

# CH 223: Lectures and Labs

### Lectures: MWF from 9 - 9:50 AM in AC 1303 (this room)

- Lectures recorded, available soon afterwards
- Lecture notes to print available (under "Problem Sets and Handouts", <u>mhchem.org/223</u>), get **CH 223 Companion** as soon as possible

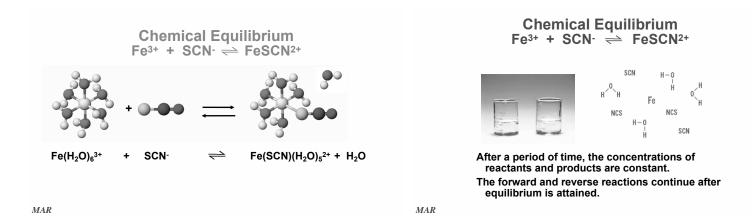
Labs (Section 01): Mondays from 1:10 - 5 PM

- Start in room AC 2501 ("the recitation")
- Move to AC 2507 ("the lab") around 3 PM
- For first day, bring a printed copy of the "Determination of an Equilibrium Constant (in class)" Lab (<u>mhchem.org/223</u>), a pair of safety glasses (Dollar store ok) and your calculator

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...more on Monday afternoon





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Phase changes:  $H_2O(s) \rightleftharpoons H_2O(liq)$ 

Examples of Chemical Equilibria



Formation of stalactites and stalagmites:  $CaCO_3(s) + H_2O(Iiq) + CO_2(g) \rightleftharpoons$  $Ca^{2+}(aq) + 2 HCO_3^{-}(aq)$ 



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For any type of chemical equilibrium of the type
a A + b B \rightleftharpoons c C + d D
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the following is a CONSTANT (at a given T)

conc. of products

$$\mathbf{K} = \frac{[A]^{a} [B]^{b}}{\mathbf{K}}$$

equilibrium constant

If K is known, we can predict concentrations of products or reactants.



Equilibrium constants, K, come from *kinetic* rate constants, k

Example: For 2  $NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$ ,

rate<sub>f</sub> = k<sub>f</sub>[NO<sub>2</sub>]<sup>2</sup>

 $rate_r = k_r[N_2O_4]$ 

When rates equal, rate<sub>f</sub> = rate<sub>r</sub>, and

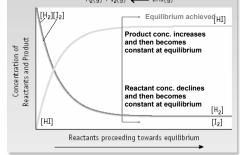
 $k_{f}[NO_{2}]^{2} = k_{r}[N_{2}O_{4}]$ 

 $[N_2O_4]/[NO_2]^2 = k_f/k_r = K$  (equilibrium)

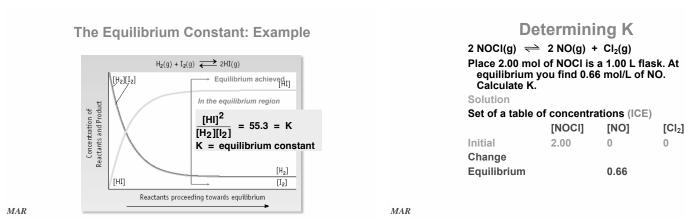
Product of two constants ( $k_f \& k_r$ ) is itself a constant (K)!

## $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

The Equilibrium Constant: Example



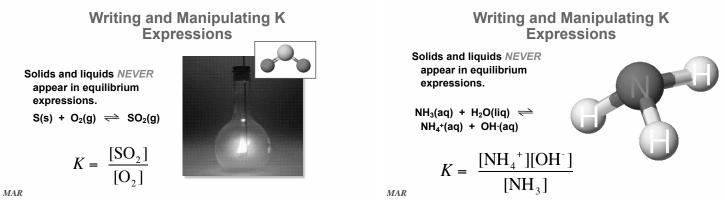




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De	termini	ng K	
2 NOCI(g) <	2 NO(g) +	· Cl₂(g)	
Place 2.00 mol equilibrium y Calculate K.			
Solution			
Set of a table of	of concentra	ations (ICE	.)
	[NOCI]	[NO]	[Cl <sub>2</sub> ]
Initial	2.00	0	0
Change	-0.66	+0.66	+0.33

**Determining K**  $2 \text{ NOCI}(g) \rightleftharpoons 2 \text{ NO}(g) + \text{CI}_2(g)$ [NOCI] [NO] [Cl<sub>2</sub>] 2.00 Initial 0 0 -0.66 +0.66 +0.33 Change 1.34 Equilibrium 0.66 0.33  $K = \frac{[NO]^2[Cl_2]}{[NOCl]^2}$  $K = \frac{[NO]^2[Cl_2]}{[NOCl]^2} = \frac{(0.66)^2(0.33)}{(1.34)^2} = 0.080$ 





