CHUKA  **UNIVERSITY**

UNIVERSITY EXAMINATIONS

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

CHEM 120: PHYSICAL CHEMISTRY I

STREAMS: BSc. CHEM **TIME: 2 HOURS**

DAY/DATE: TUESDAY 09/04/2024 **11.30 A.M. – 1.30 P.M.**

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}	$m\ s^{-1}$
Elementary charge	e	1.602 176	10^{-19}	C
Faraday's constant	$F = N_A e$	9.648 53	10^{4}	$C\ mol^{-1}$
Boltzmann's constant	k	1.380 65	10^{-23}	$J\ K^{-1}$
Gas constant	$R = N_A k$	8.314 47		$J\ K^{-1}\ mol^{-1}$
		8.314 47	10^{-2}	$dm^3\ bar\ K^{-1}\ mol^{-1}$
		8.205 74	10^{-2}	$dm^3\ atm\ K^{-1}\ mol^{-1}$
		6.236 37	10	$dm^3\ Torr\ K^{-1}\ mol^{-1}$
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}	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	$\varepsilon_0 = 1/c^2\mu_0$	8.854 19	10^{-12}	$J^{-1}\ C^2\ m^{-1}$
	$4\pi\varepsilon_0$	1.112 65	10^{-10}	$J^{-1}\ C^2\ m^{-1}$
Vacuum permeability	μ_0	4π	10^{-7}	$J\ s^2\ C^{-2}\ m^{-1}\ (= T^2\ J^{-1}\ m^3)$
Magneton				
Bohr	$\mu_B = e\hbar/2m_e$	9.274 01	10^{-24}	$J\ T^{-1}$
nuclear	$\mu_N = e\hbar/2m_p$	5.050 78	10^{-27}	$J\ T^{-1}$
g value	g_e	2.002 32		
Bohr radius	$a_0 = 4\pi\varepsilon_0\hbar^2/m_e e^2$	5.291 77	10^{-11}	m
Fine-structure constant	$\alpha = \mu_0 e^2 c/2h$	7.297 35	10^{-3}	
	α^{-1}	1.370 36	10^{2}	
Second radiation constant	$c_2 = hc/k$	1.438 78	10^{-2}	m K
Stefan–Boltzmann constant	$\sigma = 2\pi^5 k^4/15h^3c^2$	5.670 51	10^{-8}	$W\ m^{-2}\ K^{-4}$
Rydberg constant	$R = m_e e^4/8h^3 c\varepsilon_0^2$	1.097 37	10^{5}	cm^{-1}
Standard acceleration of free fall	g	9.806 65*		$m\ s^{-2}$
Gravitational constant	G	6.673	10^{-11}	$N\ m^2\ kg^{-2}$

Exact value

QUESTION ONE (30 MARKS)

a) i) In an industrial process, nitrogen is heated to 500 K in a vessel of constant volume. If it enters the vessel at 100 atm and 300 K, calculate the pressure exerted at the working temperature if it behaved as a perfect gas. (2 marks)

ii) 0.54gm of an organic liquid displaces 71.52cc of dry air at 99.80c. The barometer pressure was 691.4 mm of Hg. The compound is saturated and contains only carbon, fluoride and chlorine. There is 57% cl2 by weight. Determine its molecular formula. (2 marks)

b) i) The standard reaction enthalpy for the hydrogenation of propene

$CH_2=CHCH_3\ (g) + H_2\ (g) \rightarrow CH_3CH_2CH_3\ (g)$ is -124 kJ mol^{-1}. The standard reaction enthalpy for the combustion of propane $CH_3CH_2CH_3\ (g) + 5\ O_2\ (g) \rightarrow 3\ CO_2\ (g) + 4\ H_2O\ (l)$ is -2220 kJ mol^{-1}. Calculate the standard enthalpy of combustion of propene (3 marks)

ii) Calculate the lattice enthalpy of SrI_2 from the following data: (4 marks)

