Last Name ______________________ Student Number ______________________

First Name ______________________

Quiz 1 – 2 February 2012

Chemical Dynamics
Chem 1001N
Department of Chemistry
York University

Notes: All final answers must be in ink. All questions are to be answered.
Calculators are allowed.

Time allowed: 50 minutes; Total marks: 30

$R = 0.0821 \text{ L atm mol}^{-1}\text{ K}^{-1} = 8.314 \text{ J mol}^{-1}\text{K}^{-1}$.

$$t_{1/2} = \frac{\ln 2}{k},\quad [A] = [A]_0 - akt,\quad [A] = [A]_0 e^{-akt},\quad PV = nRT,\quad \ln\left(\frac{P_{A,0}}{P_A}\right) = akt$$

$$\frac{1}{[A]_t} = akt + \frac{1}{[A]_0},\quad k = Ae^{-\frac{E_a}{RT}},\quad \ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Marks

[5] 1 a. If the half-life of a reaction depends on the concentration of the reactant, can the reaction be first order? (answer yes or no)

$\frac{\ln 2}{k}$

Answer: no

b. What is the overall order of reaction for the following: Rate = $k[A]^{-1/2}[B]^{1/2}$?

Answer: 0 $-\frac{1}{2}+\frac{1}{2}=0$

c. Does a catalyst in a reaction increase the activation energy? (answer yes or no)

Answer: no

d. For the reaction A → products, if a plot of [A] vs. time is a straight line what is the order of the reaction?

Answer: 0

d. Are all enzymes proteins? (answer yes or no)

Answer: yes

[3] 2. The activation energy of the following reaction:

$$A\ (l) \rightarrow B\ (l) + C\ (l)$$

is 30 kJ/mol. Determine the factor by which the rate constant changes when the temperature increases from 0°C to 25°C?

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{-E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{-30\times10^3\ J/mol}{8.314\ J/mol\ K}\left(\frac{1}{273+25} - \frac{1}{273+0}\right)$$

$$\ln\frac{k_2}{k_1} = 1104$$

$$\frac{k_2}{k_1} = 3$$

✓ [6] 3. Data for the reaction G (l) + H (l) → J (l) are given below.

Experiment	[G] (M)	[H] (M)	Initial rate (M/s)
1	0.030	0.060	2.5×10^{-5}
2	0.030	0.020	2.5×10^{-5}
3	0.060	0.060	10.0×10^{-5}

a. What is the rate of reaction?

$$\text{rate} = k[G]^m [H]^n$$

use methods of initial rates

$$\frac{R_1}{R_2} = \frac{k[G]^m (0.06)^n}{k[G]^m (0.02)^n} = \frac{2.5\times10^{-5}}{2.5\times10^{-5}}$$

$$3^n = 1$$

$$n = 0$$

$$\frac{R_1}{R_3} = \frac{k(0.03)^m [H]^n}{k(0.06)^m [H]^n} = \frac{2.5\times10^{-5}}{10\times10^{-5}}$$

$$\left(\frac{1}{2}\right)^m = \frac{1}{4}$$

$$m = 2$$

$$\text{rate} = k[G]^2$$

b. What is the value of k?

use any expt

$$R_1 = k[G]^2 \Rightarrow 2.5\times10^{-5}\ \text{m/s} = k(0.03\ \text{m})^2$$

$$0.028\ \text{m}^{-1}\ \text{s}^{-1} = k$$

[8] 4. For the second order reaction A → products, the following data are obtained:

$[A] = 1.512$ M, $t = 0$ min
$[A] = 1.490$ M, $t = 1.0$ min
$[A] = 1.469$ M, $t = 2.0$ min

a. What is the average reaction rate over the first 2 min?

$$\text{rate} = \frac{-\Delta[A]}{\Delta t} = \frac{-([A_f]-[A_i])}{t_f - t_i} = -\left(\frac{1.469-1.512}{2-0}\right)$$

$$= 0.0215\ M/\text{min}$$

b. What is the rate constant, k, for this reaction?

$$\frac{1}{[A]_t} = akt + \frac{1}{[A_0]} \rightarrow \frac{1}{1.469\ M} = k(2\ \text{min}) + \frac{1}{1.512\ M}$$

$$k = 9.68 \times 10^{-3}\ M^{-1}\ \text{min}^{-1}$$

c. What is the instantaneous reaction rate at 2 min?

$$\text{rate} = k[A]^2$$

$$= (9.68 \times 10^{-3}\ M^{-1}\ \text{min}^{-1})(1.469\ M)^2$$

$$= 0.0209\ M\ \text{min}^{-1}$$

d. How long will it take for the concentration of A to drop by half the initial concentration?

