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1. Basic principles and definitions.

a. (4 pts) Which of the following are state variables:

Entropy [✓ state variable] / not a state variable

Work state variable / [✓ not a state variable]

Gibbs free energy [✓ state variable] / not a state variable

Electrical potential [✓ state variable] / not a state variable

b. (4pts) For each of the following closed systems, mark which conditions are true, which are not necessarily true, and which cannot be true.

i) Solid sucrose in the process of crystallizing from an aqueous sucrose solution:

μ[sucrose(s)] > μ[sucrose(aq)] true / not necessarily true / [✓ cannot be true]

ii) A freshwater iceberg melting in the ocean:

μ[H_2O(ice)] = μ[H_2O(ocean)] true / not necessarily true / [✓ cannot be true]

iii) An equilibrium mixture of a peptide that exists in two different configurations, state1 and state2: State 1 → State 2 kinetic rate constant, $k_1 = 100\ s^{-1}$
State 2 → State 1 kinetic rate constant, $k_{-1} = 10\ s^{-1}$

μ[state1] = μ[state2] [✓ true] / not necessarily true / cannot be true

[state1] = 0.1 x [state2] [✓ true] / not necessarily true / cannot be true

We're @ equilibrium!

c. (4 pts) For each of the following processes, state whether each of the requested quantitites is positive (+), negative (-), zero (0), or undetermined (U).

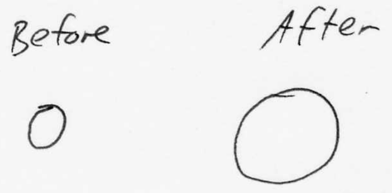
i) Spontaneous folding of a protein in an adiabatic container

$\Delta T =$ + $\Delta G =$ −

Spontaneous, so $\Delta G < 0$
Folding implies ↓ entropy, so if $\Delta G < 0$, this means $\Delta H < 0$ thus it's exothermic + thus T↑ since it's adiabatic

ii) Osmotic swelling of a red blood cell in a large bath of distilled water (37 °C, 1atm); take the red blood cell as the system. Assume the cell does not rupture.

w = + Δmass = +



more stuff inside,
∴ more mass

Swelling stretches cell membrane, ∴ work done on system

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2. (8 pts) Answer the following questions true or false. If false, explain why it is false.

   a. For the reaction $A + B \rightarrow C + D + E$, one does not need to consider the products (C, D, and E) in the rate law.

False - one has to consider the mechanism

example: DNA + RNAP → Protein

Protein feeds back at protein binding sites, which interfere with transcription.

   b. The kinetic order of a reaction cannot be deduced from the balanced reaction equation.

True

   c. Reaction orders may change over the course of a reaction.

True

   d. Since the rate of a zero-order reaction equals the rate constant, the rate cannot be increased or decreased.

False - rate can change with temp, pH

e. For an elementary reaction:

$A + 2B \rightarrow C$

Kinetic order is 1 with respect to A
2 with respect to B
3 in order overall

True

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3. The isomerization of cis-stillbene to trans-stillbene is catalyzed by the addition of iodine, I_2:

$$\text{cis} + I_2 \rightarrow \text{trans} + I_2 \qquad \text{rate constant: } k$$

Experimental data:

	Rate d[trans]/dt	$[I_2]$	[cis]
①	5.59×10^{-3}	0.05 M	0.05 M
②	1.11×10^{-2}	0.05 M	0.10 M
③	4.74×10^{-2}	0.90 M	0.10 M

(10 pts) By analyzing the above data, determine the differential rate law for this reaction in terms of [cis] and $[I_2]$ and find k.

$$\underline{\text{In general: Rate} = k[I_2]^n[\text{cis}]^m}$$

$$\frac{\text{Rate}_1 = 5.59\times10^{-3}}{\text{Rate}_2 = 1.11\times10^{-2}} = \frac{\cancel{k}[\cancel{0.05}]^n[0.05]^m}{\cancel{k}[\cancel{0.05}]^n[0.10]^m} = 1/2$$

$$\left(\frac{0.05}{0.1}\right)^m = 1/2, \Rightarrow \boxed{m = 1}$$

$$\frac{\text{Rate}_2 = 1.11\times10^{-2}}{\text{Rat}_3 = 4.74\times10^{-2}} = \frac{\cancel{k}[0.05]^n[\cancel{0.10}]^m}{\cancel{k}[0.90]^n[\cancel{0.10}]^m}$$

