

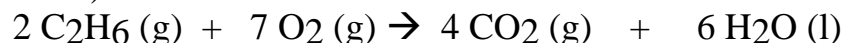
Unit 1: Kinetics and Equilibrium

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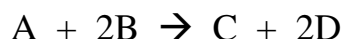
Chem 1B Fall 2009 Chapters 12, 13, 14

Chapter 12

1. What factors affect rates? Give examples of each.
2. Express the general rate of reaction in terms of the rate of change of each reactant and each product in the following reaction (this is an instantaneous rate used for relatively short time periods):



3. Write the balance equation and rate law expression for the combination reaction of NO (g) and O₂ (g) to produce NO₂ (g) if the reaction is second order in NO, first order in O₂ and 3rd order overall.
4. Rate data were collected for the following reaction at a particular temperature:



Experiment	Initial [A]	Initial [B]	Initial Rate form. C
1	0.20 M	0.10 M	4.0×10^{-4} M/min
2	0.20 M	0.30 M	1.2×10^{-3} M/min
3	0.60 M	0.30 M	3.6×10^{-3} M/min
4	0.40 M	0.20 M	?

- a) What is the order of the reaction with respect to A, B, and overall?
 - b) What is the rate law expression?
 - c) What is the value of k?
 - d) Calculate the rate for experiment 4.
5. Consider a graph where x is time in seconds and y is the concentration of reactant A in Molarity, [A]. The graph shows a straight line whose y intercept is 0.400 M and the slope is -0.0350 M/sec for the reaction: A → Products
 - a) What is the order of the reaction?
 - b) Write the rate law expression.
 - c) Determine the rate constant, k, for this reaction.
 6. The reaction $2\text{A} \rightarrow \text{products}$ is second order in A and has the form $\text{Rate} = k[\text{A}]^2$ where k has the value $6.0 \times 10^{-4} \text{ M}^{-1} \text{ min}^{-1}$. The reaction is at an initial concentration of 0.100 M and 318K.
 - a) How long is the first half-life?
 - b) How much time is required for the concentration to reach 0.085 M?

7. According to collision theory, to have an effective collision reactants must be in the proper _____ towards each other at the time of collision and have _____ to rearrange outer electrons in breaking bonds and forming new ones.
8. The following is a proposed mechanism:
- 1) $A + B \rightleftharpoons AB$ (fast, equilibrium)
 - 2) $AB + A \rightarrow A_2B$ (slow)
 - 3) $A_2B + B \rightarrow A_2 + B_2$ (fast)
- a) What is the overall equation for this mechanism?
 - b) What is the rate law expression for the mechanism?
 - c) What happens to the initial rate of formation of AB if the concentrations of A and B are both doubled?
 - d) Which letter(s) represents a reaction intermediate?
9. The activation energy for a given reaction is 95 kJ/mol . If the rate constant is 0.042 sec^{-1} at 30°C , what is the value of the rate constant at 50°C ?
10. How does a catalyst affect The activation energy? The rate? The equilibrium constant?
11. The rate and therefore the specific rate constant of a particular reaction doubles when the temperature is increased from 25°C to 40°C . Calculate the activation energy, E_a , for this reaction.
12. With regard to collision theory, ($k = Zfp$),
- a) What do each of the symbols, (k, Z, f, p) represent?
 - b) What factor is most responsible for the fact that the rate of a chemical reaction generally increases sharply with a rise in temperature?
13. Propose a plausible 3-step mechanism that fits with the information given.
- Overall reaction $2 \text{Ce}^{+4} + \text{TI}^{+1} \xrightarrow{\text{Mn}^{+2}} 2 \text{Ce}^{+3} + \text{TI}^{+3}$
 Rate = $k[\text{Ce}^{+4}][\text{Mn}^{+2}]$
 Step 1 is the rate determining slow step.
 Mn^{+3} is a reaction intermediate produced in step 1 and used up in step 2
 Mn^{+4} is a reaction intermediate produced in step 2 and used up in step 3
 TI^{+1} is not used until step 3

14. The experimentally observed rate law for the reaction: $\text{H}_2 + 2 \text{ICl} \rightarrow 2 \text{HCl} + \text{I}_2$ (all are gas) is $\text{Rate} = k[\text{ICl}][\text{H}_2]$.
- Circle the following mechanism(s) that is (are) plausible? (can be more than one)
 - For all the mechanisms identify, Reactants, Products, (Reaction Intermediates), and Catalysts
 - Identify the molecular of each step in all the mechanisms (uni-, bi-, ter-molecular).

