

CHEM 120

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: FRIDAY 20/12/2024**

**2.30 P.M – 4.30 P.M**

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**INSTRUCTIONS:**

***ANSWER QUESTION ONE AND ANY OTHER TWO QUESTIONS***

## General data and fundamental constants

Quantity	Symbol	Value	Power of ten	Units
Speed of light	$c$	2.997 925 58*	$10^8$	$\text{m s}^{-1}$
Elementary charge	$e$	1.602 176	$10^{-19}$	C
Faraday's constant	$F = N_A e$	9.648 53	$10^4$	$\text{C mol}^{-1}$
Boltzmann's constant	$k$	1.380 65	$10^{-23}$	$\text{J K}^{-1}$
Gas constant	$R = N_A k$	8.314 47		$\text{J K}^{-1} \text{mol}^{-1}$
		8.314 47	$10^{-2}$	$\text{dm}^3 \text{bar K}^{-1} \text{mol}^{-1}$
		8.205 74	$10^{-2}$	$\text{dm}^3 \text{atm K}^{-1} \text{mol}^{-1}$
		6.236 37	10	$\text{dm}^3 \text{Torr K}^{-1} \text{mol}^{-1}$
Planck's constant	$h$	6.626 08	$10^{-34}$	J s
	$\hbar = h/2\pi$	1.054 57	$10^{-34}$	J s
Avogadro's constant	$N_A$	6.022 14	$10^{23}$	$\text{mol}^{-1}$
Atomic mass constant	$m_u$	1.660 54	$10^{-27}$	kg
Mass				
electron	$m_e$	9.109 38	$10^{-31}$	kg
proton	$m_p$	1.672 62	$10^{-27}$	kg
neutron	$m_n$	1.674 93	$10^{-27}$	kg
Vacuum permittivity	$\epsilon_0 = 1/c^2 \mu_0$	8.854 19	$10^{-12}$	$\text{J}^{-1} \text{C}^2 \text{m}^{-1}$
	$4\pi\epsilon_0$	1.112 65	$10^{-10}$	$\text{J}^{-1} \text{C}^2 \text{m}^{-1}$
Vacuum permeability	$\mu_0$	$4\pi$	$10^{-7}$	$\text{J s}^2 \text{C}^{-2} \text{m}^{-1} (= \text{T}^2 \text{J}^{-1} \text{m}^3)$
Magneton				
Bohr	$\mu_B = e\hbar/2m_e$	9.274 01	$10^{-24}$	$\text{J T}^{-1}$
nuclear	$\mu_N = e\hbar/2m_p$	5.050 78	$10^{-27}$	$\text{J T}^{-1}$
g value	$g_e$	2.002 32		
Bohr radius	$a_0 = 4\pi\epsilon_0 \hbar^2 / m_e e^2$	5.291 77	$10^{-11}$	m
Fine-structure constant	$\alpha = \mu_0 e^2 c / 2h$	7.297 35	$10^{-3}$	
	$\alpha^{-1}$	1.370 36	$10^2$	
Second radiation constant	$c_2 = hc/k$	1.438 78	$10^{-2}$	m K
Stefan–Boltzmann constant	$\sigma = 2\pi^5 k^4 / 15h^3 c^2$	5.670 51	$10^{-8}$	$\text{W m}^{-2} \text{K}^{-4}$
Rydberg constant	$R = m_e e^4 / 8h^3 c \epsilon_0^2$	1.097 37	$10^5$	$\text{cm}^{-1}$
Standard acceleration of free fall	$g$	9.806 65*		$\text{m s}^{-2}$
Gravitational constant	$G$	6.673	$10^{-11}$	$\text{N m}^2 \text{kg}^{-2}$

\*Exact value

## QUESTION ONE (30MARKS)

- a) (i) A 0.5122g sample of naphthalene ( $\text{C}_{10}\text{H}_8$ ) was burned in a constant volume bomb calorimeter.

Consequently, the temperature of the water in the inner jacket rose from 20.17 °C to 24.08 °C.

