What’s New

• New HW posted and database reset. Assignment is due in two weeks.
• It’s uphill from here for a while.
• These notes will likely carry thru some, if not all, of next week.
• Exam has gone to press. 5 pages, 13 questions, approx 50% have no calculations.
• If you are prepared, then you will have ample time. If you are not, I suggest you stay home.
• First lab report due this week-no late reports accepted.
• Expect a quiz next Monday.

Elementary Reactions and the mechanism

• A chemical reaction which describes two or more species directly reacting to produce product is called elementary.
• Not surprising, most elem. reactions have only two species reacting.
• The step by step process consisting of a series of elementary reactions which yields the overall reaction is called a mechanism.
  – The sum of these elementary reactions will be the overall process.
  – When more than one step is involved, there will be a slow step called the rate determining step (rds). Only species involved up to and in the rds will appear in the rate law.
• In a reaction mechanism it is common for species to be produced (and then consumed) which don’t appear in the overall reaction. These are called intermediates.

Mechanisms and Rate Laws

• For each of the following, what is the overall reaction? Write the rate law and identify any intermediates.
  A+C⇒D+E  fast
  B+C⇒D slow, rds
  A+B⇒D fast
  B+C⇒D slow, rds
  A+C⇒E+E fast
  A+C⇒D fast
  A+B⇒E fast
  B+C⇒E slow, rds
  B+C⇒D fast
  A+C⇒N+D slow, rds
  C+N⇒M fast
  A+M⇒E+D fast
What’s the deal with catalysis?

• What is a catalyst?
• Given that a catalyst must change the value of $k$ and $k = Z \cdot e^{\frac{-E_a}{RT}}$, what do you see as ways in which catalysts could act?

Equilibrium Basics

• Any process which occurs in both directions necessarily has a point where the opposing rates will become equal. Why?
• From there on, there will be no further change in the macroscopic properties of the system (concentrations, etc), etc, and the system is said to be in a state of equilibrium. Again—it is a special state of the system.
• Microscopically, however, the forward and reverse processes continue unabated. How could you prove this?
• Both vapor pressure equilibrium and osmotic equilibrium are examples of this phenomenon. In what ways are these two processes different?

Chemical Equilibrium

• Thus far, the equilibria noted have involved physical, not chemical change.
• If a reaction is realistically chemically reversible—meaning it can occur in either direction (this is different from thermodynamic reversibility), then one can write it either way:
  – $A \Rightarrow B$ or $B \Rightarrow A$
  – the identification of products and reactants is “arbitrary” and lacks the rigidity with which one views reactions in kinetics.
  – what does “realistically chemically reversible mean”?
• $A \Leftrightarrow B$ the “$\Leftrightarrow$” is used to denote that the reaction may be occurring in either direction. As will be seen, one of the areas of interest in chemical equilibrium is the determination of the direction in which a chemical change is actually occurring.
• A system is in chemical equilibrium when the forward and reverse reactions are occurring at the same rates. Thus, despite the continual transformation of compounds into other compounds, there will be no change in the overall composition of the system.
• Again, no macroscopic changes despite constant microscopic changes
• “A reversible chemical reaction is either at equilibrium or moving toward equilibrium...” why?
## The Reaction Quotient

- In chemical equilibrium, stoichiometry and the balanced chemical equation are central. Discussion begins with the reaction quotient, \( Q_{\text{rxn}} \) or simply \( Q \).
- \[ aA + bB \rightleftharpoons cC + dD \]
- \( Q_{\text{rxn}} = \frac{[C]^c[D]^d}{[A]^a[B]^b} \)
- Only species with variable concentrations appear in \( Q_{\text{rxn}} \). What species don’t have variable concentrations? Species with fixed concentrations are assigned values of 1 in \( Q \).
- \( Q_{\text{rxn}} \) is a general function, like \( y=4x^3 \), and can (should) be evaluated for all states of a chemical system, not just the equilibrium state.
- What are \( Q \) for the following?
  - \( N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \)
  - \( 2PBr_3(g) + 3Cl_2(g) \rightleftharpoons 2PCl_3(g) + 3Br_2(g) \)
  - The reaction above if \( Br_2 \) is a liquid?
  - \( CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g) \)
  - \( 2NH_3(g) + CO_2(g) \rightleftharpoons NH_4OCONH_2(s) \)
  - \( 2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g) \)
  - \( Cr_2O_7^{2-}(aq) + H_2O(l) \rightleftharpoons 2CrO_4^{2-}(aq) + 2H^+(aq) \)
  - \( Fe_2O_3(s) + SO_3(g) + SO_2(g) \rightleftharpoons 2FeSO_4(s) \)

