THE UNIVERSITY OF ZAMBIA
Department of Chemistry

CHE2615: Basic Physical Chemistry

Test 2 Chemical Equilibrium

Instructions: Answer all questions
Duration: 1 hour

Question 1
In the reaction:

$$2NH_3 \rightarrow N_2 + 3H_2$$

Suppose that initially 0.80 mol of NH_3, 0.70 mol of H_2, and 0.40 mol of N_2 are present. At a later time t, 0.55 mol of H_2 is present. Find ξ and find the moles of NH_3 and N_2 present at t.

Question 2
$K_p^\circ = 6.51$ at 800 K for the ideal-gas reaction $2A + B \leftrightarrow C + D$. If 3.0 mol of A, 1.0 mol of B, and 4.0 mol of C are placed in an 8000 cm^3 vessel at 800 K, find the equilibrium amounts of all species.

Question 3
Calculate K_c and K_x for the reaction:

$$N_2O_4(g) \leftrightarrow 2NO_2(g)$$

for which $K_p = 0 \cdot 157$ atm at 27°C and 1 atm pressure.

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

$\Delta n = \Sigma$ Products $- \Sigma$ Reactants

THE UNIVERSITY OF ZAMBIA
SCHOOL OF NATURAL SCIENCES
DEPARTMENT OF CHEMISTRY

Basic Physical Chemistry – CHE2615 (2018/19)

25th October 2019

Test 2

Answer all questions. **Time: 1 hour 30 Minutes**

Question 1

(a) For the reaction below, if substance A is disappearing at a rate of $1.82 \times 10^{-2} molL^{-1}s^{-1}$, at what rate is C appearing?

$$3A+3B \rightarrow 5C+2D$$

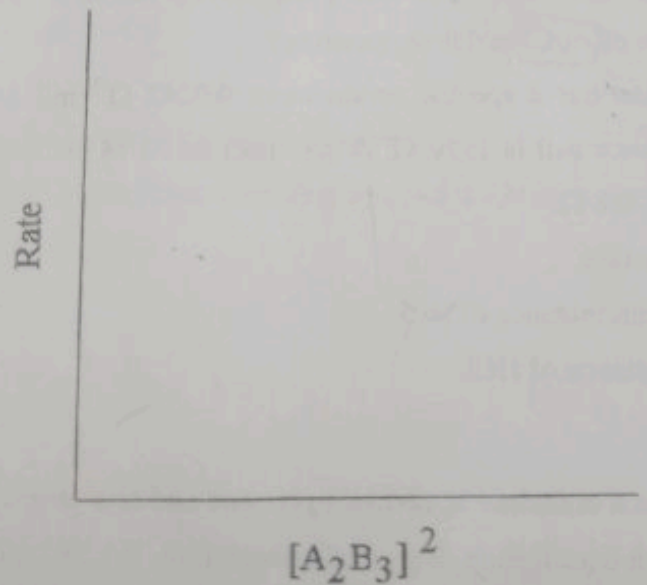
[3]

(b) The decomposition of A_2B_3 is second order with a $k = 6.5\times10^{-5}M^{-1}s^{-1}$ at 25°C. If the initial concentration is 0.50M.

(i) What is the concentration after 3min?

(ii) What is the half-life for this reaction?

(iii) Copy and complete the sketch for the above reaction



[7]

(c) The decomposition of AB is first order with a $k = 2.3\times10^{-7}s^{-1}$ at 45°C. If the initial concentration is 0.25 M, what is the concentration after 2.3 min? What is the half-life for this reaction? [5]

Question 2

(a) A CHE2615 student trying to determine the activation energy of a reaction, measures temperature in °C and the rate constant.

(i) Give the equation she can use to calculate the Activation energy. [2]

(ii) Another student suggests a plot of the data, which can be used to determine the activation energy. Which graph will she plot, draw a sketch. [5]

(iii) What is intercept of the line? [2]

(iv) What is the slope of the line? [2]

(v) How will the activation energy change if she decides to use a catalyst? [2]

(b) Identify the each term in the following equations: [2]

$$ln\frac{N}{N_0} = -\lambda t$$

Question 3

a) The limiting molar conductances of KCl, KNO_3, and $AgNO_3$ are 14.99 x 10^{-3}S m^2 mol^{-1}, 14.50 x 10^{-3}S m^2mol^{-1}, and 13.34 x 10^{-3}S m^2mol^{-1}, respectively (all at 25°C). What is the limiting molar conductance of AgCl at this temperature? [4]

b) A 0.002 M $NaNO_3$ solution has a specific conductance 0.0242 Ω^{-1} m^{-1} and its **electric resistance** (R) in conductance cell is 1650 Ω. A solutions 0.002 M HCl measured in the same cell had resistance of 468 Ω.

