THE UNIVERSITY OF ZAMBIA
SCHOOL OF NATURAL SCIENCES
DEPARTMENT OF CHEMISTRY
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TERM 2

CHE1000: INTRODUCTION TO CHEMISTRY

Tutorial Questions:

CHEMICAL KINETICS

QUESTION ONE

Consider the reaction

$$4PH_3(g) \rightarrow P_4(g) + 6H_2(g)$$

If, in a certain experiment, over a specific time period, 0.0048 mole of PH_3 is consumed in a 2.0-L container each second of reaction, what are the rates of production of P_4 and H_2 in this experiment?

QUESTION TWO

The rate of the reaction

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

depends only on the concentration of nitrogen dioxide below 225°C. At a temperature below 225°C the following date were collected:

Time/s	$[NO_2]$
0	0.500
1.20×10^3	0.444
3.00×10^3	0.381
4.50×10^3	0.340
9.00×10^3	0.250
1.80×10^4	0.174

Determine the rate Law, the integrated rate law and the value of the rate constant. Calculate $[NO_2]$ at 2.70×10^4 s after the start of the reaction.

QUESTION THREE

The decomposition of hydrogen peroxide was studied, and the following data were obtained at a particular temperature:

Time (s)	$[H_2O_2]$ (mol/L)
0	1.00
120 ±1	0.91
300 ±1	0.78
600 ±1	0.59
1200 ±1	0.37
1800 ±1	0.22
2400 ±1	0.13
3000±1	0.082
3600 ±1	0.050

Assuming that

$$Rate = -\frac{\Delta[H_2O_2]}{\Delta t}$$

determine the rate law, the integrated rate law, and the value of the rate constant. Calculate $[H_2O_2]$ at 4000. s after the start of the reaction.

QUESTION FOUR

At 40 ^{o}C, H_2O_2(aq) will decompose according to the following reaction:

$$2H_2O_2\,(aq) \rightarrow 2H_2O(l) + O_2(g)$$

The following data were collected for the concentration of H_2O_2 at various times.

Time (s)	$[H_2O_2]$ (mol/L)
0	1.000
2.16×10^4	0.500
4.32×10^4	0.250

a. Calculate the average rate of decomposition of H_2O_2 between 0 and 2.16×10^4 s. Use this rate to calculate the average rate of production of $O_2(g)$ over the same time period.

b. What are these rates for the time period 2.16×10^4s to 4.32×10^4 s?

QUESTION FIVE

$2I^-(aq) \quad + \; S_2O_8^{2-}(aq) \qquad I_2(aq) \qquad + \quad 2SO_4^{2-}(aq)$

$[I^-]_o$	$[S_2O_8^{2-}]_o$	Initial rates
0.080	0.040	12.5×10^{-6}
0.040	0.040	6.25×10^{-6}
0.080	0.020	6.25×10^{-6}
0.032	0.040	5.00×10^{-6}
0.060	0.030	7.00×10^{-6}

a) Determine the rate law
b) Calculate a value for the rate constant for each experiment and average value for the rate constant.

QUESTION SIX

A certain reaction has the following general form:

$$aA \rightarrow bB$$

At a particular temperature and $[A]_0 = 2.00 \times 10^{-2}\ M$, concentration versus time data were collected for this reaction, and a plot of ln[A] versus time resulted in a straight line with a slope value of $-2.97 \times 10^{-2}\ \text{min}^{-1}$.

a) Determine the rate law, the integrated rate law, and the value of the rate constant for this reaction.
b) Calculate the half-life for this reaction.
c) How much time is required for the concentration of A to decrease to $2.50 \times 10^{-3} M$?

QUESTION SEVEN

a) The rate constant for the gas phase decomposition of N_2O_5

$$\mathbf{N_2O_5 \rightarrow 2NO_2 + \tfrac{1}{2} O_2}$$

T (K)	**K (s^{-1})**
338	4.9×10^{-3}
318	5.0×10^{-4}
298	3.5×10^{-5}

i) Make appropriate graph using these data and determine the activation energy for this reaction

b) The reaction

$$(CH_3)_3CBr \quad + \quad OH^- \quad \rightarrow \quad (CH_3)_3COH \quad + \quad Br^-$$

in a certain solvent is first order with respect to $(CH_3)_3CBr$ and zero order with respect to OH^-. In several experiments, the rate constant *k* was determined at different temperatures. A plot of ln(*k*) versus 1/*T* was constructed resulting in a straight line with a slope value of -1.10×10^4 K and *y*-intercept of 33.5. Assume *k* has units of s^{-1}.

i) Determine the activation energy for this reaction.
ii) Determine the value of the frequency factor *A*.
iii) Calculate the value of *k* at 25^oC.

c) The activation energy for the decomposition of HI(*g*) to $H_2(g)$ and $I_2(g)$ is 186 kJ/mol. The rate constant at 555 K is 3.52×10^{-7} L/mol. s. What is the rate constant at 645 K?