## The Equilibrium Constant

- When the system is at equilibrium, all of the concentrations become constant, so \( Q_{\text{rxn}} \) must become constant. The value \( Q_{\text{rxn}} \) at the equilibrium state is called the equilibrium constant, \( K \).
- \([\text{\_\_}\_\_]\)s can be either molarities or pressures. If molarities \( \rightarrow K_c \), pressure \( \rightarrow K_p \).
- \( K \) should have dimensions—is there value in including them?
- Values of constants normally have intrinsic merit. For example, the value of \( k \), the rate constant, tells you about the intrinsic rate of the reaction and the activation energy.
- Does the value of \( K \) have the same usefulness? Why or why not?
- What about \( K > 1 \) or \( K < 1 \)? Does this tell you whether products or reactants are favored at equilibrium?

## Summary Points

- “Reversible” chemical reactions must reach a point where the rates of the forward and reverse processes become equivalent.
- At that point, all the concentrations become static, despite the continuing chemical changes.
- This is the equilibrium state.
- A general function \( Q \) describes the reaction system under all conditions. Only species with variable \([\_\_\_]\)s appear in \( Q \).
- When the system is at equilibrium \( Q=K \).
- A reversible system is either at equilibrium or moving toward equilibrium.
- Combining kinetics and equilibrium. The kinetics tells us how long it will take for a reversible reaction to reach equilibrium.
The Basics

- As you might expect, there are two basic "introductory" calculations in this area
  - Given $[\text{C}]_\text{eq}$ what is the value of $K$?
  - Given $K$, what are the $[\text{C}]$s?
- A critical issue in equilibria is learning to differentiate (and label appropriately) equilibrium and nonequilibrium $[\text{C}]$s.
- Typically, equilibrium concentrations are labeled $[\text{C}]_\text{eq}$ and non equilibrium are either unlabeled or $[\text{C}]$.

Calculating $K$

- Given the balanced equation and the equilibrium concentrations shown:
  \[ \text{COCl}_2 \rightarrow \text{CO} + \text{Cl}_2 \]
  Equilibrium Concentrations:
  - $\text{COCl}_2$: 0.070 M
  - $\text{CO}$: 0.35 M
  - $\text{Cl}_2$: 0.15 M
  What is the value of $K$?
  \[
  K = \frac{[\text{CO}]_\text{eq}[\text{Cl}_2]_\text{eq}}{[\text{COCl}_2]_\text{eq}} = \frac{(0.35)(0.15)}{0.070} = 0.75
  \]

- Given the balanced equation and the equilibrium concentrations shown:
  \[ \text{CH}_4 + 2\text{H}_2\text{S} \rightarrow \text{CS}_2 + 4\text{H}_2 \]
  Equilibrium Concentrations:
  - $\text{CH}_4$: 0.44 M
  - $\text{H}_2\text{S}$: 0.12 M
  - $\text{CS}_2$: 0.090 M
  - $4\text{H}_2$: 0.48 M
  What is the value of $K$?
  \[
  K = \frac{[\text{CS}_2]_\text{eq}[4\text{H}_2]_\text{eq}}{[\text{CH}_4]_\text{eq}[2\text{H}_2\text{S}]_\text{eq}} = \frac{(0.090)(0.48)}{(0.44)(0.12)} = 0.75
  \]
Calculating $[I]_{eq}$

- Once a value for $K$ is known, it can then be applied to determine the $[I]_{eq}$ for other reaction systems. In this area, stoichiometry is king and very careful mathematics is critical to success.

- Given the balanced equation, the $K$ value and the partial set of equilibrium concentrations shown:
  
  \[ 2\text{NOBr} \rightarrow \text{NO} + 2\text{Br} \]

  \[ K = 1.61 \times 10^{-1} \]

  Equilibrium Concentrations:
  
  $\text{NO} = 0.098 \text{M}$
  
  $\text{Br} = 0.096 \text{M}$

  - $K = 0.161 = \frac{[\text{NO}] [\text{Br}^2]}{[\text{NOBr}]^2}$
  
  - $(0.19)(0.096)^2 = 0.0175 \neq 0.161$
  
  - $(0.19)(0.096)^2 = 0.0175$
  
  - $(0.19)(0.096)^2 = 0.0175$

- Always close the circle

- Checking $(0.19)(0.096)^2 = 0.0175$

Given the balanced equation, the $K$ value and the partial set of equilibrium concentrations shown:

\[ 2\text{CO} + 2\text{NO} \rightarrow 2\text{CO}_2 + \text{N}_2 \]

\[ K = 1.82 \times 10^1 \]

Equilibrium Concentrations:

- $\text{CO} = 0.032 \text{M}$
- $\text{NO} = 0.25 \text{M}$
- $\text{N}_2 = 0.11 \text{M}$

What is the concentration of $\text{CO}_2^2$?

