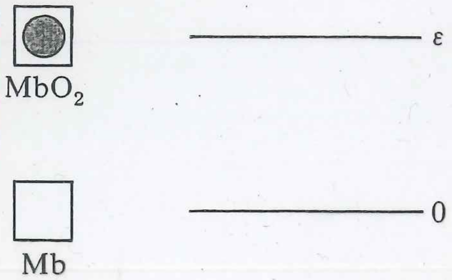

Figure 5.10 Adsorption of an O_2 by a heme, where ε is the energy of an adsorbed O_2 relative to an O_2 at infinite separation from the site. If energy must be supplied to detach the O_2 from the heme, then ε will be negative.

$\mathcal{Z}(\mu,\tau) = \sum_{N=0}^{\infty} \lambda^N Z_N(\tau)$

infinite distance, then the Gibbs sum is

$$\boxed{\mathcal{Z} = 1 + \lambda \exp(-\varepsilon/\tau).} \tag{66}$$

If energy must be added to remove the atom from the heme, ε will be negative. The term 1 in the sum arises from occupancy zero; the term $\lambda \exp(-\varepsilon/\tau)$ arises from single occupancy. These are the only possibilities. We have Mb + O_2 or MbO_2 present, where Mb denotes myoglobin, a protein of molecular weight 17 000.

Experimental results for the fractional occupancy versus the concentration of oxygen are shown in Figure 5.11. We compare the observed oxygen saturation curves of myoglobin and hemoglobin in Figure 5.12. Hemoglobin is the oxygen-carrying component of blood. It is made up of four molecular strands, each strand nearly identical with the single strand of myoglobin, and each capable of binding a single oxygen molecule. Historically, the classic work on the adsorption of oxygen by hemoglobin was done by Christian Bohr, the father of Niels Bohr. The oxygen saturation curve for hemoglobin (Hb) has a slower rise at low pressures, because the binding energy of a single O_2 to a molecule of Hb is lower than for Mb. At higher pressures of oxygen the Hb curve has a region that is concave upwards, because the binding energy per O_2 increases after the first O_2 is adsorbed.

The O_2 molecules on hemes are in equilibrium with the O_2 in the surrounding liquid, so that the chemical potentials of O_2 are equal on the myoglobin and in solution:

$$\mu(MbO_2) = \mu(O_2); \quad \Rightarrow \quad \lambda(MbO_2) = \lambda(O_2) \tag{67}$$

where $\lambda \equiv \exp(\mu/\tau)$. From Chapter 3 we find the value of λ in terms of the gas pressure by the relation

$$\boxed{\lambda = n/n_Q = p/\tau n_Q.} \tag{68}$$

We assume the ideal gas result applies to O_2 in solution. At constant temperature $\lambda(O_2)$ is directly proportional to the pressure p.

The fraction f of Mb occupied by O_2 is found from (66) to be

$$f = \frac{\lambda \exp(-\varepsilon/\tau)}{1 + \lambda \exp(-\varepsilon/\tau)} = \frac{1}{\lambda^{-1} \exp(\varepsilon/\tau) + 1}, \tag{69}$$