CHEM 1220 Lecture Notes

Matthew Rowley

Summer 2020

COURSE ADMINISTRATIVE DETAILS

- My office hours

- Intro to my research

- Introductory Quiz

- Grading details

  - Exams - 40, Final - 15, Quizzes - 15, Homework - 30
  - Online homework
  - Daily quizzes

- Importance of reading and learning on your own

- Learning resources

  - My Office Hours
  - PAL group
  - Tutoring services - https://www.suu.edu/academicsuccess/tutoring/

- Show how to access Canvas

  - Calendar, Grades, Modules, etc.
  - Sapling Homework
    * Conceptual vs. normal vs. learning curve assignments
    * Due dates are Fridays. If it is Friday and you haven't completed an assignment this week then it is time to panic!
  - Textbook

- Course Overview

  - Phases and phase changes
  - Reaction rates (kinetics)
  - Equilibrium, equilibrium, equilibrium!
  - Electrochemistry (and equilibrium)
  - Nuclear Chemistry
  - Intro to biochemistry

CHAPTER 0

―――――

1210 REVIEW

There is a whole semester of material from 1210, and these are only the topics which are *most* important for success in 1220

- Composition of atoms and ions (protons, neutrons and electrons)

- Chemical formulas and names

  · Formulas and molar masses

  · Polyatomic ion names

  · Naming ionic compounds

  · Naming binary molecular compounds

  · Naming acids

- Balancing molecular equations

- Solubility rules

- Fundamentals of acid/base chemistry

- Measurements vs. chemistry

  · Converting from measurements to moles and back

  · Stoichiometry and predicting amounts

  · Limiting reactants

- Enthalpy of reaction and heat equations

- Lewis structures

CHAPTER 12

———

LIQUIDS AND SOLIDS

Table 12.3 gives the necessary values to solve this $(186.8\,^{\circ}C)$

CHAPTER 13

———

SOLUTIONS

CHEMICAL KINETICS

Time (s)	0	5	10	15
$[B]\,(M)$	0	0.0160	0.0295	0.0503

The reaction rate changes with reactant according to the *rate law*

- For reaction aA + bB $\longrightarrow$ cC + dD, the rate law will be $rate = k\,[A]^m\,[B]^n$

- Only reactants are included in the rate law

- m and n are the reaction order with respect to each reactant, and have nothing to do with stoichiometry

- Reaction rates can be *zero order*, *first order*, and *second order* w.r.t. each reactant

- The overall reaction order is the sum of m and n

- Consider the effect of doubling the concentration of a reactant that is zero, first, and second order

- These ideas extend to reactions with more or fewer reactants than shown here

The rate law is related to the rate by: $\dfrac{\Delta\,[A]}{\nu_A\Delta t} = k\,[A]^m\,[B]^n$

The initial rate method for determining reaction order:

- Run a reaction under several different careful conditions (double $[A]$ or $[B]$)

- Measure the initial rate (rate at the very beginning of the reaction)

- Check the numbers against expectations for doubling a zero, first, and second order reactant

- There is a mathematically rigorous way to deal with this, but doubling the reactant concentrations makes it very simple

After finding the reaction orders, you can take any data point and back-calculate the value of k

Note that the units of k depend on the overall reaction order as shown in Table 14.4
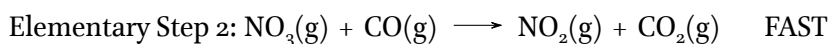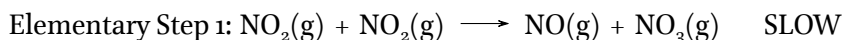
Use the data below to find the complete rate law (including the value of k) for the reaction:

aA + bB $\longrightarrow$ cC + dD
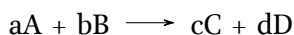
Trial	$[A]\,(M)$	$[B]\,(M)$	Initial rate (M/s)
1	0.0250	0.0250	2.04×10^{-3}
2	0.0500	0.0250	8.16×10^{-3}
3	0.0500	0.0500	1.63×10^{-2}

At $655\ K$ the rate constant is $8.15 \times 10^{-8}\dfrac{1}{M\ s}$ and at $705\ K$ the rate constant is $1.39 \times 10^{-6}\dfrac{1}{M\ s}$