$K = 18.2 = \frac{[\text{CO}_2]^2 [\text{N}_2]}{[\text{CO}]^2 [\text{NO}]^2}$

$[\text{CO}_2] = (0.11)/([0.032]^2(0.25)^2) = 18.2$

Checking $(0.11)/([0.032]^2(0.25)^2) = 18.2$

Given the balanced equation, the $K$ value and the partial set of equilibrium concentrations shown:

\[ 2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2 \]

\[ K = 4.11 \times 10^{-8} \]

Equilibrium Concentrations:

- $\text{O}_2 = 0.35 \text{M}$
- $\text{NO}_2 = 0.067 \text{M}$

What is the concentration of $\text{NO}$?

Given the balanced equation, the $K$ value and the partial set of equilibrium concentrations shown:

\[ 2\text{CO}_2 + \text{N}_2 \rightarrow 2\text{CO} + 2\text{NO} \]

\[ K = 2.16 \times 10^{-1} \]

Equilibrium Concentrations:

- $\text{N}_2 = 0.15 \text{M}$
- $\text{CO} = 0.35 \text{M}$
- $\text{NO} = 0.10 \text{M}$

What is the concentration of $\text{CO}_2$?
Suppose You’re not at Equilibrium

- The preceding treatments deal with a system wherein equilibrium has already been established. What sort of analysis can/should be made for a non-equilibrium state?
- First, let’s exam a bit of a transition case
- The table provides concentration data for the reaction shown going to equilibrium. Use the data to calculate the value of $K$.

$$2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$$

| $\text{SO}_2$ | $\text{O}_2$ | $\text{SO}_3$ |
| 0.00 | 0.20 | 0.33 |
| 0.35 | 0.40 |

How many variations can you see on this?

For any system going from an initial to the equilibrium condition, the concentration of each component has three contributors: $[\text{i}]$, $[\text{D}]$, and $[\text{eq}]$, where $[\text{eq}] = [\text{i}] + [\text{D}]$. The analysis of such systems is greatly eased by a tabular approach.

$2\text{CO}_2 + \text{N}_2 \rightarrow 2\text{CO} + 2\text{NO}$

| $\text{CO}_2$ | $\text{CO}$ | $\text{NO}$ |
| 0.440 | 0.00 | 0.053 |

$\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$

| $\text{H}_2\text{O}$ | $\text{CO}$ | $\text{CO}_2$ |
| 0.210 | 0.00 | 0.370 |
| 0.226 |

Q vs K-the key to everything

- If a system is not at equilibrium, then it must be moving toward it. Thus, there are two issues in analyzing reversible systems
  - Is it at equilibrium?
  - If not, in which direction is the reaction occurring?
- For any system which is not at equilibrium, $Q$ is constantly changing due to the net chemical change which is occurring.
- The proper evaluation of $Q$ is the key to analyzing a nonequilibrium state. If one rephrases the earlier statement using $Q$ and $K$, it reads: “$Q$ is either equal to $K$ or changing in such a fashion as to eventually equal $K$.” $Q$ can no more diverge from $K$ than a system can move away from equilibrium.
- $Q=K$-equilibrium state
- $Q>K$ or $Q<K$. System is not at equilibrium and a net reaction is occurring.
- $Q>K$ what’s happening and why?
- $Q<K$ ditto
How Complex Can Things Become?

- \( \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \) \( K=0.80 \)
- Assume all of the initial concentrations are 0.500.
- What is Q?
- In what direction is the reaction occurring?
- When equilibrium is established-what are the concentrations

Kinetics and Equilibrium

- The reaction \( \text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g) \) follows the rate law: rate=\( k [\text{N}_2\text{O}_4] \). If the rate constant is \( 6.30\times10^{-2} \text{sec}^{-1} \) and \( K=2.45 \), how long will it take for a reaction mixture containing only \( \text{N}_2\text{O}_4 \) initially to reach equilibrium?
- This is actually more complicated than it seems.

