UC Berkeley. Chem 130A. Spring 2004 Third mid-term Exam. April 14, 2004
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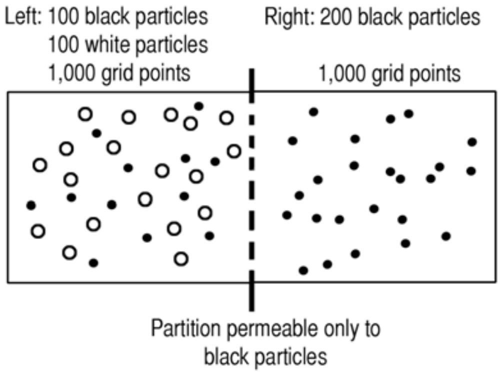
This exam totals 100 points. There are 5 questions.
(For your final grade in the course,
your score in this exam will be multiplied by 2.5)
THE TIME ALLOTTED FOR THE EXAM IS FIFTY (50) MINUTES

Show all the intermediate steps in how you work out the answers to the questions.

This exam totals 100 points. There are 4 questions.
Grading summary:

	Maximum Score	Actual Score
Q1	25	
Q2	15	
Q3	20	
Q4	20	
Q5	20	
TOTAL	100	

Q1. (25 Points)
Consider an isolated system containing 300 black particles and 100 white particles, as shown below. Initially, there are 100 white particles and 100 black particles in the left hand chamber, and 200 black particles in the right hand chamber. The two chambers are separated by a partition that is permeable only to black particles.



(A) Calculate the total entropy of the system under the initial conditions, assuming that each chamber is divided into 1000 grid boxes, each of which can contain only 1 particle, and that the particles do not interact with each other (10 points).
Hint: S = -k_b lnW. Assume that k_b = 1.
The multiplicity, W, of a chamber containing N grid boxes and N_A *particles of type A is given by:*

$$\ln W = N(\ln N - 1) - \left[N_A(\ln N_A - 1) + (N - N_A)(\ln(N - N_A) - 1)\right]$$

For left hand side, let N_A = # of black particles and N_B = # of white particles, N = total #

$$W = \frac{N!}{N_A!N_B!(N-(N_A+N_B))!}$$

$$\ln W_{LEFT} = \ln(\frac{1000!}{100!100!800!}) = 1000(\ln 1000 - 1) - [100(\ln 100 - 1) + 100(\ln 100 - 1) + 800(\ln 800 - 1)]$$

= 5907.76 – [360.52+360.52+4547.0]
= 639.03

$\ln W_{RIGHT} =$ 1000(*ln*1000-1) – [(200(*ln*200-1) + 800(*ln*(800-1)]
= 500.4

⇒ Total Entropy = 1139.4

Question 1(A) Continued.

(B) Given these initial conditions, will black particles move spontaneously from the right chamber to the left chamber?
Justify your answer by calculating the change in the total entropy of the system when one particle is moved from the right chamber to the left chamber. (10 points)

Move one black particle from right to left.

Now $\ln W_{LEFT} =$ 1000(*ln*1000-1) – [100(*ln*100-1) + 101(*ln*101-1)+799(*ln*799-1)]
= 5907.76 – [360.52+365.13+4541.0] = 641.11
$\ln W_{RIGHT} =$ 1000(*ln*1000-1) – [199(*ln*199-1) + 801(*ln*801-1)]
= 5907.76 – [854.37+4554.4] = 499.01

Total Entropy = 1140.12

Since the total entropy of the system increases, black particles will move spontaneously from right to left.

Question 1B (continued).

