EXAM 3 REVIEW
LBS 172

REACTION MECHANISMS

GENERAL
- Step by step process of bond making and breaking by which reactants become products
- Summation of steps must be equal to overall reaction
- Example: \( \text{NO}_2(g) + F_2(g) \rightarrow \text{FNO}_2 + F(g) \)
  \( \text{NO}_2(g) + F(g) \rightarrow \text{FNO}_2(g) \)
  Overall: \( 2\text{NO}_2(g) + F_2(g) \rightarrow 2\text{FNO}_2(g) \)

TERMS
- Elementary reaction: individual step in a mechanism; one chemical event
  Ex (from above rxn): \( \text{NO}_2(g) + F_2(g) \rightarrow \text{FNO}_2 + F(g) \)
- Intermediate: species that is formed and subsequently used up in the reaction
  Ex: \( F(g) \)
- Molecularity: number of particles colliding in an elementary step
  1- unimolecular
  2- bimolecular
  3- termolecular
  Ex: \( \text{NO}(g) + F(g) \rightarrow \text{FNO}_2(g) \) is a bimolecular step
- Catalyst: species that is used up by the mechanism and is subsequently reformed

RATES FOR ELEMENTARY STEPS
- Rate equation of an elementary step is based on reaction stoichiometry
  - Rate = product of rate constant and the concentrations of each reacting particle
    (Neither solids nor pure liquid reactants are used in rate equations)
  For any elementary step: \( A + B \rightarrow C + D \), rate = \( k[A][B] \)
  Ex: Rate for step \( \text{NO}_2(g) + F_2(g) \rightarrow \text{FNO}_2 + F(g) = k[\text{NO}_2][F_2] \)

RATE EQUATIONS BASED ON REACTION MECHANISMS
- The rate of any reaction is limited by its slowest step, the rate of which is often nearly the same as the overall reaction rate
- Rate determining step (RDS): the slowest elementary step in a reaction mechanism
- The RDS involves the highest total energy of all elementary steps in a given mechanism
- The rate of a rate determining step is assumed to be equal to the rate of its overall reaction
  1. \( A + B \rightarrow X + M \), Slow, large \( E_a \)
  2. \( M + A \rightarrow Y \), Fast, small \( E_a \)
  Overall: \( 2A + B \rightarrow X + Y \)
  Step 1 is RDS, so rate of overall reaction = \( k_{\text{step 1}}[A][B] \)
-In a laboratory setting, proposed mechanisms can be disproved by examining rate
dependence on reactants in RDS. Mechanisms cannot, however, be proved
correct.
-Reaction mechanisms involving an equilibrium step
  - Common case: a fast equilibrium step followed by a slow step
  
  Ex:
  
  1. \( \text{NO}_2(g) \leftrightarrow \text{NO}(g) + \text{O}(g) \) fast, equilibrium, where \( k_1 \) is constant
     for forward rxn and \( k_{-1} \) is constant for reverse reaction
  2. \( \text{O}(g) + \text{NO}_2(g) \rightarrow \text{NO}(g) + \text{O}_2(g) \) slow, \( k_2 \) is constant

  Overall: \( 2\text{NO}_2(g) \rightarrow 2\text{NO}(g) + \text{O}_2(g) \)

  -Rate equation may be written as: \( k_2[\text{O}][\text{NO}_2] \)
  -\( \text{O} \) is an immeasurable intermediate, and should not appear in the
    rate equation
  -Since in equilibrium, \( k_1[\text{NO}_2] = k_{-1}[\text{NO}][\text{O}] \), \( [\text{O}] \) can be written in
    terms of measurable species
    \( [\text{O}] = k_1[\text{NO}_2] / (k_{-1}[\text{NO}] ) \)
  -Rate equation can be written as: \( k_2 k_1[\text{NO}_2] / (k_{-1}[\text{NO}]) [\text{NO}_2] \)

**COLLISION THEORY AND ACTIVATION ENERGY**

- Collision theory states that for any reaction to occur, three conditions must be
  met:  
  1. Reacting molecules must collide
  2. Collision must have enough energy to break bonds
  3. Molecules must collide in the appropriate orientation

- Activation energy \( (E_A) \): the minimum amount of energy that must be absorbed by
  a system to cause it to react