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Writing and Manipulating K Expressions				
Adding equations for reactions				
$S(s) + O_2(g) \rightleftharpoons SO_2(g)  K_1 = [SO_2] / [O_2]$				
SO₂(g) + 1/2 O₂(g) ⇒ SO₃(g)				
$K_2 = [SO_3] / [SO_2][O_2]^{1/2}$				
NET EQUATION				
S(s) + 3/2 O₂(g) ⇒ SO₃(g)				

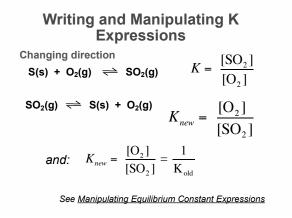
$$K_{net} = \frac{[SO_3]}{[O_2]^{3/2}} = K_1 \cdot K_2$$

$$S(s) + 3/2 O_2(g) \iff SO_3(g) \qquad K_{old} = \frac{[SO_3]}{[O_2]^{3/2}}$$

$$2 S(s) + 3 O_2(g) \iff 2 SO_3(g)$$

$$K_{new} = \frac{[SO_3]^2}{[O_2]^3}$$
$$K_{new} = \frac{[SO_3]^2}{[O_2]^3} = (K_{old})^2$$

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**Kp Expressions** 

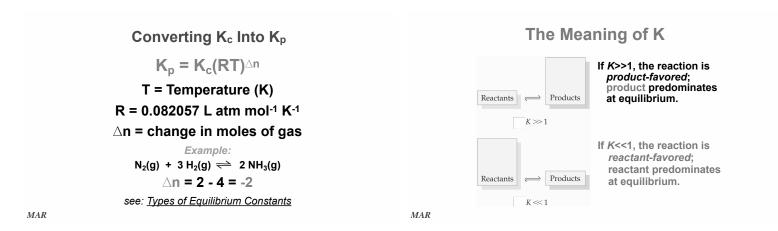
We have been writing K in terms of M (mol/L), designated by  $K_{\rm C}$ 

Equilibrium constants expressed in terms of gases designated  $K_p$  where all pressures in atm (760 mm Hg = 1 atm)

For:  $N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)$ 

$$K_{c} = \frac{[NH_{3}]^{2}}{[N_{2}][H_{2}]^{3}}$$
  $K_{p} = \frac{P_{NH_{3}}^{2}}{P_{N_{2}}P_{H_{2}}^{3}}$ 

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## The Meaning of K

Can tell if a reaction is product-favored or reactant-favored. For:  $N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)$ 

$$K_c = \frac{[\mathrm{NH}_3]^2}{[\mathrm{N}_2][\mathrm{H}_2]^3} = 3.5 \text{ x } 10^8$$

Conc. of products is much greater than that of reactants at equilibrium. The reaction is strongly productfavored. The Meaning of K

For:  $AgCl(s) \rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq)$ 

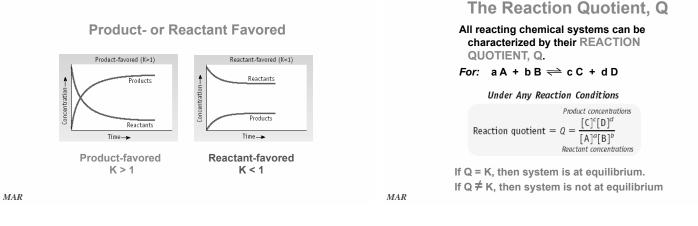
 $K_{\rm c} = [Ag^+] [CI^-] = 1.8 \times 10^{-5}$ 

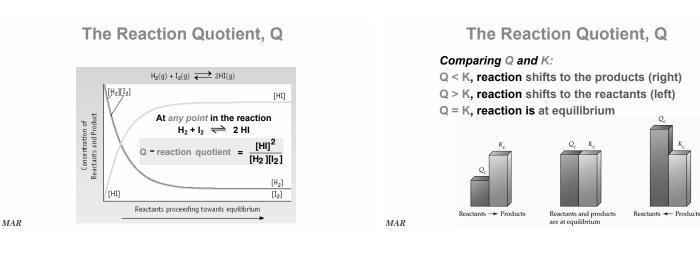
Conc. of products is **much less** than that of reactants at equilibrium.