If the effective heat capacity ( $C_v$ ) of the bomb calorimeter plus water is 5267.8JK<sup>-1</sup>, calculate  $\Delta U$  and  $\Delta H$  for the combustion of naphthalene in KJ mol<sup>-1</sup>. (2marks)

- (ii) The standard heats of formation at 298K for  $\text{CCl}_4$  (g),  $\text{H}_2\text{O}$ (g),  $\text{CO}_2$  (g) are -25.5, -57.8,-94.1 and -22.1kcal mol<sup>-1</sup> respectively. Calculate  $\Delta H_{298}^0$  for the reaction



(iii) Outline four conclusions which can be experimentally verified based on Hess's law and six applications of Hess's law (4 marks)

(iv) Determine  $K_c$  for the reaction  $\frac{1}{2} \text{N}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) + \frac{1}{2} \text{Br}_2(\text{g}) \rightleftharpoons \text{NOBr}(\text{g})$

From the following data at 298K; The equilibrium constants for the following reactions,

$2\text{NO}(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + \text{O}_2(\text{g})$  and  $\text{NO}(\text{g}) + \frac{1}{2} \text{Br}_2(\text{g}) \rightleftharpoons \text{NOBr}(\text{g})$  are  $2.4 \times 10^{30}$  and 1.4

respectively. (3marks)

(b) (i) Explain how the perfect gas equation of state arises by combination of Boyle's law, Charles's

law, and Avogadro's principle. (3marks)

(ii) Explain the term 'partial pressure' and explain why Dalton's law is a limiting law (2marks)

(iii) Explain how the compression factor varies with pressure and temperature and describe how it reveals information about intermolecular interactions in real gases. (2marks)

(iv) Given that the standard enthalpy of combustion of graphite is  $-393.51 \text{ kJ mol}^{-1}$  and that of diamond is  $-395.41 \text{ kJ mol}^{-1}$ , calculate the enthalpy of the graphite-to-diamond transition.

(3marks)

(c) (i) Discuss indicator errors in determination of end point of a titration using visual indicator.

(3marks)

(ii) Describe the preparation of buffer solution having pH of 10. (2marks)

(A student prepared 1L of an acetic acid/sodium acetate buffer that included 1M  $\text{HC}_2\text{H}_3\text{O}_2$  and

1.5M  $\text{NaC}_2\text{H}_3\text{O}_2$ . The entire solution was intended for an experiment in which 0.25mole of

$\text{OH}^-$

was expected to be generated by a reaction without changing the volume of the solution. Is there

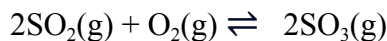
enough buffer capacity to neutralize this much strong acid without letting the pH change by more than 0.1unit? (3 marks)

(ii) Calculate the pH of a solution prepared by adding 20ml of 0.1m HOAc to 20ml of 0.1M NaOH (1 mark)

**QUESTION TWO (20 MARKS)**

- a. (i) Explain the following observation, Methyl orange is a suitable indicator for the titration of strong acid and weak base (1 mark)
- (ii) Calculate the pH at 0, 10.0, 25.0, 50.0 and 60.0 mL of 0.100 M acetic acid with 0.100 M NaOH (3 marks)
- (ii) Calculate the pH at the equilibrium point when a solution of 0.1 M acetic acid is titrated with a solution of 0.1 M NaOH.  $K_a$  for acid =  $1.9 \times 10^{-5}$  (2marks)
- (b) (i) Define order of reaction. (1mark)
- (ii) Rates of reaction double with every  $10^\circ$  rise in temperature. If this generalization holds for a reaction in the temperature ranges 298 K to 308 K, what would be the value of activation energy for their reaction?  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$  (3marks)
- (c) (i) The standard enthalpy of formation of the metallocene bis(benzene)chromium was measured in a calorimeter. It was found for the reaction  $\text{Cr}(\text{C}_6\text{H}_6)_2(\text{s}) \rightarrow \text{Cr}(\text{s}) + 2 \text{C}_6\text{H}_6(\text{g})$  that  $\Delta_r U^\ominus(583 \text{ K}) = +8.0 \text{ kJ mol}^{-1}$ . Find the corresponding reaction enthalpy and estimate the standard enthalpy of formation of the compound at 583 K. The constant-pressure molar heat capacity of benzene is  $136.1 \text{ J K}^{-1} \text{ mol}^{-1}$  in its liquid range and  $81.67 \text{ J K}^{-1} \text{ mol}^{-1}$  as a gas. (3marks)
- (ii) In the reaction  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$  at equilibrium, helium gas is injected into the vessel without disturbing the overall pressure of the system. What will be the effect on the equilibrium? (1marks)
- (iii) At  $700^\circ\text{C}$  and total pressure of one atmosphere the partial pressure at equilibrium for sulphur dioxide and oxygen are 0.27 and 0.41 atmospheres respectively. Sulphur dioxide

is oxidized to sulphur trioxide according to the following equation



Calculate the equilibrium constant,  $K_p$ , for the reaction (2marks)

(iv) State the Dalton law of partial pressures (1marks)

(v) Calculate the total pressure exerted by a mixture of 8 g of  $\text{O}_2$ , and 4g of  $\text{H}_2$  enclosed in a vessel of  $1 \text{ dm}^3$  at  $270 \text{ C}$ .  $R = 0.083 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$  (3marks)