(C) What is the chemical potential at 300K of the black particles in the left hand chamber? (5 points)

The chemical potential is the rate of change of entropy with number of particles, so:

$$\mu = -T\,\frac{\Delta S}{\Delta n} = -300 * \frac{641.11 - 639.03}{1} = -624$$

Q2. A solution containing 1 mole of molecule A and 1 mole of molecule B has a combined partial pressure of 2.5 atmospheres. When 1 more mole of A is added to the solution, the combined partial pressure rises to 2.67 atmospheres. (15 points)

(A) Assuming that A and B both obey Raoult's law, what are the partial pressures of pure A and pure B? Assume that the temperature is constant. (10 points)

Mole fraction of A = x_A
Mole fraction of B = x_B
Then total vapor pressure = $0.5P_A^* + 0.5P_B^* = 2.5$ (initially) Eq. 1
and $0.667P_A^* + 0.333P_B^* = 2.67$ (finally) Eq. 2
PA* and PB* are the vapor pressures of pure A and pure B.

Multiply Equation 1 by $\frac{0.5}{0.333} = 1.5 \Rightarrow$

$P_A^* + 0.5P_B^* = 4$ Eq. 3

Subtract Eq. 1 from Eq. 3

$\Rightarrow$ $0.5P_A^* = 1.5 \Rightarrow P_A^* = 3$ atmospheres

$\Rightarrow$ $P_B^* = 2$ atmospheres

Question 2, continued.

(B) Does the fact that A and B both obey Raoult's law mean that the A and B molecules do not interact with each other energetically? Explain your answer. (5 points)

Not necessarily. Raoult's Law will hold provided that the strength of the interaction between A and B is the same as the strengths of interactions between A-A and B-B.

Q3. (20 Points)
Consider two molecules A and B that can inter-convert chemically:
$A \Leftrightarrow B$

The B form is more stable than the A form: The chemical potential of the A form is 10 kJ/mole, while the chemical potential of the B form is 5 kJ/mole.

(A) At 300K, what is the equilibrium ratio of the concentrations of A and B ($\frac{[A]}{[B]}$)?

(10 points)

$\Delta G^\circ = \mu_B - \mu_A = -5\ kJ / mole$

At equilibrium,

$$\Delta G^\circ = -RT \ln\frac{[B]}{[A]} \Rightarrow \frac{[B]}{[A]} = e^{-\Delta G/RT} = e^{0.208x10} = 7.42$$

Or, $\frac{[A]}{[B]} = 0.135$ (either answer is OK)

(B) Since the B form is more stable than the A form why does the reaction not proceed so that the A form is completely converted to the B form? Explain your answer, assuming that the A and B forms do not interact in any way. (10 points)

Although pure B is more stable than pure A, the entropy of mixing is always such that it is most positive when both species are present.

Q 4. (20 points)

Streptavidin is a very stable vitamin binding protein of relative molecular weight M_r = 14 kDa. 56 g of pure streptavidin is dissolved in 1 liter of pure water and placed in the left hand chamber of a dialysis apparatus, in which the right hand side contains pure water. At equilibrium, at 300K, the osmotic pressure, π, on the left hand side is measured to be 2,486 Pascals.

(A) Calculate the molarity of the streptavidin solution using the formula for the osmotic pressure:

$\pi = \mathrm{M\ R\ T}$,

where M is the molarity, R is the gas constant and T is the temperature. (10 points). Also calculate the molarity of the solution from the mass of streptavidin added. (15 points)

To calculate the value of the osmotic pressure, be sure to use an appropriate value for the gas constant.

R = 0.08206 $\mathrm{LatmK^{-1}mol^{-1}}$ is convenient, because then

$\pi = \mathrm{M(molL^{-1})\ R(LatmK^{-1}mol^{-1})\ T(k)}$ = atmosphere units

Note that 1 atm = 1.01×10^{5} Pa

1 Pascal $\cong 1\times10^{-5}$ atm

From this equation,

$$M = \frac{2486x10^{-5}\,atm}{0.08206(L\,atm\,K^{-1}\,mol^{-1})300K}$$

$= 100.98\times10^{-5} = 1.0\times10^{-3}$ M

From mass and molecular weight,

M = 4×10^{-3} M. Explanation: Streptavidin forms a tetramer.