	ΔH / (kJ mol^{-1})
Sublimation of Sr (s)	+164
Ionization of Sr (g) to Sr_2 (g)	+ 1626
Sublimation of I_2 (s)	+62
Dissociation of I_2 (g)	+151
Electron attachment to I (g)	−304
Formation of SrI_2 (s) from Sr (s) and I2 (s)	−558

iii) When NH_4Cl is heated the vapour pressure at 700 K is 6.0 atm. At 732 k the vapour pressure rises to 11.0 atm .Calculate the equilibrium constants for the dissociation at these temperatures. Also calculate change in enthalpy and change in entropy at 700k. (2 marks)

c) i)A real gas in a container starts behaving ideally as the temperature is raised. Discuss (3 marks)

ii) On raising the temperature from 27^0C to 37^0C, the rate of reaction is doubled. Calculate the activation energy. (3 marks)

iii) Neutralization of all bases by acids do not necessarily occur at pH. 7. Explain. (3 marks)

d) i) 10cc of 0.1M NaOH solution are added to 50cc of 1.1M HOAc. What will be the pH of the resulting mixture? Given that k_a for HOAc=1.75x $10^{-5.}$ (2 marks)

ii) Explain why KCl or NH_4NO_3 is preferred to make salt bridge. (2 marks)

(I) Calculate the bond enthalpy of a C-O bond in methanol from the following data. (2 marks)

$C\ (s) + 2H_2\ (g) + ½\ O_2\ (g) = CH_2OH$	ΔH^o=-200.0kj mol^{-1}
$C(s) = C\ (g)$	ΔH^o = 716.8kj mol-1
$C_2H_2\ (g) = 4H\ (g)$	ΔH^o=872.0kj mol^{-1}
½ O2 (g) = O (g)	ΔH^o=249.0kj mol^{-1}

iii) State the advantages and disadvantages of TRIS buffer. (2 marks)

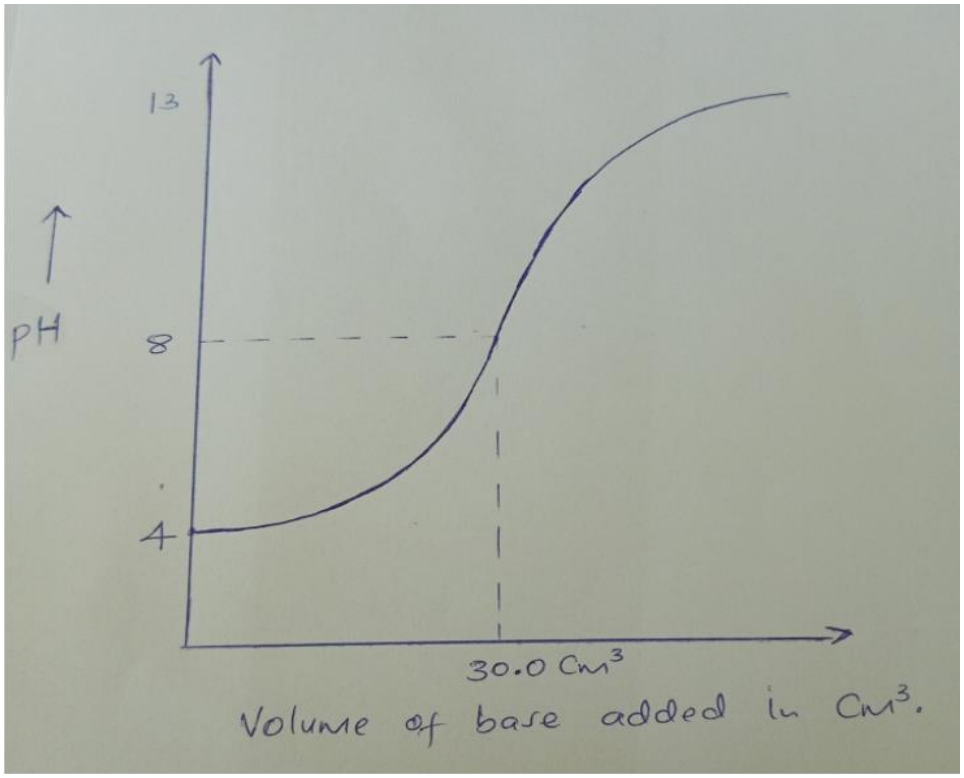
QUESTION TWO (20 MARKS)

a) (i) Distinguish between single electrode potential and standard electrode potential. (2 marks)

(ii) Explain why formal electrode potentials is always used to predict whether a given titration will occur. (2 marks)

b) (i) The total phosphate concentration in a blood is determined by spectrophotometry to be 3.0b x10^{-3} M. if the pH of the blood sample is 7.45, what are the concentrations of the $H_2PO_4^-$ and HPO_4^2 in the blood? (3 marks)

(ii) The following graph refers to the titration of 25 cm3 of 0.1M monobasic acid with a mono acid base.



