#### CHEM 116 Equilibrium Calculations

Today we will begin with the end of Lecture 15 notes that we didn't finish last week, about equilibrium. If you have already printed Lecture 15, then bring it to lecture with you, and you can avoid re-printing those pages by <u>not</u> printing pages 4 to 8 of these Lecture 16 notes. In other words, just print pages 1-3 and pages 9-16. Lecture 16 Prof. Sevian



#### Today's agenda

- A point of confusion about kinetics that arose in FSG
  - Rate expression and rate constant are different things
- Equilibrium (ch. 15, this material will be on Exam 3)
  - Summarize theory
  - General method for calculating concentrations and equilibrium constants (Initial-Change-Equilibrium table)

#### Clarifying rate vs. rate constant

• The rate law is an equation that has a form like these:

 $rate = k [reactant 1]^{m} [reactant 2]^{n} \text{ or } -\frac{d [reactant 1]}{dt} = k [reactant 1]^{m} [reactant 2]^{n}$ for a rxn:
(reactant 1) + (reactant 2)  $\rightarrow$  product  $rate = k [reactant]^{m} \text{ or } -\frac{d [reactant]}{dt} = k [reactant]^{m} \text{ for a rxn: (reactant 2)} \rightarrow (product)$ To determine the "form" of the rate equation, you have to determine
what the exponents are equal to. Exponents are called the "order"
with respect to a particular reactant. The "overall order" of a rate law
is the sum of all the exponents.

- The rate constant is *k* in the equations above
- If asked for the form of the rate law, your answer could be like:

 $rate = k [reactant 1]^2 [reactant 2]^1$  or perhaps  $rate = k [reactant]^3$ 

 If asked to determine the <u>entire</u> rate law, you will <u>also</u> have to specify the <u>value</u> of k

#### Clarifying rate law vs. concentration behavior with time

- Rate means change with time
- Rate of reaction means how a chemical's concentration changes
   with time:

 $\frac{d[\text{reactant A}]}{dt} = \text{rate of change of [A] with time}$ 

• You can integrate a rate law (using calculus) to find an expression for how the concentration of a chemical changes with time

exponent = 0  

$$\begin{aligned}
rate = k[A]^{0} \\
-\frac{d[A]}{dt} = k \rightarrow \int_{\text{when } t=0}^{\text{at time } t} d[A] = -\int_{0}^{t} k \, dt \rightarrow [A]_{t} = [A]_{0} - k \, t
\end{aligned}$$
exponent = 1  

$$\begin{aligned}
rate = k[A]^{1} \\
-\frac{d[A]}{dt} = k[A] \rightarrow \int_{\text{when } t=0}^{\text{at time } t} \frac{d[A]}{[A]} = -\int_{0}^{t} k \, dt \rightarrow \ln[A]_{t} = \ln[A]_{0} - k \, t
\end{aligned}$$
exponent = 2  

$$\begin{aligned}
rate = k[A]^{2} \\
-\frac{d[A]}{dt} = k[A]^{2} \rightarrow \int_{\text{when } t=0}^{\text{at time } t} \frac{d[A]}{[A]^{2}} = -\int_{0}^{t} k \, dt \rightarrow \frac{1}{[A]_{t}} = \frac{1}{[A]_{0}} + k \, t
\end{aligned}$$



#### Key points covered so far on Equilibrium

- *K* is called the equilibrium constant, *Q* is called the reaction quotient. The equation form is "products over reactants."
- Only the highest entropy phases appear in Q and K, because the reaction takes place only in the highest entropy phase
- *K* and *Q* have the same form (equation) for a reaction, but *Q* can have different values at different times\*, and *K* is the value that *Q* approaches asymptotically as the system reaches equilibrium
- *K* depends only on temperature (not time\*), and the same value of *K* is reached no matter what the initial concentrations of reactants or products are
- K and Q do not have units
- Under a particular set of concentrations, if Q > K, then the reaction proceeds in a direction to decrease Q (i.e., reactant concentrations [numerator] decrease and product concentrations [denominator] increase). Vice versa is also true.

\* Technically, we should speak of reaction progress, not time.

