

CHUKA



UNIVERSITY

UNIVERSITY EXAMINATIONS

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

CHEM 221: PHYSICAL CHEMISTRY II

STREAMS: BSc. CHEM

TIME: 2 HOURS

DAY/DATE: THURSDAY 24/04/2025

2.30 P.M. – 4.30 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		$\text{J K}^{-1} \text{mol}^{-1}$
		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}	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	μ_0	4π	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}	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	$a_0 = 4\pi\epsilon_0\hbar^2/m_e e^2$	5.291 77	10^{-11}	m
Fine-structure constant	$\alpha = \mu_0 e^2 c/2h$	7.297 35	10^{-3}	
	α^{-1}	1.370 36	10^2	
Second radiation constant	$c_2 = hc/k$	1.438 78	10^{-2}	m K
Stefan-Boltzmann constant	$\sigma = 2\pi^5 k^4/15h^3 c^2$	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	cm^{-1}
Standard acceleration of free fall	g	9.806 65*		m s^{-2}
Gravitational constant	G	6.673	10^{-11}	$\text{N m}^2 \text{kg}^{-2}$

*Exact value

QUESTION ONE (30 MARKS)

(a) i) Explain giving reasons the following observations;

- I. The kinetic energy of a gas increases with increasing temperature. (1½ marks)
- II. The mean free path of gas molecules increases and the number of collisions per unit time decreases with the lowering of temperature. (2 marks)
- III. Heat capacity of a diatomic gas is greater than that of a monoatomic gas. (2 marks)
- IV. Nonideal gases approach ideal behavior at low pressure and high temperatures. (2 marks)
- V. The compressibility factor is unity at Boyle temperature of a gas. (1½ marks)
- VI. The molecular attraction between gases molecules are pronounced at low temperatures. (2 marks)

VII. Gases cannot be liquefied merely by the application of pressure above their critical temperatures. (2 marks)

VIII. A Nonideal gas below its inversion temperatures shows a cooling effect in Joule-Thomson expansion. (1 mark)

(b) i) Explain how the two phase diagrams for sulfur illustrate the "problem of components" for the phase rule. (2 marks)

ii) Determine the amount of sucrose, $C_{12}H_{22}O_{11}$ that must be dissolved in 90 g of water to produce a solution over which the relative humidity is 80 %. Assume the solution is ideal. (2 marks)

iii) Dissolving a gas in a liquid is an exothermic process. Assuming an ideal gas, account for this in terms of molecular forces. Suggest a molecular explanation of the Bunsen coefficient α increase with increasing gas boiling point. (2 marks)

(c) i) Describe the similarities of the solution upper consolute point and the liquid-gas critical point. (2 marks)

ii) The hardness of an alloy is greater the more fine grained the alloy is. Explain why eutectic alloys are hard. (2 marks)

iii) Explain the direction of the influence of nonideality (for example, positive deviations from Raoult's law) on;

I. Freezing-point depression (1 mark)

II. Boiling-point elevation (1 mark)

III. Osmotic pressure compared to the ideal solution case. (1 mark)

d) Discuss and interpret the trends of the Debye length with increasing;

I. Temperature (1 mark)

II. Dielectric constant (1 mark)

III. Ionic strength. (1 mark)

QUESTION TWO (20 MARKS)

(a) i) I. State Maxwell's law of distribution of molecular speeds amongst the molecules of a gas. (1 mark)

II. Explain from part I the effect of temperature on the distribution of speeds. (1 mark)

III. Explain whether the molecules of a gas can have a high and almost zero speeds. (1 mark)

IV. Show that the most probable speed is given by $C_{mp} = \sqrt{\frac{2RT}{M}}$. (2½ marks)

(ii) I. Deduce the law of corresponding states from the Van der Waals equation. (2½ marks)

II. Explain the significance of the law. (2 marks)

(b) i) For nitrogen gas at 1 atm and 298K calculate:

I. The number of collisions each nitrogen molecule encounters in one second. (2 marks)

II. The total number of collisions in a volume of 1m³ in one second. (1 mark)

III. The mean free path of a nitrogen molecule. The collision diameter of a nitrogen molecule is 3.74×10^{-10} m. (1 mark)

ii) The following table gives the values of a, b and experimentally measured volume at 273 K and 200 atm of two Van der Waals gases A and B calculate;

	a atm.l ² .mol ⁻²	b litre.mole ⁻¹	Volume litre.mole ⁻¹
A	0.24	0.026	0.112
B	1.36	0.132	0.111

I. The compressibility factor for 1 mole of each at 273 K and 200 atm and state which one is more compressible than predicted by the ideal gas law. (2 marks)

II. The temperature at which B obeys Boyle's law over a wide range of pressure. (1 mark)

III. The temperature below which A would be subjected to Joule-Thomson expansion for liquefaction. (1 mark)

iii) For a particular gas, $b=4.42 \times 10^{-2}$ L.mol⁻¹. Determine how near the centres of the two molecules can approach. (2 marks)

