

5.9) ADSORPTION OF O₂ IN A MAGNETIC FIELD

The magnetic moment may be parallel, perpendicular, or antiparallel to the magnetic field. Hence,

$$\mathcal{Z} = 1 + \lambda \{ \exp[-(\varepsilon - \mu_B B)/\tau] + \exp(-\varepsilon/\tau) + \exp[-(\varepsilon + \mu_B B)/\tau] \}$$

$$\mathcal{Z} = 1 + \lambda \exp(-\varepsilon/\tau) [1 + 2 \cosh(\mu_B B/\tau)] \quad ,$$

where ε is the energy of an occupied site when $B = 0$. If we define $x = 3\lambda \exp(-\varepsilon/\tau)$, $1+\delta = [1 + 2 \cosh(\mu_B B/\tau)]/3$, we may write the occupancy as

$$f = \frac{x(1+\delta)}{1+x(1+\delta)} = \frac{x}{1+x} \frac{1+\delta}{1+\frac{x}{1+x}\delta} = f_0 \frac{1+\delta}{1+f_0\delta} \quad ,$$

where $f_0 = x/(1+x)$ is the occupancy when $B = 0$. For small changes δ , we may approximate

$$(1+\delta)/(1+f_0\delta) \cong 1 + (1-f_0)\delta \quad .$$

To change the occupancy f by one percent (relative to $f_0 = 0.9$), we must have $(1-f_0)\delta = 0.01$, or $\delta = 0.1$. For small δ and hence small $\mu_B B/\tau$ we may expand the hyperbolic cosine, $\cosh(\mu_B B/\tau) \cong 1 + \frac{1}{2}(\mu_B B/\tau)^2$, hence

$$\delta \cong \frac{2}{3} [\cosh(\mu_B B/\tau) - 1] \cong \frac{1}{3} (\mu_B B/\tau)^2 \cong 0.1 \quad ,$$

$$\mu_B B / \tau \cong 0.3^{\frac{1}{2}} \cong 0.548 \quad ,$$

$$B = 0.548 \tau / \mu_B \cong 2.4 \times 10^6 \text{ Gauss} \quad .$$

This number should dispense with any notions that technologically achievable magnetic fields have detectable effects on the respiratory process.

5.12) ASCENT OF SAP IN TREES

The chemical potential of water molecules in air with a relative humidity $r < 1$ differs from that in air saturated with water vapor ($r = 1$) by

$$\Delta\mu_{\text{int}} = \tau [\log(rn/n_Q) - \log(n/n_Q)] = \tau \log r < 0 \quad .$$

This is an internal chemical potential difference driving the evaporation process through the leaf surface. In steady state, any water molecule evaporating at height h must be replaced by a molecule coming up from the roots, acquiring a potential energy $\Delta\mu_{\text{ext}} = Mgh$ in the process. It acts as an external chemical potential step. The evaporation will cease when the diffusive equilibrium condition (16) has been reached:

$$\Delta\mu_{\text{ext}} = - \Delta\mu_{\text{int}} \quad ,$$

$$h = \frac{\tau}{Mg} \log (1/r) = \frac{k_B \times 298 \text{ K} \times 0.105}{18 \text{ amu} \times 981 \text{ cm s}^{-2}} \cong 1470 \text{ meter} \quad .$$

5.13) ISENTROPIC EXPANSION

(a) From (3.68), $Z_N = (Z_1)^N / N!$, where N is the number of particles and

$$Z_1 = \sum \exp[-\epsilon(\vec{n})/\tau]$$

is the single particle partition function. The vector \vec{n} designates the orbital. The occupancy of orbital \vec{n} is

$$f(\vec{n}) = (N/Z_1) \exp[-\epsilon(\vec{n})/\tau].$$

Next, from (3.49) and (3.55):

$$\begin{aligned} \sigma &= - \frac{\partial F}{\partial \tau} = + \frac{\partial}{\partial \tau} (\tau \log Z) \\ &= N \log Z - \log N! + N\tau \frac{\partial}{\partial \tau} \log Z \quad . \end{aligned}$$

The last term can be written

$$\begin{aligned}
\frac{N\tau}{Z_1} \sum \frac{\varepsilon(\vec{n})}{\tau^2} \exp[-\varepsilon(\vec{n})/\tau] &= \sum \frac{\varepsilon(\vec{n})}{\tau} f(\vec{n}) \\
&= \sum [\log N - \log Z_1 - \log f(\varepsilon_n)] f(\vec{n}) \\
&= N(\log N - \log Z_1) - \sum f(\vec{n}) \log f(\vec{n}).
\end{aligned}$$

With this

$$\sigma = N \log N - \log N! - \sum f(\vec{n}) \log f(\vec{n}).$$

But, from Stirling's formula, (A.29), $N \log N - \log N! = N = \sum f(\vec{n})$, hence

$$\sigma = \sum f(\vec{n}) [1 - \log f(\vec{n})]. \quad (S1)$$

(b) From (3.59), all orbital energies depend on the volume like $\varepsilon \propto L^{-2} = v^{-2/3}$. Hence, the partition function and with it the occupancies depend on τ and V only through the product $\tau v^{2/3}$. If this product is constant, the occupancies will be constant and therefore, because of (S1), the entropy will be constant.

