Chang 11th edtion

****ASSIGNED PROBLEMS****

Remember You Have the Option to do the On-line Connect Homework Instead.

Chapter 13 Rates of ReactionsSuggested Problems for – KINETICS: Rates and Mechanisms of Chemical Reactions. *To be done in your HOMEWORK NOTEBOOK* see syllabus for details.

Order in [A]	Rate Law*	Integrated Rate Law $y = mx + b$ form	Linear Graph ? vs t	Slope of Line Equals	Half life Equations
0	rate = k	$[A]_t = -kt + [A]_0$	$[A]_t$	-k	$t_{1/2} = [A]_0/2k$
1	rate = k[A]	$\ln[A]_t = -kt + \ln[A]_0$	$\ln[A]_t$	-k	$t_{1/2} = 0.693/k$
2	rate = $k[A]^2$	$1/[A]_t = kt + 1/[A]_0$	$1/[A]_t$	k	$t_{1/2} = 1/k[A]_0$

*Since the units of rate are concentration/time, the units of k (the rate constant) must dimensionally agree. So for each order, k will have different units and these units can be used to tell one which equation to use. A [ ] means the concentration of the enclosed species.

Arrhenius Equation:

logarithmic form (used in graphing to find E_a): $\ln k = \ln A + [(-E_a/R)(1/T)]$

note: form is $y = b + mx$ where $y = \ln k$, $m = -E_a/R$, $x = 1/T$, and $b = \ln A$ so a plot of ln k against 1/T would be a straight line with the slope = $-E_a/R$.

Two Point form: *$\ln(k_2/k_1) = (E_a/R)(1/T_1 - 1/T_2)$ using this form, a rate constant can be calculated at different temperatures. *Note: there are different forms of this equation which are derived by different algebraic manipulations.

Chapter 13 "Chemical Kinetics": Read the chapter and look through the "summary of Facts and Concepts on page 610 and the Review questions 13.1- 13.4 on page 611. The Key Equations on are page 610.

Assigned Problems (pages 611-622): **6, 8,** (read and understand 9-12), **14** (read the surrounding text to first find the rate law), **16** (you must determine the value of k to do b), **18,** (read and understand 22-24), **26, 28,** (read and understand 31-35), **38, 40, 42, 44, 46,** (read and understand 48-54), **56, 57, 58,** (read and understand 59-64), **66, 68, 70, 74a and b, 78, 82, 88, 92, 94, 96, 100, 102** (try using computer graphing), **106, 110, 116, 118, 134.**

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Chapter 14
HOMEWORK

Chemical
NOTEBOOK

Equilibrium. To be done in your
see syllabus for details.

For reaction: $aA + bB \Leftrightarrow cC + dD$

$K_c = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$ "products raised to their coefficients over reactants raised to their coefficients" Solids (and water in high concentrations) are ignored.

$Q = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$

Capital K is the equilibrium <u>constant</u> .
Capital Q is the reaction <u>quotient</u>.   At equilibrium Q = K.

We also have a K_p which is often used for gases. Instead of Molarity, [ ], the gas concentrations are expressed as their pressure. $K_p = K_c(RT)^{\Delta n}$ where "delta n" is the change in moles of **gas** in the reaction.

If two or more reactions can be summed up to give a third reaction, then the equilibrium constant for that reaction is the product of the equilibrium constants of those reactions.

It is often helpful to use and I.C.E. (initial, change, equilibrium) chart in setting up and solving problems.

*****Be sure to read and study **Le Chatelier's principle**.

<u>**Chapter 14 "Chemical Equilibrium"**</u>: Read the chapter and look through the "summary of Facts and Concepts on page 656 and the Review questions 14.1- 14.12 on page 657. The Key Equations on are page 656.

<u>**Assigned problems (page 658-667):**</u> **14, 16, 18, 20, 22, 24, 26, 28, 30, 32**, (read and understand 33 and 34), **36**, (read and understand 38), **40, 42, 46a, 48** (perfect square), **54, 56, 58, 60, 62, 68, 70, 72, 86, 94, 100, 102.**

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Chapter 15: Acids and Bases:

(Seven Strong Acids: $HClO_4$, $HClO_3$, H_4SO_4, HI, HBr, HCl, HNO_3 [the corressponding Br and I oxyacids are also strong). All the other acids will be considered weak acids unless otherwise stated.