Determine the activation energy and frequency factor for this reaction $\left(218\dfrac{kJ}{mol} \text{ and } 1.91 \times 10^{10}\dfrac{1}{M\ s}\right)$

Elementary Step 1: $NO_2(g) + NO_2(g) \longrightarrow NO(g) + NO_3(g)$ SLOW

Elementary Step 2: $NO_3(g) + CO(g) \longrightarrow NO_2(g) + CO_2(g)$ FAST

The two steps add up to the total equation

$NO_3(g)$ is produced in the first step, then consumed in the second step, so it never shows up in the overall reaction

This makes $NO_3(g)$ an *intermediate*

Intermediates are different from transition states because they are energetically stable (minimum in the reaction coordinate diagram)

Intermediates may sometimes be observed directly in the course of the reaction, or they may be so dilute or so short-lived that they cannot be observed

Figure 14.19 shows the reaction coordinate diagram for a two-step reaction like this one

Elementary steps each have their own reaction rates:

- The rate law for an elementary step depends on the *molecularity* of the step

  · Unimolecular steps have only one reactant: AB $\longrightarrow$ A + B

  · Bimolecular steps involve an encounter between two molecules: A + B $\longrightarrow$ C or 2 A $\longrightarrow$ B

  · Termolecular steps are very rare, but can occur

- The rate law can be inferred from the stoichiometry of the step

- · AB $\longrightarrow$ A + B   gives $rate = k\,[AB]$

- · A + B $\longrightarrow$ C   gives $rate = k\,[A]\,[B]$

- · 2 A $\longrightarrow$ B   gives $rate = k\,[A]^2$

○ While each step has its own rate, the overall reaction can only proceed at the rate of the *slowest* step

○ The slowest step is therefore called the *rate-limiting* step of the reaction

○ Looking at the reaction of NO_2 and CO above, the first step is slower so the overall reaction rate will be $rate = k\,[NO2]^2$

Any proposed mechanism must, at a minimum, add up to the total equation, and produce a rate law consistent with observations

This is not conclusive proof of a mechanism's validity, as one could contrive infinite mechanisms within these two constraints

Some elementary steps are reversible, and establish an equilibrium (subject of the next chapter):

○ Consider the reaction $2\,NO(g) + Cl_2(g) \longrightarrow 2\,NOCl(g)$ $rate = k\,[NO]^2\,[Cl]$

○ This observed rate law seems consistent with a single-step *termolecular* mechanism, but termolecular reactions are exceptionally rare

○ An alternative proposed mechanism is:

$NO(g) + Cl_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NOCl_2(g)$ FAST

$NOCl_2(g) + NO(g) \overset{k_2}{\longrightarrow} 2\,NOCl(g)$ SLOW

○ The first step will reach an equilibrium, where the forward rate will equal the reverse rate
$k_1\,[NO]\,[Cl_2] = k_{-1}\,[NOCl_2]$

○ Rearrange this to give the equilibrium concentration of the intermediate $[NOCl_2] = \dfrac{k_1}{k_{-1}}\,[NO]\,[Cl_2]$

○ The reaction rate is ultimately determined by the formation of product in the second step:
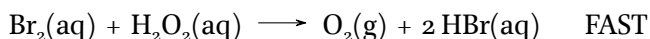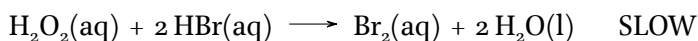$rate = k_2\,[NOCl_2]\,[NO]$

○ Substitute in our expression for $[NOCl_2]$

$rate = k_2\left(\dfrac{k_1}{k_{-1}}\,[NO]\,[Cl_2]\right)[NO] = \dfrac{k_2 k_1}{k_{-1}}\,[NO]^2\,[Cl_2]$

Consider the reaction: $2\,NO(g) + O_2(g) \longrightarrow 2\,NO_2(g)$ $\Delta H_{rxn} = -116.2\dfrac{kJ}{mol}$

○ The observed rate law is: $rate = k \left[NO\right]^2 \left[O_2\right]$

○ A proposed mechanism is:

$NO(g) + O_2(g) \rightleftharpoons NO_3(g)$ FAST

$NO(g) + NO_3(g) \longrightarrow 2\,NO_2(g)$ SLOW

○ Is the reaction mechanism consistent with the observed rate law?

