Chemistry 271, Section 21xx
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Your Name: Key

Your SID #:

General Chemistry and Energetics
Exam I (100 points total)

Your Section #:

March 7, 2011

N = 184

You have 50 minutes for this exam.

Exams written in pencil or erasable ink will not be re-graded under any circumstances.

Explanations should be concise and clear. I have given you more space than you should need. There is extra space on the last page if you need it.

You will need a calculator for this exam. No other study aids or materials are permitted.

Partial credit will be given, *i.e.*, if you don't know, guess.

Useful Equations:

$K_a = [H^+][A^-]/[HA]$

$pH = -\log([H^+])$

$K_b = [BH^+][HO^-]/[B]$

$F = ma$

$e^{i\pi} + 1 = 0$

$PV = nRT$

$K_w = [H^+][HO^-] = 10^{-14}$

$pH = pK_a + \log([A^-]/[HA])$

$pH\ (e.p.) = (pK_{a1} + pK_{a2})/2$

$R = 0.08206\ L\cdot atm/mole\ K$

$0\ °C = 273.15\ K$

$pK_a = -\log(K_a)$

$K_p = K_c(RT)^{\Delta n}$

$P^2/a^3 = 4\pi^2/MG$

$\nabla\times E = -\partial B/\partial t$

Honor Pledge: At the end of the examination time, please write out the following sentence and sign it, or talk to me about it:

"I pledge on my honor that I have not given or received any unauthorized assistance on this examination."

+1 point extra credit for filling in this box

1. (20 pts) Fill in the Blanks

Read the whole sentence before you fill in the blanks.

(a; 2 pts) K_c and K_p are equal if the number of moles of gas (+2) does not change during the reaction.

(b; 2 pts) The value of the reaction quotient Q approaches the equilibrium constant (+2) as the reaction progresses.

(c; 4 pts) At equilibrium, the rates of forward and reverse reactions are constant (+2) and are the same (+2) as each other.

(d; 4 pts) The conjugate base (+2) of a weak acid is a strong base whose pK_b can be predicted from the pK_a of the weak acid using the equation $pK_b = 14 - pK_a$ or $K_b = K_w / K_a$ (+2)

(e; 2 pts) K_w is the equilibrium constant for the water self-dissociation reaction (+2)

(f; 2 pts) The concentration of a solid or a pure liquid is constant as long as some of it is still present, so it is not included in (+2) the reaction quotient expression.

(g; 4 pts) Ideal gases are defined by two properties: the particles have no excluded volume (+2) volume and they do not (+2) attract each other.

Score for the page______

2. (28 pts) Chemical Equilibria [Adapted from Oxtoby].

(a; 18 pts) Explain the effect of each of the following stresses on the position of the following equilibrium:

$$3\ NO\,(g) \rightleftharpoons N_2O\,(g) + NO_2\,(g)$$

reactant left

prod right

The reaction as written is exothermic (releases heat). In each case, briefly explain which way the equilibrium shifts and explain why. The five cases are independent of each other.

(i) N_2O (g) is added to a mixture at equilibrium without changing the volume or the temperature.

(+3) Adding product → drive equilibrium toward reactants

LEFT

(ii) The volume of the equilibrium mixture is reduced at constant temperature.

(+3) Pressure increases → equilibrium shifts to reduce # of moles of gas → shifts to the right

(iii) The equilibrium mixture is cooled at constant volume.

(+3) for everyone

Unknowable - depends on exact values of ΔH and T

Questions (iv) and (v) are frequently answered incorrectly. Hint: Think about the *Q* and its ingredients.

(iv) Gaseous argon (which does not react) is added to the equilibrium mixture and the <u>total</u> gas pressure and the temperature are maintained constant. (Hint: how would this be done?)