(i) Calculate the cell constant. [3]

(ii) Determines specific conductance of HCl. [3]

(iii) Find the molar conductance of HCl. [4]

Question 4

When nitrogen tetroxide is held in a container at constant pressure and near room temperature or higher, it rather quickly reaches an equilibrium degree of dissociation. If 1.588 g of nitrogen tetroxide gives a total pressure of 1.0133 bar when partially dissociated in a 500 cm^3 glass vessel at 25 C.

a) What is the extent of reaction? [4]

b) What is the value of K_p? [7]

c) What is the extent of reaction at a total pressure of 0.5 bar? [4]

Question 5

a) The reaction taking place in the cell:

$$Mg(s) \,|\, Mg^{2+}(aq), Cl^{-}(aq) \,|\, Cl_2\,(g, 1\ atm) \,|\, Pt$$

is found to have an entropy change of -337.3 $JK^{-1}\ mol^{-1}$ under standard conditions. What is the temperature coefficient for the cell? [4]

b) Consider the cell:

$$Ag|AgBr(s)|KBr(aq, 0.050\ M)||\ Cd(NO_3)_2(aq, 0.010\ M)|Cd.$$

[3]

i) Write the cell reaction.

ii) Given that

$AgBr + e^- \rightarrow Ag + Br^-$ 0.0713V

$Cd^{2+} + 2e^- \rightarrow Cd$ - 0.403 V

[3]

Write the Nernst equation for the cell.

iii) Use the Debye–Hückel limiting law and the Nernst equation to estimate the cell potential at 25°C. [5]

THE UNIVERSITY OF ZAMBIA
CHEMISTRY DEPARTMENT

CHE 2615/2415 quiz 1

Duration 10 minutes

1. The properties of a closed system change following the relation between pressure and volume as $\mathbf{pV = 3.0}$ where p is in bar V is in m^3. Calculate the done when pressure increases from 1.5 bar to 7.5 bar.

AUSTIN GERRARD

THE UNIVERSITY OF ZAMBIA
Department of Chemistry

CHE2615: Basic Physical Chemistry

Assignment/Tutorial Sheet 2: ELECTROCHEMICAL CELL
Due date: 24th October 2019 at 16:00hrs in room 322 (submit Q2 and Q7)

1. A 0.002 M $NaNO_3$ solution has a specific conductance 0.0242 Ω^{-1} m^{-1} and its **electric resistance** (R) in conductance cell is 1650 Ω. A solutions 0.002 M HCl measured in the same cell had resistance of 468 Ω.

   (i) Calculate the cell constant.
   (ii) Determines specific conductance of HCl.
   (iii) Find the molar conductance of HCl.

2. The quantity l/A of a conductance cell is called the cell constant. Find the cell constant for a conductance cell in which the conductance of a 0.100 M KCl solution is 0.01178 S at 25 °C. The equivalent conductance for 0.100 M KCl at 25 °C is 128.96 S cm^2 mol^{-1}. If a 0.0500 M solution of an electrolyte has a measured conductance of 0.00824 S using this cell, what is the equivalent conductance of the electrolyte?

3. Consider a cell $Zn(s)|ZnCl_2(0.000772\ M)||\ AgCl(s)|Ag(s)$ at 25°C, with a measured emf 1.2475V.

   (i) Write the overall cell reaction
   (ii) Calculate the mean activity coefficient and activity of $ZnCl_2$ using the Debye-Huckel limiting law (show your working)
   (iii) Calculate the emf of the cell

4. The solubility of AgCl in water at 25°C is 1.274×10^{-5} mol dm^{-3}. Assuming that the Debye-Huckel limiting law applies,
   a) Calculate ΔG° for the process $AgCl(s) \rightarrow Ag^+(aq) + Cl^-(aq)$
   b) Calculate the solutbility of AgCl in an 0.005 M solution of K_2SO_4

5. The following data has been reported for the cell:

   $Ag(s)|AgBr(s)|HBr(aq)|Br_2(g,1atm)|Pt(s)$

   The right electrode is the cathode.

t(°C)	442.3	456.0	490.9	521.4	538.3	556.2
E(V)	0.8031	0.7989	0.7887	0.7803	0.7751	0.7702

   (a) Perform quadratic regression fitting of the above data.
   (b) Calculate the emf of the cell at 500.0 °C.
   (c) Find the temperature coefficient for this cell in V K^{-1}.

AUSTIN BANDA (KB) BANDA KALECA.