$$\frac{1}{[A]_t} = akt + \frac{1}{[A_0]}$$

$$1/\tfrac{1.512\ M}{2} = (9.68 \times 10^{-3})\ M^{-1}\ \text{min}^{-1}\ t + \frac{1}{1.512\ M}$$

$$68.3\ \text{min} = t$$

✓ [8] 5. Hydrogen iodide is thought to form via the following mechanism:

(1) $I_2(g) \rightarrow 2I(g)$
(-1) $2I(g) \rightarrow I_2(g)$
(2) $H_2(g) + 2I(g) \rightarrow 2HI(g)$

$$I_{2(g)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2I_{(g)}$$

$$H_{2(g)} + 2I_{(g)} \xrightarrow{k_2} 2HI_{(g)}$$

a. What is the overall reaction corresponding to this mechanism?

$$I_2 + H_2 \rightarrow 2HI$$

b. If you assume that reactions (1) and (-1) are in rapid equilibrium and reaction 2 is rate determining, what is the rate equation corresponding to this mechanism?

from (2) rate $= k_2[H_2][I]^2$

need to get rid of $[I]$

from rapid =brium

rate (1) = rate (-1)

$$k_1[I_2] = k_{-1}[I]^2$$

$$\frac{k_1}{k_{-1}}[I_2] = [I]^2$$ substitute

$$\text{rate} = \frac{k_1}{k_{-1}}[I_2][H_2]$$

c. What is a potential problem with this mechanism?

stop (2) is trimolecular

Answers

Last Name ____________ ~~Student Number~~ ____________

First Name ____________

[redacted]

Quiz 2 – 1 March 2012

Chemical Dynamics
Chem 1001N
Department of Chemistry
York University

Notes: All final answers must be in ink. All questions are to be answered. Calculators are allowed.

Time allowed: 50 minutes; Total marks: 30

R = 0.0821 L atm mol^{-1} K^{-1} = 0.08315 L bar mol^{-1} K^{-1} = 8.314 J mol^{-1} K^{-1}.

$pH = pK_a + \log\frac{[A^-]}{[HA]}$, $PV = nRT$, $K_p = K_c(RT)^{\Delta n_{gas}}$, $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

Marks

[5] 1 N_2O_3 (g) decomposes to NO (g) and NO_2 (g) with a ΔH° = 40.5 kJ mol^{-1} according to the equilibrium:

$$N_2O_3\,(g) \rightleftharpoons NO\,(g) + NO_2\,(g)$$

What effect will the following changes have on the position of the equilibrium? Circle the correct answer

(a) more N_2O_3 (g) is added, volume stays fixed:

shift left [✓ shift right] stay the same

(b) more NO_2 (g) is added, volume stays fixed:

[✓ shift left] shift right stay the same

(c) the volume of the reaction flask is increased:

shift left [✓ shift right] stay the same

(d) the temperature is lowered:

[✓ shift left] shift right stay the same

(e) add He (g) while keeping the volume fixed:

shift left shift right [✓ stay the same]

[2] ✓ 2

Consider the following reaction:

$3H_2 (g) + N_2 (g) \leftrightarrows 2NH_3 (g)$

For this reaction the value of K_p is 6.5×10^{-3} at 723 K. For the following mixture indicate if the system is at equilibrium, and if it is not, indicate the direction in which the reaction will proceed to achieve equilibrium.

Pressure of NH_3 = 60 atm, pressure of H_2 = 150 atm, pressure of N_2 = 80 atm

$$Q = \frac{P_{NH_3}^2}{P_{H_2}^3 P_{N_2}} = \frac{60^2}{150^3 \; 80} = 1.3 \times 10^{-5}$$

$$Q < K_p$$

not at equilibrium, rxn goes to right

[5] 3 ✓

Calculate the pH and concentration of the benzoate ion in a 50 mM solution of benzoic acid (K_a=6.3×10^{-5}).

$$H_2O + HA \rightleftarrows A^- + H_3O^+$$

I	0.050	0	0
C	$-x$	x	x
E	$0.05-x$	x	x

$$K = \frac{[A^-][H_3O^+]}{[HA]} = \frac{x^2}{0.05-x} = 6.3 \times 10^{-5}$$

$x << 0.05$

$x = 1.8 \times 10^{-3}$

$[A^-] = 1.8 \times 10^{-3}$ M

$pH = -\log(1.8 \times 10^{-3}) = 2.7$

[9] 4 ✓ For the reaction $PCl_5 (g) \leftrightarrows PCl_3 (g) + Cl_2 (g)$, K_p is 1.8 at 523 K.

a) What is the value of K_c for this reaction?

