

# Chemistry 120

## Equilibrium

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### What We Know

- Observations
  - Many reactions do not give 100% yield
  - Composition of reaction mixture changes over time and then stops changing
  - Isotopic scrambling
  - Above true in all states of matter and in solution
- Direction of Spontaneous Change shown by  $\Delta G^0$ 
  - Sign and magnitude related to amounts

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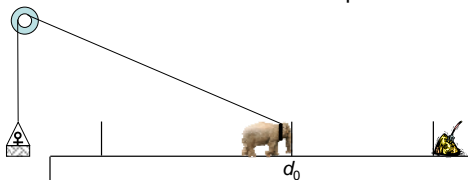
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### $\Delta G$ and the Extent of Reaction

- Analogous to Relationship between Work that could be done vs. Work actually done
  - Recall  $\Delta G$  tells us about non-expansion work



Work elephant can do or has done can be written in terms of its position relative to  $d_0$ .

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## $\Delta G$ and the Extent of Reaction

- In general  $\Delta G(T, p, n_i)$ 
  - But in a chemical reaction  $T$  and  $p$  are constant while  $n_i$  change
- Can define  $\Delta G_{reaction}$  as amount of Energy available to do Work by changing Composition
  - Define  $\Delta G$  at a standard set of conditions and measure everything relative to it

$$\Delta G_{reaction} = \Delta G^0 + R \cdot T \cdot \ln Q$$

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## Reaction Quotient

- For a Reaction:  $x A + y B \rightleftharpoons m C + n D$  define  $Q$  with *Activities* (for solutions) or *Fugacities* (for gases)

$$Q = \frac{a_C^m a_D^n}{a_A^x a_B^y} \quad Q = \frac{f_C^m f_D^n}{f_A^x f_B^y}$$

- Pure substances in their own separate phase (and ideal solvents):  $a = 1$  or  $f = 1$
- Assume ideal dilute solutions (concentration  $\approx$  activity) and ideal gases (partial pressure  $\approx$  fugacity)

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## $\Delta G_{reaction}, Q$ and Chemical Reactions

- Under Standard Conditions
  - All activities/fugacities equal 1
  - So,  $\Delta G_{reaction} = \Delta G^0$
- If not Standard then  $\Delta G_{reaction} \neq \Delta G^0$ 
  - System will try to change to alleviate
- In a Chemical Reaction only Activities can change over Time (with  $T$  and  $p$  constant)
  - Changing activities cause  $Q$  to change until  $\Delta G_{reaction} = 0$  (all work has been done)

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## Equilibrium Constant

- When  $\Delta G_{\text{reaction}} = 0$  there is no net Change and *Equilibrium* is achieved
  - Does not mean that nothing happens
- Q when  $\Delta G_{\text{reaction}} = 0$  is *Equilibrium Constant, K*

$$\Delta G^0 = -R \cdot T \cdot \ln K$$

- $K$  is  $\Delta G$  written in terms of amount of material
- Magnitude of  $K$  relative to  $\Delta G^0$
- Value of  $R$  ( $8.314510 \text{ J}\cdot\text{K}^{-1}\cdot\text{mole}^{-1}$ )
- Units of  $K$

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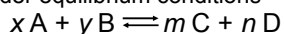
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## Equilibrium Constant

- Same form as Q, so same Approximations to get useable Form
  - Pure substances in own separate phase
  - Ideal solvents and gases, dilute solutions
  - Difference is that concentrations or pressures are under equilibrium conditions



$$K_c = \frac{[C]^m [D]^n}{[A]^x [B]^y} \quad K_p = \frac{p_C^m p_D^n}{a p_A^x p_B^y}$$

- Examples

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## Rules for Manipulating Equilibrium Constants

- Common Manipulations of  $K$ 
  - Change stoichiometric coefficients:  $K = K^x$
  - Reverse reaction:  $K = 1/K$
  - Interchange  $K_p$  and  $K_c$ :  $K_p = K_c \cdot (RT)^{\Delta n}$
  - Add reactions, multiply their equilibrium constants to get new  $K$
- Result of  $G$  being a State Function
- Examples

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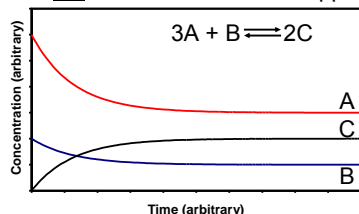
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## Kinetic View of Equilibrium

- Kinetic Criterion for Equilibrium is System Composition has stopped changing
  - Rate forward reaction = rate reverse reaction
  - Does not mean reaction has stopped!



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## Kinetic View of Equilibrium

- Can always write Rate of forward Reaction in terms of Reactants, and reverse Reaction in terms of Products
  - Actual rate law depends on reaction
- So, at Equilibrium

Forward Rate = Reverse Rate

$$k_{\text{forward}}[\text{reactants}] = k_{\text{reverse}}[\text{products}]$$

$$K = \frac{[\text{products}]}{[\text{reactants}]} = \frac{k_{\text{forward}}}{k_{\text{reverse}}}$$

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## Calculating Equilibrium Constants

- In a Solution that is in equilibrium with solid  $\text{AuCl}_3$ ,  $[\text{Au}^{3+}] = 3.30 \times 10^{-7} \text{ M}$  and  $[\text{Cl}^-] = 9.90 \times 10^{-7} \text{ M}$ . What is  $K_c$  for the reaction  $\text{AuCl}_3(\text{s}) \rightleftharpoons \text{Au}^{3+}(\text{aq}) + 3 \text{Cl}^-(\text{aq})$ ?