UNIVERSITY OF ZAMBIA
DEPARTMENT OF CHEMISTRY

CHE2615 **TUTORIAL SHEET 1** **OCTOBER 2019**

1. Fuel cells provide an attractive alternative energy source. They require an H2 feed stream to operate. Consider a fuel cell based on the direct conversion of methanol to form hydrogen:

$$H_2O(g) + CH_3OH(g) \leftrightarrow CO_2(g) + 3H_2(g)$$

The reaction is carried out at 60oC and low pressure, with a feed of twice as much water as methanol. The equilibrium extent of reaction is $\xi = 0.87$. How many moles of H_2 can be produced per mole of CH_3OH in the feed? What is the mole fraction of H_2?

2. Acetic acid is esterified in the liquid phase with ethanol at 100°C and atmospheric pressure to produce ethyl acetate and water according to the reaction:

$$CH_3COOH(l) + C_2H_5OH(l) \rightarrow CH_3COOC_2H_5(l) + H_2O(l)$$

If initially there is one mole each of acetic acid and ethanol, estimate the mole fraction of ethyl acetate in the reacting mixture at equilibrium. Given that:

Name	ΔH^o_{f298}	ΔG^o_{f298}
CH_3COOH	- 484,500	- 389,900
C_2H_5OH	- 277,690	- 174,780
$CH_3COOC_2H_5$	- 480,000	- 332,200 J
H_2O	- 285,830	- 237,129

3. Consider the association of potassium atoms in the vapor phase to form dimers.

$2K(g) \rightleftharpoons K_2(g)$

Suppose we start with 2 moles of K(g) and no dimers. Derive an expression for K_p (T) in terms of ξ, the extent of reaction at equilibrium, and the pressure, P.

4. Nitrogen trioxide dissociates according to the reaction

$N_2O_3\ (g) = NO_2\ (g) + NO\ (g)$

When one mole of N_2O_3 (g) is held at 25 °C and 1 bar total pressure until equilibrium is reached, the extent of reaction is 0.30. What is $\Delta_r G°$ for this reaction at 25 °C?

5. At 55 °C and 1 bar the average molar mass of partially dissociated N_2O_4 s 61.2 mol^{-1}.
Calculate
(a) ξ and K for the reaction $N_2O_4\ (g) = 2NO_2\ (g)$.
(b) Calculate ξ at 55 °C if the total pressure s reduced to 0.1 bar.

AUSTIN GERRARD BANDA.

THE UNIVERSITY OF ZAMBIA

DEPARTMENT OF CHEMISTRY

CHE 2615/2415 TUTORIAL/ASSIGNMENT

Answer all questions and submit solutions by 12:00 hrs. Friday, 2nd September 2019

for Open other Systems

Q1. What is (a) a system (b) an open system (c) an isolated system (d) a closed system? What is the definition of a property of a system? Pressure, temperature, mass, volume, density, total energy; are these properties intensive or extensive?

Q2. a) What is the first law of thermodynamics?

b) What is the classical sign convention for heat and work?

Q3. Three kilograms of nitrogen gas at 27oC, 0.15 MPa are compressed isothermally to 0.3 MPa in a piston-cylinder device. Show that nitrogen can be expected to behave as an ideal gas during this process and determine the minimum work of compression, in kJ. For nitrogen: R = 0.2968 kJ/(kgK), T_{cr} = 126.2K, P_{cr} = 3.39MPa.

Q4. Air undergoes a constant pressure cooling process in which the temperature decreases by 100°C. What is the magnitude and direction of the work for this process? Assume that air behaves as an ideal gas and that R_{air} = 0.287 kJ/kg K.

Q5. a) Starting from the definition of enthalpy, show that Cp = Cv + R for an ideal gas.

b) How is the specific heat ratio (k) defined?

Q6. Suppose that a chemical reaction is caused to occur in a bulb to which is attached a capillary tube having a cross-section area of 2.50mm^3. The tube is open to the atmosphere (pressure = 101.325 kPa), and during the course of the reaction the rise in capillary is 2.40 cm. Calculate the work done by the reaction system.

Q7. Suppose that water is boiling at its boiling point is maintained in a cyclinder that has a frictionless piston. For equilibrium to be established, the pressure that must be applied to the piston is 1 atm (101.325 kPa). Suppose that we now reduce the external pressure by an infinitesimal amount in order to have a reversible expansion. If the piston sweeps out a volume of 2.00 dm^3, what is the work done by the system?

AUSTIN GERRARD BANDA

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Basic Physical Chemistry – CHE2615 (2019)

Tutorial sheet 1 (Knietics)

Submit all the questions on Monday 30th September 2019 before 12:00 hrs.

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1. Consider the decomposition of N_2O_5 to give NO_2 and O_2:

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

	Concentration (M)		
Time (s)	$[N_2O_5]$	$[NO_2]$	$[O_2]$
0	0.0200	0	0
100	0.0169	0.0063	0.0016
200	0.0142	0.0115	0.0029
300	0.0120	0.0160	0.0040
400	0.0101	0.0197	0.0049
500	0.0086	0.0229	0.0057
600	0.0072	0.0256	0.0064
700	0.0061	0.0278	0.0070

(a) Calculate the average rate of the reaction.