$0.08314 \text{ bar L K}^{-1} \text{ mol}^{-1}$

$$K_p = K_c (RT)^{\Delta n \text{ gas}}$$

$$1.8 = K_c (523) (\underline{0.8315})^1$$

$$K_c = 0.041$$

b) If 0.10 moles of PCl_3 and 0.10 moles of Cl_2 were introduced into a 1.0 L flask, how many moles of PCl_5 would be produced?

	PCl_5	PCl_3	Cl_2
i	0	0.1	0.1
c	x	$-x$	$-x$
e	x	$0.1 - x$	$0.1 - x$

$$K_c = \frac{[Cl_2][PCl_3]}{[PCl_5]} = \frac{(0.1 - x)(0.1 - x)}{x}$$

$$x K_c = x^2 - 0.2x + 0..01$$

$$0 = x^2 - 0.241x + 0.01$$

$$x = \frac{0.241 \pm \sqrt{(0.241)^2 - (4)(1)(0.01)}}{(2)(1)}$$

$$x = 0.0535$$

moles PCl_5 = 0.053 moles

c) Calculate the concentrations of PCl_3, Cl_2 and PCl_5 present at equilibrium if 0.10 moles of PCl_3, 0.10 moles of Cl_2 and 0.10 moles of PCl_5 were introduced into a 1.0 L flask.

$Q = \frac{(0.1)(0.1)}{0.1} = 0.1$ $Q > K_c$ rxn goes to lft

	PCl_5	PCl_3	Cl_2
i	0.1	0.1	0.1
c	x	$-x$	$-x$
e	$0.1+x$	$0.1-x$	$0.1-x$

$K_c = 0.042 = \frac{(0.1-x)^2}{0.1+x} \hookrightarrow 0.042x + 0.0042 = x^2 - 0.2x + 0.01$

$0 = x^2 - 0.242x + 5.8\times10^{-3}$

use quadratic $x = 0.027$

$[PCl_3] = [Cl_2] = 0.1 - 0.027 = 0.073$ M

$[PCl_5] = 0.1 + x = 0.127$ M

[5] 5 ✓ The pK_a of formic acid is 3.74. A buffer is made by mixing 1.10 L of 10.0 mM formic acid with 100 mL of 20.0 mM NaOH. What is the pH of this buffer?

moles formic acid $= 11 \times 0.01 = 0.011$ moles

moles base $= (0.1)(0.02) = 2\times10^{-3}$

after base reacts with acid

moles formic acid $= 0.011 - 0.002 = 0.009 = [HA]$

moles formate = moles base = $0.002 = [A^-]$

$pH = pK_a + \log\frac{[A^-]}{[HA]} = pK_a + \log\frac{n_{A^-}}{n_{HA}}$

$= 3.74 + \log\left(\frac{0.002}{0.009}\right)$

$= 3.09$

[4] 6 The pK_b value of ammonia is 4.74. The pH value of the buffer made of ammonia and ammonium chloride is equal to 9.26.

✓ a) Calculate the ratio of conjugate base to conjugate acid for this buffer.

$$pH = pK_a + \log \frac{A^-}{HA}$$

$$9.26 = 9.26 + \log \frac{A^-}{HA}$$

14 - 4.74

$$\frac{A^-}{HA} = 1$$

✓ b) Is this solution a good buffer? Briefly explain your answer.

yes $\frac{A^-}{HA}$ is between 0.1 and 10

Answers

Last Name ____________ Student Number ____________

First Name ____________

Quiz 3 – 22 March 2012

Chemical Dynamics
Chem 1001N
Department of Chemistry
York University

Notes: All final answers must be in ink. All questions are to be answered.
Calculators are allowed.

Time allowed: 50 minutes; Total marks: 30

R = 0.0821 L atm mol^{-1} K^{-1} = 0.08315 L bar mol^{-1} K^{-1} = 8.314 J mol^{-1} K^{-1} k=1.38-66 JK^{-1}N$_a$=6.022x10^{23}

$$pH = pK_a + \log\frac{[A^-]}{[HA]},\ \Delta G = \Delta H - T\Delta S,\ S = k\ln W,\ \Delta S = \frac{q_{rev}}{T},\ x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$\Delta G = \Delta G^\circ + RT\ln Q_{eq},\ \ln K_{eq} = -\frac{\Delta H^\circ}{R}\frac{1}{T} + \frac{\Delta S^\circ}{R},\ \Delta G^\circ = -RT\ln K_{eq},\ pH = pK_a + \log\frac{[A^-]}{[HA]}$$

Marks

[4] 1. For each reaction indicate the whether sign of ΔS is positive, negative or not possible to determine from the information given. Briefly justify your answers (use less than 12 words).

a) $H_2O(s) \rightarrow H_2O(l)$

positive

solid to liquid

b) $(NH_4)_2SO_4(s) \rightarrow 2NH_3(g) + H_2O(g) + SO_3(g)$

positive

solid to gas

c) $CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$

not possible to determine

same number of gas molecules on each side

d) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

negative

fewer gas molecules in products than reactants

[6] ✓ 2 a. What is the solubility of AgCl if its solubility product is 1.8×10^{-10}?