○ What is the value of k in terms of the elementary step rate constants?

○ Draw a basically accurate reaction coordinate diagram for this reaction

Reaction mechanisms can become complex and interesting for certain reactions (harpoon mechanism and collisional activation)

$H_2O_2(aq) + 2\,HBr(aq) \longrightarrow Br_2(aq) + 2\,H_2O(l)$ SLOW

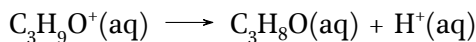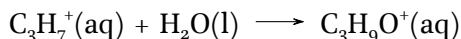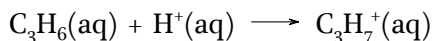$Br_2(aq) + H_2O_2(aq) \longrightarrow O_2(g) + 2\,HBr(aq)$ FAST

Note that the HBr is consumed in the first step, but regenerated in the second step

Catalysts can be *homogeneous* (HBr above) or *heterogeneous* (catalytic converters)

(not in the book) Catalysts can operate in several ways:

○ Heterogeneous catalysts confine reactants to a surface, increasing the encounter frequency

○ Enzymes hold the reactants in precise configurations, improving the steric component of the frequency factor and stabilizing the activated complex

○ Homogeneous catalysts produce new compounds which shift electron density and weaken bonds which must be broken for the reaction to proceed
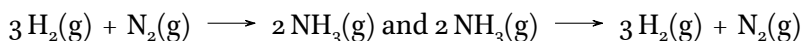
Analyze the following reaction mechanism:

$C_3H_6(aq) + H^+(aq) \longrightarrow C_3H_7^+(aq)$

$C_3H_7^+(aq) + H_2O(l) \longrightarrow C_3H_9O^+(aq)$

$C_3H_9O^+(aq) \longrightarrow C_3H_8O(aq) + H^+(aq)$

○ Give the total overall reaction

○ Identify any catalysts and intermediates

CHEMICAL EQUILIBRIUM

$$3\,H_2(g) + N_2(g) \longrightarrow 2\,NH_3(g) \text{ and } 2\,NH_3(g) \longrightarrow 3\,H_2(g) + N_2(g)$$
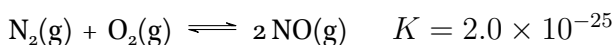
Such reactions will reach an equilibrium

- o Equilibrium is when the forward reaction rate and the reverse reaction rate are equal

- o The concentrations of reactants and products remains steady indefinitely once equilibrium is reached

- o Figure 15.2 shows how the amounts of reactant and product shift over time until equilibrium is reached

- o Equilibrium is a dynamic state – reactions continue, they merely balance each other

- o The precise concentrations at equilibrium will depend on the starting conditions

The above two reactions can be combined into one equation: $3\,H_2(g) + N_2(g) \rightleftharpoons 2\,NH_3(g)$

Equilibrium can be reached whether you start with reactants or start with products (Figure 15.1)

Note that $N_2(g)$ alone or $H_2(g)$ alone cannot lead to equilibrium from the reactant side – both are needed

$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g) \quad K = 2.0 \times 10^{-25}$$

$$2\,NO(g) + O_2(g) \rightleftharpoons 2\,NO_2(g) \quad K = 6.4 \times 10^9$$

$5.00\ mol$ H_2 and $0.500\ mol$ I_2 are reacted in a $1.00\ L$ chamber and at equilibrium $[HI] = 0.900\ M$. Find the value of K_C (324)

Consider the reaction $CO(g) + H_2O(g) \rightleftharpoons H_2(g) + CO_2(g) \quad K_C = 5.80$

Find the equilibrium conditions if initial concentrations are: $[CO] = [H_2O] = 0.0125\ M$

Often the equilibrium expression will lead to a quadratic equation when solving for x

The quadratic formula is: $ax^2 + bx + c = 0 \rightarrow x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

Consider the reaction: $I_2(g) \rightleftharpoons 2\,I(g) \quad K_{P,1000K} = 0.260$

Find the equilibrium conditions if a reaction chamber is initially charged with $0.200\ atm$ I and $0.00500\ atm$ I_2

Some quadratic equations can be greatly simplified by recognizing when x is small compared to initial amounts

- If x is small, then it can be neglected from any species with an initial amount

- First solve the equation *assuming* that x can be neglected

- Compare the solved value of x to the amounts it was neglected from

- If x is less than 5% of those values then your simplification was valid

- If not, then you must go back and solve the complete quadratic equation

Consider the reaction $HCOOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCOO^-(aq)$ $K_C = 1.8 \times 10^{-4}$

Find the equilibrium conditions for a solution that begins with $[HCOOH] = 0.250 \; M$

How would the reaction shift if each species is added or removed in turn?

