the seismic velocity structure in the outer 100 km of the lunar interior. In this report we briefly describe the data, the inversion techniques, and the velocity model and its compositional significance in the light of laboratory measurements of velocities characteristic of lunar and terrestrial rocks.

Data used in the study of the earth's interior have come from a large number of earthquakes of all magnitudes and from numerous artificial sources (such as underground nuclear explosions) and have been recorded at more than a thousand seismic stations. In the case of the moon the natural seismicity (the number and energy of moonquakes) is many orders of magnitude lower than that of the earth (*1*). With only three