

Physics 353: Problem Set 4 - SOLUTIONS

1 Heme groups revisited.

Heme group. 
$$Z = \sum_N \sum_{\text{states}} e^{\mu N / \tau} e^{-\epsilon(N) / \tau} \quad (\text{general})$$

$$= \underbrace{1}_{N=0 \text{ oxygen}} + \underbrace{e^{\mu / \tau} e^{-\epsilon / \tau}}_{N=1 \text{ oxygen}}$$

occupied probability 
$$f = \frac{1}{3} e^{\mu / \tau} e^{-\epsilon / \tau} = \frac{e^{\mu / \tau} e^{-\epsilon / \tau}}{1 + e^{\mu / \tau} e^{-\epsilon / \tau}} = f$$

What is  $\mu$ ? Diff. equilibrium w/ surrounding  $O_2$ :  $\mu = \mu_{\text{surrounding}}$   
 $= \tau \ln\left(\frac{n}{n_Q}\right)$ . so  $e^{\mu / \tau} = n / n_Q$

$$\Rightarrow f = \frac{(n/n_Q) e^{-\epsilon / \tau}}{1 + (n/n_Q) e^{-\epsilon / \tau}}$$
 Simplifying: 
$$f = \frac{n}{n_Q e^{\epsilon / \tau} + n}$$

Ideal gas:  $P = n \tau$  (note  $n = N/V$ ), so 
$$f = \frac{P / \tau}{n_Q e^{\epsilon / \tau} + P / \tau}$$

or 
$$f = \frac{P}{\tau n_Q e^{\epsilon / \tau} + P}$$
 Define 
$$P_0 \equiv \tau n_Q e^{\epsilon / \tau}$$

$$\Rightarrow \boxed{f = \frac{P}{P_0 + P}}$$

## 2, A hydrogen-like atom.

Hydrogen-like atom.  $z = \sum_N \sum_{\text{states}(N)} \lambda^N e^{-E(N)/\tau}$

$$z = \underbrace{e^{+\delta/2\tau}}_{N=0} + \underbrace{\lambda e^{+\delta/2\tau}}_{N=1} + \underbrace{\lambda e^{-\delta/2\tau}}_{N=1} + \underbrace{\lambda^2 e^{-\delta/2\tau}}_{N=2}$$

$$\langle N \rangle = \frac{1}{z} \lambda \left( \frac{\partial}{\partial \lambda} z \right). \quad \frac{\partial}{\partial \lambda} z = e^{+\delta/2\tau} + e^{-\delta/2\tau} + 2\lambda e^{-\delta/2\tau}$$

$$\Rightarrow \langle N \rangle = \frac{\lambda e^{+\delta/2\tau} + \lambda e^{-\delta/2\tau} + 2\lambda^2 e^{-\delta/2\tau}}{e^{+\delta/2\tau} + \lambda e^{+\delta/2\tau} + \lambda e^{-\delta/2\tau} + \lambda^2 e^{-\delta/2\tau}}$$

$$\langle N \rangle = 1, \text{ so } \cancel{\lambda e^{+\delta/2\tau}} + \cancel{\lambda e^{-\delta/2\tau}} + 2\lambda^2 e^{-\delta/2\tau} = e^{+\delta/2\tau} + \cancel{\lambda e^{+\delta/2\tau}} + \cancel{\lambda e^{-\delta/2\tau}} + \lambda^2 e^{-\delta/2\tau}$$

$$\Rightarrow \lambda^2 e^{-\delta/2\tau} = e^{+\delta/2\tau} \Rightarrow \lambda^2 = e^{+\delta/\tau} \Rightarrow e^{\mu/\tau} = e^{+\delta/\tau}$$

$$\Rightarrow \boxed{\mu = \delta}$$

## 3 The Langmuir model of adsorption.

a.  $\Omega = \frac{A!}{N!(A-N)!}$ .  $\sigma \equiv \ln \Omega = \ln A! - \ln N! - \ln(A-N)!$

