

### News dujour

- Database reset -new HW posted
- When is the next exam?
- Lab Report for Group I due this week. Real simple-just flow diagram with unknown identified and answer to the odd numbered questions..

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### Mathematics of K

- $aA + bB \rightleftharpoons cC + dD$   $K=2.4$
- What is K for the following
- $cC + dD \rightleftharpoons aA + bB$
- $2aA + 2bB \rightleftharpoons 2cC + 2dD$
- $1/3 * cC + 1/3 * dD \rightleftharpoons 1/3 * aA + 1/3 * bB$
- Write Q for  $A + B \rightleftharpoons 2C$  call it Q1
- Write Q for  $2B \rightleftharpoons$  Call it Q2
- Write Q for  $A + 3B \rightleftharpoons 2C + D$  Call it Q3
- Mathematically, how are they related?
- Where do you think this is heading?

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### Combining equilibria

- The three basic questions to be asked/answered are:
  - Is the reaction needed (what is the unique connection between the contributor and the target equation-if there isn't one-what's Plan B)?
  - Is the contributor (in terms of the unique connection) on the correct side of the reaction?
  - Is the contributor (in terms of the unique connection) present in the needed quantity?
- The operations
  - Reverse reaction  $K_{rev} = 1/K_{forward}$
  - Multiply the reaction by  $x \Rightarrow K=K^x$
  - The final K is obtained by taking the product of the Ks for contributors
  - A tabular approach greatly facilitates the analysis of these systems.
- $2C_2H_6O(l) + O_2(g) \rightleftharpoons 2C_2H_4O(l) + 2H_2O(l)$ 
  - I)  $2CO_2(g) + 3H_2O(g) \rightleftharpoons C_2H_4O(l) + 3O_2(g)$   $K=0.100$
  - II)  $2CO_2(g) + 2H_2O(g) \rightleftharpoons C_2H_4O(l) + 5/2O_2(g)$   $K=0.120$
- $H_2S(g) + 2O_2(g) \rightleftharpoons H_2SO_4(l)$ 
  - I)  $SO_3(g) + H_2O(g) \rightleftharpoons H_2SO_4(l)$   $K=0.164$
  - II)  $SO_2(g) + H_2O(l) \rightleftharpoons H_2S(g) + 2O_2(g)$   $K=0.148$
  - III)  $H_2O(l) \rightleftharpoons H_2O(g)$   $K=6.58$

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- $C_2H_6(g) \rightleftharpoons C_2H_2(g) + 2H_2(g)$ 
  - I)  $C_2H_2(g) + 5/2O_2(g) \rightleftharpoons 2CO_2(g) + H_2O(g)$        $K = 3.60$
  - II)  $H_2O(g) \rightleftharpoons H_2(g) + 1/2O_2(g)$        $K = 0.333$
  - III)  $C_2H_6(g) + 7/2O_2(g) \rightleftharpoons 2CO_2(g) + 3H_2O(g)$        $K = 2.44$
  
- $H_2S(g) + 2O_2(g) \rightleftharpoons H_2SO_4(l)$ 
  - I)  $SO_3(g) + H_2O(g) \rightleftharpoons H_2SO_4(l)$        $K = 0.505$
  - II)  $H_2S(g) + 2O_2(g) \rightleftharpoons SO_3(g) + H_2O(l)$        $K = 3.59$
  - III)  $H_2O(g) \rightleftharpoons H_2O(l)$        $K = 0.1622$
  
- $NH_3(g) + 1/2O_2(g) \rightleftharpoons H_2O(l) + N_2H_4(l)$ 
  - I)  $2NH_3(g) + 3N_2O(g) \rightleftharpoons 4N_2(g) + 3H_2O(g)$        $K = 0.286$
  - II)  $2N_2H_4(l) \rightleftharpoons 2N_2(g) + 4H_2(g)$        $K = 0.350$
  - III)  $N_2O(g) + 3H_2(g) \rightleftharpoons N_2H_4(l) + H_2O(l)$        $K = 0.49$
  - IV)  $H_2O(l) \rightleftharpoons H_2(g) + 1/2O_2(g)$        $K = 0.153$

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### Messing with an equilibrium system

- If a system is at equilibrium and something is done to move it away from the equilibrium condition, what will happen and why?
- In general, how would you describe this process in terms used to date (Q and K)
- What types of stress will always disturb the equilibria?
- What will never disturb the equilibria?
- What will sometimes disturb the equilibria?