QUESTION THREE (20 MARKS)

a) i) Explain giving reasons the following observations;

I. A solution of benzene and toluene behaves nearly ideal while that of ethanol; and water or chloroform and acetone shows considerable deviations from ideality. (2 marks)

II. An azeotrope although distills unchanged in composition at a given pressure, yet it is not a chemical compound. (2 marks)

ii) Suggest how we can draw a phase diagram for pure water as a system. (2½ marks)

Explain how it will influence your consideration if water has;

I. Some air dissolved in it. (1 mark)

II. 5% heavy water mixed with it. ($1\frac{1}{2}$ marks)

III. Been obtained from a well. (1 mark)

b) i) Latent heat of fusion of water is 6025 joules per mole and can be treated as constant. Normal melting point of ice is 0°C . Determine the melting point of ice if the pressure on it is;

I. Reduced to 0.006 atmosphere (2 marks)

II. Increased to 5 atmospheres (1 mark)

ii) A mixture of water and an organic liquid A, immiscible in water, distills at 95°C when the external pressure is 635 mm Hg.

I. Calculate the molecular weight of A if the distillate contains 40% by weight of water. ($1\frac{1}{2}$ marks)

II. Calculate the weight of water required for the steam distillation of 500g of A if its molecular weight be 160awu. ($1\frac{1}{2}$ marks)

iii) At 300 K two pure liquids A and B have vapour pressures of 200 and 500 torr. Calculate mole percent of A and B in the liquid and vapour phases of a mixture C which has vapour pressure of 350 torr. (2 marks)

c) Account for the following;

I. Zinc sulphide alone is precipitated when hydrogen sulphide is passed into an aqueous solution containing Zn^{2+} and Mn^{2+} ions and dilute acetic acid. (0.5 mark)

II. Magnesium hydroxide is not precipitated from solutions of magnesium salts by ammonia solution in the presence of ammonium chloride. (0.5 mark)

III. A concentrated solution of calcium chloride gives no precipitate with ammonia solution, but with sodium hydroxide solution a precipitate forms immediately. (1 mark)

QUESTION FOUR (20 MARKS)

(a) i) Explain why the boiling point of a solvent is elevated and its freezing point is depressed by the addition of a solute. ($1\frac{1}{2}$ marks)

ii) Explain the effect of the following situation on determination of molecular weight of a substance by the cryoscopic method;

- I. If some solvent is lost from the measured quantity before solution is made in it. (1 mark)
- II. Some solution is lost after making the solution, before the freezing point of solution is measured. (1 mark)
- III. If some of the weighed solute added remains undissolved. (1 mark)
- IV. If the solvent has already got some soluble non-interacting impurity in it. (1 mark)
- V. If the thermometer used has a correction of $+1^{\circ}\text{C}$ all over the scale. (1 mark)
- b) i) Phenol is one of those substances which partially associates into double molecules when dissolved in water. If a solution of 1.880 g of phenol in 100 g of water freezes at -0.210°C , calculate the degree of association of phenol molecules at the freezing point of the solution. Molal freezing point constant of water is 1.86°C . (3 marks)
- ii) Blood plasma has the following composition (milli-equivalents per litre). Calculate its osmotic pressure at 37°C . $\text{Na}^+=138$, $\text{Ca}^{2+}= 5.2$, $\text{K}^+= 4.5$, $\text{Mg}^{2+}= 2.0$, $\text{Cl}^- = 105$, $\text{HCO}_3^- = 25$, $\text{PO}_4^{3-} = 2.2$, $\text{SO}_4^{2-} = 0.5$, proteins=16, others=1.0. (4 marks)
- iii) In a constant temperature room two solutions A and B are kept under a bell jar till they reach a state of equilibrium. If solution A has 0.020 mole of cane sugar dissolved in 100g of water and solution B has 0.010 mole of urea dissolved in 100g of water, determine the equilibrium concentrations. (4 marks)
- iv) A solution is made by dissolving 5.00g of $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ in 100 g of water. Determine the vapour pressure and lowering of vapour pressure for this solution at 25°C when vapour pressure of pure water is 23.756 torr. ($2\frac{1}{2}$ marks)

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	$1 \text{ kg m}^{-1} \text{ s}^{-2}$ 1 N m^{-2}	pascal, Pa
Energy	$1 \text{ kg m}^2 \text{ s}^{-2}$ 1 N m 1 Pa m^3	joule, J
Power	$1 \text{ kg m}^2 \text{ s}^{-3}$ 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}

