CHEM 116 – Honors and Majors General and Analytical Chemistry I

2 Exams, 6 Quizzes, 7 Labs, 9 Weeks HWK - 595 points (1245 in course)

EII: AVE = 108 (72%)   Range: 49 - 148

EI: AVE = 87 (58%)

A	100	120
B	70	90
C	50	70
D	40	60

Class Averages

EXAM	195	65%
QZ	37	61%
LAB	118	84%
HWK	73	77%

Course Grade Estimate

Q1 6.0	Q4 7.8	Q6 6.1
Q3 4.2	Q5 6.5	Q7 6.1
E1 19	E5 16	L5 18
E2 17	E7 12***	
L3 18	SP 17	

A	75%	
B	65%	class average 72.1%
C	50%	GPA 3.1
D	40%	7+

Chemical Equilibrium

"When a system is in chemical equilibrium, a change in one of the parameters of the equilibrium produces a shift in such a direction that, were no other actors involved in this shift, it would lead to a change of opposite sign in the parameter involved."
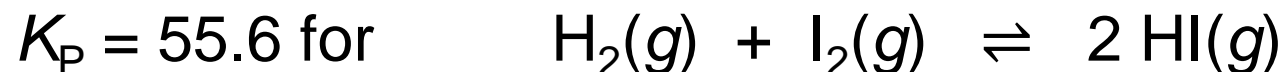
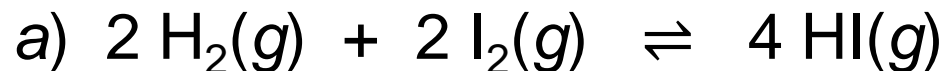**Henri Louis Le Châtelier, 1888**

END OF WEEK SWITCHING TO HARRIS TEXT

6.8 Le Châtelier's Principle
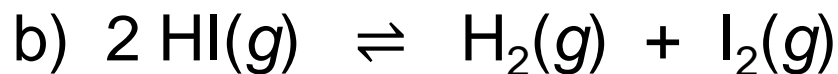
6.9 Equilibria Involving Real Gases (Activity)
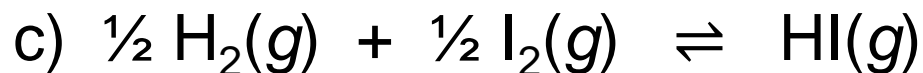
Relationship of K's of Related Equilibria

$$K_P = 55.6 \text{ for} \qquad H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$$

EX 5. For the above reaction ($K_P = P^2_{HI} / P_{H2}\, P_{I2}$) what is K_P for:

a) $2\,H_2(g) + 2\,I_2(g) \rightleftharpoons 4\,HI(g)$

      multiply all coefficients by n => $K_{new} = K_o^{\,n}$

b) $2\,HI(g) \rightleftharpoons H_2(g) + I_2(g)$

      reverse reaction (multiply by -1) => $K_{new} = K_o^{-1} = 1\,/\,K_o$

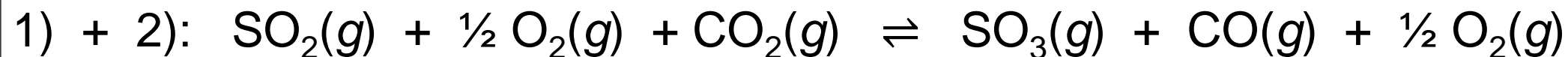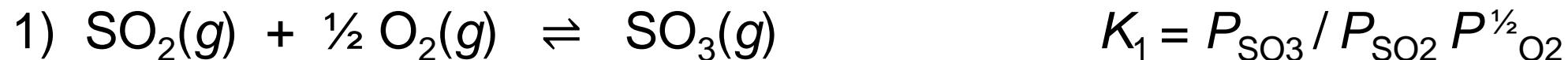c) $\frac{1}{2}\,H_2(g) + \frac{1}{2}\,I_2(g) \rightleftharpoons HI(g)$

      multiply all coefficients by $n = \frac{1}{2}$ => $K_{new} = K_o^{\,1/2} = \sqrt{K_o}$

Relationship of *K*'s of Simultaneous Equilibria

EX 6. Find the equilibrium constant for

$$SO_2(g) + CO_2(g) \rightleftharpoons SO_3(g) + CO(g)$$

if you know the equilibrium constants for the following reactions:

1) $SO_2(g) + \frac{1}{2} O_2(g) \rightleftharpoons SO_3(g)$ $K_1 = P_{SO3} / P_{SO2} P^{\frac{1}{2}}_{O2}$

2) $CO_2(g) \rightleftharpoons CO(g) + \frac{1}{2} O_2(g)$ $K_2 = P_{CO} P^{\frac{1}{2}}_{O2} / P_{CO2}$

1) + 2): $SO_2(g) + \frac{1}{2} O_2(g) + CO_2(g) \rightleftharpoons SO_3(g) + CO(g) + \frac{1}{2} O_2(g)$
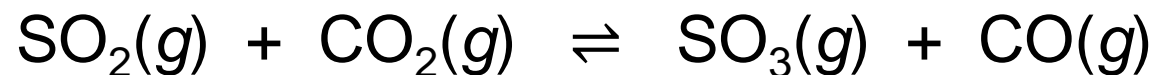
$K = (P_{SO3} / P_{SO2} P^{\frac{1}{2}}_{O2})(P_{CO} P^{\frac{1}{2}}_{O2} / P_{CO2}) = K_1 K_2$ add reactions, multiply *K*'s

Relationship of *K*'s of Simultaneous Equilibria

EX 6. Find the equilibrium constant for

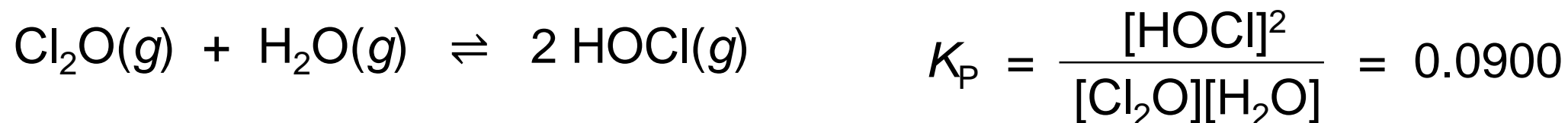$$PCl_5(g) \;\rightleftharpoons\; PCl_3(g) \;+\; Cl_2(g)$$

if you know the equilibrium constants for the following reactions:

1) $PCl_5(s) \;\rightleftharpoons\; PCl_3(g) \;+\; Cl_2(g)$ $\qquad\qquad K_1 = P_{PCl3}\,P_{Cl2}$

2) $PCl_5(s) \;\rightleftharpoons\; PCl_5(g)$ $\qquad\qquad\qquad\qquad K_2 = P_{PCl5}$

1) − 2): $PCl_5(s) \;+\; PCl_5(g) \;\rightleftharpoons\; PCl_3(g) \;+\; Cl_2(g) \;+\; PCl_5(s)$
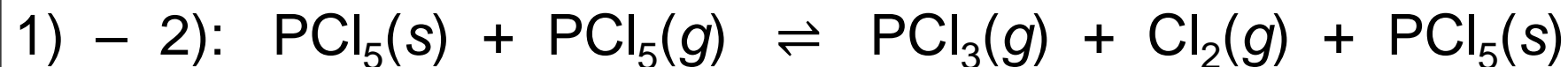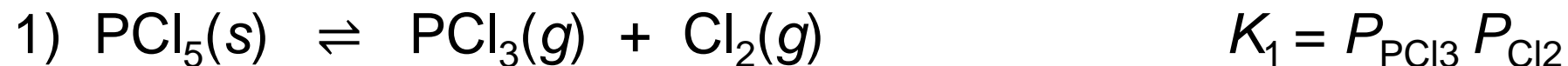
$$(P_{PCl3}\,P_{Cl2}) \,/\, P_{PCl5} \;=\; K_1 \,/\, K_2 \quad \text{subtract reactions, divide } K\text{'s}$$