Question 4, continued.

(B) Are the two values of the molarity the same? If not, what is the most reasonable explanation for the difference? (5 points)

Streptavidin forms a stable tetramer.

Q 5 (20 Points)

Consider a drug or ligand, L, that binds to two proteins, P and Q.

$L + P \Leftrightarrow L.P$ and
$L + Q \Leftrightarrow L.Q$

The dissociation constant, K_P, for the first binding equilibrium is 10^{-10}, where
$K_P = \frac{[L][P]}{[L.P]}$.
The dissociation constant, K_Q, for the second binding equilibrium is 10^{-6}, where
$K_Q = \frac{[L][Q]}{[L.Q]}$.

(A) The fractional occupany, Y, of the Q protein is given by:
$$Y = \frac{[L.Q]}{[L.Q]+[Q]}$$
Show that Y can be expressed in terms of K_Q and [L] by the following equation:
$$Y = \frac{[L]}{[L]+K_Q}$$

Show all the steps and logic of how you work out the answer.
(10 points)

$$Y = \frac{[LQ]}{[LQ]+[Q]} \quad (1)$$
$$K_Q = \frac{[L][Q]}{[LQ]} \Rightarrow [LQ] = \frac{[L][Q]}{K_Q} \quad (2)$$
Substituting (2) in (1)
$$Y = \frac{\frac{[L][Q]}{K_Q}}{\frac{[L][Q]}{K_Q}+[Q]} = \frac{[L][Q]}{[L][Q]+K_Q[Q]} = \frac{[L]}{[L]+K_Q}$$

(B) What is the concentration of the ligand ([L]) that will result in only 10% fractional occupancy of Q (i.e., only 10% of Q protein is bound to the drug)? (5 points)

When Y = 10%

$$0.1 = \frac{[L]}{[L]+10^{-6}}$$

$$0.1[L]+10^{-7} = [L]$$

10^{-7} = 0.9[L]

[L]=1.11x10^{-7} M

(C) What is the fractional occupancy of the other protein (P) at the same concentration (i.e., the concentration at which Q is only 10% occupied)? (3 points)

$$Y = \frac{[L]}{[L]+K_P}$$ where $K_P = 10^{-10}$

$$Y = \frac{1.11x10^{-7}}{1.11x10^{-7}+10^{-10}} \approx 1$$

(D) Comment on the implications of these observations for drug design, given that P is the desired target and Q is an undesired target of the drug. (2 points)

When a drug has very low dissociation constant for the desired target it can be delivered at a low enough concentration to saturate the desired target while minimizing cross-reaction.

-END OF EXAM-

$V = n_1\overline{V}_1 + n_2\overline{V}_2$	(Volume of a solution)	(7.6)
$\overline{G}_i = \mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j}$	(Definition of chemical potential)	(7.7)
$\Delta_{\text{mix}}G = nRT(x_1 \ln x_1 + x_2 \ln x_2)$	(Gibbs energy of mixing)	(7.11)
$\Delta_{\text{mix}}S = -nR(x_1 \ln x_1 + x_2 \ln x_2)$	(Entropy of mixing)	(7.12)
$P_1 = X_1 P_1^*$	(Raoult's law)	(7.16)
$\mu_1(l) = \mu_1^*(l) + RT \ln x_1$	(Chemical potential of solvent in an ideal solution)	(7.17)
$P_2 = Kx_2$	(Henry's law)	(7.18)
$P_2 = K'm$	(Henry's law)	(7.19)
$a_1 = \frac{P_1}{P_1^*}$	(Activity of solvent)	(7.21)
$a_1 = \gamma_1 x_1$	(Definition of activity coefficient)	(7.22)
$\mu_2(l) = \mu_2^\circ(l) + RT \ln a_2$	(Chemical potential of solute in a real solution)	(7.25)
$\mu_2(l) = \mu_2^\circ(l) + RT \ln \frac{m_2}{m^\circ}$	(Chemical potential of solute in an ideal solution)	(7.27)
$\Delta P = x_2 P_1^*$	(Vapor-pressure lowering)	(7.33)
$\Delta T = K_{\text{b}} m_2$	(Boiling-point elevation)	(7.39)
$\Delta T = K_{\text{f}} m_2$	(Freezing-point depression)	(7.40)
$\pi = MRT$	(Osmotic pressure)	(7.46)