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### LeChatelier Effects

- The perturbing of an equilibrium system and its subsequent response is called a LeChatelier effect. The system responds in a manner that "relieves the stress" and reestablishes the equilibrium state How would the system respond to each of the following? Use Q vs K to explain the effect.
- Add reagent
- Add product
- Remove reagent
- Remove product
- $q > 0$ 
  - Increase T
  - Decrease T
- $q < 0$ 
  - Increase T
  - Decrease T

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### Volume changes -anthropomorphic view

- Predicting the effect of volume changes on equilibria can be done by using the “relieve the stress “ approach.
  - If the volume increases, the system will adjust in a fashion as to occupy more volume => produce more moles
  - If the volume decreases, the system will adjust in a fashion as to occupy less volume => produce fewer moles
  - $\Delta n$ =moles prods-moles reagents
  - $\Delta V=V_2-V_1$
- special case:  $\Delta n=0$
- The four cases
- $\Delta V>0 \Delta n>0$
- $\Delta V>0 \Delta n<0$
- $\Delta V<0 \Delta n>0$
- $\Delta V<0 \Delta n<0$

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### Volume Changes -Q vs K view

- The preceding discussion, although it will yield the correct results, is largely baloney.
- When the volume of the system is changed, which concentrations are changed?
- If V increases, how are the concentrations changed?
- If V decreases?
- Will Q change and can you predict how? In other words, since all of the [ ]s are changed will the effect be greater on the numerator or denominator of Q?
- what about  $\Delta n=0$  here?
- The four cases (Q vs K view)
- $\Delta V>0 \Delta n>0$
- $\Delta V>0 \Delta n<0$
- $\Delta V<0 \Delta n>0$
- $\Delta V<0 \Delta n<0$

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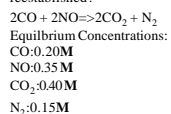
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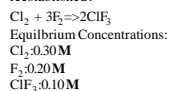
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### Handling LeChatelier Quantitatively

- For the reaction below, at equilibrium with the concentrations shown. If [CO] is changed to 0.30, what will all of the concentrations be once equilibrium is reestablished?



- For the system below, at equilibrium with the concentrations shown, if the volume is doubled, what will the new concentrations be once equilibrium is reestablished?



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### General Analysis of dynamic changes

- $aA + bB \rightleftharpoons cC + dD$
- The above reaction, initially not at equilibrium, will be described at equilibrium by the following general equation

$$\frac{([C]_i + or - cx)^c ([D]_i + or - dx)^d}{([A]_i + or - ax)^a ([B]_i + or - bx)^b} = K$$

- If  $Q < K$ , which means the reaction will proceed L to R to reach equilibrium, then the signs in the numerator will be positive and those in the denominator, negative

$$\frac{([C]_i + cx)^c ([D]_i + dx)^d}{([A]_i - ax)^a ([B]_i - bx)^b} = K$$

- For  $Q > K$ , the opposite will be the case

$$\frac{([C]_i - cx)^c ([D]_i - dx)^d}{([A]_i + ax)^a ([B]_i + bx)^b} = K$$

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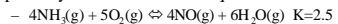
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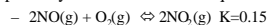
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- For the reaction below, if the initial concentrations are all 0.10 and K is as shown, write the equation that would permit you to solve for the equilibrium concentrations



- For the reaction below, if the initial concentrations are all 0.50 and K is as shown, write the equation that would permit you to solve for the equilibrium concentrations




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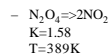
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### $K_p$ vs $K_c$

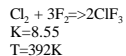
- In the following problems, all species are gaseous unless otherwise noted

- Given the balanced equation and the value of  $K_c$



What is the value of  $K_p$ ?

- Given the balanced equation and the value of  $K_c$



What is the value of  $K_p$ ?

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### More on Volume Changes

- $M_1V_1 = M_2V_2$
- We always want  $M_2 = M_1 \cdot (V_1/V_2)$  and  $M_1 = [ ]_{eq}$
- For the reaction at equilibrium
  - $aA + bB \rightleftharpoons cC + dD$
  - $K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$
- After the volume change, each new  $[ ]_i$  will be equal to  $[ ]_{eq} \cdot (V_1/V_2)$
- Further  $Q = ([C]_{eq}(V_1/V_2))^c \dots$  And so on
- As with the  $K_p$  and  $K_c$ , the  $V_1/V_2$  terms can be factored out and combined ultimately yielding
- $Q = K \cdot (V_1/V_2)^{\Delta n} (V_1/V_2)^{\Delta n}$
- Is what this predicts in terms of  $Q$  vs  $K$  consistent with the anthropomorphic approach?
- The ? becomes: Is  $(V_1/V_2)^{\Delta n} >, < \text{ or } = 1$ ?

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### Some More Practice

- $C_2H_6(g) \rightleftharpoons C_2H_4(g) + 2H_2(g)$ 
  - I)  $C_2H_2(g) + 5/2O_2(g) \rightleftharpoons 2CO_2(g) + H_2O(g)$   $K = 3.60$
  - II)  $H_2O(g) \rightleftharpoons H_2(g) + 1/2O_2(g)$   $K = 0.333$
  - III)  $C_2H_6(g) + 7/2O_2(g) \rightleftharpoons 2CO_2(g) + 3H_2O(g)$   $K = 2.44$
- For the reaction below, if the initial concentrations are all 0.10 and  $K$  is as shown, write the equation that would permit you to solve for the equilibrium concentrations
  - $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$   $K = 2.5$
- For the reaction below, if the initial concentrations are all 0.50 and  $K$  is as shown, write the equation that would permit you to solve for the equilibrium concentrations
  - $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$   $K = 0.15$

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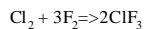
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For the system below, at equilibrium with the concentrations shown, if the volume is doubled, what will the new concentrations be once equilibrium is reestablished?