If the total pressure and T are constant, volume must be increasing

Therefore partial pressures drop. (+3)

$$Q = \frac{[N_2O][NO_2]}{[NO]^3}$$ and the reaction shifts to

increase total pressure of N_2O NO_2, NO

Therefore shifts to the left (+3)

Score for the page____________

(v) Gaseous argon is added to the equilibrium mixture <u>without</u> changing the volume or temperature. (Hint: what will the effect on Q be?)

total pressure goes up but partial pressures do not change

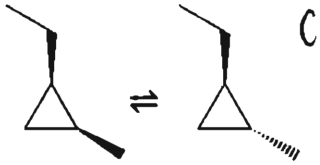
$Q = \frac{[NO_2][N_2O]}{[NO]^3}$ does not change ⊕3

Trans

At equilibrium at 425.6 °C, a sample of *cis*-1-methyl-2-ethylcyclopropane is 73.6 % converted to the *trans* form (i.e. 73.6 % of the material is found in the *trans* form at equilibrium):

cis: 26.4%

cis ⇌ *trans*



(b; 4 pts) Compute the equilibrium constant *K* for this reaction at 425.6 °C.

$K = \left(\frac{73.6}{26.4}\right) = \underbrace{2.79}_{+2}$

3 sig #

+2

(c; 6 pts) Suppose that 0.525 mol of the *cis* compound is initially placed in a 15.0 L vessel and is then heated to 425.6 °C. Compute the equilibrium partial pressure of the *cis* and *trans* compounds. [Hint: you don't actually need the answer to part ~~(a)~~ b to solve this.]

Initial $P_{cis} = \frac{0.525\ mol}{15.0\ L} \cdot 0.08206\ L\cdot atm/mol\,K \cdot (425.6 + 273.15)\,K$

$= 2.01\ atm$

this set up [illegible] //

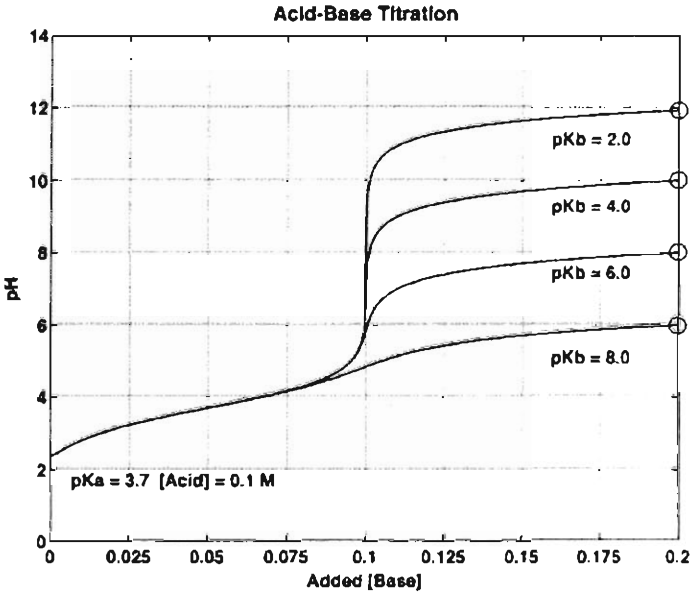
⊕2

So final $P_{\cancel{cis}\ trans} = 0.736 \times 2.01 = 1.48\ atm$ ⊕2

$P_{\cancel{trans}\ cis} = 0.264 \times 2.01 = 0.530\ atm$ ⊕2

Score for the page____________

3. (22 pts) Acid-base equilibria



Consider four separate titrations of a weak acid HA ($pK_a = 3.7$) with four different weak bases B2, B4, B6, and B8, with pK_b's = 2, 4, 6, and 8 respectively.

The family of titration curves is shown in the graph at the right. The total concentration of acid is 0.1 M and the final concentration of base is 0.2 M. Ignore dilution.

(a; 6 pts) What is the dominant reaction occurring in the solution as HA and B are mixed?
Explain why all the titration curves look the same on the left half of the graph.

(+3) $\underline{HA + B \rightleftharpoons A^- + BH^+}$ lies far to the right for any base

So the ~~B~~ pK_b of the base doesn't make much
(+3) difference to the amount of A^- we get

(b; 6 pts) When the final total concentrations of acid and base are 0.1 M and 0.2 M respectively, what are the concentrations [B] and [BH^+], approximately (no ICE tables!). Using the base dissociation equilibrium, justify the circled pH values on the right hand side of the graph: show the calculation only once since it is the same for all of them.