$$0.234 = (0.0556)^n \Rightarrow \log(0.234) = n\log(0.0556)$$

$$n = \frac{\log(0.234)}{\log(0.0556)} = \boxed{1/2 = n}$$

$$\text{Rate}_1 = 5.59\times10^{-3} = k(0.05)^{1/2}(0.05)$$

$$\boxed{k = \frac{5.59\times10^{-3}}{1.12\times10^{-2}} = 0.5}$$

$$\boxed{\text{Rate Law: } \frac{d[\text{trans}]}{dt} = 0.5[I_2]^{1/2}[\text{cis}]}$$

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4. Oxides of sulfur are important in pollution.

Compound	ΔH_f^0 (kJ/mol)	ΔS_f^0 (J/ K mol)
O_2 (g)	0	205.1
H_2O (g)	-241.8	188.7
SO_2 (g)	-296.8	248.2
SO_3 (g)	-395.7	256.8
H_2SO_4 (g)	-814.0	156.9

The oxidation of SO_2 in air can occur: $1/2\ O_2 + SO_2 \leftrightarrow SO_3$

a. (10 pts) Find the equilibrium ratio of SO_3 to SO_2 in air at 25 °C. The partial pressure of O_2 in air is 0.21 atm and you may ignore involvement of H_2SO_4 for this part.

$$\Delta G_f^\circ(SO_3) = -395.7\ kJ/mol - (298k)(0.257\ kJ/k\ mol) = -472.3\ kJ/mol$$

$$\Delta G_f^\circ(SO_2) = -296.8\ kJ/mol - (298k)(0.248\ kJ/k\ mol) = -370.7\ kJ/mol$$

$$\Delta G_f^\circ(O_2) = 0 - (298k)(0.205\ kJ/k\ mol) = -61.1\ kJ/mol$$

$$\Delta G^\circ_{rxn} = -472.3 + [370.7 + \tfrac{1}{2}(61.1)] = -71.05\ kJ/mol$$

$$K = e^{-\Delta G^\circ/RT} = \frac{P_{SO_3}}{P_{O_2}^{1/2} P_{SO_2}} \Rightarrow \frac{P_{SO_3}}{P_{SO_2}} = (0.21\ bar)^{1/2} e^{71.05\times10^3/(8.314)(298)}$$

$$= \boxed{1.3\times10^{12}}$$

b. (10 pts) In general, the atmosphere contains an excess amount of H_2O which can react with SO_3 as follows: $H_2O + SO_3 \leftrightarrow H_2SO_4$

What form of sulfur do you expect to be the dominant form in the atmosphere? Briefly Explain your conclusion.

$$\Delta G_f(H_2SO_4) = -814 - (298)(0.157) = -860.8\ kJ/mol$$

$$\Delta G_f(H_2O) = -241.8 - (298)(0.189) = -298.12\ kJ/mol$$

$$\Delta G_{rxn} = -860.8 + [472.3 + 298.12] = -90.38\ kJ/mol$$

$$k = e^{-\Delta G_{rxn}/RT} \gg 1 \quad + \text{ since } \quad k = \frac{[H_2SO_4]}{[SO_3][H_2O]}$$

I expect H_2SO_4 to be the dominant form.

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5. (20 pts) Some bacteria cells create a pH gradient and voltage across the cell membrane using light to pump protons from inside the cell to the outside. This pH gradient is then used to synthesize ATP. Assume 2 protons are transported back into the cell to synthesize one ATP molecule.

The reaction is: ADP + HPO_4^{2-} ←→ ATP + H_2O $\Delta G^0 = 31$ kJ/mol
In the cell: [ADP] = 100 μm [ATP] = [HPO_4^{2-}] = 1 mM
Voltage across cell membrane = 100 mV with inside negative relative to outside

Assuming that all of the energy of the protons can be utilized to synthesize the ATP, what pH difference between inside and outside is needed for this reaction to occur spontaneously?

