

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

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

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

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

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)

Answer: no

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

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 $A \rightarrow \text{products}$, 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?

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

$$\ln \left(\frac{k_2}{k_1} \right) = \frac{-30 \times 10^3 \text{ J/mol}}{8.314 \text{ J/mol K}} \left(\frac{1}{273+25} - \frac{1}{273+0} \right)$$

$$\ln \frac{k_2}{k_1} = 1.109$$

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

[6] 3. Data for the reaction $G(l) + H(l) \rightarrow J(l)$ 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?

rate = $k [G]^m [H]^n$
 use methods of initial rates

$$\frac{R_1}{R_2} = \frac{k [G]^m (0.06)^n}{k [G]^m (0.02)^n} = \frac{2.5 \times 10^{-5}}{2.5 \times 10^{-5}}$$

$$3^n = 1$$

$$n = 0$$

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

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

$$m = 2$$

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

b. What is the value of k ?

use any rept

$$R_1 = k [G]^2 \Rightarrow 2.5 \times 10^{-5} \text{ m/s} = k (0.03 \text{ m})^2$$

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

[8] 4. For the second order reaction $A \rightarrow \text{products}$, the following data are obtained:

$$[A] = 1.512 \text{ M}, t = 0 \text{ min}$$

$$[A] = 1.490 \text{ M}, t = 1.0 \text{ min}$$

$$[A] = 1.469 \text{ M}, t = 2.0 \text{ min}$$

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

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{[A_f] - [A_i]}{t_f - t_i} = -\left(\frac{1.469 - 1.512}{2 - 0}\right)$$
$$= 0.0215 \text{ M/min}$$

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

$$\frac{1}{[A]_t} = akt + \frac{1}{[A]_0} \rightarrow \frac{1}{1.469 \text{ M}} = k(2 \text{ min}) + \frac{1}{1.512 \text{ M}}$$

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

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

$$\text{rate} = k[A]^2$$
$$= (9.68 \times 10^{-3} \text{ M}^{-1} \text{ min}^{-1})(1.469 \text{ M})^2$$
$$= 0.0209 \text{ M min}^{-1}$$

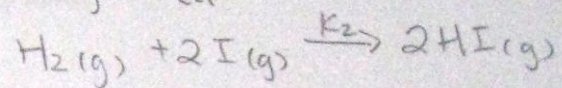
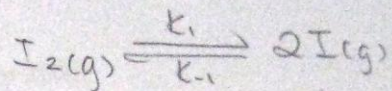
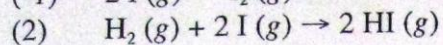
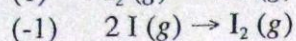
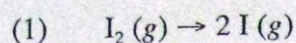
✓ d. How long will it take for the concentration of A to drop by half the initial concentration?

$$\frac{1}{[A]_t} = akt + \frac{1}{[A]_0}$$
$$\frac{1}{\frac{1.512 \text{ M}}{2}} = (9.68 \times 10^{-3} \text{ M}^{-1} \text{ min}^{-1})t + \frac{1}{1.512 \text{ M}}$$

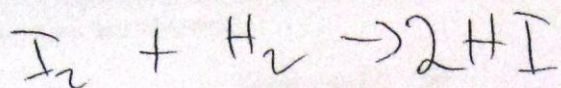
$$68.3 \text{ min} = t$$

✓ [8]

5. Hydrogen iodide is thought to form via the following mechanism:



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



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) $\text{rate} = k_2 [\text{H}_2] [\text{I}]^2$

need to get rid of $[\text{I}]$

from rapid equilibrium

$$\text{rate (1)} = \text{rate (-1)}$$

$$k_1 [\text{I}_2] = k_{-1} [\text{I}]^2$$

$$\frac{k_1}{k_{-1}} [\text{I}_2] = [\text{I}]^2 \quad \text{substitute}$$

$$\text{rate} = \frac{k_1}{k_{-1}} [\text{I}_2] [\text{H}_2]$$

c. What is a potential problem with this mechanism?

step (2) is trimolecular

Answers

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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;