#### Which chemicals are part of the expression for Q?

- Determine phase (liquid, gas, aqueous) the reaction takes place in
- Only chemicals that are in that phase are part of the reaction quotient, because chemicals in other phases remain in those phases
- In an aqueous reaction, spectator ion concentrations do not change, so spectator ions are not part of the reaction quotient either
- Examples: 1.  $N_2(g) + 3 H_2(g) \leftrightarrows 2 NH_3(g)$   $Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$   $Q_p = \frac{(p_{NH_3})^2}{(p_{N_2})(p_{H_2})^3}$ 2.  $2 S(s) + 3 O_2(g) \leftrightarrows 2 SO_3(g)$   $Q_c = \frac{[SO_3]^2}{[O_2]^3}$   $Q_p = \frac{(p_{SO_3})^2}{(p_{O_2})^3}$ 3.  $Cu(NO_3)_2(aq) + Zn(s) \leftrightarrows Zn(NO_3)_2(aq) + Cu(s)$ net ionic reaction:  $Cu^{2+}(aq) + Zn(s) \leftrightarrows Zn^{2+}(aq) + Cu(s)$   $Q = \frac{[Zn^{2+}]}{[Cu^{2+}]}$ 4.  $PbCl_2(s) \leftrightarrows Pb^{2+}(aq) + 2 Cl^{-}(aq)$   $Q = \frac{[Pb^{2+}][Cl^{-}]^2}{1} = [Pb^{2+}][Cl^{-}]^2$

An easy way to remember it: only the highest entropy phases appear in Q

## Concentration (moles per unit volume) of a pure solid or liquid has a constant value

In a liquid-aqueous reaction

 $\mathrm{H}^{+}(aq) + \mathrm{OH}^{-}(aq) \leftrightarrows \mathrm{H}_{2}\mathrm{O}(l)$ 

 $[H^+] = \frac{moles \text{ of } H^+ \text{ ions}}{\text{liter of solution}}$  and  $[OH^-] = \frac{moles \text{ of } OH^- \text{ ions}}{\text{liter of solution}}$  typically on order of 10<sup>-7</sup> M

By contrast, in one liter of water, moles of H<sub>2</sub>O (*l*) is approximately

 $1000 \ mL \times \frac{1.00 \ g}{mL} \times \frac{1 \ mol}{18.02 \ g} = 55.5 \ mol$  so when 10<sup>-7</sup> moles of H<sub>2</sub>O (*l*) react, the effect is negligible

In a reaction involving a pure solid or liquid

"Molarity" of a solid or liquid is moles of solid or liquid per volume taken up. If you double the amount of solid or liquid used in the reaction, then the "molarity" of the solid or liquid stays the same. Since the reaction quotient only involves quantities that change when the reaction occurs, then pure solids or liquids do not appear in *Q*.

#### Converting between $K_c$ and $K_p$

- Use gas law, pV = nRT
- Or partial pressure of a component gas in a mixture:

Concentration is moles per liter (n/V)



#### Another example of converting between $K_c$ and $K_p$

Remember, this is valid only for gas phase reactions  $N_2(g) + 3 H_2(g) \leftrightarrows 2 NH_3(g)$  $K_p = \frac{(p_{\rm NH_3})^2}{(p_{\rm N})(p_{\rm H_1})^3}$  and pV = nRT and  $[X] = \frac{\text{moles of } X}{\text{volume in liters}}$ For any gas,  $p_X = \frac{n_X RT}{V} = \left(\frac{n_X}{V}\right) RT = [X](RT)$ Therefore.  $K_{p} = \frac{(p_{\rm NH_{3}})^{2}}{(p_{\rm N_{2}})(p_{\rm H_{2}})^{3}} = \frac{([\rm NH_{3}](RT))^{2}}{([\rm N_{2}](RT))([\rm H_{2}](RT))^{3}}$  $=\frac{[NH_3]^2}{[N_2][H_2]^3}\left(\frac{(RT)^2}{(RT)(RT)^3}\right)$  $=\frac{[NH_3]^2}{[N_2][H_2]^3}\left(\frac{1}{(RT)^2}\right)=K_c(RT)^{-2}$ 

Generally speaking,  

$$K_p = K_c (RT)^{\Delta n}$$
  
where  
 $\Delta n = \sum_{products} n - \sum_{reactants} n$ 

#### $K_{\rm c}$ vs. $K_{\rm p}$ : Different equilibrium constants?

• For an aqueous system, it only makes sense to use molarities  $Cu^{2+}(aq) + Zn(s) \leftrightarrows Zn^{2+}(aq) + Cu(s)$ 

$$K_c = \begin{bmatrix} \operatorname{Zn}^{2+} \\ \operatorname{Cu}^{2+} \end{bmatrix}$$