Interpreting Value of the Equilibrium Constant

$$H_2(g) \ + \ \tfrac{1}{2}\,O_2(g) \ \rightleftharpoons \ H_2O(g)$$

$$K \ = \ \frac{[H_2O]}{[H_2][O_2]^{\frac{1}{2}}} \ = 5.6 \times 10^{40}$$

$$Cl_2O(g) \ + \ H_2O(g) \ \rightleftharpoons \ 2\,HOCl(g)$$

$$K_P \ = \ \frac{[HOCl]^2}{[Cl_2O][H_2O]} \ = 0.0900$$

$$N_2(g) \ + \ O_2(g) \ \rightleftharpoons \ 2\,NO_2(g)$$

$$K_P \ = \ \frac{[NO_2I]^2}{[N_2][O_2]} \ = 4.7 \times 10^{-31}$$
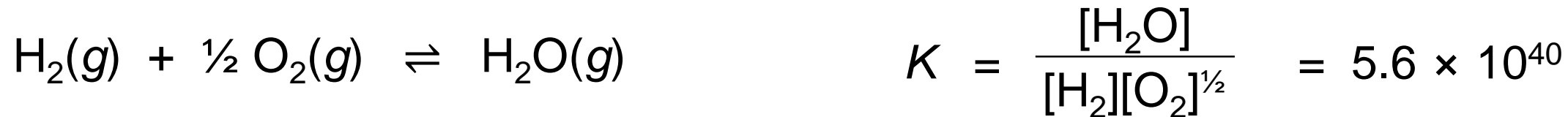
$K > 1$ => product-favored; $K \gg 1$ => reaction essentially complete
$K < 1$ => reactant-favored; $K \ll 1$ => essentially no reaction

Solving Equilibrium Problems

Find K given initial partial pressures and one equilibrium partial pressure.

EX 8. 4.00 atm of H_2(g) and 2.00 atm of I_2(g) are mixed and allowed to react. When equilibrium is reached 3.76 atm of HI(g) is formed. What is K_P for the reaction?
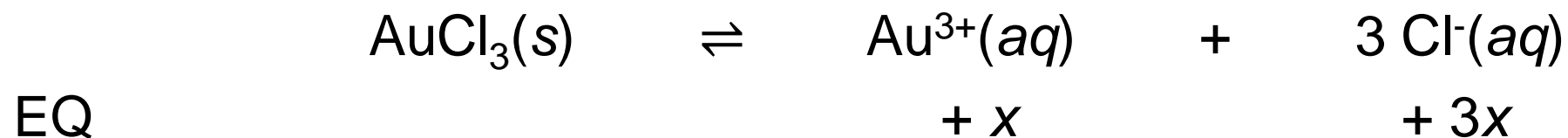
	H_2(g)	+	I_2(g)	⇌	2 HI(g)
I	4.00 atm		2.00 atm		0
C	- x		- x		+ 2x
E	4.00 - x		2.00 - x		3.76 atm = 2x => x = 1.88
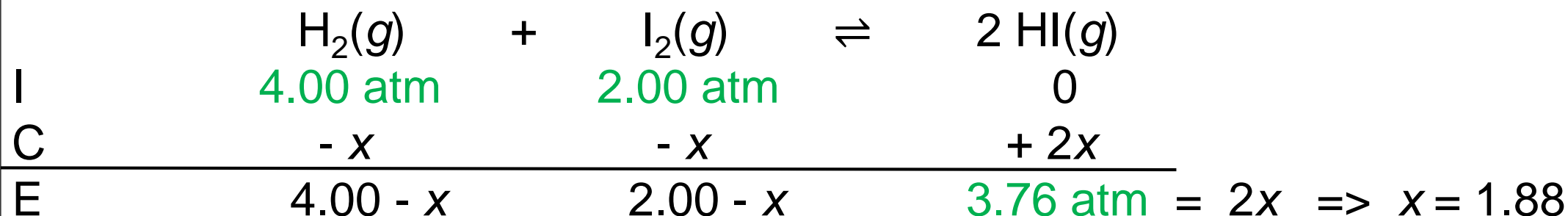
$$K_P = \frac{P^2_{HI}}{P_{H2}P_{I2}} = \frac{(1.88)^2}{(4.00\text{-}1.88)\ (2.00\text{-}1.88)} = \mathbf{55.6}$$

Solving Equilibrium Problems

Given K_{sp} for dissolution of a solid, find ion concentrations.

EX 11. What are the equilibrium concentration of the ions at 25°C if Ksp = 3.2×10^{-25}?

$$AuCl_3(s) \quad \rightleftharpoons \quad Au^{3+}(aq) \quad + \quad 3\,Cl^-(aq)$$

EQ $\qquad\qquad\qquad\qquad\qquad +x \qquad\qquad\qquad +3x$

$$K_{sp} = x\,(3x)^3 = 27\,x^4 \Rightarrow x = (K_{sp}/27)^{1/4}$$

$$= [\,(3.2 \times 10^{-25})/27\,]^{1/4}$$

$$= 3.3 \times 10^{-7} = [Au^{3+}]$$

$$9.9 \times 10^{-7} = [Cl^-]$$

Solving Equilibrium Problems

Treating systems with a small equilibrium constant

EX 13. If 2.00 mol of HBr were placed in a 1.00 L vessel at 1495 K what would be the equilibrium concentration of all species if $K = 2.86 \times 10^{-5}$?