INTERNATIONAL ATOMIC MASSES*

Name	Symbol	Atomic Number	Atomic Mass	Name	Symbol	Atomic Number	Atomic Mass
Actinium	Ac	89	[227]	Mendelevium	Md	101	[258]
Aluminium	Al	13	26.9815385(7)	Mercury	Hg	80	200.592(3)
Americium	Am	95	[243]	Molybdenum	Mo	42	95.95(1)
Antimony	Sb	51	121.760(1)	Neodymium	Nd	60	144.242(3)
Argon	Ar	18	39.948(1)	Neon	Ne	10	20.1797(6)
Arsenic	As	33	74.921595(6)	Neptunium	Np	93	[237]
Astatine	At	85	[210]	Nickel	Ni	28	58.6934(4)
Barium	Ba	56	137.327(7)	Niobium	Nb	41	92.90637(2)
Berkelium	Bk	97	[247]	Nitrogen	N	7	14.007
Beryllium	Be	4	9.0121831(5)	Nobelium	No	102	[259]
Bismuth	Bi	83	208.98040(1)	Osmium	Os	76	190.23(3)
Bohrium	Bh	107	[270]	Oxygen	O	8	15.999
Boron	B	5	10.81	Palladium	Pd	46	106.42(1)
Bromine	Br	35	79.904	Phosphorus	P	15	30.973761998(5)
Cadmium	Cd	48	112.414(4)	Platinum	Pt	78	195.084(9)
Calcium	Ca	20	40.078(4)	Plutonium	Pu	94	[244]
Californium	Cf	98	[251]	Polonium	Po	84	[209]
Carbon	C	6	12.011	Potassium	K	19	39.0983(1)
Cerium	Ce	58	140.116(1)	Praseodymium	Pr	59	140.90766(2)
Cesium	Cs	55	132.90545196(6)	Promethium	Pm	61	[145]
Chlorine	Cl	17	35.45	Protactinium	Pa	91	231.03588(2)
Chromium	Cr	24	51.9961(6)	Radium	Ra	88	[226]
Cobalt	Co	27	58.933194(4)	Radon	Rn	86	[222]
Copernicium	Cn	112	[285]	Rhenium	Re	75	186.207(1)
Copper	Cu	29	63.546(3)	Rhodium	Rh	45	102.90550(2)
Curium	Cm	96	[247]	Roentgenium	Rg	111	[281]
Darmstadtium	Ds	110	[281]	Rubidium	Rb	37	85.4678(3)
Dubnium	Db	105	[270]	Ruthenium	Ru	44	101.07(2)
Dysprosium	Dy	66	162.500(1)	Rutherfordium	Rf	104	[267]
Einsteinium	Es	99	[252]	Samarium	Sm	62	150.36(2)
Erbium	Er	68	167.259(3)	Scandium	Sc	21	44.955908(5)
Europium	Eu	63	151.964(1)	Seaborgium	Sg	106	[269]
Fermium	Fm	100	[257]	Selenium	Se	34	78.971(8)
Ferrovium	Fv	114	[289]	Silicon	Si	14	28.085
Fluorine	F	9	18.998403163(6)	Silver	Ag	47	107.8682(2)
Francium	Fr	87	[223]	Sodium	Na	11	22.98976928(2)
Gadolinium	Gd	64	157.25(3)	Strontium	Sr	38	87.62(1)
Gallium	Ga	31	69.723(1)	Sulfur	S	16	32.06
Germanium	Ge	32	72.630(8)	Tantalum	Ta	73	180.94788(2)
Gold	Au	79	196.966569(5)	Technetium	Tc	43	[97]
Hafnium	Hf	72	178.49(2)	Tellurium	Te	52	127.60(3)
Hassium	Hs	108	[270]	Terbium	Tb	65	158.92535(2)
Helium	He	2	4.002602(2)	Thallium	Tl	81	204.38
Holmium	Ho	67	164.93033(2)	Thorium	Th	90	232.0377(4)
Hydrogen	H	1	1.008	Thulium	Tm	69	168.93422(2)
Indium	In	49	114.818(1)	Tin	Sn	50	118.710(7)
Iodine	I	53	126.90447(3)	Titanium	Ti	22	47.867(1)
Iridium	Ir	77	192.217(3)	Tungsten	W	74	183.84(1)
Iron	Fe	26	55.845(2)	Ununoctium	Uuo	118	[294]
Krypton	Kr	36	83.798(2)	Ununpentium	Uup	115	[289]
Lanthanum	La	57	138.90547(7)	Ununtrium	Uut	113	[285]
Lawrencium	Lr	103	[262]	Uranium	U	92	238.02891(3)
Lead	Pb	82	207.2(1)	Vanadium	V	23	50.9415(1)
Lithium	Li	3	6.94	Xenon	Xe	54	131.293(6)
Livermorium	Lv	116	[293]	Ytterbium	Yb	70	173.045(10)
Lutetium	Lu	71	174.9668(1)	Yttrium	Y	39	88.90584(2)
Magnesium	Mg	12	24.305	Zinc	Zn	30	65.38(2)
Manganese	Mn	25	54.938044(3)	Zirconium	Zr	40	91.224(2)
Meitnerium	Mt	109	[278]				