- The proportion of molecules in a sample that have energy at or above \( E_A \) is
directly related to the speed of their reaction

- Reaction coordinate diagram
  - Shows chemical potential energy over time during a reaction

Ex:
· The energy of the reactants at left is higher than the energy of the products at right, therefore the reaction is exothermic (reactants would have lower $E$ than products if endothermic)
· $E_A$ is the difference from the beginning $E$ of the sample and the energy required for the sample to react
· When the sample has reached $E_A$, there is enough energy to break the appropriate bond(s), this occurs at the peak. A single peak represents one step
· New bonds are created to form products. To begin a reverse reaction, $E_A'$ must be added to the products to reach the peak

-Effects of Temperature
· Heating a sample has the effect of increasing the fraction of molecules in a sample having higher energies. This in turn increases the fraction of molecules at or above the activation energy barrier and therefore increases the rate of reaction
· Heat does not change concentration of reactants, so for the rate to increase, an increase in temperature must increase the rate constant
· Arrhenius equation: rate constant $k = Ae^{-E_A/(RT)}$, where $A$ is a parameter called the frequency factor, $R$ is the gas constant, $E_A$ is activation energy, and $T$ is temperature

EQUILIBRIUM

EQUILIBRIUM CONSTANT AND REACTION QUOTIENT

- Equilibrium constant
· Reaction: $aA + bB \leftrightarrow cC + dD$ at equilibrium
Equilibrium constant $K_{eq} = ([C]^c[D]^d)/([A]^a[B]^b)$
· $K_{eq}$ may only be expressed at equilibrium
· $K_{eq}$ depends only on the reaction and temperature
· $K_{eq}$ has no units
· Solid and liquid reactants and products are omitted in $K_{eq}$ calculations
· $K_{eq}$ may be written as $K_c$, as it is based on concentrations
· From equation for $K_{eq}$, if $K_{eq} << 1$, then reaction is reactant favored; if $K_{eq} >> 1$, then reaction is product favored

- Equilibrium constant can be written in terms of partial pressures for reactions involving gasses
· Reaction: $aA(g) + bB(g) \leftrightarrow cC(g) + dD(g)$ at equilibrium
$K_p = (P_C^c * P_D^d) / (P_A^a * P_B^b)$
· By the ideal gas law, $K_p = K_c(RT)^{\Delta n}$, where $\Delta n$ = change in moles of gas

- Reaction quotient, $Q$
· Reaction: $aA + bB \leftrightarrow cC + dD$
$Q = ([C]^c[D]^d)/([A]^a[B]^b)$
· $Q$ is the same expression as $K_{eq}$, but it may be expressed when a system is not in equilibrium. System is at equilibrium if $Q = K_{eq}$
· $Q$ can be used to predict concentration changes as systems approach equilibrium
- If $Q < K$, reaction will shift right, converting more reactants into products to reach equilibrium.
- If $Q > K$, reaction will shift left, converting more products into reactants.
  
  · $Q$ can be applied similarly to partial pressures, and compared to $K_p$.

LeChatelier’s Principle and rates:
  
  · Equilibrium will react to a stress to reach equilibrium.
  
  · This can be explained with rates.
  
  Ex: $\text{Co}^{2+} + 4\text{Cl}^- \leftrightarrow \text{CoCl}_4^{2-}$. If $\text{Cl}^-$ is added, $Q$ will decrease, rxn will make more $\text{CoCl}_4^{2-}$ to reach equilibrium. Why?
  
  At equilibrium: $k[\text{Cl}^-][\text{Co}^{2+}] = k[\text{CoCl}_4^{2-}]$, if $\text{Cl}^-$ is added, the rate of the forward reaction increases, increasing $[\text{CoCl}_4^{2-}]$ and then increasing the reverse reaction to stabilize at equilibrium.

· In endothermic reactions, the addition of heat has the same effect on rate as the addition of reactant.

· In exothermic reactions, the addition of heat has the same effect on rate as the addition of product.

EQUILIBRIUM CALCULATIONS:

- General steps to solve equilibrium problems:
  1. Write out equation.
  2. Use $Q$ to determine shift.
  3. Set up ICE table, use balanced equation to find ratios.
  4. Plug in Eq values into $K$ expression.
  5. Solve for variable change.
  6. Use change to find equilibrium concentrations.
  7. Check answer.