$AgCl \rightleftarrows Ag^+ + Cl^-$

if S = solubility

$S^2 = 1.8\times10^{-10}$

$S = 1.3\times10^{-5}$ m

✓ b. Calculate the molar solubility of AgCl in 0.04 M NaCl.

	AgCl	Ag^+	Cl^-
i	–	–	0.04
c	–	S	S
e	–	S	S+0.04

$K_{sp} = 1.8\times10^{-5} = [A^+][Cl^-]$

$= S(S+0.04)$

assume $S < 0.04$

$1.8\times10^{-5} = S(0.04)$

4.5×10^{-4} m $= S$

[5] 0 3. Will AgCl precipitate after adding 10 mL of 1×10^{-6} M NaCl to 1 L of 0.1 M $AgNO_3$ (K_{sp} of AgCl = 1.8×10^{-10})? Support your answer with a calculation.

moles Cl^- = 10×10^{-3} L × 1×10^{-6} M

= $1.\times10^{-8}$ moles

moles Ag^+ = 1L × 0.1M

= 0.1 moles

$[Cl^-] = \frac{1\times10^{-8}\text{ moles}}{1.01L} = 9.9\times10^{-9}$ M

$[Ag^+] = \frac{0.1}{1.01} = 0.099$ M

$Q = [Cl^-][Ag^+] = (9.9\times10^{-9})(0.099)$

$= 9.8\times10^{10}$

$Q > K_{sp}$

ppt will form

[4] ✓ **4**. For a given reaction if a plot of $\ln K_{eq}$ versus 1/T has a slope of 0 K what is the value of ΔH°? If in the same plot the y intercept has a value of 4.0 is the reaction spontaneous? Briefly explain your answer.

$\Delta H^\circ =$ 0 kJ/mol

using $\ln K_{eq} = \frac{-\Delta H^0}{R}\frac{1}{T} + \frac{\Delta S^0}{R}$

slope $= 0 = -\frac{\Delta H^0}{R} \rightarrow \Delta H^0 = 0$

y intercept $\frac{\Delta S^0}{R} = 4$

$\Delta S^0 = 4R$

this will always be positive

spontaneous

[4] ✓ **5**. For the decomposition of calcium carbonate into calcium oxide and carbon dioxide the values of ΔH° and ΔS° for this reaction are 178 kJ and 161 J K^{-1}, respectively. Above which temperature is this reaction spontaneous?

$\Delta G = \Delta H - T\Delta S = 0$

$\Delta H = T\Delta S$

$178 \times 10^3 \text{ J/mol} = T \ 161 \text{ J/K}$

$1106 \,^\circ K = T$

at T greater than 1106 °K

[7] 6 (a) Use the data below to determine ΔH°, ΔS°, ΔG° and K_{eq} for the following reaction at 25°C.

$$PCl_5(g) \leftrightharpoons PCl_3(g) + Cl_2(g)$$

	ΔH°$_f$ (kJ mol^{-1})	S° (J mol^{-1})
PCl_5 (g)	-375.0	364.5
PCl_3(g)	-287.0	311.7
Cl_2(g)	0.000	223.0

$\Delta H = -287 + 0 - -375 = 88$ kJ/mol

$\Delta S = 311.7 + 223 - 364.5 = 170.2$ J/mol/K

$\Delta G = \Delta H - T\Delta S \Rightarrow \Delta G = 88\times10^{3} - (25+273)(170.2)$

$= 37.3$ kJ/mol

$\Delta G = -RT \ln K_{eq} \Rightarrow K_{eq} = e^{-\Delta G/RT} = e^{37.3\times10^{3}/8.314\cdot298}$

$= 2.29\times10^{-7}$

ΔH°= 88 kJ mol^{-1} ΔS°= 170.2 J mol^{-1} K^{-1}

ΔG°= 37.3 kJ/mol K_{eq}= 2.92×10^{-7}

(b) For the reaction above (part a) is this reaction spontaneous under the conditions stated?

no ΔG is (+)

(c) Calculate the equilibrium constant (K_{eq}) for this reaction at 400° C. Briefly state the assumption(s) you are making when doing this.

$K_{eq} = e^{-\Delta G/RT} = e^{37.3\times10^{3}/8.314\cdot(273+400)}$

K_{eq} = 1.27×10^{-3}

Assumptions:

ΔG° independent of temperature