

CHUKA



UNIVERSITY

UNIVERSITY EXAMINATIONS

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

CHEM 322: PHYSICAL CHEMISTRY III

STREAMS: BSc.

TIME: 2 HOURS

DAY/DATE: TUESDAY 19/12/2023

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

CHEM 322: PHYSICAL CHEMISTRY III**QUESTION ONE (30 marks)**

1. a.i) Find the difference in the work done when 500 ml of a gas at a pressure of 2 atmospheres is compressed to 100 ml reversibly and (a) isothermally (b) adiabatically (γ for the gas is 1.35)

[3 marks]

ii) the coefficient of thermal expansion, α is defined as $\alpha = \frac{1}{V} \left(\frac{dV}{dT} \right)_P$ while the compressibility k is defined as $k = -\frac{1}{V} \left(\frac{dV}{dP} \right)_T$. Evaluate them for an ideal gas and prove that $\left(\frac{dP}{dT} \right)_V = \frac{\alpha}{k}$. (3marks)

iii) Show that $\left(\frac{\partial \alpha}{\partial P} \right)_T + \left(\frac{\partial k}{\partial T} \right)_P = 0$ [3 marks]

iv) $\left(\frac{\partial E}{\partial V} \right)_T = 0$, Show that $\left(\frac{\partial E}{\partial P} \right)_T = 0$ [2 marks]

v) A sample of gas changes in volume from 4.00 L to 6.00 L against an external pressure of 1.50 atm, and simultaneously absorbs 1000 J of heat. What is the change in the internal energy of the system? [2 marks]

b.i) 16 gm of O_2 at $27^\circ C$ and 10 atm undergoes reversible adiabatic expansion to 1 atm.

I) Calculate the final temperature, work done, ΔU , and ΔH . If the same expansion takes place reversibly against a constant pressure of 1 atm, [2 marks]

II) What will be the final temperature, W , ΔU , and ΔH [2 marks]

III) if the same expansion takes place against a constant pressure of 1 atm but till the volume is trebled (then pressure is raised to match the internal pressure), what will be the final temperature, W , ΔU and ΔH [2 marks]

ii) If 1 mol of an ideal gas undergoes a reversible polytropic expansion, $PV^n = C$ holds where n and c are constants with $n > 1$.

a) Calculate the work done if the gas expands from V_1 to V_2 litres with $T_1 = 300K$ and $T_2 = 200K$ with $n=2$ [2 marks]

b) If $C_v = 5R/2$, calculate Q , ΔU and ΔH [2 marks]

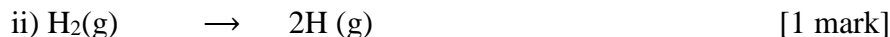
iii) One mole of oxygen expands adiabatically against a constant external pressure of 1 atmosphere until the pressure balances. The initial temperature and Volume are $200^\circ C$ and 20L respectively.

a) Explain whether the process is reversible or not. [1 mark]

- b) Calculate the final temperature, Work done and the change in entropy. [2 marks]
- c) Will the quantities be different if n moles of oxygen were taken. Give a reason. Assume ideal behavior [1 mark]
- d) Calculate ΔU and ΔH [2 marks]
- c) A compressor designed to compress air is used instead to compress helium. It is found that the Compressor Overheats. Explain this effect, assuming that the compression is approximately adiabatic and starting pressure is the same for both gases [1 mark]

QUESTION TWO (20 marks)

- 2 a. i) Explain how on the basis of the efficiency of reversible heat engine, the thermodynamic scale of temperature was developed by Lord kelvin [3 mark]
- ii) Calculate the amount of heat supplied to carnot's cycle working between 368K and 288K if the maximum work obtained is 895 joules [0.5 mark]
- iii) predict in which of the following processes entropy increases or decreases
- a) A liquid crystallizes into a solid [1 mark]
- b) The temperature of a crystalline solid is raised from 0K to 115K
1mark
- c) The following reactions are carried out



- b. i) the Joule –thomson coefficient for van der Waals is given by

$$\mu_{JT} = \frac{1}{C_{P,M}} \left[\frac{2a}{RT} - b \right] = \left(\frac{\partial T}{\partial P} \right)_H$$

Calculate the value for the isothermal compression of 1 mole of nitrogen from 1 to 500 atmospheres at 300K, $a=0.1353\text{nm}^4\text{mol}^{-2}$, $b= 0.039 \times 10^{-3} \text{ m}^3\text{mol}^{-1}$. [3 marks]

- ii) One mole of air at 750 K is expanded reversibly and adiabatically from 1 dm³ to 10 dm³. Taking $C_{v,m}$ for air as 20.92JK⁻¹mol⁻¹ and assuming ideal behavior, calculate the final temperature, ΔE , ΔH , and ΔW (2 marks)
- iii) Calculate the molar entropy change of mixing 0.2 mole of oxygen and 0.6 mole of nitrogen at 25⁰c assuming that they are gases [1.5 marks]
- iv) To what pressure must a certain ideal gas ($\gamma=1.4$) at 373K and 1-atmosphere pressure be compressed adiabatically in order to raise its temperature to 773K? (1mark)

c A mole of an ideal monoatomic gas at 20 atm. And 300k is expanded adiabatically against a constant pressure of 10 atm. Calculate the entropy change for the gas. [5 marks]