$$2\ HBr(g) \quad \rightleftharpoons \quad H_2(g) \quad + \quad Br_2(g)$$

	2 HBr(g)	H$_2$(g)	Br$_2$(g)
I	2.00 M	0	0
C	- 2x	+ x	+ x
E	2.00 − 2x	x	x

$$K = \frac{x^2}{(2.00 - 2x)^2} \Rightarrow \sqrt{K} = x / (2.00 - 2x)$$

ignore 2x since K small => x small
(not ignored then x= 0.01058)

$$x = 2\sqrt{K} = 2\sqrt{(2.86 \times 10^{-5})} = 0.01069$$

[HBr] = 2.00 − 2(0.01069) = 1.9786 => **1.98 M**   **[H$_2$] = [Br$_2$] = 0.01 M**

Solving Equilibrium Problems

Systems requiring a quadratic equation

EX 14. At a particular temperature $K = 9.1 \times 10^{-4}$. Determine the concentration of all ions in a solution that is initially 2.0 M $FeSCN^{2+}$.

$$FeSCN^{2+}(aq) \rightleftharpoons Fe^{3+}(aq) + SCN^-(aq)$$

EQ $\qquad$ $2.00 - x$ $\qquad\qquad$ x $\qquad\qquad$ x
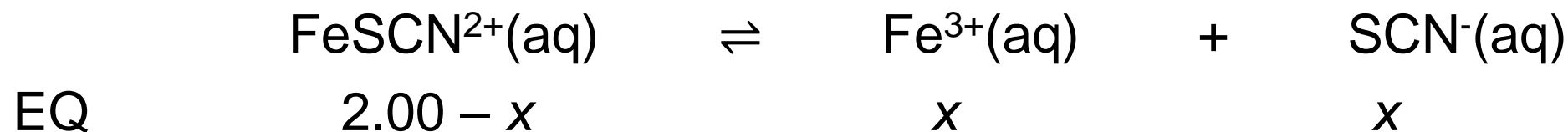
$$K = \frac{x^2}{2.00 - x} \qquad \text{or} \qquad x^2 + xK - 2K = 0$$

for $ax^2 + bx + c = 0$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$x = -9.1 \times 10^{-4} \pm \sqrt{(9.1 \times 10^{-4})^2 - 4(2)(9.1 \times 10^{-4})}$

$= $ **0.042 M** $=$ **$[Fe^{3+}]$** $=$ **$[SCN^-]$** $\qquad$ **$[FeSCN^{2+}] = $ 2.0 M**

$- 0.043$ M unphysical

$x = 0.04266$

Le Châtelier's Principle

"When a system is in chemical equilibrium, a change in one of the parameters of the equilibrium produces a shift in such a direction that, were no other actors involved in this shift, it would lead to a change of opposite sign in the parameter involved."

Henri Louis Le Châtelier, 1888

I.   change of **temperature** at constant pressure

II. change of **total pressure** at constant temperature
   a) add or remove gaseous reactant or product at constant volume
   b) change volume of container
   c) add inert gas (one not involved in the reaction) at constant volume

III. change of **concentration/partial pressure** at constant volume (same as **II** a)

Le Châtelier's Principle – Change P (T Constant)