- To avoid using the quadratic formula, the addition or subtraction of a variable change ($x$) in a $K$ expression can be neglected only if the addition/subtraction of $x$ does not significantly affect the number that is being added to/subtracted from.

- How to use an ICE table:

Ex: $\text{C(graphite)} + \text{CO}_2(g) \leftrightarrow 2\text{CO(g)}$. The system was kept at constant volume at 1000K until equilibrium was reached. At this temperature, $K = 0.021$. The initial concentration of $\text{CO}_2$ was 0.012M. Calculate the equilibrium concentration of $\text{CO}$.

<table>
<thead>
<tr>
<th></th>
<th>C(graphite)</th>
<th>CO$_2$(g)</th>
<th>2CO(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>0.012</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-</td>
<td>-x</td>
<td>$\pm 2x$</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>-</td>
<td>0.012-x</td>
<td>2x</td>
</tr>
</tbody>
</table>

With these assumptions, we can set $K = 0.021 = (2x)^2 / (0.012-x)$. If the $-x$ in the denominator is neglected, then $x$ is calculated as 0.008, which significantly effects the concentration of $\text{CO}_2$. So the quadratic formula must be used.

$x$ is correctly calculated to be 0.0057. The equilibrium concentration of CO then is calculated to be $2(0.0057) = 0.0114M$. 

ACIDS AND BASES

ACIDS BASES AND THEIR REACTIONS

-Bronsted definitions:
  Acid: a substance that can donate a proton to any other substance
  Base: a substance that can accept a proton from any other substance

-Reactions
  · Involve the transfer of a proton (H⁺)
  · Acid + Base ↔ Conjugate Base + Conjugate Acid
  · Acids and their conjugate bases differ only by the presence of one proton, as do bases and their conjugate acids
  Ex: HCO₃⁻(aq) + H₂O(l) ↔ H₃O⁺(aq) + CO₃²⁻(aq)
    Acid Base Conj. Acid Conj. Base
  The acid HCO₃⁻ and its conjugate base CO₃²⁻ differ by only one H⁺
  The base H₂O and its conjugate acid H₃O⁺ differ by only one H⁺
  Ex: NH₃(aq) + H₂O(l) ↔ NH₄⁺(aq) + OH⁻(aq)
    Base Acid Conj. Acid Conj. Base

-Strong Acids
  · HCl, HBr, HNO₃, HI, H₂SO₄, HClO₄
  · These create a complete forward reaction, not an equilibrium reaction.
    The conjugate bases are relatively too weak to induce reverse reactions.
    Ex: HCl(aq) + H₂O → H₃O⁺(aq) + Cl⁻(aq), Cl⁻ is too weak of a base to pull a proton from H₃O⁺ in this system, so the reaction is one way
  · All other (weak) acids create bases with sufficient strength to maintain equilibrium. The stronger the acid, the weaker its conjugate base.

-Strong Bases
  · NaOH, KOH, LiOH, Ba(OH)₂, H⁺, RO⁻, R⁻, NH₂⁻
  · These create a complete forward reaction, not an equilibrium reaction.
    The conjugate acids are relatively too weak to induce reverse reactions.
    Ex: H⁺ + H₂O → H₂ + OH⁻(aq), H₂ has nearly no acid strength, so the reaction is one way
  · All other (weak) bases create acids with sufficient strength to maintain equilibrium. The stronger the base, the weaker its conjugate acid.

-Monoprotic, Polyprotic, and Amphiprotic
  · Monoprotic acids/bases: Bronstead acids/bases that are capable of donating/accepting one proton
    Ex: acid: HCl, base: NaOH
  · Polyprotic acids/bases: Bronstead acids/bases that are capable of donating/accepting more than one proton
    Ex: acid: H₂SO₄, base: CO₃²⁻
  · Amphiprotic: describes species that can behave either as Bronstead acids or bases
    Ex: Water as base: H₂O(l) + HCl(aq) → H₃O⁺(aq) + Cl⁻(aq)
    Water as acid: H₂O(l) + NH₃(aq) ↔ NH₄⁺(aq) + OH⁻(aq)
Lewis Acids
Electron acceptors that, although do not donate H\(^+\) themselves, increase the acidity of solution. Transition metal cations are Lewis acids. Ex: Fe\(^{2+}\), as in hard water. Fe\(^{2+}\) attracts 6 H\(_2\)O molecules in an octahedral pattern. O-H bonds in water weaken due to the pulling of e\(^-\) by Fe\(^{2+}\). H\(^+\) is then more easily removed by a base, resulting in a more acidic solution.