I. State with reasons whether the acid and the base are weak or strong (1 mark)

II. If several indicators are available having pka values 2.0, 4.0, 6.0, 8.0, 10.0, and 12.0. State with reasons which one would be most suitable for this titration. (1 mark)

c) i) From the following information on bond enthalpy, calculate the enthalpy of formation gaseous isoprene $CH_3C\ (CH_2)\ CHCH_2$. Bond energies of H-H, C-H, C-C AND C=C is35.94 $kJmol^{-1}$, 415.8 $kJmol^{-1}$, 347.7 $kJmol^{-1}$, 600.7 $kJmol^{-1}$ respectively. The enthalpy of sublimation of carbon is 716.68 $kJmol^{-1}$. If the enthalpy of formation of gaseous isoprene obtained from the combustion is 8.79 $kJmol^{-1}$, how would you account in the two values? (2 marks)

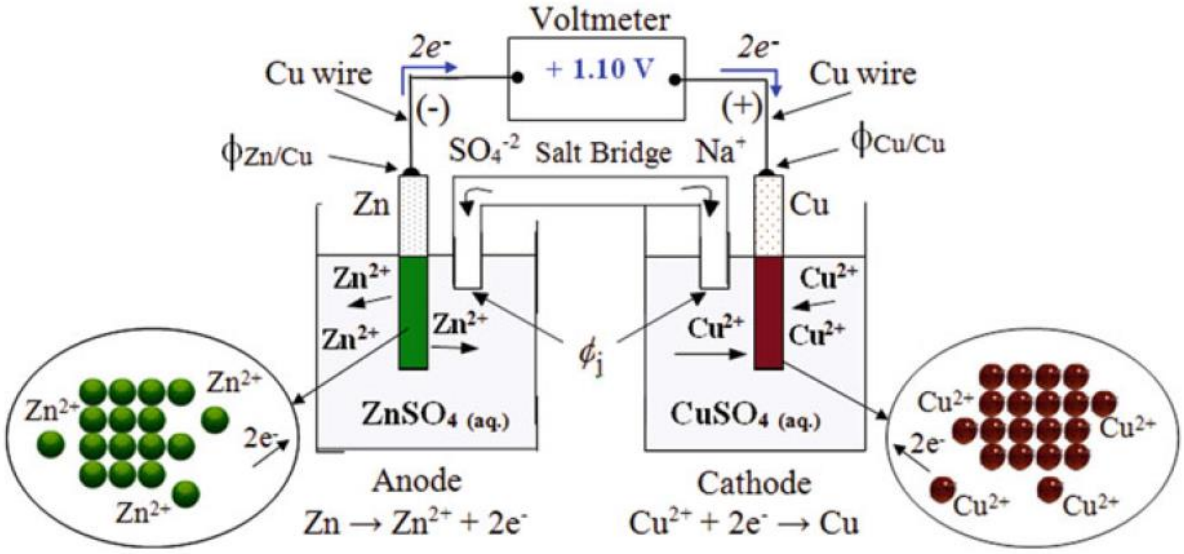
ii) Describe how the syringe method can be used to determine the relative molecular mass of a gas and vapour. (3 marks)

d) i) Explain how temperature affects the rate of a reaction. (2 marks)

ii) Describe the two types of intermolecular interactions responsible for deviations from ideal gas behavior, and indicate the direction of their effect on the pressure. (4 marks)

QUESTION THREE (20 MARKS)

a) Use the figure below to answer the following questions



(i) Define the galvanic electrode potential for the cell shown above using the interfacial potentials involved in the electrochemical process. (1 mark)

(ii)Describe what happens in the galvanic cell shown above when electrons leave the Cu terminal at the Cu-Zn interface. (2 marks)

(iii) Explain why an electrode potential difference occurs in the cell above (2 marks)