Energy from gradient:

$$\Delta_m G = RT\ln\frac{[H^+]_{in}}{[H^+]_{out}} + zF\overset{\phi_{in}-\phi_{out}}{\Delta V}$$

Energy to make ATP:

$$\Delta_A G = \Delta_A G^\circ + RT\ln\left(\frac{[ATP]}{[ADP][HPO_4^{2-}]}\right)$$

For 2 H^+ ions:

$$\boxed{2\Delta_m G = \Delta_A G}$$

$$2RT\ln\frac{[H^+]_{in}}{[H^+]_{out}} + 2zFV = \Delta G^\circ + RT\ln\frac{[ATP]}{[ADP][HPO_4]}$$

$$2\ln\frac{[H^+]_{in}}{[H^+]_{out}} - \ln\frac{[ATP]}{[ADP][HPO_4]} = \frac{\Delta G^\circ - 2zFV}{RT}$$

$$\underset{exp}{\ln\left(\frac{[H^+]^2_{in}}{[H^+]^2_{out}}\cdot\frac{[ADP]\cancel{[HPO_4]}}{\cancel{[ATP]}}\right)} = \underset{exp}{''}$$

$$\frac{[H^+]^2_{in}}{[H^+]^2_{out}} = \frac{1}{[ADP]}\cdot\exp\left(\frac{\Delta G^\circ - 2zFV}{RT}\right)$$

⋮ $\left(\text{Solve for } \frac{[H^+]_{in}}{[H^+]_{out}}\right)$

$$\Delta pH = -\log[H^+]_{in} - \left(-\log[H_{out}]\right) = -\log\frac{[H^+]_{in}}{[H^+]_{out}}$$

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6. A single stranded oligonucleotide that has complementary ends can form a base-paired loop. For the oligonucleotide $A_5C_6U_5$:

```
                                   k1          CC
AAAAACCCCCCUUUUU                 ←  →     AAAAA    C
                                  k-1      UUUUU    C        loop
      SS                                        CC
```

(10 pts) At 25°C, you measure the forward rate constant $k_1 = 2 \times 10^3\ s^{-1}$. You also measure the equilibrium concentrations of the loop, $[Loop]_{eq} = 0.42$ mM, and single strand, $[SS]_{eq} = 0.58$ mM. What is the rate constant for Loop → SS, k_{-1}?

$$\frac{d[SS]}{dt} = k_{-1}[Loop] - k_1[SS] \qquad \frac{d[loop]}{dt} = k_1[SS] - k_{-1}[loop]$$

@ equilibrium $\frac{d[loop]}{dt} = 0$ and $k_1[SS] = k_{-1}[loop]$

$$K_{eq} = \frac{[loop]}{[SS]} = \frac{k_1}{k_{-1}} = \frac{0.42\,mM}{0.58\,mM}$$

$$k_{-1} = \left(\frac{0.58\,mM}{0.42\,mM}\right)\underset{\overset{\uparrow}{k_1}}{\left(2 \times 10^3\,s^{-1}\right)} = \boxed{2.76 \times 10^3\ s^{-1}}$$

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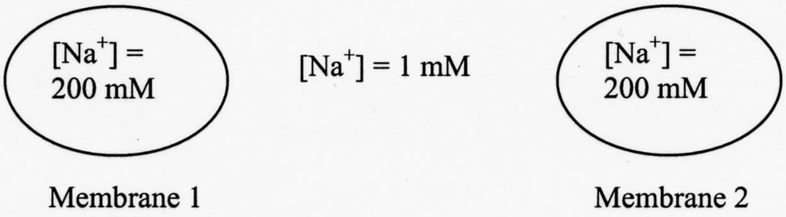
7. Consider two spherical membranes vesicles(10 µm in diameter) initially enclose a solution of 200 mM Na^+. The membranes contain pores and are leaking Na^+ to the outside environment, which is 1mM in Na^+.



a. (5 pts) You study two different membrane compositions, each with identical pores, and find that membrane 2 is leaking Na^+ more slowly than membrane 1. Can you deduce anything about the charge densities of the two membranes from this information? If so, what?

$\sigma_2 > \sigma_1$

(A more positive charge density on #2 slows Na^+'s ability to cross the membrane. In other words, the Na^+ doesn't want to get near the more positively charged membrane)

b. (5 pts) Which of the membranes vesicles will have a higher Na^+ concentration inside at equilibrium? Assume the pores in these membranes are not ion selective and ignore small deviations resulting from counterions to the membrane charges.