Strong Bases: Group 1 and Group II from $Ca(OH)_2$ on down. (There are stronger bases about which you will learn in organic chemistry.)

KEY EQUATIONS:

$[H^+][OH^-] = $ $K_w = 1.0 \times 10^{-14}$ at 25°C, but value changes with temperature.
pH = $-log[H^+]$ **note this is log base 10, not natural log.**
pOH= $-log[OH^-]$
pH + pOH = 14 <u>@ 25°C</u>

For weak acids and bases:

$K_a = [H^+][A^-]/[HA]$ or $[H_3O^+][A^-]/[HA]$ $K_b = [HB^+][OH^-]/[B]$

Also: $K_aK_b = K_w = 1 \times 10^{-14}$ @ 25°C

<u>**Chapter 15 : "Acids and Bases"**</u>: Read the chapter and look through the "summary of Facts and Concepts on page 711 and the Review questions 15.1- 15.2 on page 711. The Key Equations on are page 710.

<u>**Assigned problems (page 711-719)**</u>:   Know definitions of acids and bases. **4, 6, 8**, (read and understand 9-14), **16, 18, 20, 22** (assume 25°C), **24, 26**, (read and understand 27-30), **33, 34, 36, 38**, (read and understand 39-42), **44, 46** (you will need to look up the K_a value), **48, 50**, (read and understand 51-52), **54, 56, 58**, (read and understand 59-60), **64, 68, 70, 72,** (read and understand 73-76), **78, 80, 82, 84, 91, 92, 94, 98, 102, 104, 110, 112, 116, 130, 134, 149.**

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Chapter 16: Acid-Base Equilibria and Solubility Equilibria.

(Seven Strong Acids: $HClO_4$, $HClO_3$, H_4SO_4, HI, HBr, HCl, HNO_3 (analogous acids $HBrO_4$, HIO_4, $HBrO_3$, and HIO_3 are also strong). All the other acids will be considered weak acids unless otherwise stated.

Strong Bases: Group 1 and Group II from $Ca(OH)_2$ on down. (There are stronger bases about which you will learn in organic chemistry.)

KEY EQUATIONS:

$[H^+][OH^-] =$ $K_w = 1.0$ x 10^{-14} at 25^oC, but value changes with temperature.
pH = -log$[H^+]$ **note this is log base 10, not natural log.**
pOH= -log$[OH^-]$
pH + pOH = 14 **@ 25^oC**

For weak acids and bases:

$K_a = [H^+][A^-]/[HA]$ or $[H_3O^+][A^-]/[HA]$ $\qquad$ $K_b = [HB^+][OH^-]/[B]$

Also: $K_aK_b = K_w = 1$ x 10^{-14} @ 25^oC

Henderson-Hasselbach equation: $pH = pK_a + \log\dfrac{[conj.base]}{[acid]}$

Try deriving an equivalent pOH = pK_b expression from $\mathbf{K_b = \dfrac{[conj.\,acid][OH^-]}{[base]}}$

Chapter 16 " Acid-Base Equilibria and Solubility Equilibria": Read the chapter and look through the "summary of Facts and Concepts on page 766 and the Review questions 16.1- 16.4 on page 766. The Key Equations on are page 765.

Assigned Problems (pages 766-775): (On many of these problems you will have to look up the values of K_a or K_b, also be sure to look at Henderson-Hasselbach equation.) **6, 10, 12, 14, 16, 18, 20, 24, 26, 28** (this problem is similar to the lab dealing with the molar mass of a weak acid), **30, 34, 36, 40** (this problem is similar to the lab dealing with the molar mass of a weak acid), (read and understand 41-42), **46, SOLUBILITY:** (read and understand 47-52), **54, 58, 60, 64,** (read and understand 65), **68, 70, 72, 74, 82, 84** (You must use table 16.4), **110, 128, 142, 145, 146.**

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Chapter 17 "Entropy, Free Energy, and Equilibrium *Be sure to Review Chapter 6 (Thermochemistry)*

": Read the chapter and look through the "summary of Facts and Concepts on page 805 and the Review questions 17.1- 17.4 on page 806. The Key Equations on are page 805.