QUESTION EIGHT

The rate of the reaction

$$NO_2(g) \quad + \quad CO(g) \quad \rightarrow \quad NO(g) + \quad CO_2(g)$$

depends only on the concentration of nitrogen dioxide below 225 ^oC. At a temperature below 225^oC, the following data were collected:

Time (s)	**[NO2] (mol/L)**
0	0.500
1.20×10^3	0.444
3.00×10^3	0.381
4.50×10^3	0.340
9.00×10^3	0.250
1.80×10^4	0.174

Determine the rate law, the integrated rate law, and the value of the rate constant. Calculate $[NO_2]$ at 2.70×10^4 s after the start of the reaction.

CHEMICAL EQUILIBRIA; AND ACID-BASE EQUILIBRIA

QUESTION ONE

a) Write the equilibrium expression (K) for each of the following gas-phase reactions.
   i) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$
   ii) $SiH_4(g) + 2Cl_2(g) \rightleftharpoons 2SiCl_4(g) + 2H_2(g)$
   iii) $2PBr_3(g) + 3Cl_2(g) \rightleftharpoons 2PCl_3(g) + 3Br_2(g)$
   iv) $NH_3(g) \rightleftharpoons ½N_2(g) + 3/2H_2(g)$

b) Write the equilibrium expression (K_p) for each reaction in the above question.

QUESTION TWO

a) Predict the shift in the equilibrium position that will occur for each of the following reactions when the volume of the reaction is increased:
   i) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
   ii) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
   iii) $H_2(g) + F_2(g) \rightleftharpoons 2HF(g)$
   iv) $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$
   v) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

b) At a particular temperature, 12 mol $SO_3(g)$ is placed into a 3.0L rigid container, and the SO_3 dissociates by the reaction

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$$

At equilibrium 3.0 mol SO_2 is present. Calculate the K for this reaction.

c) At 35 ^oC, $K= 1.6 \times 10^{-5}$ for the reaction:

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

Calculate the concentrations of all species at equilibrium for each of the following original mixture

i) 2.0 mol pure NOCl in a 2.0 L
ii) 1.0 mol NOCl and 1.0 mol NO in a flask 1.0 L

d) At 327 ^oC, the equilibrium concentrations are $[CH_3OH] = 0.15\ M$, $[CO] = 0.24\ M$, $[H_2] = 1.1\ M$

$$CH_3OH(g) \rightleftharpoons CO(g) + 2H_2(g)$$

-Calculate K_p at this temperature.

QUESTION THREE

At 25 ^{o}C, K= 0.090 foe the reaction

$H_2O(g) + Cl_2O(g) \rightleftharpoons 2HOCl(g)$

Calculate the concentration of all species at equilibrium for each of the following cases:

a) 1.0g H_2O and 2.0g Cl_2O are mixed in a 1.0 L flask.
b) 1.0 mol pure HOCl is placed in a 2.0 L flask

ACIDS AND BASES

QUESTION ONE

a) For each of the following aqueous reactions, identify the **acid**, the **base,** the **conjugate base**, and the **conjugate acid**.

i) $H_2O + H_2CO_3 \rightleftharpoons H_3O^+ + HCO_3^-$
ii) $C_5H_5NH^+ + H_2O \rightleftharpoons C_5H_5N + H_3O^+$
iii) $HCO_3^- + C_5H_5NH^+ \rightleftharpoons H_2CO_3 + C_5H_5N$

b) At 40 ^{o}C the values of K_w is 2.92 x10^{-14}.
i) Calculate the $[H^+]$ and $[OH^-]$ in pure water at 40 ^{o}C.
ii) What is the pH of pure water at 40 ^{o}C?
iii) If the hydroxide ion concentration in solution is 0.10 M, what is the pH at 40^{o}C?

QUESTION TWO

Values of K_w as a function of temperature are as follows:

Temperature (^{o}C)	**K_w**
0	1.14 x10^{-15}
25	1.00 x10^{-14}
35	2.09 x10^{-14}
40	2.92 x10^{-14}
50	5.47 x10^{-14}

a) Is the autoionization of water exothermic or endothermic?
b) Calculate [H+] and [OH-] in a neutral solution at 50.^{o}C.