Stirling  $\ln N! \approx N \ln N - N$

$$\Rightarrow \sigma \approx A \ln A - A - N \ln N + N - (A-N) \ln(A-N) + A - N$$

$$= A \ln A - N \ln N - (A-N) \ln(A-N)$$

b.  $\mu \equiv -\tau \left. \frac{\partial \sigma}{\partial N} \right|_{u, v} = -\tau \left[ -\frac{N}{N} + \ln N + \left( \frac{A-N}{A-N} \right) + \ln(A-N) \right]$

$$= -\tau \ln \left( \frac{A-N}{N} \right)$$

$$\Rightarrow \mu = \tau \ln \left( \frac{N}{A-N} \right) = \underline{\underline{\mu = \tau \ln \left( \frac{f}{1-f} \right)}} \text{ using } N=fA.$$

c. Equilibrium:  $\mu_{\text{surface}} = \mu_{\text{gas}}$

$$\tau \ln\left(\frac{f}{1-f}\right) + \epsilon = \tau \ln\left(\frac{n}{n_Q z_{\text{int}}}\right)$$

$\uparrow$  surface part       $\uparrow$  surface part       $\uparrow$  gas

$$\Rightarrow \ln\left(\frac{f}{1-f}\right) = -\frac{\epsilon}{\tau} + \ln\left(\frac{n}{n_Q z_{\text{int}}}\right)$$

$$\Rightarrow \frac{f}{1-f} = \left[\exp\left(-\frac{\epsilon}{\tau}\right)\right] \frac{n}{n_Q z_{\text{int}}}$$

$$\Rightarrow f = \frac{n}{n_Q z_{\text{int}}} e^{-\epsilon/\tau} - f \frac{n}{n_Q z_{\text{int}}} e^{-\epsilon/\tau}$$

$$\Rightarrow f \left(1 + \frac{n}{n_Q z_{\text{int}}} e^{-\epsilon/\tau}\right) = \frac{n}{n_Q z_{\text{int}}} e^{-\epsilon/\tau}$$

$$\Rightarrow f = \frac{\frac{n}{n_Q z_{\text{int}}} e^{-\epsilon/\tau}}{1 + \frac{n}{n_Q z_{\text{int}}} e^{-\epsilon/\tau}} = \frac{n}{n_Q z_{\text{int}} e^{\epsilon/\tau} + n}$$

Define  $K(\tau) \equiv n_Q z_{\text{int}} e^{\epsilon/\tau} \Rightarrow \boxed{f = \frac{n}{K(\tau) + n}}$

Note: It would be fine to define K as 1/this instead.

d. What should  $\frac{n}{f}$  vs.  $n$  look like?

Rearrange,  $K(\tau) + n = \frac{n}{f}$ , so we expect a straight line with intercept  $K(\tau)$ . The data show a straight line & are therefore consistent w/ a Langmuir model. We can "read off"  $K(\tau) \approx 20 \text{ nM}$

$$\text{From } f = \frac{n}{K+n}, fK = n(1-f) \Rightarrow n = \frac{fK}{1-f}$$

$$f = 0.1 \rightarrow n = 2.3 \text{ nM} \quad f = 0.95 \rightarrow n = 380 \text{ nM}$$

4 Biopolymer growth: Kittel & Kroemer 9.4.

(a) First consider  $l\text{-mer} + N\text{-mer} \rightleftharpoons (N+1)\text{-mer}$ .

Chem. equilibrium:  $\mu_l + \mu_N - \mu_{N+1} = 0$

Ideal gas  $\mu = \tau \ln(\rho / \rho_Q z_{int})$ .

$$\Rightarrow \tau \ln\left(\frac{[l]}{\rho_Q(l) z_{int}(l)}\right) + \tau \ln\left(\frac{[N]}{\rho_Q(N) z_{int}(N)}\right)$$

$$= \tau \ln\left(\frac{[N+1]}{\rho_Q(N+1) z_{int}(N+1)}\right) \quad \text{exp. both sides}$$

$$\Rightarrow \frac{[l]}{\rho_Q(l) z_{int}(l)} \frac{[N]}{\rho_Q(N) z_{int}(N)} = \frac{[N+1]}{\rho_Q(N+1) z_{int}(N+1)}$$

$$\Rightarrow [N+1] = [l][N] / K_N, \quad \text{where } K_N = \frac{\rho_Q(l) \rho_Q(N) z_{int}(l) z_{int}(N)}{\rho_Q(N+1) z_{int}(N+1)}$$