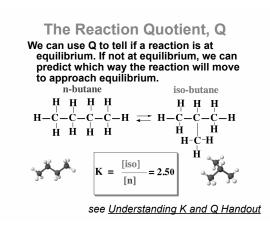
The reaction is strongly reactant-favored.

The reverse reaction Ag⁺(aq) + Cl·(aq) ⇐ AgCl(s) is product-favored,

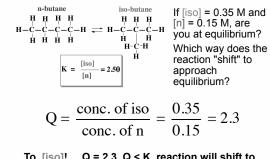
 $K_{rev} = 1/1.8 \times 10^{-5} = 5.6 \times 10^{4}$ 



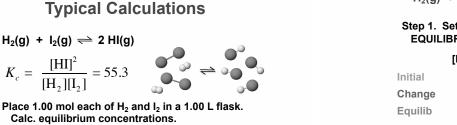




The Reaction Quotient, Q



To [iso]! Q = 2.3, Q < K, reaction will shift to "right" (product side, or [iso])



 $H_2(g) + I_2(g) \rightleftharpoons 2 HI(g), K_c = 55.3$ 

Step 1. Set up ICE table to define EQUILIBRIUM concentrations.

	[H <sub>2</sub> ]	[l <sub>2</sub> ]	[HI]
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where x is defined as am't of  $H_2$  and  $I_2$  consumed on approaching equilibrium.

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 $H_2(g) + I_2(g) \rightleftharpoons 2 HI(g), K_c = 55.3$ 

Step 2. Put equilibrium concentrations into  $\ensuremath{\mathsf{K}_c}$  expression.

$$K_c = \frac{[2x]^2}{[1.00-x][1.00-x]} = 55.3$$

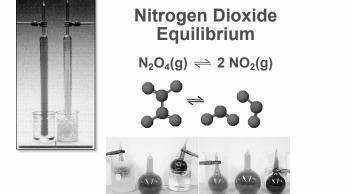
 $H_2(g) + I_2(g) \implies 2 HI(g), K_c = 55.3$ 

Step 3. Solve K<sub>c</sub> expression - take square root of both sides.  $7.44 = \frac{2x}{1.00 - x}$ 7.44 (1.00 - x) = 2x7.44 - 7.44x = 2xx = 7.44 / 9.44 = 0.788Therefore, at equilibrium $[H_2] = [I_2] = 1.00 - x = 0.21 \text{ M}$ [HI] = 2x = 1.58 M

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N <sub>a</sub> O <sub>4</sub> (	Dioxide Equ g) $\Rightarrow$ 2 No $\frac{1}{2}$ = 0.0059	$D_{\alpha}(\mathbf{n})$		
If initial concentration of $N_2O_4$ is 0.50 M, what are the equilibrium concentrations?				
Step 1. Set up an equilibrium table				
	[N <sub>2</sub> O <sub>4</sub> ]	[NO <sub>2</sub> ]		
Initial	0.50	0		
Change				
Equilib				

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Nitrogen Dioxide Equilibrium $N_2O_4(g) \iff 2 NO_2(g)$					
$K_c = \frac{[NO_2]^2}{[N_2O_4]} = 0.0059 \text{ at } 298 \text{ K}$					
If initial concentration of N <sub>2</sub> O <sub>4</sub> is 0.50 M, what are the equilibrium concentrations?					
Step 1. Set up an equilibrium table					
	[N <sub>2</sub> O <sub>4</sub> ]	[NO <sub>2</sub> ]			
Initial	0.50	0			
Change	-X	+2x			
Equilib	0.50 - x	2x			

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Nitrogen Dioxide Equilibrium  $N_2O_4(g) \rightleftharpoons 2 NO_2(g)$ Step 2. Substitute into K<sub>c</sub> expression and solve.  $K_c = 0.0059 = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(2x)^2}{(0.50 - x)}$ Rearrange: 0.0059 (0.50 - x) = 4x<sup>2</sup> 0.0029 - 0.0059x = 4x<sup>2</sup> 4x<sup>2</sup> + 0.0059x - 0.0029 = 0 This is a QUADRATIC EQUATION ax<sup>2</sup> + bx + c = 0 a = 4 b = 0.0059 c = -0.0029 CH 223: report both values of x who

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CH 223: report **both** values of x when performing quadratic calculations