\( K_c \) and \( K_p \)

- \( \text{aA} + \text{bB} \rightleftharpoons \text{cC} + \text{dD} \)
- \( K_c=[\text{C}]^c[\text{D}]^d/[\text{A}]^a[\text{B}]^b \)
- \( K_p=P_c^cP_d^d/P_a^aP_b^b \)
- \( P=nRT/V \) \( n/V=M \)
- \( K_p=(\text{C})^{RT}(\text{D})^{RT}/(\text{A})^{RT}(\text{B})^{RT} \)
- \( \Delta n=\text{(# of gaseous products)-(# of gaseous reactants)} \)
- \( K_p=[\text{C}]^c/[\text{A}]^a[\text{B}]^b(\text{RT})^{c-a} \)
- \( \Delta n=0 \text{ or } K_p=K_c \)
Mathematics of \( K \)

- \( aA + bB \not\rightarrow cC + dD \quad K=2.4 \)

- What is \( K \) for the following
  - \( cC + dD \not\rightarrow aA + bB \)
  - \( 2aA + 2bB \not\rightarrow 2cC + 2dD \)
  - \( 1/3*cC + 1/3*dD \not\rightarrow 1/3*aA + 1/3*bB \)

- Where do you think this is heading?

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?

- Reverse reaction \( K_{rev} = 1/K_{forward} \)
- Multiply the reaction by \( x \) \( \Rightarrow K = K \cdot x \)
- The final \( K \) is obtained by taking the product of the \( K \)s for contributors

- \( 2\text{C}_2\text{H}_6\text{O}(l) + \text{O}_2(g) \not\Rightarrow 2\text{C}_2\text{H}_4\text{O}(l) + 2\text{H}_2\text{O} (g) \) \( K = 0.100 \)
  - \( 2\text{C}_2\text{H}_6\text{O}(l) + 2\text{H}_2\text{O}(g) \not\Rightarrow 2\text{C}_2\text{H}_4\text{O}(l) + 2\text{O}_2(g) \) \( K = 0.120 \)

- \( \text{H}_2\text{S}(g) + 2\text{O}_2(g) \not\Rightarrow \text{H}_2\text{SO}_4(l) \)
  - \( \text{SO}_2(g) + \text{H}_2\text{O}(g) \not\Rightarrow \text{H}_2\text{SO}_4(l) \) \( K = 0.164 \)
  - \( \text{SO}_3(g) + \text{H}_2\text{O}(g) \not\Rightarrow \text{H}_2\text{SO}_4(l) \) \( K = 0.148 \)
  - \( \text{H}_2\text{O}(l) \not\Rightarrow \text{H}_2\text{O}(g) \) \( K = 6.58 \)

- \( \text{C}_2\text{H}_6(g) \not\Rightarrow \text{C}_2\text{H}_6(g) + 2\text{H}_2(g) \)
  - \( \text{C}_2\text{H}_6(g) + 5/2\text{O}_2(g) \not\Rightarrow 2\text{CO}_2(g) + \text{H}_2\text{O}(g) \) \( K = 3.60 \)
  - \( \text{H}_2\text{O}(g) \not\Rightarrow \text{H}_2\text{O}(g) + 1/2\text{O}_2(g) \) \( K = 0.333 \)
  - \( \text{C}_2\text{H}_6(g) + 3\text{O}_2(g) \not\Rightarrow 2\text{CO}_2(g) + \text{H}_2\text{O}(g) \) \( K = 2.44 \)

- \( \text{H}_2\text{S}(g) + 2\text{O}_2(g) \not\Rightarrow \text{H}_2\text{SO}_4(l) \)
  - \( \text{SO}_2(g) + \text{H}_2\text{O}(g) \not\Rightarrow \text{H}_2\text{SO}_4(l) \) \( K = 0.505 \)
  - \( \text{SO}_3(g) + 2\text{O}_2(g) \not\Rightarrow \text{H}_2\text{SO}_4(l) + \text{H}_2\text{O}(l) \) \( K = 3.59 \)
  - \( \text{H}_2\text{O}(g) \not\Rightarrow \text{H}_2\text{O}(l) \) \( K = 0.162 \)
Yet another one

- $2\text{NH}_3(g) + \frac{1}{2}\text{O}_2(g) \rightleftharpoons \text{H}_2\text{O}(l) + \text{N}_2\text{H}_4(l)$
- $2\text{NH}_3(g) + 3\text{N}_2\text{O}(g) \rightleftharpoons 4\text{N}_2(g) + 3\text{H}_2\text{O}(g)$ $K = 0.286$
- $2\text{N}_2\text{H}_4(l) \rightleftharpoons 2\text{N}_2(g) + 4\text{H}_2(g)$ $K = 0.350$
- $\text{N}_2\text{O}(g) + 3\text{H}_2(g) \rightleftharpoons 4\text{N}_2\text{H}_4(l) + \text{H}_2\text{O}(l)$ $K = 0.49$
- $\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2(g) + \frac{1}{2}\text{O}_2(g)$ $K = 0.153$