 For a gas system, you could use either molarities or partial pressures
 N<sub>2</sub> (g) + 3 H<sub>2</sub> (g) ≒ 2 NH<sub>3</sub> (g) at 25 °C

$$K_{c} = \frac{[\mathrm{NH}_{3}]^{2}}{[\mathrm{N}_{2}][\mathrm{H}_{2}]^{3}} = 3.8 \times 10^{8} \qquad K_{p} = \frac{(p_{\mathrm{NH}_{3}})^{2}}{(p_{\mathrm{N}_{2}})(p_{\mathrm{H}_{2}})^{3}} = 1.08 \times 10^{5} \text{ when pressures in atm}$$

- Sometimes it is easier to work with partial pressures (e.g., if there are inert gases also in the mixture)
- If you're working with a gas phase equilibrium, you need to know which value of K is given, and you need to know how to convert between them
- Remember that in a gas system, you can use the ideal gas law
- Remember that molarity = moles of the chemical per unit volume

### Values of $K_{eq}$ have been measured for many reactions

$$2 \operatorname{NO}_2(g) \leftrightarrows \operatorname{N}_2\operatorname{O}_4(g)$$
 at 25 °C  $K_c = \frac{[\operatorname{N}_2\operatorname{O}_4]}{[\operatorname{NO}_2]^2} = 171.0$ 

$$CH_{3}COOH(aq) + H_{2}O(l) \leftrightarrows H_{3}O^{+}(aq) + CH_{3}COO^{-}(aq)$$
  
at 25 °C  
$$K = \frac{[H_{3}O^{+}][CH_{3}COO^{-}]}{K}$$

$$K_{a} = \frac{\left[\text{H}_{3}\text{O}^{+}\right]\left[\text{CH}_{3}\text{COO}^{-}\right]}{\left[\text{CH}_{3}\text{COOH}\right]} = 1.8 \times 10^{-5}$$

 $N_2H_4(aq) + H_2O(l) \leftrightarrows N_2H_5^+(aq) + OH^-(aq)$ at 25 °C

$$K_{b} = \frac{\left[N_{2}H_{5}^{+}\right]\left[OH^{-}\right]}{\left[N_{2}H_{4}\right]} = 8.5 \times 10^{-7}$$

 $PbBr_2(s) \leftrightarrows Pb^{2+}(aq) + 2 Br^-(aq)$  at 25 °C  $K_{sp} = [Pb^{2+}][Br^-]^2 = 6.6 \times 10^{-6}$ 

# ICE tables make it easy to keep track of the stoichiometry

ICE = initial, change, at equilibrium

- Initial: the non-equilibrium conditions initially present (i.e., initial concentrations or partial pressures – must use one of these, not moles)
- **Change**: as reaction proceeds in one direction or the other, if *x* moles/volume (or *x* atm of partial pressure) of one chemical react, stoichiometry dictates how much of the other chemicals will react or form
- Equilibrium: what was initially present, plus the change, equals the equilibrium values

Using the **equilibrium expression**, K=..., will often result in an equation in which you have to solve for *x*. Once you solve for *x*, you can calculate everything else.

#### A simple example of using ICE

Practice Exercise on p. 645

Sulfur trioxide decomposes at high temperature in a sealed container:

 $2 \operatorname{SO}_3(g) \leftrightarrows 2 \operatorname{SO}_2(g) + \operatorname{O}_2(g)$ 

Initially, the vessel is charged at 1000 K with SO<sub>3</sub> (*g*) at a partial pressure of 0.500 atm. At equilibrium, the SO<sub>3</sub> partial pressure is 0.200 atm. Calculate the value of  $K_p$  at 1000 K.

partial pressures	2 $SO_3(g)$	$\Rightarrow$ 2 SO <sub>2</sub> (g)	$+ O_2(g)$
Initial	0.500 atm	0 atm	0 atm
Change	- 2 <i>x</i>	+ 2x	+ <i>x</i>
Equilibrium	0.200 = 0.500 - 2	<i>x</i> 2 <i>x</i>	X

# If you know the value of $K_c$ and the initial conditions you can figure out the final concentrations – Use an ICE table

To complement Practice Exercises on pp. 644-645

At some temperature,  $K_c$  = 33 for the reaction

$$H_2(g) + I_2(g) \leftrightarrows 2 HI(g)$$

If the initial concentrations of both  $\rm H_2$  and  $\rm I_2$  are 6.00  $\times$  10<sup>-3</sup> mol/L, find the concentration of each reactant and product at equilibrium.