Nitrogen Dioxide Equilibrium  $N_2O_4(g) \rightleftharpoons 2 NO_2(g)$ Solve the quadratic equation for x.  $ax^2 + bx + c = 0$  a = 4 b = 0.0059 c = -0.0029  $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$   $x = \frac{-0.0059 \pm \sqrt{(0.0059)^2 - 4(4)(-0.0029)}}{2(4)}$  $x = -0.00074 \pm 1/8(0.046)^{1/2} = -0.00074 \pm 0.027$  Nitrogen Dioxide Equilibrium  $N_2O_4(g) \rightleftharpoons 2 NO_2(g)$   $x = \frac{-0.0059 \pm \sqrt{(0.0059)^2 - 4(4)(-0.0029)}}{2(4)}$ x = -0.00074 ± 1/8(0.046)<sup>1/2</sup> = -0.00074 ± 0.027 x = 0.026 or -0.028 But a negative value is not reasonable. Conclusion: x = 0.026 [N\_2O\_4] = 0.50 - x = 0.47 M [NO\_2] = 2x = 0.052 M

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CH 223: report **both** values of *x* when performing quadratic calculations

# Le Chatelier's Principle

Temperature, changes in volume, changes in pressure and changes in concentration affect equilibria.

The outcome is governed by LE CHATELIER'S PRINCIPLE

"...if a system at equilibrium is disturbed, the system tends to shift its equilibrium position to counter the effect of the disturbance."



Henri Le Chatelier, 1850 - 1936

### Temperature effects change the numeric value of K

Consider the fizz in a soft drink  $CO_2(g) + H_2O(Iiq) \rightleftharpoons CO_2(aq) + heat$ 

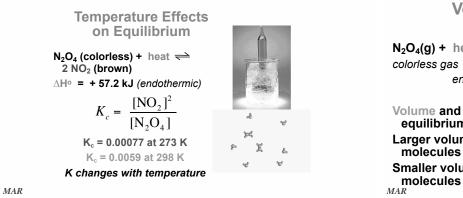
**Decrease T.** What happens to equilibrium position? To value of *K*?

 $K = [CO_2] / P (CO_2)$ 

K increases as T goes down because [CO<sub>2</sub>] increases and P(CO<sub>2</sub>) decreases.

Increase T. Now what? Equilibrium shifts left and K decreases. see: <u>Le Chatelier's Guide</u>





### Volume & Pressure Effects on Equilibrium

N<sub>2</sub>O<sub>4</sub>(g) + heat ⇒ 2 NO<sub>2</sub>(g) colorless gas brown gas endothermic

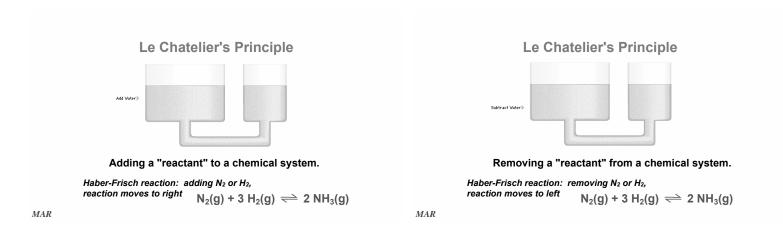
Volume and Pressure changes affect equilibrium Larger volume / Less Pressure = more

Smaller volume / Higher Pressure = fewer

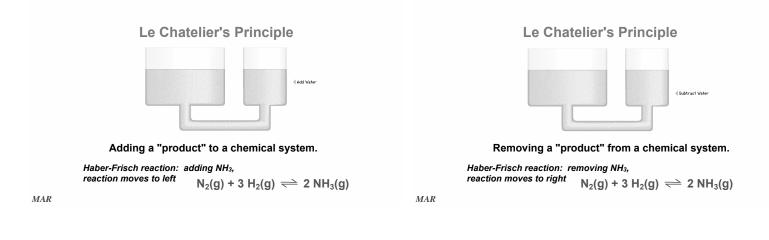


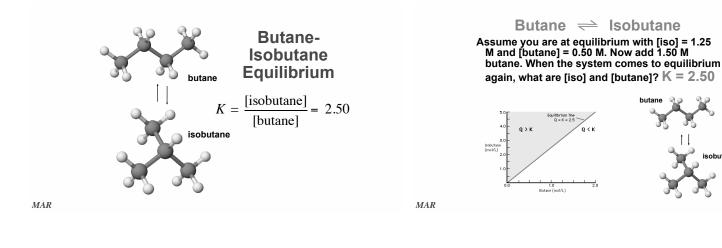
NH<sub>3</sub> EQUILIBRIUM AND EXTERNAL EFFECTS **Production** Concentration changes ---> no change in K - only the position of equilibrium changes. Catalyst for the We can use the "water U-tube" to Haber-Frisch reaction is mostly demonstrate this phenomena Fe with some KOH (and connect to Haber-Frisch) Haber-Frisch reaction:  $N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)$  $N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)$  $K = 3.5 \times 10^8$  at 298 K Water U-tube MAR

