CHUKA  **UNIVERSITY**

UNIVERSITY EXAMINATIONS

EXAMINATION FOR THE AWARD OF DEGREE OF BACHELOR OF SCIENCE IN CHEMISTRY

CHEM 120: PHYSICAL CHEMISTRY 1

STREAMS: **TIME: 2 HOURS**

DAY/DATE: TUESDAY 23/03/2021 **11.30 A.M – 1.30 P.M**

INSTRUCTIONS:

Answer question one and any other two questions

USEFUL DATA

1 cal = 4.184J

1 atm = 101.325k pa = 760 Torr

1 L atm = 101.325 J

$\theta\,℃$ = **T° k -273.15/0**$℃ = 273$

1 J = 1 kg $m^2 s^{-2}$ **= 1 AVS**

1 N = 1 kgm s^{-2}

1 pa = 1N M^{-2}**=1 kg** $m^{-1}s^{-2}$ **1J**m^{-3}

C= 3.0 x 10^8 **m5**

R = 8.314J $K^{-1}mol^{-1} = 8.314\,x\,10^{-2}$ **L bar** $k^{-1}mol^{-1}$

R = 8.20574 x 10^{-2} **L atm** $k^{-1}mol^{-1}$

R = 6.23637 x 10^1 L**Torr** $k^{-1}mol^{-1}$

H= 6.62608 x 10^{-34}**JS**

F = NA e = 9.64853 x 10^4 **(**mol^{-1}

h= $\frac{h}{2\pi}$ **= 1.05457 x** 10^{-34} **JS**

K = 1.38065 x $10^{-23} J K^{-1}$

e=1.602176 x $10^{-19} C$

1 $m^3 = 10^3 dm^3$

QUESTION ONE (30 MARKS)

1.(a)(i) Briefly discuss how kinetic theory explains the existence of a minimum temperature, ok. [3 marks]

(ii) Write short notes on how kinetic theory explains the greater effusion rate of a gas with a low formula mass compared to one with a higher formula mass. [3 marks]

(iii) Calculate the density of moist air in gm $litre^{-1}$ of moist air at 298.15k and I bar pressure when dry air contains 79% nitrogen and 21% oxygen by volume. The relative humidity of moist air is 60% . The aqueous tension at 298.15k is 0.032 bar { R = 0.0821L atm $K^{-1} mol^{-1}$ 1 atm = 1.01325 bar } [3 marks]

(b) (i) From an economic point of view, why would an industrial corporation want to know about the factors that affect the rate of a reaction. [5 marks]

(ii) The reaction iodine with hypochloride ion ocl- (which is found in liquid bleach) follows the equation : O $Cl^{-¿+I^{-¿\rightarrow OI^{-¿+Cl^{-¿¿}}¿}}$

It is a rapid reaction that gives the following rate data

Initial concentration

$mol\,L^{-1}$

$ocl^{-¿¿}$ $[I^{-¿¿}$ Rate of formation of $cl^{-¿(mol\,L^{-1}5^{-1})¿}$

1.7×10^{-3}	1.7×10^{-3}	1.75×10^{4}
3.4×10^{-3}	1.7×10^{-3}	3.5×10^{4}
1.7×10^{-3}	3.4×10^{-3}	3.50×10^{4}

(I) Determine the rate law for the reaction. [2½ marks]

(II) Calculate the value of the rate constant with its correct units.

(c) The reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ is endothermic, with $\Delta H° = +56.9 k¿$. How will the amount of NO_2 at equilibrium be affected by:

(i) Adding $N_2O_4(g)$ [1 mark]

(ii) Lowering the pressure by increasing the volume of the container. [1 mark]

(iii) Raising the temperature. [1½ marks]

(iv) Adding a catalyst to the system? [1½ marks]

(v) Which of the above changes will alter the value of K_c [½ mark]

(d) 25ml of a 0.15M solution of the ammonia solution ($K_b = 1.75 x\, 10^{-5}$ ¿ is titracted with 0.3 M H_2SO_4.. Calculate the pH at the ;

(i) Start of titration [2 marks]

(ii) After addition of 4ml, 6.25 ml and 10ml of titrant. [5 marks]

QUESTION TWO (20 MARKS)

2.(a) (i) Calculate the electron affinity of chlorine from the following data at 298K.

Na(g) = $Na^{+}¿(g)+e^{-}¿\Delta H° = 499.8\, KJ¿¿$

½ $cl_2(g) = cl(g)\, \Delta H° = +120.9\, KJ$

Na(s) = Na(g) $\Delta H° = +108.3\, KJ$

Na(s) +½ $cl_2(g)$= Nacl(s) $\Delta H = 411.3\, KJ$

$Na^{+}¿(g)+cl^{-}¿(g) = Nacl(s) \Delta H° = -975.4\, KJ¿¿$

(ii) Using the data (all values in KJ mol^{-1} at 298K) given below. Calculate the bond enthalpies of c-c and C- H bonds.