1) Pressure induced phase transition

$$H_2O(s) \quad \rightleftharpoons \quad H_2O(l)$$
$$d = 0.917 \quad\quad d = 0.999$$
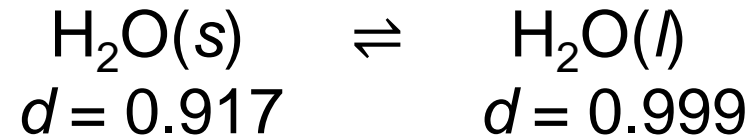
Density = m/V =>liquid water has a larger volume available to a given mass of molecules than ice does. Therefore, ice melts under pressure (remember that the phase diagram for water has a negative slope for the solid/liquid coexistence line).
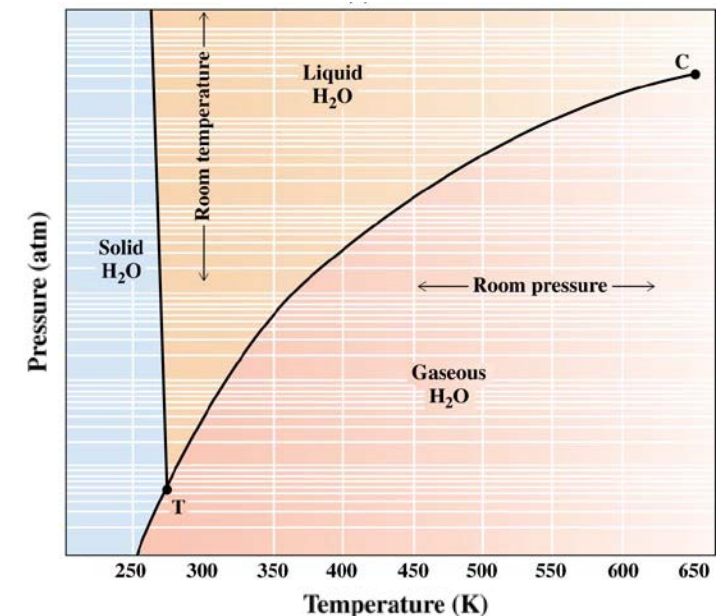
Le Châtelier's Principle – Change P (T, V Constant)

Law of Mass Action

For   aA + bB   <=>   cC + dD the equilibrium constant K is

$$K = \frac{P^c_C \, P^d_D}{P^a_A \, P^b_B}$$

2) add inert gas (one that does not participate in the chemical equilibrium

Since $P_i = n_i RT/V$, the partial pressures of all gases participating in the equili-brium reaction are unaffected by the presence of the inert gas. Hence so is the equilibrium constant.

Le Châtelier's Principle – Change P (T, V Constant)

Law of Mass Action

For   aA + bB   <=>   cC + dD the equilibrium constant K is

$$K = \frac{P^c_C \, P^d_D}{P^a_A \, P^b_B}$$

3) add gaseous reactant or product

Since $P_i = n_i RT/V$, partial pressures of all other gases participating in the equilibrium reaction are unaffected. But K would change and it is a constant! Therefore if added gas were a reactant, K would decrease unless equilibrium shifts to products => equilibrium must shift to products. Similarly, were the added gas a product, the equilibrium would shift toward reactants.

Le Châtelier's Principle – Change P (T, V Constant)

Law of Mass Action

For   aA + bB   <=>   cC + dD the equilibrium constant K is

$$K = \frac{P^c_C \, P^d_D}{P^a_A \, P^b_B}$$

4) decrease volume by compression (consider 4-fold decrease)

Since $P_i = x_i P_{TOT}$, each P_i in K (actually Q until new equilibrium established) increases 4-fold. If total # of moles of reactant gases in balanced chemical equation same as total # of moles of product gases then no effect - powers that P_i are raised to in numerator of K same as in denominator.
P increase shifts equilibrium to side with fewer moles in balanced equation.

Le Châtelier's Principle – Change *T* (*P* Constant)

Exothermic reactions gives off heat, endothermic reactions require heat

a) the following reaction is exothermic

$$N_2(g) \; + \; 3\,H_2(g) \; \rightleftharpoons \; 2\,NH_3(g) \qquad \text{+ heat}$$
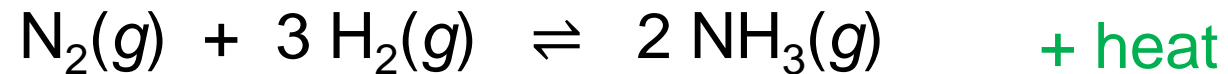
b) the following reaction is endothermic

$$\text{+ heat} \qquad N_2(g) \; + \; O_2(g) \; \rightleftharpoons \; 2\,NO(g)$$

analogy with the stress imposed by adding or removing a gaseous reactant if one were to consider heat as a "reactant" in the case of an endothermic reaction and as a "product" for an exothermic reaction.