Molarity	$\mathrm{H}_{2}\left( g\right) \qquad +$	$\mathrm{I}_{2}\left(g\right)$	Ħ	$2 \operatorname{HI}(g)$
Initial	$6.00  imes 10^{-3} \text{ M}$	$6.00  imes 10^{-3} \text{ M}$		0 M
Change	- <i>x</i>	- <i>x</i>		+ 2 <i>x</i>
Equilibrium	$(6.00 \times 10^{-3}) - x$	$(6.00 \times 10^{-3}) - x$		2x

#### Many variations on the theme

Graphite and carbon dioxide are kept at 1000 K until the reaction

$$C(s, graphite) + CO_2(g) \leftrightarrows 2 CO(g$$

has come to equilibrium. At this temperature, K = 0.021. The initial concentration of CO<sub>2</sub> is 0.012 M. Calculate the equilibrium concentration of CO.

Molarity	C (s, graphite)	+ $\operatorname{CO}_2(g)$	₽	2 CO (g)
Initial		0.012 M		0 M
Change		- <i>x</i>		+ 2 <i>x</i>
Equilibrium		0.012 – <i>x</i>		2x

#### Key points about equilibrium constants

- Reaction quotient (Q) and equilibrium constant (K) have the same form (expression).
- Q and K both depend on temperature. Q and K have no units.
- K is the value of Q at equilibrium conditions. There are many nonequilibrium conditions, so Q can have many values. There is only one value for K at a given temperature.
- Comparing Q (at some conditions) to K (a constant) will tell you which direction a reaction must proceed in order to move toward equilibrium.
- K (or Q) can be expressed in terms of concentrations (for any situation) or partial pressures (only for gases). You can convert between K<sub>p</sub> and K<sub>c</sub> for a gas phase equilibrium, using the ideal gas law.
- Initial-change-equilibrium tables help to keep track of the stoichiometry. The key is to figure out what to set *x* equal to. After that, solving equilibrium problems is algebra.

#### Some relationships among K values

- Multiplying a reaction by a number
- Adding up reactions to total an overall reaction

#### Multiplying Rxns by a Number



#### Summing reactions to an overall rxn



# Relating equilibrium constants and reactions

- If you <u>multiply</u> a reaction by a number (e.g., x(-1) or x2), you do the same to the <u>exponent</u> of the equilibrium constant
- If you <u>add</u> two reactions together to get an overall reaction, then the <u>product</u> of the two equilibrium constants is the overall  $K_{eq}$
- [Mathematical simplification: The first statement is a specific instance of the second statement (e.g., doubling the same reaction is the same as adding it to itself, in which case you would square the *K* value)]

#### Disturbing a chemical equilibrium

- When a system is at equilibrium, it remains at equilibrium, unless an outside force disturbs it (Newton? No, le Chatelier ©)
- The system reacts by opposing the outside force to partially un-do its effects
- · Some outside forces cause the equilibrium to shift and others don't
- What does "shift" mean? A change in the final concentrations of all chemical in the reaction

First, you have to figure out if K changes as a result of the outside force

- Outside forces that do not change the value of K
  - Addition or removal of a reactant or product
  - Volume change (for gas phase reaction)
  - Addition or removal of an inert gas (for gas phase reaction)
- Outside force that changes the value of K
  - Temperature change



#### Let's begin with a system that achieves equilibrium

Then, once it is at equilibrium, add some NO<sub>2</sub> to the flask



Mathematic $K_c = \frac{[N_2O_4]}{[NO_2]^2}$	C <b>ally, wha</b> t =171 at this	t happ tempera	Dened?	Initially at equilibrium: $2 \operatorname{NO}_2 \leftrightarrows \operatorname{N}_2\operatorname{O}_4$ Add some $\operatorname{NO}_2$
	$2 \operatorname{NO}_2(g)$	ţ	$N_2O_4\left(g\right)$	
Initial (non-eq)	3.52 M		0 M	$Q = \frac{[N_2O_4]}{[NO_4]^2} = \frac{0}{(2.52)^2} = 0$
First change	- 2 <i>x</i>		+x	$[100_2]$ (3.32)
First equilibrium	0.100 M		1.71 M	$K = \frac{\left[N_2 O_4\right]}{\left[N O_2\right]^2} = \frac{1.71}{\left(0.100\right)^2} = 171$
Disturbance creates new initial (non-eq)	0.100+0.900 =1.000 M		1.71 M	$Q = \frac{[N_2O_4]}{[NO_2]^2} = \frac{1.71}{(1.00)^2} = 1.71$
Second change	- 2 <i>x</i>		+x	
Second equilibrium	0.112 M		2.15 M	$K = \frac{\left[N_2 O_4\right]}{\left[NO_2\right]^2} = \frac{2.15}{\left(0.112\right)^2} = 171$

Conclusion: Equilibrium is re-established. The system reacted to partially un-do the disturbance, using up some of the  $NO_2$  that was added.