QUESTION THREE

a) An antacid purchased at a local drug store has a pOH of 2.3. Calculate the pH, $[H^+]$, and $[OH^-]$ of this solution. Is the antacid acidic or basic?

b) Calculate the pH of each of the following solutions of a strong acid in water.

i)	0.10 *M* HCl	iii)	$1.0x\ 10^{-11}$ *M* HCl
ii)	5.0 *M* HCl	iv)	$6.2\ x10^{-12}$ *M* HNO_3

c) For propanoic acid ($HC_3H_5O_2$, $Ka = 1.3x10^{-5}$), determine the concentration of **all** species present, the pH, and the percent dissociation of a 0.100 *M* solution.

QUESTION FOUR

Complete the following information in the table given below:

	pH	**pOH**	**[H+]**	**[OH-]**	**Acidic, basic, or neutral**
Solution (a)	6.88				
Solution (b)				$8.4x10^{-14}$ M	
Solution (c)		3.11			
Solution (d)			$1.0x10^{-7}$		

	pH	**pOH**	**[H+]**	**[OH-]**	**Acidic, basic, or neutral**
Solution (a)	9.63				
Solution (b)				$3.9x10^{-6}$ M	
Solution (c)			0.027 M		
Solution (d)		12.2			
Solution (e)	**-1.0**				

BUFFERS

QUESTION ONE

a) Which of the following can be classified as buffer solutions?
   - i) 0.25 *M* HBr 1 0.25 *M* HOBr
   - ii) 0.15 *M* $HClO_4$ 1 0.20 *M* RbOH
   - iii) 0.50 *M* HOCl 1 0.35 *M* KOCl
   - iv) 0.70 *M* KOH 1 0.70 *M* $HONH_2$
   - v) 0.85 *M* H_2NNH_2 1 0.60 *M* $H_2NNH_3NO_3$

b) A certain buffer is made by dissolving $NaHCO_3$ and Na_2CO_3 in some water. Write equations to show how this buffer neutralizes added H^+ and OH^-.

c) Calculate the pH of each of the following solutions.

- i) 0.100 *M* propanoic acid ($HC_3H_5O_2$, $K_a = 1.3 \times 10^{-5}$)
- ii) 0.100 *M* sodium propanoate ($NaC_3H_5O_2$)
- iii) Pure H_2O
- iv) A mixture containing 0.100 *M* $HC_3H_5O_2$ and 0.100 *M* $NaC_3H_5O_2$
- v) Calculate the pH of each of the following buffered solution; 0.50 *M* $C_2H_5NH_2$/0.25 *M* $C_2H_5NH_3Cl$

QUESTION TWO

a) Consider a buffer solution where [weak acid] > [conjugate base]. How is pH of the solution relate to the pK_a value of the weak acid? If [conjugate base] > [weak acid], how
is pH related to pK_a?

b) Consider the titration of 40.0 mL of 0.200 *M* $HClO_4$ by 0.100 *M* KOH. Calculate the pH of the resulting solution after the following volumes of KOH have been added

- i. 0.0 mL
- ii. 10.0 mL
- iii. 40.0 mL
- iv. 80.0 mL
- v. 100.0 mL

SOLUBILITY PRODUCT QUESTIONS

QUESTION ONE

a) Write a balanced equation for dissolution reactions and the corresponding solubility product expressions for each of the solids:

i. $AgC_2H_3O_2$ iii. $Ca_3(PO_4)_2$

ii. $Al(OH)_3$ iv. Ag_2CO_3

b) Use the following data to calculate the K_{sp} value for each solid.

i) The solubility of CaC_2O_4 is 4.8 x10^{-5} mol/L.
ii) The solubility of $Pb_3(PO_4)_2$ is 6.2 x10^{-12} mol/L.
iii) The solubility of Li_2CO_3 is 7.4 x10^{-2} mol/L.

c) The K_{sp} for silver sulfate (Ag_2SO_4) is 1.2 x10^{-5}. Calculate the solubility of silver sulfate in each of the following:

i) water
ii) **b.** 0.10 *M* $AgNO_3$
iii) **c.** 0.20 *M* K_2SO_4
iv) Comment on your results in *i-iii.*

QUESTION TWO

a) The K_{sp} of $Al(OH)_3$ is 2x10^{-32}. At what pH will a 0.2 M Al^{3+} solution begin to show precipitation of $Al(OH)_3$?

b) A solution contains 1.0 x 10^{-6} *M* $Sr(NO_3)_2$ and 5.0 x 10^{-7} *M* K_3PO_4. Will $Sr_3(PO_4)_2(s)$ precipitate? [K_{sp} for $Sr_3(PO_4)_2$ = 1.0 x 10^{-31}].

c) A solution is prepared by mixing 50.0 mL of 0.10 *M* $Pb(NO_3)_2$ with 50.0 mL of 1.0 *M* KCl. Calculate the concentrations of Pb^{2+} and Cl^- at equilibrium. [K_{sp} for $PbCl_2(s)$ is 1.6 x10^{-5}.]