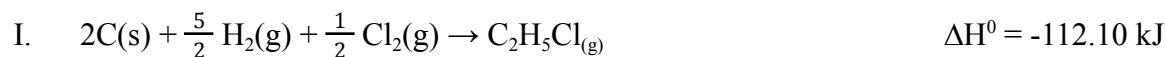
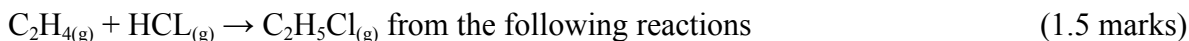
### QUESTION THREE (20MARKS)

a. (i) Discuss the following using suitable examples

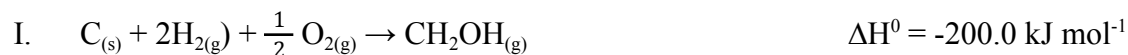
(I) Hess law of Constant heat summation (2 marks)

(II) Bond enthalpies (2 marks)

(ii) Calculate the enthalpy of the reaction



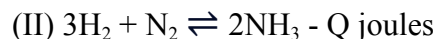
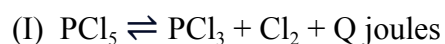
(iii) Calculate the bond enthalpy for a C-O bond in methanol from the following data: (2 marks)



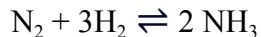
(iv) Define on what is meant by chemical equilibrium being a dynamic equilibrium` (1 mark)

(v) State Le Chatelier-Braun principle and discuss its application to the following reactions:

(3 marks)



(vi) The equilibrium constant for the formation of ammonia according to the equation



At 500°C is  $1.5 \times 10^{-5} \text{ atm}^{-2}$ . If a start be made with  $\text{N}_2$  and  $\text{H}_2$  in the stoichiometric ratio, calculate what fraction of the reactants will be converted to ammonia at total pressures of 1 atmosphere and 500 atmospheres respectively, maintained throught. (4 marks)

(vii) Real gases do not obey ideal gas equation under all conditions. Explain. (1 mark)

(viii) What are reversible and irreversible cells? Explain with a suitable example (0.5 mark)

(ix) Manganese sulphate reacts with acids according to the following equation

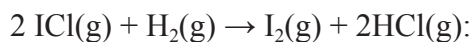


State, giving a reason, what would happen to the equilibrium if

- I. Water is added to the equilibrium mixture (1mark)
- II. Hydrogen chloride is bubbled into the equilibrium mixture (1mark)
- III. pH of equilibrium mixture is increased. (1mark)

#### QUESTION FOUR (20 MARKS)

(a) The following kinetic data ( $v_0$  is the initial rate) were obtained for the reaction



Experiment	$[\text{ICl}]_0/(\text{mmol dm}^{-3})$	$[\text{H}_2]_0/(\text{mmol dm}^{-3})$	$v_0/(\text{mol dm}^{-3} \text{ s}^{-1})$
1	1.5	1.5	$3.7 \times 10^{-7}$
2	3.0	1.5	$7.4 \times 10^{-7}$
3	3.0	4.5	$22 \times 10^{-7}$
4	4.7	2.7	?

- I. Write the rate law for the reaction. (3 marks)
- II. From the data, determine the value of the rate constant. (3 marks)
- III. Use the data to predict the reaction rate for experiment 4. (2 marks)

- a) Define the terms in  $\ln k = \ln A - \frac{Ea}{RT}$  and discuss the conditions under which the expression is valid. (2 marks)
- b) Distinguish between galvanic and electrolytic cells. (3 marks)
- c) Calculate the final pressure of O<sub>2</sub> in the following experiment: a collapsed polythene bag of 30 L capacity is partially blown up by the addition of 10 L of N<sub>2</sub> at 0.965 atm at 298 K. Subsequently, enough O<sub>2</sub> is pumped into the bag so that at the temperature of 298 K and external pressure of 0.990 atm, the bag contains a volume of 30 L. (2marks)
- d) Consider the cell Pt(s)|H<sub>2</sub>(g,p<sup>⊖</sup>)|HCl(aq)|AgCl(s)|Ag(s), for which the cell reaction is  $2 \text{AgCl}_{(s)} + \text{H}_{2(g)} \rightarrow 2 \text{Ag}_{(s)} + 2 \text{HCl}_{(aq)}$ . At 25°C and a molality of HCl of 0.010 mol kg<sup>-1</sup>, E<sub>cell</sub> = + 0.4658 V.
- (i) Write the Nernst equation for the cell reaction. (1 mark)
- (ii) Calculate ΔrG for the cell reaction. (3 marks)
- (iii) Assuming that the Debye–Hückel limiting law holds at this concentration, calculate E<sup>⊖</sup>(AgCl/Ag,Cl<sup>-</sup>). (3 marks)