ACID AND BASE MEASURES
- \(2\text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq)\)
  \(K_w = [\text{H}_3\text{O}^+][\text{OH}^-]\). At 25\(^\circ\)C, \(K_w = 1*10^{-14}\) for all aqueous solutions
- \(\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log[\text{H}^+]\)
- \(\text{pOH} = -\log[\text{OH}^-]\)
- \(\text{pH} + \text{pOH} = 14\) for all aqueous solutions
- Solution is acidic if: \([\text{H}_3\text{O}^+] > [\text{OH}^-]\), \(\text{pH} < 7\), \(\text{pOH} > 7\)
- Solution is basic if: \([\text{H}_3\text{O}^+] < [\text{OH}^-]\), \(\text{pH} > 7\), \(\text{pOH} < 7\)
- Solution is neutral if: \([\text{H}_3\text{O}^+] = [\text{OH}^-] = 1*10^{-7}\text{M}\), \(\text{pH} = \text{pOH} = 7\)

EQUILIBRIUM CONSTANTS FOR ACIDS AND BASES
- For a general acid HA:
  \(\text{HA}(aq) + \text{H}_2\text{O}(l) \leftrightarrow \text{H}_3\text{O}^+ + \text{A}^-(aq)\)
  \(K_a = ([\text{H}_3\text{O}^+][\text{A}^-]) / [\text{HA}]\)
  \(K_a\) is directly related to acid strength
- For a general weak base B:
  \(\text{B}(aq) + \text{H}_2\text{O}(l) \leftrightarrow \text{BH}^+(aq) + \text{OH}^-(aq)\)
  \(K_b = ([\text{BH}^+][\text{OH}^-]) / [\text{B}]\)
  \(K_b\) is directly related to base strength
- \(K_a \times K_b = K_w\) for all aqueous solutions
- Logarithmic measures
  \(\cdot \text{pK}_a = -\log K_a\)
  \(\text{pK}_a\) is indirectly related to acid strength
  \(\cdot \text{pK}_b = -\log K_b\)
  \(\text{pK}_b\) is indirectly related to base strength

PREDICTING pH OF A SALT SOLUTION
- Consider the ions of the salt
- Conjugate bases of weak acids are basic, while those of strong acids are neutral
- Conjugate acids of weak bases are acidic, while those of strong bases are neutral
- Alkali metal cations have no effect on pH
- Transition metal cations are acidic (Lewis acids)
- Ex: NaNO\(_3\) ions: Na\(^+\) has no effect on pH. NO\(_3^-\) is the conjugate base of HNO\(_3\), a strong acid, therefore it is neutral. So NaNO\(_3\) solution is neutral.

EQUILIBRIUM CALCULATIONS
- Use the same techniques as non-acid/base equilibrium calculations discussed above
- Use given pH and/or pOH information to find [H\(_3\)O\(^+\)] and/or [OH\(^-\)]
-Use $K_w = K_a \cdot K_b$ to convert between $K_a$ and $K_b$
-In problems with polyprotic acids or bases, a full cycle of calculations are necessary for each donation/acceptance of a proton. E.g., three ICE tables will be necessary to find end concentrations of all species in a reaction with a triprotic acid.

BUFFERS
-Buffer: a solution that resists pH changes
-Composed of a weak acid and a weak base for conjugate acid/base pair
-Most effective when $pH \approx pK_a$, generic: $[A^-] \approx [HA]$
-Buffer capacity: measure of how much acid or base a buffer can absorb without significant pH changes; affected by total amount of $A^-$ and HA present
-Finding pH of a buffer (2 options)
  1. Do an equilibrium calculation
  2. Use Henderson Hasselbach equation
     - $pH = pK_a + \log([A^-]/[HA])$
     - $pOH = pK_b + \log([H^\beta^-]/[B])$
     - Only can be used when the variable change ($x$) in the equilibrium calculation is insignificant