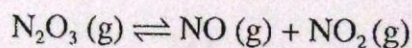
Total marks: 30

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

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

Marks

[5] 1 N_2O_3 (g) decomposes to NO (g) and NO_2 (g) with a $\Delta H^\circ = 40.5 \text{ kJ mol}^{-1}$ according to the equilibrium:



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:

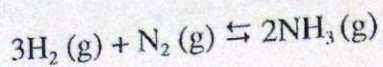
shift left

shift right

stay the same

[2] ✓ 2

Consider the following reaction:



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 $\text{NH}_3 = 60$ atm, pressure of $\text{H}_2 = 150$ atm, pressure of $\text{N}_2 = 80$ atm

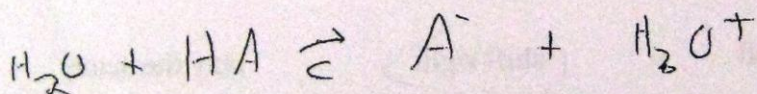
$$Q = \frac{P_{\text{NH}_3}^2}{P_{\text{H}_2}^3 P_{\text{N}_2}} = \frac{60^2}{150^3 \cdot 80} = 1.3 \times 10^{-5}$$

$$Q < K_p$$

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 ($K_a = 6.3 \times 10^{-5}$).



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

$$K = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]} = \frac{x^2}{0.05 - x} = 6.3 \times 10^{-5}$$

$$x \ll 0.05$$

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

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

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

[9] ✓ For the reaction $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$, K_p is 1.8 at 523 K.

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

$$K_p = K_c (RT)^{\Delta n_{\text{gas}}}$$
$$1.8 = K_c (523) (0.08314)^1$$

0.08314 bar L K⁻¹ mol⁻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	$0.1 - x$	$0.1 - x$

$$K_c = \frac{[\text{Cl}_2][\text{PCl}_3]}{[\text{PCl}_5]} = \frac{(0.1-x)(0.1-x)}{x}$$

$$x K_c = x^2 - 0.2x + 0.01$$

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

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

$$x = 0.0535$$

$$\text{moles } \text{PCl}_5 = 0.053 \text{ moles}$$

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.

$$Q = \frac{(0.1)(0.1)}{0.1} = 0.1$$

(2) K_c rxn goes to left

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

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

$$0 = x^2 - 0.242x + 5.8 \times 10^{-3}$$

use quadratic $x = 0.027$

$$[\text{PCl}_3] = [\text{Cl}_2] = 0.1 - 0.027 = 0.073 \text{ M}$$

$$[\text{PCl}_5] = 0.1 + x = 0.127 \text{ M}$$

15] The $\text{p}K_a$ 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?

$$\text{moles formic acid} = 1.1 \times 0.01 = 0.011 \text{ moles}$$

$$\text{moles base} = (0.1)(0.02) = 2 \times 10^{-3}$$

after base reacts with acid

$$\text{moles formic acid} = 0.011 - 0.002 = 0.009 = [\text{HA}]$$

$$\text{moles formate} = \text{moles base} = 0.002 = [\text{A}^-]$$

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

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

$$= 3.09_4$$

- [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.

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

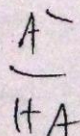
$$9.26 = 9.26 + \log \frac{A^-}{HA}$$

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

$$14 - 4.74$$

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

Yes



is between

0.1 and 10

Answers

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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

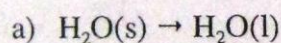
$$R = 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1} = 0.08315 \text{ L bar mol}^{-1} \text{ K}^{-1} = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \quad k = 1.38 \times 10^{-23} \text{ J K}^{-1} \quad N_a = 6.022 \times 10^{23}$$

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

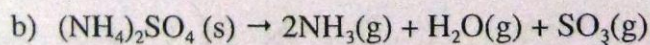
$$\Delta G = \Delta G^\circ + RT \ln Q_{\text{eq}}, \quad \ln K_{\text{eq}} = -\frac{\Delta H^\circ}{R} \frac{1}{T} + \frac{\Delta S^\circ}{R}, \quad \Delta G^\circ = -RT \ln K_{\text{eq}}, \quad \text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

Marks

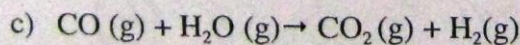
- [4] 1. For each reaction indicate the whether sign of ΔS is positive, negative or not possible to determine from the information given. Briefly justify your answers (use less than 12 words).