5.14) MULTIPLE BINDING OF O₂

We assume that the four O₂ binding sites are independent. The Gibbs sum for a single binding site would be

$$\tilde{\mathcal{Z}}_1 = 1 + \lambda \exp(-\epsilon/\tau).$$

For four independent binding sites

$$\begin{aligned} \tilde{\mathcal{Z}}_4 &= (\tilde{\mathcal{Z}}_1)^4 = [1 + \lambda \exp(-\epsilon/\tau)]^4 \\ &= 1 + 4\lambda \exp(-\epsilon/\tau) + \dots + \lambda^4 \exp(-4\epsilon/\tau). \end{aligned}$$

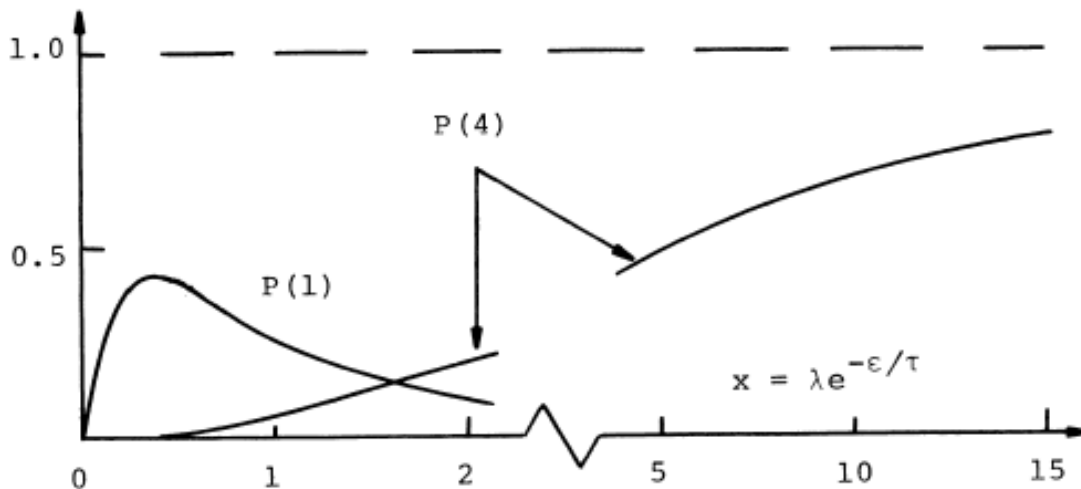
Here the first term corresponds to no occupancy, the second term to occupancy of one of the binding sites, and the last term to occupancy of all four binding sites.

$$(a) \quad P(1) = 4\lambda \exp(-\epsilon/\tau) / \tilde{\mathcal{Z}} = 4x / (1+x)^4,$$

where $x = \lambda \exp(-\epsilon/\tau)$. The probability starts linearly with λ , goes through a maximum $P(1) = 27/64$ at $x = 1/3$, and then falls off towards zero.

$$(b) \quad P(4) = \lambda^4 \exp(-4\epsilon/\tau) / \tilde{\mathcal{Z}} = [x / (1+x)]^4.$$

This starts proportionally to λ^4 , then levels out slowly and approaches $P(4) = 1$ asymptotically.



5.15) EXTERNAL CHEMICAL POTENTIAL

(a) Moving the system to a height h without a change in the state of the system otherwise, adds the potential energy $NMgh$ to the state of the system. This added energy is the same for all states of the system, hence we add a factor $\exp(-NMgh/\tau)$ to every term in the partition function, and therefore to the partition function itself,

$$Z(h) = Z(0) \times \exp(-NMgh/\tau).$$

From (3.55) we obtain the Helmholtz free energy:

$$F(h) = -\tau \log Z(h) = -\tau \log Z(0) + NMgh = F(0) + NMgh.$$

From this and the definition (5) of the chemical potential, by differentiation with respect to N ,

$$\mu(h) = \mu(0) + Mgh.$$

(b) In the barometric problem $\mu(h) = \mu(0)$ because the two systems were in diffusive equilibrium with each other. If we simply lift a system by h it would not be in diffusive equilibrium with an otherwise identical system left behind on the ground: On diffusive contact, particles would flow from the upper to the lower system until the chemical potentials have equilibrated.