Strong Acids and Bases_____

END OF WEEK SWITCHING TO HARRIS TEXT

OVERVIEW of this material in Harris:

6-1, 6-2, 6-5 – 6-7

omitting the thermodynamics

7.1 The Nature of Acids and Bases
7.2 Acid Strength
7.3 The pH Scale
7.4 Calculating the pH of Strong Acid Solutions
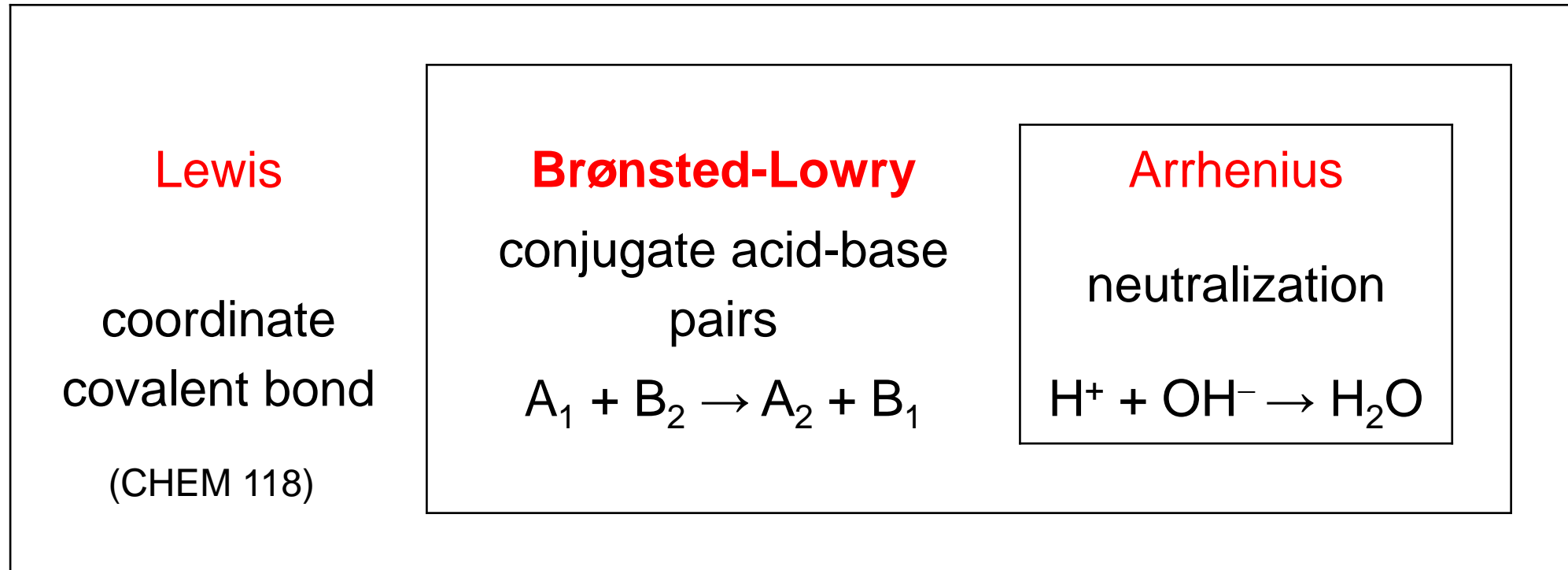**7.6 Bases (just the strong ones)**

FRIDAY QUIZ ON CHEMICAL EQUILIBRIUM

Nature of Acids and Bases

acid: accepts electron pair   donates H^+ produces H^+
base: donates electron pair   accepts H^+ produces OH^-

Lewis

coordinate

covalent bond

(CHEM 118)