Assigned Problems (pages 806-813): (read and understand 7-8), **10, 12, 14,** (read and understand 15-16), **18** (refer to appendix 3), **20,** (read and understand 21-22), **24, 26, 28** (note the difference between ΔG^o and ΔG), **32, 46, 52, 56, 58, 60, 62, 64, 66, 70, 74, 86, 94** (you must first calculate ΔH).

$\Delta U = q + w$ (some books use $\Delta E = q + w$)
ΔH = negative, <u>favors</u> spontaneity
ΔH = positive, <u>favors</u> non-spontaneity

$\Delta H = H_{final} - H_{initial}$

$\Delta H = H(products) - H(reactants)$

$$\Delta H^o_{rxn} = \sum m\Delta H^o_f(products) - \sum n\Delta H^o_f(reac\tan ts)$$

ΔS = positive, <u>favors</u> spontaneity

ΔS = negative, <u>favors</u> non-spontaneity

reversible process: $\Delta S_{universe} = 0$

Irreversible process: $\Delta S_{universe} > 0$

$\Delta S = q_{rev}/T$ (@ constant T)

$\Delta S = \Delta H_{vap}/T_{boiling}$

$$\Delta S^o = \sum m\Delta S^o_f(products) - \sum n\Delta S^o_f(reac\tan ts)$$

ΔG = negative, the reaction **is** spontaneous in the forward direction.

ΔG = zero, the reaction **is** at equilibrium.

ΔG = positive, **the reaction in the forward direction is nonspontaneous** and work must be supplied from the surroundings to make it occur. However, the reverse reaction will be spontaneous.

$G = H - TS$ (_relate this formula to table 19.4 on page 735_)

$\Delta G = \Delta H - T\Delta S$

$$\Delta G^o = \sum m\Delta G^o_f(products) - \sum n\Delta G^o_f(reac\tan ts)$$

$\Delta G = \Delta G^o + RTlnQ$ @equilibrium $\Delta G = 0$ so $\Delta G^o = -RTlnK$

ΔG^o negative: K>1   (the more negative ΔG^o, the larger the value of $K_{equilibrium}$)

ΔG^o zero: K=1

ΔG^o positive: K<1

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Chapter 18 "Electrochemistry ": Read the chapter and look through the "summary of Facts and Concepts on page 850 and the Review questions 18.1- 18.13 on page 851. The Key Equations on are page 850.

Assigned Problems (pages 851-860):   2, (read and understand 3-10), **12, 14, 16, 18, 20, 24, 26a,&b,** (read and understand 29), **32, 36,** (read and understand 37, 45), **48, 52a&b, 70, 104.**

A = C/s   J = V•C   F = 9.65 x 10⁴ C/mole (of e⁻s)=9.65 x 10⁴ J/V•mole (of e⁻)

1 V = 1 J/C   R = 8.314J/mol•K

$E^o = E^o_{ox} + E^o_{red}$ (a positive value is spontaneus) note: this is a different equation than that found in your book

$\Delta G = -nFE$ $\Delta G = -nFE^o$

Nerst Equation : $E = E^o - \dfrac{RT}{nF}lnQ$ or @ $25^o C$ $E = E^o - \dfrac{0.0257}{n}lnQ$

$$\ln K = \frac{nE^o}{0.0257} \ @ \ 25^o C$$

Chapter 19 "Nuclear Chemistry ": Read the chapter and look through the "summary of Facts and Concepts on page 893 and the Review questions 19.1- 19.6 on page 894. The Key Equations on are page 892.

Assigned Problems (pages 894-899): 8, (read and understand 9-14), **18, 20, 22a, 26, 28, 30, 34, 38,** (read and understand 41-50), **56, 64, 70, 72, 74, 88.**

NOTE: Nuclear decay is just __first order kinetics.__ The formulas below are really the same as the formulas for 1ˢᵗ order kinetics. The variables are changed from [A]ₒ and [A]ₜ to Nₒ and Nₜ and the equations have been rearranged.

$$\ln \frac{N_t}{N_o} = -kt \quad \textbf{\underline{or}} \quad \ln N_t = -kt + \ln N_o \qquad \textbf{\underline{and}} \qquad k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{t_{1/2}}$$

$$\ln N_t = -\lambda t + \ln N_o \qquad\qquad \lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{t_{1/2}}$$