

5.4) ACTIVE TRANSPORT

$$\begin{aligned} \Delta\mu &= \mu(\text{sap}) - \mu(\text{pond}) = \tau \log[n(\text{sap})] - \tau \log[n(\text{pond})] \\ &= \tau \log[n(\text{sap})/n(\text{pond})] = \tau \log 10^4 . \end{aligned}$$

At $T = 300\text{K}$: $\tau = 0.0259 \text{ eV}$. Hence $\tau = 0.238 \text{ eV}$. Because potassium is singly ionized, this corresponds to a voltage

of 0.238 V .

5.6) GIBBS SUM FOR A TWO LEVEL SYSTEM

(a) There are three states:

Occupancy N:	0	1	1	
Energy:	0	0	ϵ	

$$\mathcal{Z} = 1 + \lambda + \lambda \exp(-\epsilon/\tau) . \quad (76)$$

(b) $\langle N \rangle = \frac{1}{\mathcal{Z}} [0 \times 1 + 1 \times \lambda + 1 \times \lambda \exp(-\epsilon/\tau)]$

$$= (\lambda/\mathcal{Z}) [1 + \exp(-\epsilon/\tau)] \quad (77)$$

(c) The thermal average occupancy of the state at energy ϵ is given by the last term in the expression for $\langle N \rangle$,

$$\langle N(\epsilon) \rangle \cong \frac{\lambda}{\mathcal{Z}} \exp(-\epsilon/\tau) . \quad (78)$$

(d) $U = \frac{1}{\mathcal{Z}} [0 \times 1 + 0 \times \lambda + \epsilon \times \lambda \exp(-\epsilon/\tau)]$

$$= (\epsilon \lambda / \mathcal{Z}) \exp(-\epsilon/\tau) = \langle N(\epsilon) \rangle \epsilon .$$

(e) Adding a state with occupancy $N = 2$ and energy $\varepsilon + 0 = \varepsilon$ contributes an additional term $\lambda^2 \exp(-\varepsilon/\tau)$ to \mathcal{Z} :

$$\begin{aligned}\mathcal{Z} &= 1 + \lambda + \lambda \exp(-\varepsilon/\tau) + \lambda^2 \exp(-\varepsilon/\tau) \\ &= (1+\lambda)[1+\lambda \exp(-\varepsilon/\tau)].\end{aligned}\tag{79}$$

This has the form $\mathcal{Z} = \mathcal{Z}_0 \mathcal{Z}_\varepsilon$ of the Gibbs sum for two independent systems, one with the fixed energy 0 independent of occupancy, and one with the energy 0 if empty and ε if occupied. Both systems can be occupied with either zero or one particle, and the occupancy of one is independent of the occupancy of the other.

5.7) STATES OF POSITIVE AND NEGATIVE IONIZATION

N :	0	1	1	2
ε :	$-\delta/2$	$-\Delta/2$	$+\Delta/2$	$+\delta/2$

$$\begin{aligned}\mathcal{Z} &= \exp(\delta/2\tau) + \lambda[\exp(\Delta/2\tau) + \exp(-\Delta/2\tau)] + \lambda^2 \exp(-\delta/2\tau) \\ \langle N \rangle &= 0 + \lambda[\exp(\Delta/2\tau) + \exp(-\Delta/2\tau)] + 2\lambda^2 \exp(-\delta/2\tau).\end{aligned}$$

To obtain $\langle N \rangle = 1$ the right-hand sides of the two last lines must be equal: $\lambda^2 \exp(-\delta/2\tau) = \exp(+\delta/2\tau)$, or

$$\lambda^2 = \exp(\delta/\tau) \quad .$$

Because of (60) this implies $\mu = \delta/2$. The quantity Δ has dropped out.

5.8) CARBON MONOXIDE POISONING

With the abbreviations $x = \lambda_A \exp(-\varepsilon_A/\tau)$ and $y = \lambda_B \exp(-\varepsilon_B/\tau)$ we have the Gibbs sum $\mathcal{Z} = 1 + x + y$. The fraction of sites occupied by O_2 is

$$f = x/\mathcal{Z} = x/(1+x+y) \quad .\tag{S1}$$

(a) No CO means $\lambda_B = 0$, $y = 0$; hence $x = f/(1-f) = 0.9/0.1 = 9$, and $\epsilon_A = -\tau \log(x/v_A) = -\tau \log(9 \times 10^5) = -13.7 \tau = 0.366 \text{ eV}$, where we have used $\tau = 8.62 \times 10^{-5} \text{ eV K}^{-1} \times 310 \text{ K} = 0.0267 \text{ eV}$.

(b) We solve (S1) for y : $y = x/f - (1+x) = 80$. Thus, $\epsilon_B = -\tau \log(y/\lambda_B) = -\tau \log(80 \times 10^7) = -20.5\tau = -0.548 \text{ eV}$. We see that CO is more tightly bound by about 6.8τ . This means that a relatively small concentration of CO can make the binding sites inaccessible to O_2 . This is why CO is such a poison.