Brønsted-Lowry

conjugate acid-base
pairs

$A_1 + B_2 \rightarrow A_2 + B_1$

Arrhenius

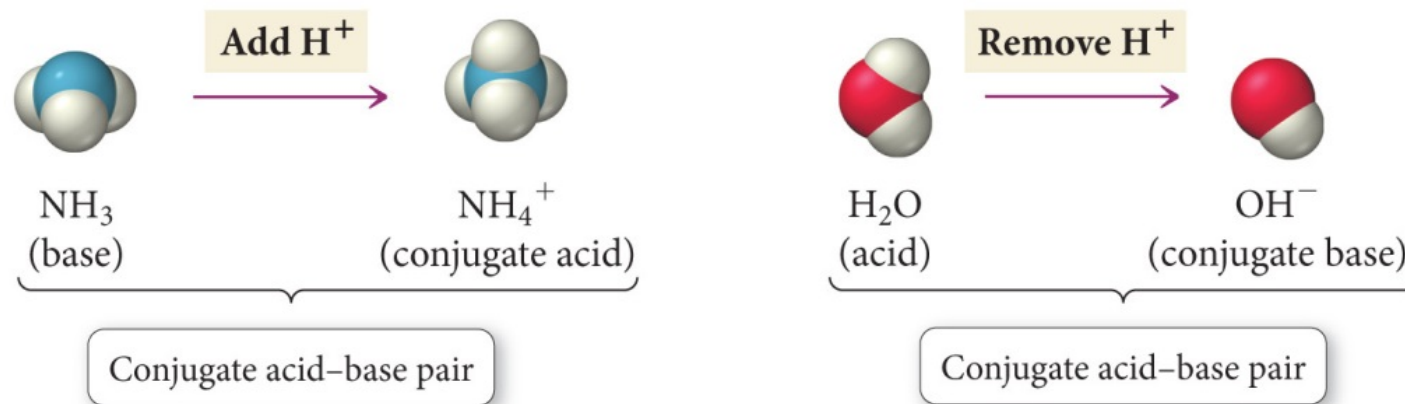neutralization

$H^+ + OH^- \rightarrow H_2O$

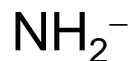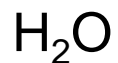problem: most general   must have H   need aqueous solution

Brønsted-Lowry: Conjugate Acid-Base Pairs

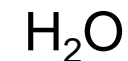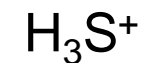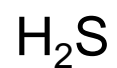| Add H$^+$		Remove H$^+$	
NH_3 (base)	NH_4^+ (conjugate acid)	H_2O (acid)	OH^- (conjugate base)
Conjugate acid–base pair		Conjugate acid–base pair	

EX 1. For each of the following write the formula of its conjugate.

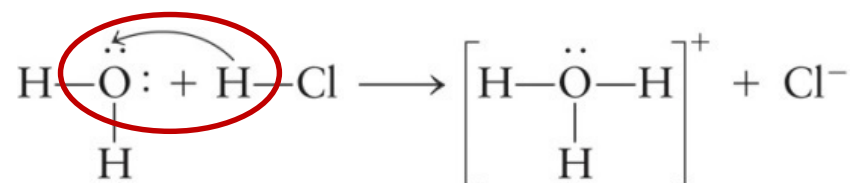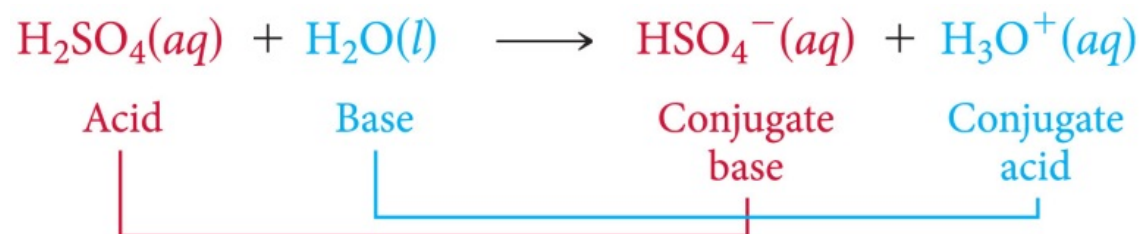| ACIDS		BASES	
HCl	Cl$^-$	NH_3	NH_4^+
H_2O	OH$^-$	H_2S	H_3S^+
NH_3	NH_2^-	NaOH	H_2O
CH_3COOH	CH_3COO^-	O^{2-}	OH$^-$
SH$^-$	S^{2-}	CN$^-$	HCN

Brønsted-Lowry: Acid-Base Pair Chemistry

acids – proton donors => form a species [acid – H^+] called **conjugate base**

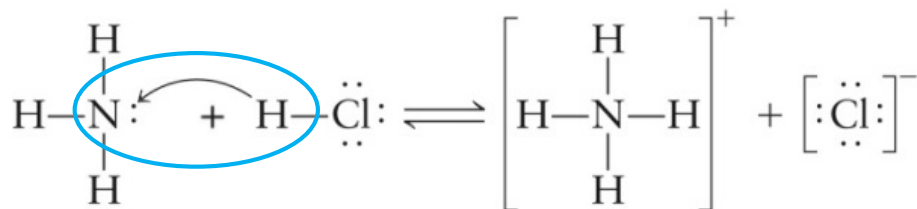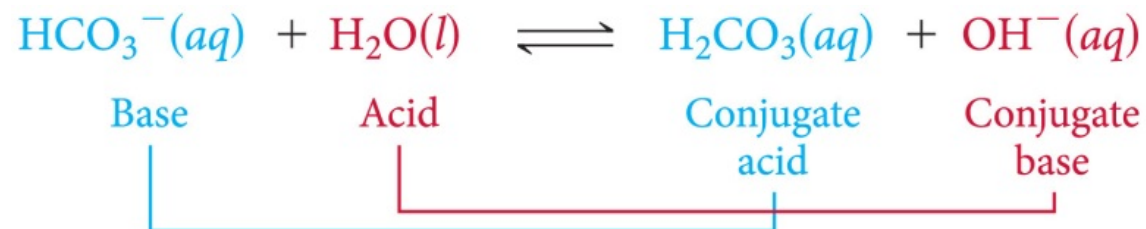strong acid or base often uses reaction arrow