$\Delta_{\text{r}}G^\circ = -RT \ln K_P$	(Relation between $\Delta_{\text{r}}G^\circ$ and K_P)	(9.7)
$\Delta_{\text{r}}G = \Delta_{\text{r}}G^\circ + RT \ln Q$	(Gibbs energy change of a reaction)	(9.9)
$\gamma = \frac{f}{P}$	(Fugacity coefficient)	(9.11)
$\ln \frac{K_2}{K_1} = \frac{\Delta_{\text{r}}H^\circ}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$	(van't Hoff equation)	(9.18)
$\ln K = -\frac{\Delta_{\text{r}}H^\circ}{RT} + \frac{\Delta_{\text{r}}S^\circ}{R}$	(van't Hoff equation)	(9.19)

Useful Fundamental Constants and Conversions:

1 atm = 760 torr = 1.013×10^5 Pa
1 cal = 4.184 J
1 R (gas constant) = 8.314 J K^{-1} mol^{-1} = 0.08206 L atom K^{-1} mol^{-1}
Avogadro's Constant, $N_A = 6.022 \times 10^{23}$ mol^{-1}
Boltzmann Constant, $k_B = 1.381 \times 10^{-23}$ J K^{-1}

SI Base Units

Base Quantity	Name of Unit	Symbol
Length	meter	m
Mass	kilogram	kg
Time	second	s
Electrical current	ampere	A
Temperature	kelvin	K
Amount of substance	mole	mol
Luminous intensity	candela	cd

Derived Units in the SI System

Physical Quantity	Name	Symbol	Units
Energy	Joule	J	$kg\ m^2\ s^{-2}$
Force	Newton	N	$kg\ m\ s^{-2}$
Power	Watt	W	$kg\ m^2\ s^{-3}$
Electric charge	Coulomb	C	A s
Electrical resistance	Ohm	Ω	$kg\ m^2\ s^{-3}\ A^{-2}$
Electrical potential difference	Volt	V	$kg\ m^2\ s^{-3}\ A^{-1}$
Electrical capacity	Farad	F	$A^2\ s^4\ kg^{-1}\ m^{-2}$
Frequency	Hertz	Hz	s^{-1}

Some Commonly Used Non-SI Units

Unit	Quantity	Symbol	Conversion Factor
Angstrom	Length	Å	$1\ Å = 10^{-10}\ m = 100\ pm$
Calorie	Energy	cal	$1\ cal = 4.184\ J$
Debye	Dipole moment	D	$1\ D = 3.3356 \times 10^{-30}\ C\ m$
Gauss	Magnetic field	G	$1\ G = 10^{-4}\ T$
Liter	Volume	L	$1\ L = 10^{-3}\ m^3$

Prefixes Used with SI Units

Prefix	Symbol	Meaning
Tera-	T	1,000,000,000,000, or 10^{12}
Giga-	G	1,000,000,000, or 10^9
Mega-	M	1,000,000, or 10^6
Kilo-	k	1,000, or 10^3
Deci-	d	1/10, or 10^{-1}
Centi-	c	1/100, or 10^{-2}
Milli-	m	1/1,000, or 10^{-3}
Micro-	μ	1/1,000,000, or 10^{-6}
Nano-	n	1/1,000,000,000, or 10^{-9}
Pico-	p	1/1,000,000,000,000, or 10^{-12}