**Table F.2** A selection of derived units

Physical quantity	Derived unit*	Name of derived unit
Force	$1 \text{ kg m s}^{-2}$	newton, N
Pressure	$1 \text{ kg m}^{-1} \text{ s}^{-2}$ $1 \text{ N m}^{-2}$	pascal, Pa
Energy	$1 \text{ kg m}^2 \text{ s}^{-2}$ $1 \text{ N m}$ $1 \text{ Pa m}^3$	joule, J
Power	$1 \text{ kg m}^2 \text{ s}^{-3}$ $1 \text{ J s}^{-1}$	watt, W

\* Equivalent definitions in terms of derived units are given following the definition in terms of base units.

**Table F.3** Common SI prefixes

Prefix	y	z	a	f	p	n	$\mu$	m	c	d
Name	yocto	zepto	atto	femto	pico	nano	micro	milli	centi	deci
Factor	$10^{-24}$	$10^{-21}$	$10^{-18}$	$10^{-15}$	$10^{-12}$	$10^{-9}$	$10^{-6}$	$10^{-3}$	$10^{-2}$	$10^{-1}$
Prefix	da	h	k	M	G	T	P	E	Z	Y
Name	deca	hecto	kilo	mega	giga	tera	peta	exa	zeta	yotta
Factor	10	$10^2$	$10^3$	$10^6$	$10^9$	$10^{12}$	$10^{15}$	$10^{18}$	$10^{21}$	$10^{24}$

# PERIODIC TABLE OF THE ELEMENTS

		Metals														VIIA 17		0 18																	
		Nonmetals										IIIA 13		IVA 14		VA 15		VIA 16		H 1		He 2													
		Metalloids																																	
1	IA 1	1 H 1.008											IIIA 13		5 B 10.81	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.9984	10 Ne 20.1797	VIIA 17		0 18												
2		3 Li 6.941	4 Be 9.0122																																
3		11 Na 22.9898	12 Mg 24.3050	IIIB 3	IVB 4	VB 5	VIB 6	VIIA 7	VIII 8 9 10			IB 11	IIIB 12	13 Al 26.9815	14 Si 28.085	15 P 30.9738	16 S 32.06	17 Cl 35.453	18 Ar 39.948																
4		19 K 39.0983	20 Ca 40.078	21 Sc 44.9559	22 Ti 47.867	23 V 50.9415	24 Cr 51.9961	25 Mn 54.9380	26 Fe 55.845	27 Co 58.9332	28 Ni 58.6934	29 Cu 63.546	30 Zn 65.38	31 Ga 69.723	32 Ge 72.63	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.798																
5		37 Rb 85.4678	38 Sr 87.62	39 Y 88.9058	40 Zr 91.224	41 Nb 92.9064	42 Mo 95.96	43 Tc (98)	44 Ru 101.07	45 Rh 102.9055	46 Pd 106.42	47 Ag 107.8682	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.760	52 Te 127.60	53 I 126.9045	54 Xe 131.293																
6		55 Cs 132.9055	56 Ba 137.327	57 La 138.9055	58 Ce 140.9076	59 Pr 140.9076	60 Nd 144.242	61 Pm (145)	62 Sm 150.36	63 Eu 151.964	64 Gd 157.25	65 Tb 158.9254	66 Dy 162.500	67 Ho 164.9303	68 Er 167.259	69 Tm 168.9342	70 Yb 173.054	71 Lu 174.9668	72 Hf 178.49	73 Ta 180.9479	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.217	78 Pt 195.084	79 Au 196.9666	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.9804	84 Po (209)	85 At (210)	86 Rn (222)		
7		87 Fr (223)	88 Ra (226)	89 Ac (227)	90 Th 232.0381	91 Pa 231.0359	92 U 238.0289	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)	104 Rf (265)	105 Db (268)	106 Sg (271)	107 Bh (270)	108 Hs (277)	109 Mt (276)	110 Ds (281)	111 Rg (280)	112 Cn (285)	113 Uut (284)	114 Fl (289)	115 Uup (288)	116 Lv (293)	117 Uus (294)	118 Uuo (294)		

\*Lanthanide Series

58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
140.9076	140.9076	144.242	(145)	150.36	151.964	157.25	158.9254	162.500	164.9303	167.259	168.9342	173.054	174.9668

Note: Atomic masses are 2009 IUPAC values (up to four decimal places). More accurate values for some elements are given in the table inside the back cover.

\*\* Actinide Series

90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr
232.0381	231.0359	238.0289	(237)	(244)	(243)	(247)	(247)	(251)	(252)	(257)	(258)	(259)	(262)