			<u>Molecularity</u>
<u>Mechanism 1</u>	Step 1	$\text{H}_2 + 2 \text{ICl} \rightarrow 2 \text{HCl} + \text{I}_2$	Slow _____
<u>Mechanism 2</u>	Step 1	$2\{ \text{ICl} \rightleftharpoons \text{I} + \text{Cl} \}$	Fast _____
	Step 2	$\text{I} + \text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{HI}$	Slow _____
	Step 3	$\text{HI} + \text{I} + \text{Cl} \rightarrow \text{HCl} + \text{I}_2$	Fast _____
<u>Mechanism 3</u>	Step 1	$2\text{ICl} \rightarrow \text{Cl}_2 + \text{I}_2$	Slow _____
	Step 2	$\text{Cl}_2 + \text{H}_2 \rightarrow 2 \text{HCl}$	Fast _____
<u>Mechanism 4</u>	Step 1	$\text{H}_2 + \text{ICl} \rightarrow \text{HCl} + \text{HI}$	Slow _____
	Step 2	$\text{ICl} + \text{HI} \rightarrow \text{HCl} + \text{I}_2$	Fast _____

15. Explain why a mixture of natural gas and air formed by leakage of gas from a pipe can stand for a long time without reacting but explodes if a spark is introduced.
16. Describe the characteristics of the specific rate constant, k . Include if and how k and its units are affected by temperature, time, concentration, overall order, catalyst, etc.
17. a) The table shows concentration changes with time as a reaction $\text{A} \rightarrow \text{products}$ takes place. Fill in the table.

time (hour)	[A] (Molarity)	$\ln[\text{A}]$	$1/[\text{A}]$
0	0.200 M		
1	0.100 M		
3	0.050 M		
4	0.040 M		
7	0.025 M		

- What order is the reaction? Zero First Second
- Plot a graph labeling the axes appropriately for the determined order, which will give a straight line.
- Calculate the value of the specific rate constant, k .
- How long will it take [A] to reduce to 0.085 M?
- How long is the first half-life of this reaction?
- How long is the third half-life of this reaction?

Chapter 13

18. Do most reactions go to completion (all reactants forming all products until one reactant is used up)?
19. a) Write the equilibrium constant (K_C or K_P) for the following reaction:
 $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g}) \quad \Delta H = -198.4 \text{ kJ/mol rxn}$
- b) Does K remain constant as...
- 1) temperature varies?
 - If temperature increases how will the equilibrium shift? How does K change?
 - 2) initial concentrations vary?
 - If you start with only products instead of reactants how does K change?
 - 3) reaction coefficients vary?
 - If the equation is written as $\text{SO}_2 + 1/2 \text{O}_2 \rightleftharpoons \text{SO}_3$, how does K change?
- c) if $K \ll 1$ then are products or reactants favored?
- d) How are K_C and K_P different? By what equation are they related?
- e) What is the difference between Q and K ?
20. What is Le Chatelier's Principle? Explain the meaning of STRESS added to a system at equilibrium and how the system reacts.
21. For the reaction $\text{Br}_2(\text{g}) + \text{F}_2(\text{g}) \rightleftharpoons 2\text{BrF}(\text{g}) \quad K_C = 54.7$
- a) What are the equilibrium concentrations of all the gases if the initial concentrations of bromine and fluorine were both 0.100-M with no BrF?
 - b) What are the equilibrium concentrations if the initial concentrations of all three gases (Br_2 , F_2 , & BrF) start at 0.100 M?
22. The system below is at equilibrium and has the following concentrations in a 1.00 L flask: $[\text{H}_2\text{O}_2]$ and $[\text{CO}]$ both are 0.37 M while $[\text{H}_2\text{O}] = [\text{CO}_2] = 0.74 \text{ M}$. If 0.75 moles of ONLY hydrogen peroxide are added, calculate the new equilibrium concentrations.
- $$\text{H}_2\text{O}_2(\text{g}) + \text{CO}(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g}) + \text{CO}_2(\text{g})$$
23. For the reaction at a 25°C temperature: $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$
If $K_C = 250$, what is K_P ?
24. What is the equilibrium constant (K_C , K_P , K_{eq}) expression for ...
- a) $\text{MgCO}_3(\text{s}) \rightleftharpoons \text{MgO}(\text{s}) + \text{CO}_2(\text{g})$
 - b) $2\text{HCl}(\text{aq}) + \text{Mg}(\text{s}) \rightleftharpoons \text{H}_2(\text{g}) + \text{MgCl}_2(\text{aq})$
 - c) $\text{Fe}^{+3}(\text{aq}) + \text{SCN}^{-1}(\text{aq}) \rightleftharpoons \text{FeSCN}^{+2}(\text{aq})$
25. What is the value of K_{eq} when $\Delta G = -150 \text{ kJ/mol}$ at 25°C ? $\Delta G = -RT \ln K_{\text{eq}}$