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## Calculating Equilibrium Constants

- Ammonium carbamate decomposes according to the balanced chemical equation:  
 $(\text{NH}_4)_2\text{C}_2\text{O}_4(\text{s}) \rightleftharpoons 2 \text{NH}_3(\text{g}) + \text{CO}_2(\text{g})$   
If the pressure of gas above the solid is 0.116 atm, what is  $K_p$ ?

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## What $K$ means

- No Reaction truly goes 100% to Products so Equilibrium is more general Treatment
  - $K = 1$  equal distribution between reactants and products ( $\Delta G \approx 0$ )
  - $K > 1$  products favored ( $\Delta G < 0$ )
  - $K < 1$  reactants favored ( $\Delta G > 0$ )
- Predicting Composition of Equilibrium Mixtures for a Reaction
  - How to force a reaction that does not go to completion to give more product?

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## Using the Reaction Quotient

- Recall  $Q$  has same form as  $K$  but Conditions are not at Equilibrium
  - Use to determine direction of chemical change
- For Reaction as written, if
  - $Q > K$  reaction goes to left
  - $Q < K$  reaction goes to right
  - $Q = K$  reaction at equilibrium

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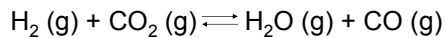
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### Calculating Equilibrium Conditions

- The reaction shown below has  $K_c$  equal to 4.40 at 2000 K. If a 4.68 L vessel is charged with 1.00 mol each of  $H_2$  and  $CO_2$ , what is the concentration of all species when equilibrium is attained?



- Repeat the problem, but now start with 1.00 mole of  $H_2O$  and 1.00 mole of  $CO$

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### Calculating Equilibrium Conditions

- Note that Concentrations of all Species were the same regardless of whether started with Products or Reactants
  - Equilibrium constant is constant
- Achieving same State regardless of Starting Point Hallmark of Equilibrium
  - Demonstration of equilibrium

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### Solving Equilibrium Problems

- Few Problems are Perfect Squares
  - Look for them first, but don't look too hard
- Many Problems require Quadratic
- Some Problems are Cubic or Higher
  - Be sure nothing overlooked
  - Look for simplifying approximations
  - If all else fails use a computer to solve
- Simplifying Approximations can be made when  $K < \sim 0.001$  or  $K > \sim 1000$

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### Solving Equilibrium Problems

- If  $K$  is very large or small, Equilibrium lies well toward one Side
- Make Simplifying Assumptions
  - When  $K$  is large, and given reactants, assume reaction goes to completion (converted completely to products) and then comes back to establish equilibrium
  - When  $K$  is small, and given reactants, assume that the amount of change in reactants is negligible compared to total amount

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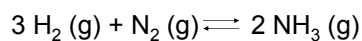
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### Calculating Equilibrium Conditions

- At 25.0 °C  $K_c$  for the following reaction is  $3.5 \times 10^8$ . If the initial concentration of  $N_2$  is 0.25 M and that of  $H_2$  is 0.75 M, what are the concentrations when equilibrium is attained?



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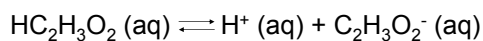
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### Calculating Equilibrium Conditions

- At 25.0 °C  $K_c$  for the following reaction is  $1.8 \times 10^{-5}$ . If the initial concentration of  $HC_2H_3O_2$  is 0.100 M, what are the concentrations of all species present in solution when equilibrium is attained?



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## Disturbing Equilibrium

- Le Châtelier's Principle
  - Disturbing a system at equilibrium causes it to respond in such a way as to relieve the stress
- System Stressors
  - Add or remove reactants
  - Remove or add products
  - Change volume
  - Change temperature
  - Pressure change has no effect!

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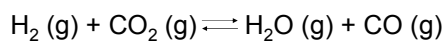
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## Changing Amount of Reactant



- The reaction shown above has  $K_c$  equal to 4.40 at 2000 K. If the initial  $[\text{H}_2]$  and  $[\text{CO}_2]$  are 0.214 M, equilibrium concentrations are
  - $[\text{H}_2] = 0.069 \text{ M}$        $[\text{H}_2\text{O}] = 0.145 \text{ M}$
  - $[\text{CO}_2] = 0.069 \text{ M}$        $[\text{CO}] = 0.145 \text{ M}$

What will the new concentrations be if  $[\text{H}_2]$  is made 0.100 M?

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## Changing Amount of Reactants or Products

- Equilibrium shifts to Left when
  - Products added
  - Reactants removed
- Equilibrium shifts to Right when
  - Products removed
  - Reactants added
- If you have a Reaction that does not convert completely to Products, what do you do?

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## Changing Volume

- Changes Concentration and/or Partial Pressures
  - Increasing volume causes shift toward side with more particles
  - Decreasing volume causes shift toward side with fewer particles
  - Equilibria with the same number of particles on each side do not change with volume
- How do we change Volume?
  - In gas, can change  $V$  by changing  $p$
  - In solution, add more solvent

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## Dependence of $K$ on Temperature

$$\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2}$$

- van't Hoff Equation
  - Derivable from  $\Delta G = -R \cdot T \cdot \ln K$
  - If  $\Delta H^\circ < 0$ ,  $K$  decreases as  $T$  increases
  - If  $\Delta H^\circ > 0$ ,  $K$  increases as  $T$  increases
- Shortcut: treat Heat as a Product ( $\Delta H < 0$ ) or a Reactant ( $\Delta H > 0$ )

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## Catalysts and Equilibrium

- Catalysts increase Rate of Reaction in both Forward and Reverse Direction
  - No effect on  $K$
  - Only affects rate at which equilibrium is attained
- Equilibrium is a Thermodynamic Property of the System ( $\Delta G = -R \cdot T \cdot \ln K$ )
  - Only changed by things that change  $\Delta G$
  - Rate of reaction not directly related to  $\Delta G$

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