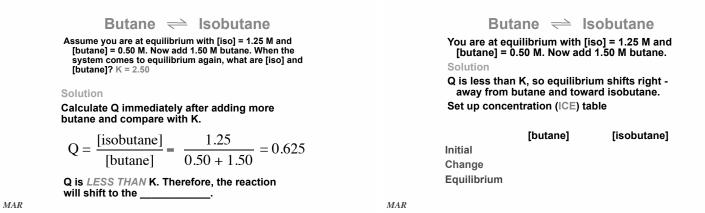




Page III-13-8 / Chapter Thirteen Lecture Notes







**Butane** 
$$\rightleftharpoons$$
 **Isobutane**  
You are at equilibrium with [iso] = 1.25 M and  
[butane] = 0.50 M. Now add 1.50 M butane.  
Solution  

$$K = 2.50 = \frac{[isobutane]}{[butane]} = \frac{1.25 + x}{2.00 - x}$$

$$x = 1.07 M$$
At the new equilibrium position,  
[butane] = 0.93 M and [isobutane] = 2.32 M  
Equilibrium has shifted toward isobutane.  
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**Le Chatelier's Principle**-  
**Overview**  
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**End of Chapter 13** 

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#### See:

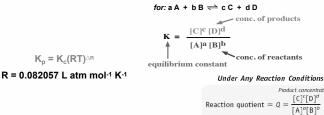
- Chapter Thirteen Study Guide
- Chapter Thirteen Concept Guide
- Types of Equilibrium Constants
- · Important Equations (following this slide)
- · End of Chapter Problems (following this slide)

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Important Equations, Constants, and Handouts from this Chapter:



Handouts.

4. 5.

• Manipulating Equilibrium Constant Expressions

End of Chapter Problems: Answers

[l<sub>2</sub>] = 0.00614 M, [l] = 0.00480 M a. right b. left c. right d. left

1. K<sub>c</sub> = [CO]<sup>2</sup> / [CO<sub>2</sub>] or K<sub>p</sub> = P<sub>CO<sup>2</sup></sub> / P<sub>CO2</sub> 2. No, Q < K, reaction will proceed to the right (more products) 3. K = 1.2

· Types of Equilibrium Constants

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Le Chatelier's Principle

Product concentrations

 $Q = \frac{[A]^{a}[B]^{b}}{[A]^{a}[B]^{b}}$ Reactant concent

End of Chapter Problems: Test Yourself

- Write an equilibrium constant expression for the following reaction: C(s) +  $CO_2(g) \rightleftarrows 2 \ CO(g)$ 1.
- 2. K = 5.6 x 10<sup>-12</sup> at 500 K for the dissociation of iodine molecules to iodine atoms: I<sub>2</sub>(g)  $\rightleftharpoons$  2 I(g) A mixture has [I<sub>2</sub>] = 0.020 mol/L and [I] = 2.0 x 10<sup>-8</sup> mol/ L. Is the reaction at equilibrium (at 500 K)? If not, which way must the reaction proceed to reach equilibrium? 3. The reaction:  $PCI_5(g) \rightleftharpoons PCI_3(g) + CI_2(g)$  was examined at 250 °C. At
- equilibrium, [PCIs] = 4.2 x 10<sup>5</sup> mol/L, [PCIs] = 1.3 x 10<sup>-2</sup> mol/L, and [CI<sub>2</sub>] = 3.9 x 10<sup>3</sup> mol/L. Calculate K for the reaction. 4. The equilibrium constant for the dissociation of iodine molecules to iodine atoms: I<sub>2</sub>(g)  $\approx$  2 I(g) is 3.76 x 10<sup>-3</sup> at 1000 K. Suppose 0.105 mol of I<sub>2</sub> is
- placed in a 12.3 L flask at 1000 K. What are the concentrations of  $\mathsf{I}_2$  and  $\mathsf{I}$
- block and 120 model to equilibrium? Dinitrogen trioxide decomposes to NO and NO<sub>2</sub> in an endothermic process  $(\Delta H = 40.5 \text{ kJ/mol}): N_2O_3(g) \approx NO(g) + NO_2(g)$  Predict the effect of the 5. following changes on the position of the equilibrium (left, right, or no change): b. adding more  $N_2O_3(g)$ b. adding more  $N_2O_3(g)$ c. increasing the volume of the reaction flask d. lowering the temperature

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