26. In the Haber process NH_3 is manufactured from N_2 and H_2 . At 25°C , $K_p = 3.6 \times 10^8$. To increase the rate of reaction the reaction is run at a higher temperature. Use the van't Hoff equation to calculate K_p at 450°C



Van't Hoff eq. $\ln(K_{T2}/K_{T1}) = \Delta H/R (1/T_1 - 1/T_2)$

REVIEW from Ch 4

27. What volume of 18.0 M H_2SO_4 is required to prepare 1.50 L of 2.00 M H_2SO_4
28. What is the difference between an equivalence point and an end point?
29. What is the M of KOH if you have 38.7 ml of KOH solution, and 43.2 ml of 0.223 M HCl is required to react with all the KOH in a titration reaction?
30. What does it mean to be a strong electrolyte? Which types of substances will be strong electrolytes? What are the strong acids? What are the strong soluble bases?
31. For the following double displacement reactions, **predict** the products and **balance** the reactions, **include terms** (s), (l), (g), & (aq): Use **NR** for no reaction.
- a) $\text{KNO}_3(\text{aq}) + (\text{NH}_4)_3\text{PO}_4(\text{aq}) \rightarrow$
- b) $\text{HCl}(\text{aq}) + \text{K}_2\text{SO}_3(\text{aq}) \rightarrow$
- c) $\text{NaCl}(\text{aq}) + \text{AgNO}_3(\text{aq}) \rightarrow$

Chapter 14

32. Give a definition for an acid and a base for each of the 3 theories; Arrhenius, Bronsted-Lowry, and Lewis.
33. What is the acid, base, conjugate base and acid in the equation below?
- $$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$$
34. a) What are some properties of an acid? a base?
b) List the strong acids and strong bases.
c) Describe the relationship between the strength of a strong acid and its conjugate base.
d) What is the relationship between the bond strength of a binary acid and the acid strength?
e) What is the relationship between the oxidation state of an oxyacid with the same central atom and the acid strength?
f) What other factors affect acid strength? (carboxylic acids, small highly charged metal ions)
35. When would a soluble salt be basic? neutral? acidic? or unsure without knowing K_b or K_a values?
Write the molecular equation, complete ionic equation, and net ionic equation for the following salts, indicate whether each salt is: basic, acidic, neutral, or unsure. NaCl , NH_4NO_3 , KF , $\text{CH}_3\text{NH}_3\text{NO}_2$

36. What is the concentration of hydroxide ions in 0.25M Ba(OH)₂?
37. Water will autoionize, what does that mean? K_W is the equilibrium constant for water $K_W = [H^+][OH^-] = 1 \times 10^{-14} = K_a K_b$ at 25°C. $pH + pOH = 14$. What is the pH range for acid? neutral? and base solutions?
38. For 0.020 M HCl calculate $[H^+]$, pH, pOH, $[OH^-]$
39. For cyanic acid write the ionization equation. What is the $[HCN]$, $[CN^-]$, $[H^+]$, pH, % ionization in a 0.040 M HCN solution. K_a of HCN = 4.9×10^{-10}
40. Given that the pH of a NH₃ solution is 10.95. Calculate the molarity of NH₃ in this solution. $K_b = 1.8 \times 10^{-5}$
41. Calculate the concentrations of $[H^+]$, $[OH^-]$, $[H_2S]$, $[HS^-]$, and $[S^{2-}]$ in 1.00 M H₂S solution. K_{a1} of H₂S = 9.5×10^{-8} , K_{a2} of HS⁻ = 1×10^{-19}
42. What is the hydrolysis constant, K_b of CN⁻ if K_a of HCN = 4.9×10^{-10} . Calculate the $[OH^-]$, pOH, pH and % hydrolysis of CN⁻ in a solution that contains 0.22 M KCN.
43. Look up the appropriate K_a and K_b constants. Would NH₄CN be acidic, neutral, or basic?