$\Delta H°$(combustion) $C_2H_6 = -1556.45$

$\Delta H°$(combustion) $C_2H_6 = -2217.52$

$\Delta H°_{C}(S) \rightarrow C(g) = +719.65$

$\Delta H°_{H} \rightarrow +436.0$

$\Delta H°F\, H_2O(L) \rightarrow -285.8$

$\Delta H° CO_{2(g)} \rightarrow -393.30$ [5 marks]

(b) From the data at 298K

$½H_2(g) + ½O_2(g) = \text{OH(g)}\ \Delta H° = 42.09\text{KJ}\ mol^{-1}$

$H_2(g) + ½O_2(g) = H_2O\text{(g)}\ \Delta H° = 241.83\ \text{KJ}\ mol^{-1}$

$H_2(g) = 2H(g)\ \ \Delta H° = 435.94\text{KJ}\ mol^{-1}$

$O_2(g) + 2O(g)\ \Delta H° = 495.04\text{KJ}\ mol^{-1}$

Compute $\Delta H°$ for reaction

(i)OH(g) = H(g) +Og [1½ marks]

(ii)$H_2O(g)$ = 2H(g) + O(g) [1½ marks]

(iii) $H_2O(g) = H(g) + OH(g)$ [1½ marks]

(c) CO_2 reacts with graphite to form CO. Based on the following data given below, calculate ΔE (change in internal energy for the reaction)

$C_{graphite} + CO_2(g) \rightarrow 2CO(g)$

Δ H (enthalpy change) at 25°C and 1.0 bar pressure = 172.46KJ. Density of graphite = 2.25g cm^{-1} {R=8.314J $mol^{-1}K^{-1}$, I bar = $10^5\, pa$, 1 pa = 1NM^{-2} = 1kg $m^{-1}s^{-2}$ = 1Jm^{-3}}

[4½ marks]

(d)(i) Calculate the potential of the electrochemical cell shown above. [1½ marks]

(ii) Calculate the concentration of $Fe^{3+¿¿}$ in an electrochemical cell similar to that shown above, if the concentration of HCL in the left hand cell is 1.0m, the concentration of Fe cl_2 in the right hand cell is 0.0151m and the measured potential is +0.546v.

$Agcl_{(s)} + e^{-¿¿} \rightleftharpoons Ag(s) + cl^{-¿+0.223¿}$ E° at $25° V$

$Fe^{3+¿¿} + e^{-¿ \rightleftharpoons Fe^{2+¿+0.771¿¿}}$ F = 96,487 [1½ marks]

QUESTION THREE (20 MARKS)

3.(a) (i) Write short notes on the following:

(I) Indicator errors in determination of end point of a titration using visual indicator. [6 marks]

(II) Selection of pH indicator for a particular titration. [2 marks]

(ii) Discuss Buffer capacity. [3 marks]

(iii) Calculate the buffer capacity of a buffer solution containing 0.4M NH_3 and 0.2M NH_4cl [$pk_b = 4.76¿$ [3 marks]

(b) For the isomerization of cyclopropane to propene.

△ → = propene

Cyclopropane C_3H_7

C_3H_7

The following data were obtained

T°C	477	523	577	623
K,S^{-1}	0.00018	0.0027	0.030	0.26

Calculate without using graph;

(i) Frequency factor. [5 marks]

(ii) The activation energy. [½ mark]

(iii) Fraction of molecules with minimum energy for reaction at temperature 523℃. [R = 8.314J $mol^{-1}K^{-1}$ [½ mark]

QUESTION FOUR (20 MARKS)

4.(a) (i) For the reaction

$N_2(g)+3H_2(g)\rightleftharpoons 2NH_3(g)+Heat$

Write expression for K_c and K_p and show how they are related when the initial moles of $N_2(g)$ and $H_2(g)$ were different. [6 marks]

(ii) 16.4g potassium iodine was dissolved in 500cm^3 of water and about 1.0g of iodine was dissolved in 100 cm^3 of benzene. The two solutions were then mixed and allowed to stand subsequent titrations showed 10 cm^3 of the benzene layer was equivalent of 5.1 cm^3 of m/10 sodium thiosulphate while 50 cm^3 of the aqueous layer was equivalent to 2.9 cm^3 of m/10 thiosulphate.The distribution coefficient between benzene and water is 130. Calculate the value of equilibrium reaction $KI+I_2+KI_3$

[I = 126.9043, 0 = 15.9994, k = 39.0989, S = 32.066J

(b) (i) Comment on the following statement: " Gases cannot be liquefied unless their temperature are lowered to values equal to or below their critical temperature. [12 marks]

(ii) The compressibility factor z for N_2 at -50℃ and 800—atm pressure is 1.95 and at 100℃ and 200 atm it is 1.10. A certain mass of nitrogen occupied a volume of 1.0 litre at -50℃ and 800 atm. Calculate the volume occupied by the same quality of nitrogen at 100℃ and 200 atm. [1½ marks]

(c) In an experiment to determine the percentage of gaseous mixture at 25℃, a gas cylinder was evacuated and a gas Y was let in until the pressure was one atmosphere. The cylinder was then weighted and compressed inert gas X was forced in until W grams had been added. If the volume of the cylinder was 82 litres, calculate the;

(i) Mass of gas x that gives a mixture of composition 20 mole percent Y and 80 mole percent X given the molar mass of X is 20g. [3 marks]

(ii) Total pressure of the final of mixture. [1½ marks]