Changing volume

- If the reaction volume changes, all the concentrations or pressures will change together

- The effect this has depends on the stoichiometry of the reaction

- Consider the reaction $3\,H_2(g) + N_2(g) \rightleftharpoons 2\,NH_3(g)$ – How will the reaction quotient change if the volume doubles?

- The shift depends on Δ_n, considering only the moles of gas or aqueous substances

- If volume increases (dilution), the reaction will shift to the side with *more* moles

- If volume decreases (concentration), the reaction will shift to the side with *fewer* moles

- If $\Delta_m = 0$, then the reaction is unaffected by dilution and concentration

- Figure 15.6 illustrates this principle

Temperature changes

- Unlike with the other changes, a change in T will actually change the value of K

- How K changes depends on ΔH_{rxn}

- We will explore this relationship mathematically later, but for now we can use a trick to determine the direction of the shift

- Consider "heat" as a reactant for endothermic reactions, and as a product for exothermic reactions

- Heat is not really a product or reactant (how many g of heat are produced)

- ○ Lowering T removes heat and the reaction will respond just like removing any other reactant or product

- ○ Raising T adds heat and will have the same effect as adding any other reactant or product

Equilibrium is often not the most important factor in industrial settings. The Haber process is run at high temperatures to increase the reaction rate even though it pushes equilibrium toward reactants

Addition of a catalyst has *no* effect on the equilibrium position

CHAPTER 16

ACID-BASE THEORY

$$Al^{3+}(aq) + 6\,H_2O(l) \longrightarrow Al(H_2O)_6^{3+}(aq)$$
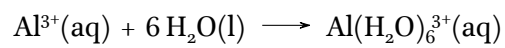
Carbonic acid makes gas due to Lewis acid action: $H_2CO_3(aq) \rightleftharpoons CO_2(g) + H_2O(l)$

CHAPTER 17

AQUEOUS EQUILIBRIA

CHEMICAL THERMODYNAMICS

		ΔH_{rxn}
		$+$	$-$
ΔS_{rxn}	$+$	Spontaneous @ High T	Always Spontaneous
	$-$	Never Spontaneous	Spontaneous @ Low T

We can find the threshold temperature by solving the Gibbs energy equation for $\Delta G_{rxn} = 0 \rightarrow 0 = \Delta H_{rxn} - T\Delta S_{rxn}$

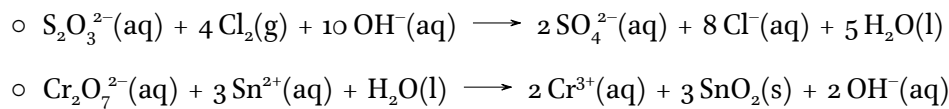This simplifies to: $T_{threshold} = \dfrac{\Delta H_{rxn}}{\Delta S_{rxn}}$

ELECTROCHEMISTRY

$$Cr_2O_7^{2-}(aq) + 3\,Sn^{2+}(aq)2\,H^+(aq) \longrightarrow 2\,Cr^{3+}(aq) + 3\,SnO_2(s) + H_2O(l)$$
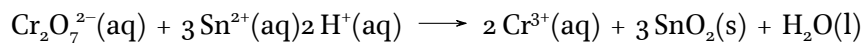
To balance in basic conditions, add four steps:

1. For each $H^+(aq)$ ion in the equation, add one OH^- ion to *both* sides

2. Combine H^+ and OH^- ions on the same side to form H_2O

3. Cancel out any H_2O that appears on both sides

4. Verify that all atoms and total charges are balanced

Balance the previous two equations in base instead of in acid:

- $S_2O_3^{2-}(aq) + 4\,Cl_2(g) + 10\,OH^-(aq) \longrightarrow 2\,SO_4^{2-}(aq) + 8\,Cl^-(aq) + 5\,H_2O(l)$
- $Cr_2O_7^{2-}(aq) + 3\,Sn^{2+}(aq) + H_2O(l) \longrightarrow 2\,Cr^{3+}(aq) + 3\,SnO_2(s) + 2\,OH^-(aq)$

NUCLEAR CHEMISTRY

Isotope	Mass (u) or $\left(\frac{g}{mol}\right)$
$^{238}_{92}U$	238.00033
$^{234}_{90}Th$	233.99423
$^{4}_{2}He$	4.00151

○ Adding up the products gives a mass $0.00459 \; \frac{g}{mol}$ less than the mass of $^{238}_{92}U$

○ This change is mass can be used to find the energy released: $\Delta E = \delta m c^2$ (convert to kg)

○ So, the reaction released $4.125 \times 10^{11} \; \frac{J}{mol}$, or $4.125 \times 10^8 \; \frac{kJ}{mol}$

○ Note that this is 100,000 times more energy than any chemical reactions

○ This is an α-decay reaction, fission and fusion reactions are still more energetic!

Nuclear reactions are often described as converting mass into energy – this is a bit misleading – rather, energy has its own mass, and enough energy is lost that we can observe it when we measure mass

| Particle	Mass (u) or $\left(\frac{g}{mol}\right)$
proton $^{1}_{1}p$	1.00728
neutron $^{1}_{0}n$	1.00866
$^{4}_{2}He$	4.00151

○ The mass of $^{4}_{2}He$ is less than the sum of its parts by $0.03037 \; \frac{g}{mol}$!

○ This discrepancy is called the mass defect

○ The mass defect is due to binding energy holding all nucleons together in a stable nucleus

The binding energy per nucleon increases sharply through the small elements until it reaches a maximum at Fe, and begins to slowly drop

This means that it is energetically favorable to combine small elements up until Fe, and it is energetically favorable to break down large elements down until Fe

ORGANIC CHEMISTRY

$$ROH + R'OH \xrightarrow{\text{H}_2\text{SO}_4} ROR' + H_2O$$
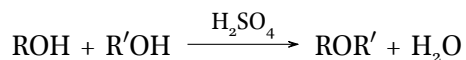
Ethers contain two alkyll groups linked through an O

- Ethers are named by the longer alkyl chain, with the other alkyl chain making a substituent with an -oxy ending (methoxyethane)

- An older convention is to just name the two alkyl groups and end with ether (ethyl methyl ether)

- Ethers are structural isomers of alcohols with the general formula of $C_nH_{2n+2}O$

Amines contain a nitrogen bound to one or more alkyl groups

- Amines are named by listing the alkyl groups and ending with amine

- Figure 21.18 shows primary, secondary, and tertiary amines

$$RCOOH + R'OH \longrightarrow RCOOR' + H_2O$$

Esters are named by the carboxylic acid name with an -oate ending, and the alcohol's parent alkyl name (methylpropanoate)

Esters will often have pleasant aromas (think banana laffy-taffys)

Esters linkages can also be used to form polymers, covered in the next section

Amides are like esters, but with an amine in place of the alcohol ($RCONR'R''$)

- Amides are also formed by condensation reactions
  $$RCOOH + NHR'R'' \longrightarrow RCONR'R'' + H_2O$$

- Amides are named like esters, but with the -amide ending (methylethylpropanamide)

- Amide bonds can also be used to form polymers, like proteins made from amino acids

Table 21.7 summarizes how to recognize and name these classes of organic compounds

CHAPTER 22

COORDINATION CHEMISTRY

CHAPTER 23

———

BIOCHEMISTRY

ERRATA

○ Figure 12.38 is inconsistent on how it shades the sliced faces of the ions (green or gray)

○ The equation embedded in Figure 14.4 is correct in the textbook but wrong on the lecture slides

○ The reaction presented in section 14.5, $2\,NO(g) + Cl_2(g) \longrightarrow N_2(g) + 2\,NOCl(g)$ should not have any N_2 on the product side

○ Section 22.5 presents $[CO(NH_5)Cl]Br$ and $[CO(NH_3)_5Br]Cl$ but $[CO(NH_5)Cl]Br$ should be $[CO(NH_3)_5Cl]Br$