(+3) $[B] = 0.1\ M$ $[BH^+] = 0.1\ M$ because half of the base has reacted w/ HA to give $A^- + BH^+$

$$K_b = \frac{[BH^+][HO^-]}{[B]} \quad \text{so} \quad [HO^-] = K_b \frac{[B]}{[BH^+]} = K_b$$

(+3) hence $pOH = pK_b$ $pH = 14 - pK_b$

Score for the page____________

(c; 10 pts) The exact calculation of the titration curve of HA with B is complicated, especially at low concentrations of HA and B. We would like to solve for the six concentrations [HA], [A^-], [B], [BH^+], [H^+], and [HO^-] given the K_a for HA, the K_b for B, and the input concentrations CA and CB. Write down the six equations that we would need to solve for the six variables.

(+1) $[HA]+[A^-]=C_A$

(+1) $[BH^+]+[B]=C_B$

(+2) $K_a=\frac{[H^+][A^-]}{[HA]}$

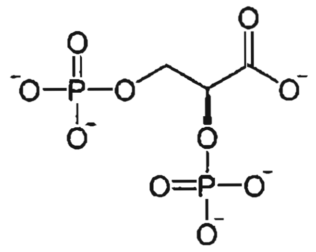
(+2) $K_b=\frac{[BH^+][HO^-]}{[B]}$

$K_w=[H^+][HO^-]$ (+1)

(+3) $[H^+]+[BH^+]=[A^-]+[HO^-]$

3. (30 pts) Hemoglobin and Linkage

The molecule 2,3-bisphosphoglycerate (2,3-BPG) controls short-term adaptation to high altitude. It binds to T-state hemoglobin about 250-fold more tightly than it does to R-state hemoglobin. We know that the R and T states also interconvert.



(a; 8 pts) Given the three equilibria below, provide a linkage argument to show that the equilibrium constant for the interconversion of R•BPG and T•BPG is 25000.

R•BPG ⇌ R + BPG $K_{diss,R}=3.0\times10^{-3}$ M

T•BPG ⇌ T + BPG $K_{diss,T}=1.2\times10^{-5}$ M

R ⇌ T $K_{RT}=100$

R•BPG ⇌ T•BPG $K_{RTBPG}=?$

Show that $K_{RTBPG}=25000$:

$$\begin{tikzcd}
R\cdot BPG \arrow[r, shift left, "3\times10^{-3}"] \arrow[d, shift right, "K=?"'] & R+BPG \arrow[l, shift left, "1"] \arrow[d, shift right, "2"'] \\
T\cdot BPG \arrow[u, shift right, "4"'] \arrow[r, shift left, "3"] & T+BPG \arrow[l, shift left, "1.2\times10^{-5}"] \arrow[u, shift right, "K=100"']
\end{tikzcd}$$

(+3) for adding equilibria or writing square

$\boxed{K_1K_2=K_4K_3}$ (+3)

$K_{RTBPG}=\frac{3\times10^{-3}\cdot100}{1.2\times10^{-5}}=250\cdot100$
$=25000$

(+2) for calculation

Score for the page____________

(b; 12 pts) The mathematics of linkage is complicated. We will consider simplified cases. First, consider oxygen binding in the absence of BPG. The R state binds O_2 about 100 times better than the T state:

$R{\bullet}O_2 \rightleftharpoons R + O_2$ $K_{O,R} = 1.3 \times 10^{-4}$ atm $= [R][O_2]/[R{\cdot}O_2]$

$T{\bullet}O_2 \rightleftharpoons T + O_2$ $K_{O,T} = 1.3 \times 10^{-2}$ atm

$R \rightleftharpoons T$ $K_{RT} = 100$

If we find in the end that [R] = 1.5 μM and $[O_2] = 2.6 \times 10^{-2}$ atm (assumed constant) use the equilibria above to give the concentrations of $R{\bullet}O_2$, T, and $T{\bullet}O_2$. The calculation is very straightforward: since I give you the equilibrium concentrations of R and O_2 you do not need an ICE table.