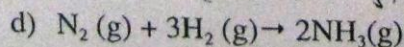
positive
solid to liquid



positive
solid to gas



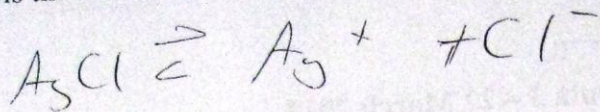
not possible to determine
same number of gas molecules on
each side



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} ?



if $S = \text{solubility}$

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

$$S = 1.34 \times 10^{-5} \text{ M}$$

✓ 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

$$K_{sp} = 1.8 \times 10^{-10} = [\text{Ag}^+][\text{Cl}^-]$$

$$= S(S + 0.04)$$

assume $S < 0.04$

$$1.8 \times 10^{-10} = S(0.04)$$

$$4.5 \times 10^{-9} \text{ M} = S$$

- [5] 3. Will AgCl precipitate after adding 10 mL of 1×10^{-6} M NaCl to 1 L of 0.1 M AgNO₃ (K_{sp} of AgCl = 1.8×10^{-10})? Support your answer with a calculation.

$$\begin{aligned} \text{moles Cl}^- &= 10^{-3} \text{ L} \times 1 \times 10^{-6} \text{ M} \\ &= 1 \times 10^{-9} \text{ moles} \end{aligned}$$

$$\begin{aligned} \text{moles Ag}^+ &= 1 \text{ L} \times 0.1 \text{ M} \\ &= 0.1 \text{ moles} \end{aligned}$$

$$[\text{Cl}^-] = \frac{1 \times 10^{-9} \text{ moles}}{1.01 \text{ L}} = 9.9 \times 10^{-9} \text{ M}$$

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

$$\begin{aligned} Q &= [\text{Cl}^-][\text{Ag}^+] = (9.9 \times 10^{-9})(0.099) \\ &= 9.8 \times 10^{-10} \end{aligned}$$

$$Q > K_{sp}$$

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.

$$\Delta H^\circ = \underline{0 \text{ kJ/mol}}$$

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

$$\text{slope} = 0 = -\frac{\Delta H^\circ}{R} \Rightarrow \Delta H^\circ = 0$$

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

$$\Delta S^\circ = 4R$$

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?

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

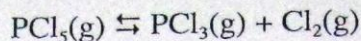
$$\Delta H = T\Delta S$$

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

$$1106^\circ\text{K} = T$$

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 .



	ΔH_f° (kJ mol ⁻¹)	S° (J mol ⁻¹)
$\text{PCl}_5(\text{g})$	-375.0	364.5
$\text{PCl}_3(\text{g})$	-287.0	311.7
$\text{Cl}_2(\text{g})$	0.000	223.0

$$\Delta H = -287 + 0 - (-375) = 88 \text{ kJ/mol}$$

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

$$\Delta G = \Delta H - T\Delta S \rightarrow \Delta G = 88 \times 10^3 - (298)(170.2) = 37.3 \text{ kJ/mol}$$

$$\Delta G = -RT \ln K_{eq} \Rightarrow K_{eq} = e^{-\Delta G/RT} = e^{-37.3 \times 10^3 / (8.314 \times 298)} = 2.29 \times 10^{-7}$$

$$\Delta H^\circ = 88 \text{ kJ/mol} \quad \Delta S^\circ = 170.2 \text{ J/mol} \cdot \text{K}^{-1}$$

$$\Delta G^\circ = 37.3 \text{ kJ/mol} \quad K_{eq} = 2.29 \times 10^{-7}$$

- (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.

$$K_{eq} = e^{-\Delta G/RT} = e^{-37.3 \times 10^3 / (8.314 \times (273 + 400))}$$

$$K_{eq} = 1.27 \times 10^{-3}$$

Assumptions:

ΔG° independent of temperature