Equilibrium Concentrations:

$Cl_2$ : 0.30M

$F_2$ : 0.20M

$ClF_3$ : 0.10M

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### A Quick Review of the basics of acid/bases

- Refer to sec 4.2(p. 130) and 4.8 (p. 149)
- Arrhenius
  - **Acid:** produces an acidic aqueous solution:  $[H^+] > [OH^-]$  via hydrolysis  $HA + H_2O \rightleftharpoons A^- + H_3O^+$
  - **Base:** produces a basic aqueous solution:  $[H^+] < [OH^-]$  via hydrolysis  $B + H_2O \rightleftharpoons BH^+ + OH^-$  (this is not quite correct for soluble salts of hydroxide-why?)
- Bronsted-Lowry
  - Acid: proton,  $H^+$ , donor-note it is a **cation** which is donated
  - Base: proton,  $H^+$ , acceptor
  - Proton transfer  $HA + B \rightleftharpoons A^- + BH^+$ , Again,  $H^+$  was transferred. The following is **incorrect**:
    - $HA + B \rightleftharpoons A + BH$
  - Conjugate pairs  $HA$  and  $A^-$   $B$  and  $BH^+$ -two species related by a proton.

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### Identifying Acids and Bases

- You are responsible for knowing the common strong acids: HCl, HBr, HI, HNO<sub>3</sub>, HClO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub>. The common strong bases are KOH and NaOH. There are other strong acids and bases known.
- **Neutrals**-the conjugate bases of the strong, monoprotic acids are neutral. Ex: NO<sub>3</sub><sup>-</sup>. What are the other neutrals. How might they be "presented?"
- **Other conjugates:** all other conjugates (of the weak species) are weak
- The formula of a chemical compound is usually presented in a fashion that indicates whether the compound has acid/base character. Proper identification is the crucial first step in analyzing acid/ base systems. You should look for the following
  - Is there a leading H? In most cases that hydrogen is acidic. Ex: HNO<sub>2</sub>
  - Does the compound end in CO<sub>2</sub>H? This is a carboxylic acid-the most common weak acid type. Ex: CH<sub>3</sub>CO<sub>2</sub>H.
  - Does the compound end in NH<sub>x</sub> (x=0,1,2,3). These are nitrogen bases, the most common type of weak bases. NH<sub>3</sub>, CH<sub>3</sub>NH<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>NH, (CH<sub>3</sub>)<sub>3</sub>N
  - Ions- generally anions will be bases and cations will be acids as they are often formed by the loss (anions) and gain (cations) of H. That is the question you need to ask-can this ion be viewed as having been formed by the loss or gain of a proton? ClO<sub>2</sub><sup>-</sup> (weak base); C<sub>6</sub>H<sub>5</sub>NH<sup>+</sup> (weak acid)

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### Presenting Hydrolysis Reactions

- Acid/base hydrolysis reactions will generally involve the exchange of a proton between a solute and a water. Water may be either the acid or the base.
- A "generic" reaction looks something like this
  - $HA(B) + H_2O \rightleftharpoons A^-(HB^+) + H_3O^+(OH^-)$
  - Make note of the charges. An  $H^+$  is being transferred.
  - Also, these are reversible so can be written in the reverse of what's above. The reverse, however, is not hydrolysis.
- Write hydrolysis reactions for the following: HBr, CH<sub>3</sub>NH<sub>2</sub>, F<sup>-</sup>, C<sub>2</sub>H<sub>5</sub>CO<sub>2</sub>H, (CH<sub>3</sub>)<sub>3</sub>NH<sup>+</sup>

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### Presenting proton transfer reactions

- The key to the BL definition of acids and bases is the proton transfer reaction. Whether a species donates or accepts a proton determines its acid/base categorization.
- The generic proton transfer reaction:  
 $HA + B \rightleftharpoons A^- + HB^+$
- Proton transfer reactions have far more variety possible than hydrolysis. Each of the following is a proton transfer reaction.
  - $NH_3 + HCl \rightleftharpoons NH_4^+ + Cl^-$
  - $HS^- + NO_2^- \rightleftharpoons S^{2-} + HNO_2$
  - $CH_3CO_2H + SO_4^{2-} \rightleftharpoons CH_3CO_2^- + HSO_4^-$
  - $NH_4^+ + HCO_2^- \rightleftharpoons NH_3 + HCO_2H$

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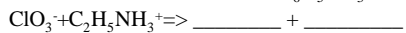
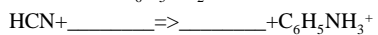
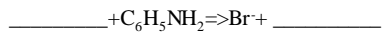
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### More on Proton Transfer

Complete the following proton transfer reactions.  
Identify the acid and the base in each.



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