(iv) Why are Cu^{2+} cations electroplated on the *Cu* electrode surface in the figure above? (1 mark)

(v) Calculate the equilibrium constant at 25^0C for the electrochemical cell shown above (2 marks)

b) (i) Derive the Arrhenius equation from the general definition of the activation energy of any rate reaction process (3 marks)

(ii) Determine the Arrhenius constants *B* and *Ae* using the derived equation and the following data for the dissociation constants: *Ksp*@300 D 10^{11}, *Ksp*@350 D 3*Ksp*@300 between 300 and 350K. It is assumed that the activity coefficients approach 1 in diluted electrolyte solution and that *Ksp* follows an Arrhenius type trend. Recall that *Ksp* can be expressed in terms of concentrations. (3 marks)

(iii) 16.4g potassium iodide was dissolved in 500cm^3 of water and about 1.0g of iodide was dissolved in 100cm3 of benzene. The two solutions were then mixed and allowed to standard. Subsequent titrations showed 10cm3 of the benzene layer was equivalent of 5.1cm^3 of M/10 sodium thiosulphate (vi) solution while 50cm3 of the aqueous layer was equivalent to 2.9cm3 of M/10 thiosulphate. The distribution coefficient of iodine between the benzene and water is 130. Calculate the value of the equilibrium constant of the equilibrium. (3 marks)

$KI+I_2 = KI_3$

c) Calculate the buffer capacity of 500ml of a buffer which contains 0.06M NH_4CL and 0.08M NH_4OH ($Kb=1.75 \times 10^{-5}$) (3 marks)

QUESTION FOUR (20MARKS)

a) (i) Explain theories of acid base indicators. (2 marks)

(ii)A car tyre (i.e. an automobile tire) was inflated to a pressure of 24 lb in^{-2} (1.00 atm = 14.7 lb in^{-2}) on a winter's day when the temperature was −5°C. What pressure will be

found, assuming no leaks have occurred and that the volume is constant, on a subsequent summer's day when the temperature is 35°C? What complications should be taken into account in practice? (2 marks)

iii) A mixture of SO_2 and O_2 in the molar ration of 2:1 was kept over platinum catalyst in a reaction vessel at 6500c, the total pressure at equilibrium was found to be 10am. If 60% SO_2 be converted to SO_3, calculate Kp for $2SO_2 + O_2 \rightarrow 2SO_3$ (2 marks)

(iv) In the reaction $COCl_2 \rightarrow CO + Cl_2$ at 550°C, when the initial pressures of CO and Cl_2 are 250mmHg and 280mmHg respectively, the equilibrium pressure is found to be 380 mmHg. Calculate the degree of dissociation of cocl2 at 1atm. What will be the extent of dissociation when N2 at s pressure of 0.4 atm is present, and if the total pressure is (I) 1atm (II) 1.4atm (3 marks)

b)

i. The compressibility factor of O_2 is 0.927at 0°C and 100atm pressure. Calculate the weight of O_2 necessary to fill a cylinder of 100litres capacity at the given condition. (2 marks)

ii. The equilibrium constant, Kp for the reaction $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$ is 5.04×1017 atm^{-1} at 25°C. Calculate $\Delta G°$. (1 mark)

iii. Carbon dioxide upon heating with carbon at high temperature is reduced to carbon monoxide: $CO_2(g) + C(s) \rightarrow 2CO(g)$ Kp for the reaction is 1.90 atm. In a particular experiment the total pressure at equilibrium was found to be 2.00 atm. What were the partial pressures of CO and CO2? (2 marks)

c)

i. Calculate the grams of ammonium chloride and the volume of 5M sodium hydroxide which should be added to 100ml to prepare a buffer of pH 10 with a salt concentration of 0.2M (Kb for ammonia =1.75*10-5, N=14.0067,cl=35.453,H=1.00794.(2 marks)

ii. *Tris* (hydroxymethyl) aminomethane [$(HOCH2)_3CNH_2$—Tris, or THAM] is a weak base frequently used to prepare buffers in biochemistry. Its K_b is 1.2×10^{-6} and pK_b is 5.92. The corresponding pK_a is 8.08, which is near the pH of the physiological buffers, and so it exhibits good buffering capacity at physiological pH. What weight of THAM must be taken with 100 mL of 0.50 *M* HCl to prepare 1 L of a pH 7.40 buffer? (2 marks)

iii.The total carbon dioxide content *(*$HCO_3^- + CO_2$) in a blood sample is determined by acidifying the sample and measuring the volume of CO_2 evolved with a Van Slyke manomeric apparatus. The total concentration was determined to be 28.5 mmol/L.
The blood pH at 37°C was determined to be 7.48. What are the concentrations of HCO_3^- and CO_2 in the blood? (2 marks)
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Table F.2 A selection of derived units