$$R \circ O_2 \rightleftharpoons R + O_2 \qquad \boxed{[R{\cdot}O_2] = [R][O_2]/K_{O_2}} = 1.5\,\mu M \cdot \frac{2.6\times10^{-2}}{1.3\times10^{-4}}$$

(+2)

$$= \underline{300\,\mu M} \text{ (+1)}$$

(+2) $\boxed{[T] = K_{RT}[R]} = \underline{\overset{150}{\cancel{[illegible]}}\,\mu M}$ (+1)

$$\boxed{[T{\cdot}O_2] = [T][O_2]/K_{O,T}} = \frac{150\,\mu M \cdot 2.6\times10^{-2}}{1.3\times10^{-2}} = \underline{300\,\mu M} \text{ (+1)}$$

(+2)

Calculate the fraction of the total hemoglobin that is bound to oxygen, i.e. calculate $([R{\bullet}O_2]+[T{\bullet}O_2])/([R{\bullet}O_2]+[T{\bullet}O_2]+[R]+[T])$.

(79.8%)

$$\frac{[R{\cdot}O_2]+[T{\cdot}O_2]}{[R{\cdot}O_2]+[T{\cdot}O_2]+[R]+[T]} = \frac{600\,\mu M}{600 + 1.5 + \overset{150}{\cancel{[illegible]}}} = \boxed{80\%}$$

(+1) for idea of filling in from above

(+1) for numbers

(+1)

(c; 10 pts) Next will consider the case when [BPG] is present, at high enough concentration so that all of the hemoglobin is in the BPG-bound form, and we will assess the effect of BPG on oxygen binding. We assume that the dissociation constants for the R and T states are the same with and without BPG.

$R{\bullet}BPG{\bullet}O_2 \rightleftharpoons R{\bullet}BPG + O_2$	$K_{O,R} = 1.3 \times 10^{-4}$ atm $= [R\cdot BPG][O_2]/[R\cdot BPG\cdot O_2]$
$T{\bullet}BPG{\bullet}O_2 \rightleftharpoons T{\bullet}BPG + O_2$	$K_{O,T} = 1.3 \times 10^{-2}$ atm
$R{\bullet}BPG \rightleftharpoons T{\bullet}BPG$	$K_{RTBPG} = 25000$

(+2)

Based on LeChatelier, circle whether more or [✓ less] Hb is bound to O_2 in the presence of BPG versus in its absence. If [R•BPG] = 10 nM and $[O_2] = 2.6 \times 10^{-2}$ atm (assumed constant) calculate the concentrations of $R{\bullet}BPG{\bullet}O_2$, T•BPG, and $T{\bullet}BPG{\bullet}O_2$. What fraction of the total hemoglobin is bound to oxygen?

$$[R\cdot BPG\cdot O_2] = \frac{[R\cdot BPG][O_2]}{K_{O,R}} = 10\,nM \times \frac{2.6\times10^{-2}\,atm}{1.3\times10^{-4}\,atm} = 2\,\mu M$$ (+2)

$$[T\cdot BPG] = K_{RTBPG}\,[R\cdot BPG] = 25000 \cdot 10\,nM = 250\,\mu M$$ (+2)

$$[T\cdot BPG\cdot O_2] = \frac{[T\cdot BPG][O_2]}{K_{O,T}} = 250\,\mu M \cdot \frac{2.6\times10^{-2}\,atm}{1.3\times10^{-2}\,atm} = 500\,\mu M$$ (+2)

$$\%\,bound = \frac{[R\cdot BPG\cdot O_2] + [T\cdot BPG\cdot O_2]}{[R\cdot BPG\cdot O_2] + [T\cdot BPG\cdot O_2] + [R\cdot BPG] + [T\cdot BPG]} = \frac{502}{502 + 0.01 + 250}$$ (+2)

$$= \frac{502}{752} = 67\,\%$$

Page	Score
1	/1
2	/20
3	/15
4	/13
5	/12
6	/18
7	/12
8	/10
Total	**/101**

Score for the page____________