#### Changing the volume (in a gaseous equilibrium)

- Consider the same NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub> system
- You may find the following review helpful (on your own) http://myphlip.pearsoncmg.com/altproducts/demo/ab2page.cfm?vbcid=9018&vid=10000#oa213641

Initially at equilibrium:		$2 \operatorname{NO}_2(g)$	₽	$N_2O_4\left(g\right)$
$2 \operatorname{NO}_{2}(g) \leftrightarrows \operatorname{NO}_{4}(g)$	First equilibrium	0.100 M		1.71 M
Halving of the volume Causes doubling in pressures and	Disturbance creates new initial (non-eq)	0.200 M		3.42 M
BUT by an EQUAL factor	Change	- 2 <i>x</i>		+ <i>x</i>
$Q = \frac{[N_2O_4]}{[NO_4]^2} = \frac{3.42}{(0.200)^2} = 85.5$	Second equilibrium	0.142 M		3.45 M
$[NO_2]$ (0.200)				

Conclusion: Equilibrium is re-established. The system reacted to partially un-do the disturbance. The reaction proceeded in the direction that reduces the pressure by decreasing the number of molecules.

#### Changing the pressure by adding an inert gas

- Consider what would happen if the total pressure in the previous example were increased not by changing the volume but instead by adding an inert gas
- Mathematically, neither the concentrations nor the partial pressures of each gas change in this case

	$2 \operatorname{NO}_2(g)$	⇆	$N_2O_4\left(g\right)$
First equilibrium	0.100 M		1.71 M
Disturbance creates no change	0.100 M		1.71 M



## You can use the effect on *K* of temperature change to determine whether a rxn is exo- or endothermic

- Trick: you can pretend that heat is a reactant or product for the purpose of figuring out le Chatelier's principle (but remember that heat is not matter)
- Changing from lower temperature to higher temperature caused the equilibrium to shift in favor of NO<sub>2</sub>
- · Which one of these correctly describes the observed behavior?



Conclusions:

- The reaction must be \_\_\_\_\_
- As the temperature increases, the value of K \_\_\_\_\_

#### Example: Disturbing a chemical equilibrium

*Similar to Practice Exercises on pp. 655-656.* Explain the effect in each case. Assume each system is at equilibrium before the disturbance occurs.

- a) 2 NOCl (g)  $\leftrightarrows$  2 NO (g) + Cl<sub>2</sub> (g)  $\Delta H_{rxn}^{o} = +77.1 kJ$ What would happen if the temperature were decreased?
- b)  $H_2(g) + CO_2(g) \leftrightarrows H_2O(g) + CO(g)$ What would happen if the volume were increased?
- c) C (s) + CO<sub>2</sub> (g) ≒ 2 CO (g) What would happen if suddenly more CO<sub>2</sub> were added? More C?

# d) C (s) + CO<sub>2</sub> (g) ≒ 2 CO (g) An increase in temperature causes the CO concentration to increase. What is the sign of ∠H?

#### Summary of le Chatelier's principle

If you take a system that is at equilibrium and then disturb it, it will come back to equilibrium in a particular way: It will partially un-do the disturbance

- If you add a chemical that is involved in the equilibrium, the new equilibrium will be shifted toward the direction that uses up some of the new chemical that was added (K<sub>eq</sub> will not change)
- If you change the pressure or the volume in a gas phase reaction, the new equilibrium will shift in the direction that reduces the disturbance ( $K_{eq}$  will not change)
- If you add heat, the new equilibrium will be shifted toward the direction that uses up some of the heat that was added and the value of  $K_{eq}$  will also change, since you changed T

#### Important equilibria

- Weak acids and weak bases (ch. 16)
- Buffers, acid-base titrations (ch. 17)
- Solubility equilibria (ch. 17)
- Oxidation-reduction, separated so as to generate voltage (ch. 20)