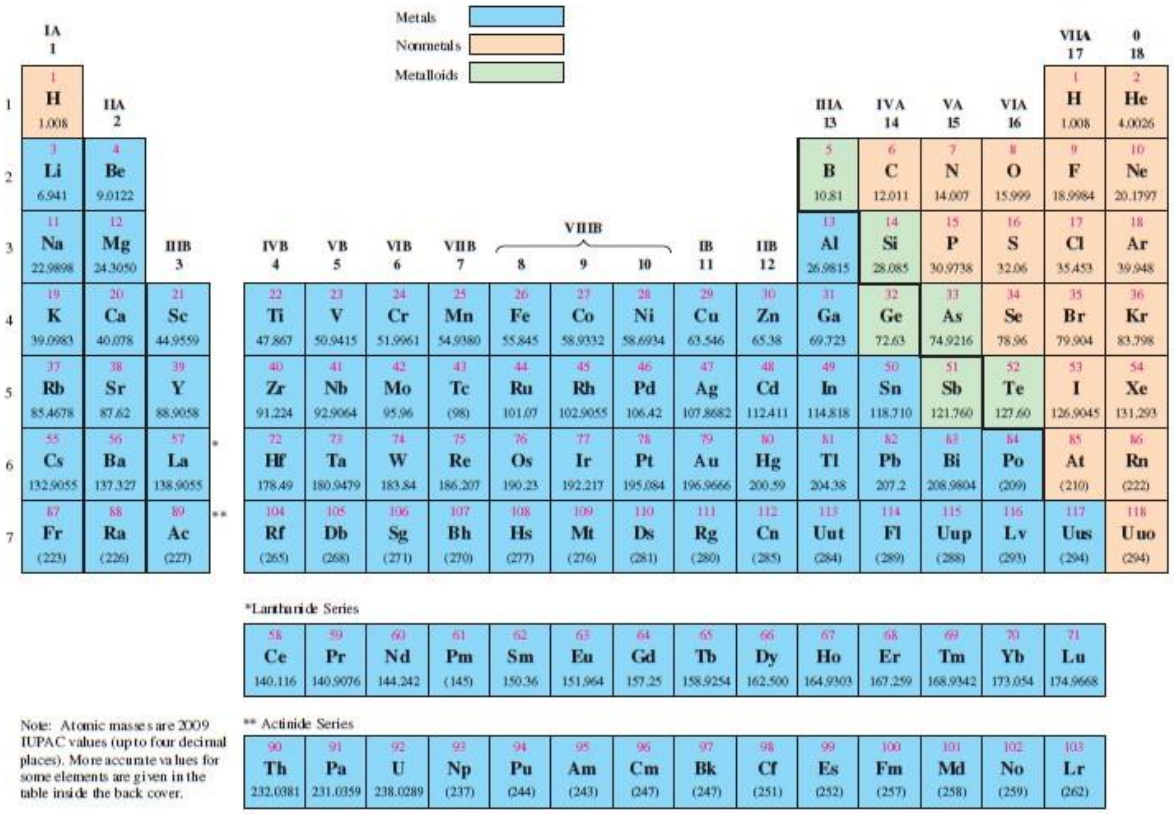
Physical quantity	Derived unit*	Name of derived unit
Force	$1\ kg\ m\ s^{-2}$	newton, N
Pressure	$1\ kg\ m^{-1}\ s^{-2}$ $1\ N\ m^{-2}$	pascal, Pa
Energy	$1\ kg\ m^2\ s^{-2}$ $1\ N\ m$ $1\ Pa\ m^3$	joule, J
Power	$1\ kg\ m^2\ s^{-3}$ $1\ J\ s^{-1}$	watt, W

* 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	μ	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



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.