$K_N$  accounts for all concentration-independent parameters.

$$\text{Similarly } [N] = [l][N-1] / K_{N-1}, \quad [N-1] = \frac{[l][N-2]}{K_{N-2}}, \text{ etc.},$$

$$\text{up to } [2] = [l][1] / K_1.$$

$$\text{Therefore } [N+1] = \frac{[l]}{K_N} \frac{[l]}{K_{N-1}} \frac{[l]}{K_{N-2}} \dots \frac{[l]}{K_1} [1]$$

$$\Rightarrow [N+1] = \frac{[l]^{N+1}}{K_1 K_2 K_3 \dots K_N}$$

(b) Note the  $K_N$  expression above. Since  $F = -\tau \ln Z$ ,

we can write  $z_{int}$  in terms of the (internal) free

energy:  $z_{int} = e^{-F/\tau}$ .  $\Rightarrow$

$$K_N = \frac{\rho_Q(l) \rho_Q(N)}{\rho_Q(N+1)} \exp\left[\frac{1}{\tau} (F_{N+1} - F_N - F_l)\right]$$

(c) From above  $\frac{[N+1]}{[N]} = \frac{[I]}{K_N}$ . Is this  $> 1$  or  $< 1$ ?

$$\text{If } \Delta F = F_{N+1} - F_N - F_1 = 0,$$

$$K_N = \frac{n_Q(1) n_Q(N)}{n_Q(N+1)} \approx n_Q(1).$$

$$n_Q(1) = \left( \frac{2\pi h^2}{m\tau} \right)^{-3/2}, \text{ where } m = 200 \times 1.67 \times 10^{-27} \text{ kg.}$$

$$\tau = 310 \text{ K} \times k_B = 4.28 \times 10^{-21} \text{ J}$$

$$\Rightarrow n_Q(1) = \left( \frac{2\pi (1.1) 10^{-68}}{200 \cdot (1.67) \cdot 10^{-27} \cdot (4.28) \times 10^{-21}} \right)^{-3/2}$$

$$= (4.89 \times 10^{-23})^{-3/2} = .0029 \times 10^{36}$$

$$= n_Q(1) = 2.9 \times 10^{33} \text{ m}^{-3}$$

$$\text{We assume } [I] = 10^{20} \text{ cm}^{-3} = 10^{26} \text{ m}^{-3}$$

$$\text{Therefore } \frac{[N+1]}{[N]} \approx \frac{10^{26} \text{ m}^{-3}}{10^{33} \text{ m}^{-3}} = 10^{-7}.$$

A chain of  $N+1$  links is much rarer than a chain of  $N$  links, which is much rarer than  $N-1$  etc.

$$(d). \quad K_N = \frac{n_Q(1) n_Q(N)}{n_Q(N+1)} \exp\left(\frac{\Delta F}{\tau}\right) \approx n_Q(1) \exp\left(\frac{\Delta F}{\tau}\right).$$

$$\text{We need } \frac{[I]}{K_N} > 1, \text{ i.e. } \frac{[I]}{n_Q(1) \exp\left(\frac{\Delta F}{\tau}\right)} > 1$$

$$\Rightarrow \exp\left(-\frac{\Delta F}{\tau}\right) > \frac{n_Q(1)}{[I]} = \frac{2.9 \times 10^{33} \text{ m}^{-3}}{10^{26} \text{ m}^{-3}} = 3 \times 10^7$$

$$\Rightarrow -\frac{\Delta F}{\tau} > 17.2 \text{ (taking logs)}$$

$$\Rightarrow \Delta F < (-7.4 \times 10^{-20} \text{ J})$$

$$\text{i.e. } \underline{\underline{\Delta F < (-0.46 \text{ eV})}}$$