Since we can ignore the counterions (i.e. $\lambda \ll$ radius),
↑ Debye Length.

the Na^+ ions inside the bulk part of the vesicles will be experiencing the same environment. Thus, both vesicles will have the same equilibrium $[Na^+]$. The charged membrane here was just affecting the kinetics of the system, not the equilibrium!

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8. A spherical protein, P, of diameter, R, dimerizes (P + P → PP). Assume the proteins rearrange upon dimerization so that the dimer is also spherical with volume equal to twice the volume of the original protein. Recall that volume = 4/3 πr^3 ; and R = 2r.

$$\longrightarrow V = \frac{4}{3}\pi r^3$$

$$\downarrow$$

$$r = \sqrt[3]{\frac{3}{4\pi} V}$$

$$\downarrow$$

$$\frac{r_{small}}{r_{big}} = \left(\frac{\cancel{\frac{3}{4\pi}} V_{small}}{\cancel{\frac{3}{4\pi}} V_{big}}\right)^{1/3} = \left(\frac{1}{2}\right)^{1/3}$$

a. (5 pts) What will be the percent increase or decrease in the diffusion coefficient?

Diffusion coefficient $D = \frac{k_B T}{6\pi\eta r}$ (Chang p. 882)

So $$\frac{D_{big}}{D_{small}} = \left(\frac{\frac{1}{r_{big}}}{\frac{1}{r_{small}}}\right) = \frac{r_{small}}{r_{big}} = \left(\frac{1}{2}\right)^{1/3}$$

so $D_{big} = 0.794 D_{small}$

So D_{big} is 79.4% of D_{small}

b. (5 pts) What will be the percent increase or decrease in the sedimentation coefficient?

$$s = \frac{m(1-\bar{v}\rho)}{f}$$

m = mass,
$\bar{v}$ = partial specific volume
ρ = density of solution

See p897, but you probably don't know this section!

So $$\frac{s_{big}}{s_{small}} = \frac{\left(\frac{m_{big}\,\cancel{(1-\bar{v}_{big}\rho)}}{f_{big}}\right)}{\left(\frac{m_{small}\,\cancel{(1-\bar{v}_{small}\rho)}}{f_{small}}\right)}$$

$\bar{v}_{big} = \bar{v}_{small}$

$f_{big} = 6\pi\eta r_s$ ← radius of solute (our protein)

$$\frac{m_{big}}{m_{small}} = 2$$

$$\frac{s_{big}}{s_{small}} = 2\cdot\frac{\left(\frac{1}{r_{big}}\right)}{\left(\frac{1}{r_{small}}\right)} = 2\cdot\left(\frac{1}{2}\right)^{1/3} = 1.587$$

So s_{big} = 158.7% of s_{small}

More solutions for problems 7and 8

#7(a). Slower transport in membrane 2 means that the barrier for the process in membrane 2 is greater than that in 1. This barrier is arising from different electrical potentials in both membranes which then come from corresponding charge densities. In other words, the charge densities in membrane 2 must be more positive than in 1 since Na+ is feeling greater barrier (or repulsion) in membrane 2 in its passing.

#7(b). Although the kinetics for these two membranes are different due to different electrical potentials as described above, it doesn't mean that the thermodynamic equilibrium is different as well. In fact, since the differences in electrical potential between INSIDE and OUTSIDE are the same for both membranes (which we more or less assume), the final composition will be the same for both. What is different is just the time that take for both systems to reach (the same) equilibrium. Remember we derived that equilibrium composition is only dependent on delta_Pi as long as the size of vesicle is large enough compared to Debye length (last midterm).

#8(a). Diffusion coefficient (D) is inversely proportional to the radius of a spherical particle (coming from the resistance part, or viscosity). That the volume of the a spherical protein doubled means that the radius increased by a factor of 2^(1/3) = 1.26 (note V=4/3*pi*r^3). Therfore, D must be reduced to (1/1.26) *D1=0.79*D1, where D1 is the diffusion coefficient for a monomer protein. As a result, percent decreae in diffusion coefficient for a dimer formation is 21%.

#8(b). Inappropriate question to ask basen on the materials we had.