$$H_2SO_4(aq) \; + \; H_2O(l) \longrightarrow \; HSO_4^-(aq) \; + \; H_3O^+(aq)$$

Acid   Base   Conjugate   Conjugate
base   acid

reaction when acid dissolved in water

bases – proton acceptors => form a species [base + H^+] called **conjugate acid**

weak acid or base uses equilibrium arrow
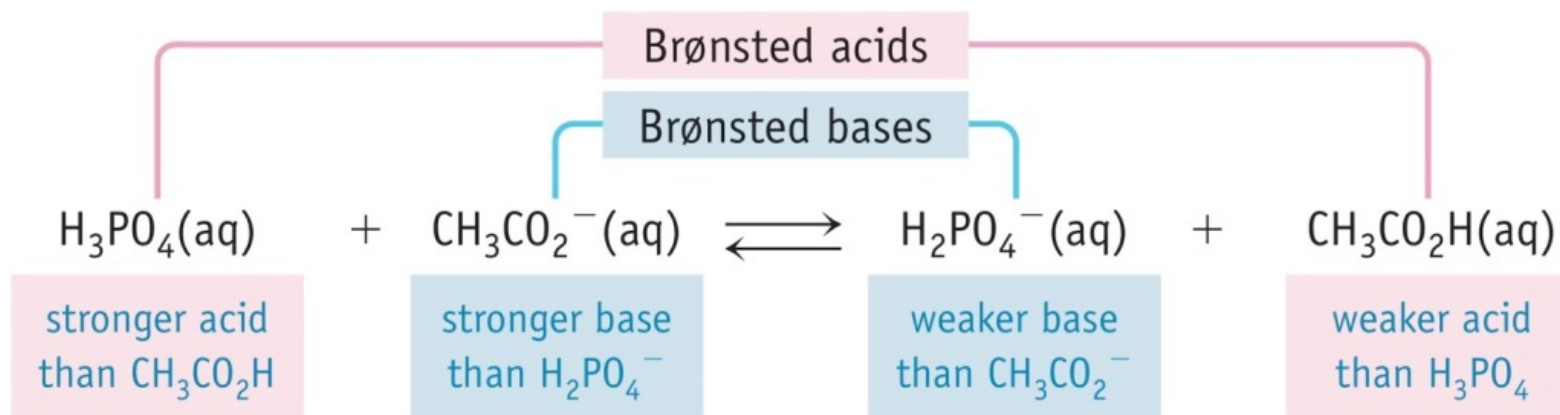
$$HCO_3^-(aq) \; + \; H_2O(l) \; \rightleftharpoons \; H_2CO_3(aq) \; + \; OH^-(aq)$$

Base   Acid   Conjugate   Conjugate
acid   base

nonaqueous reaction in liquid ammonia   reaction when base dissolved in water

Brønsted-Lowry: Acid-Base Pair Chemistry

two acids competing to give up H$^+$ – the stronger acid "wins"

Brønsted acids

Brønsted bases

$H_3PO_4(aq)$ + $CH_3CO_2^-(aq)$ $\rightleftharpoons$ $H_2PO_4^-(aq)$ + $CH_3CO_2H(aq)$

| stronger acid than CH_3CO_2H | stronger base than $H_2PO_4^-$ | weaker base than $CH_3CO_2^-$ | weaker acid than H_3PO_4 |

two bases competing for the acidic proton – the stronger base "wins"

EX 3. From the Brønsted-Lowry point of view, which is the stronger acid in the following reaction:

$$H_2SO_4(aq) + HNO_3(aq) <=> HSO_4^-(aq) + H_2NO_3^+(aq)$$