(b) Calculate the average rate of decomposition of N_2O_5 and average rate of formation of O_2 between 600- 700 s.

(c) Calculate the instantaneous rate at 300s.

2. The reaction of nitric oxide with hydrogen at 1280°C is:

$$2NO(g) + 2H2(g) \rightarrow N2(g) + 2H2O(g)$$

From the following data, determine the rate law and rate constant with its units .

EXPERIMENT	[NO] (M)	$[H_2]$ (M)	Initial Rate (M/minute)
1	0.010	0.010	0.0070
2	0.020	0.030	0.196
3	0.010	0.020	0.014

3. The rate of decomposition of azomethane ($C_2H_6N_2$) was studied by monitoring the partial pressure of the reactant as a function of time.
Determine the order of reaction and calculate the rate constant for the reaction.

Time (s)	0	100	150	200	250
P (mm Hg)	284	220	193	170	150

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CHE2615: PHYSICAL CHEMISTRY ASSIGNMENT 2 September 2022

18

1. A sample of nitrogen collected in the laboratory occupies a volume of 725 mL at a pressure of 0.971 atm. What volume will the gas occupy at a pressure of 1.40 atm, assuming the temperature remains constant?
2. Chlorine gas is collected by water displacement at a temperature of 19°C. The total volume is 1.45 L at a pressure of 156.5 kPa. Assume that no chlorine gas dissolves in the water. What is the volume of chlorine corrected to STP?
3. If you placed 3 moles of N_2 and 4 moles of O_2 in a 35 L container at a temperature of 25^0 C, what will the pressure of the resulting mixture of gases be?
4. I have a balloon that can hold 100 L of air. If I blow up the balloon with 3 moles of oxygen gas as a pressure of 1 atmosphere, what is the temperature of the balloon?
5. An ideal monoatomic gas initially at 298 K and a pressure of 5 atm is expanded to a final pressure of 1 atm: (a) Isothermally and reversibly (b) isothermally against a constant pressure of 1 atm. Calculate for each expansion: (i) the final temperature of the gas (ii) the heat absorbed by the gas (iii) the change in internal energy of the gas (iv) the enthalpy change of the gas.
6. Determine the entropy change that takes place when 1 mole of ammonia (a) passes from liquid state to gaseous state at its boiling point, – 33 °C (b) as a gas at – 33 °C comes to room temperature, 25 °C. Assume that the heat capacity is constant at 8.9 $cal°C^{-1}mol^{-1}$. $\Delta H_{vap} = 5570$ cal mol^{-1}.
7. Iodine crystals sublime at 25 °C and atmospheric pressure according the equation shown below.

$$I_2(s) \rightleftarrows I_2(g)$$

It is found that the enthalpy change is 9.41 kcal mol^{-1} and the change in entropy is 20.6 $cal°C^{-1}mol^{-1}$. At what temperature will solid iodine be in equilibrium with the iodine gas?

8. What is the change in entropy if a sample of solid magnesium is heated from 27 °C to 227 °C at 1 atm. The specific heat capacity in the region 0 – 600 °C varies according to the expression

$$Cp = 26.0 + 5.46 \times 10^{-2}T - 28.6 \times 10^{4}\, T^{-2}$$

9. Calculate the enthalpy change of formation of $Ca(OH)_2(s)$ from its elements using the following thermochemical data: use the Hess's cycle

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$	$\Delta H° = -286$ kJ
$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s)$	$\Delta H° = -64$ kJ
$Ca(s) + \frac{1}{2}O_2(g) \rightarrow CaO(s)$	$\Delta H° = -634$ KJ

10. Calculate the quantity of heat required to (a) convert 1 L of water at 30 °C to water at 60 °C and (b) heat a 1 kg block of aluminium from 30 °C to 60 °C. Assume that the specific heat of water and aluminium is 1 cal $g^{-1}°C^{-1}$ respectively.
11. Calculate the change in the entropies of the system and the surroundings, and the total change in entropy, when the volume of a sample of argon gas of mass 21 g at 298 K and 1.50 bar increases from 1.20 dm^3 to 4.60 dm^3 in (a) an isothermal reversible expansion, (b) an isothermal irreversible expansion against $p_{ex} = 0$, and (c) an adiabatic reversible expansion.
12. Calculate ΔS (for the system) when the state of 2.00 mol diatomic perfect gas molecules, for which $C_{p,m} = 7/2\ R$, is changed from 25° C and 1.50 atm to 135° C and 7.00 atm. How do you rationalize the sign of ΔS?

SUBMIT SOLUTIONS TO QUESTIONS: 3 – 7, 8, 11 BY WEDNESDAY 19 SEPTMBER.