QUESTION THREE (20 marks)

3 a. i) the equilibrium constant K_P for a reaction $A+B \rightleftharpoons C+D$ is 10^{-12} at 327°C and 10^{-7} at 427°C . Calculate the enthalpy of the reaction. ($R=8.314\text{JK}^{-1}\text{mol}^{-1}$) [2 marks]

ii) Briefly describe the importance of the third law [3 marks]

iii) C_v for a metal is $3.04\text{ JKT}^{-1}\text{mol}^{-1}$ at 20K. Calculate the absolute entropy in $\text{JK}^{-1}\text{mol}^{-1}$ at 20K [2 marks]

(iv) Calculate the vapor pressure of water at 90.0°C if its value at 100.0°C is 76.0 cm. The mean heat of vaporization of water in the temperature range 90° and 100°C is 542 calories per gram. (1 mark)

(v) Prove that entropy change for 1 mole of an ideal gas is given by

$$\Delta s = 2.303C_v \log \frac{T_2}{T_1} + 2.303 R \log \frac{V_2}{V_1} \quad [1.5\text{marks}]$$

b.i) Explain how the Validity of the third law of thermodynamics can be tested [2 marks]

ii) Calculate the entropy change that takes place during the conversion of 1 mol of ice at 273.1K and one atm, pressure into steam at 373.1K and one atm pressure given that the molar fusion of ice ΔH_f is 6.00 KJmol^{-1} at 273.1K and molar heat of vaporization of water, ΔH_v at 373.1K IS 40.60 kJmol^{-1} . Assume that the molar heat capacity C_p in this temperature range is constant at $75.2\text{ JK}^{-1}\text{mol}^{-1}$ [2 marks]

iii) The following reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ the free energy changes at 25°C and 35°C are -33.089 and -28.018 KJ respectively. Calculate the heat of the reaction. [1.5 marks]

iv) The ClBrO_3 molecule can have four possible arrangements with nearly the same energy. calculate the residual entropy of the ClBrO_3 molecule. [1 mark]

c. show that the efficiency of a reversible Carnot cycle is $T_2 - T_1 / T_2$ where T_2 and are temperature of the source and the sink [4 marks]

QUESTION FOUR (20 MARKS)

4.a) In biological cells that have a plentiful supply of O_2 , glucose is oxidized completely to CO_2 and H_2O by a process called *aerobic oxidation*. Muscle cells may be deprived of O_2 during vigorous exercise and, in that case, one molecule of glucose is converted to two molecules of lactic acid ($CH_3CH(OH)COOH$) by a process called *anaerobic glycolysis*

(i) When 0.3212 g of glucose was burned in a bomb calorimeter of calorimeter constant 641 J K^{-1} the temperature rose by 7.793 K. Calculate [1.5marks]

- (I) the standard molar enthalpy of combustion,
- (II) The standard internal energy of combustion,
- (III) The standard enthalpy of the formation of glucose.

(b) (i) What is the biological advantage (in kilojoules per mole of energy released as heat) of complete aerobic oxidation compared with anaerobic glycolysis to lactic acid? [1mark]

ii) Concerns over the harmful effects of chlorofluorocarbons on stratospheric ozone have motivated a search for new refrigerants. One such alternative refrigerant is 1,1,1,2-tetrafluoroethane (refrigerant HFC-134a). Tillner-Roth and Baehr published a compendium of thermophysical properties of this substance (*J. Phys. Chem. Ref. Data* **23**, 657 (1994)), from which properties such as the Joule–Thomson coefficient μ can be computed.

(I) Compute μ at 0.100 MPa and 300 K from the following data (all referring to 300 K): (2.5marks)

p/MPa	0.080	0.100	0.12
Specific enthalpy/(kJ kg^{-1})	426.48	426.12	425.76

(The specific constant-pressure heat capacity is 0.7649 kJ K^{-1} kg^{-1} .)

(II) Compute μ at 1.00 MPa and 350 K from the following data (all referring to 350 K):

(2 marks)

p/MPa	0.80	1.00	1.2
Specific enthalpy/(kJ kg^{-1})	461.93	459.12	456.15

(The specific constant-pressure heat capacity is 1.0392 kJ K^{-1} kg^{-1} .)

c) (i) Nitric acid hydrates have received much attention as possible catalysts for heterogeneous reactions that bring about the Antarctic ozone hole. Worsnop *et al.* investigated the thermodynamic stability of these hydrates under conditions typical of the polar winter stratosphere

(*Science* **259**, 71 (1993)). They report thermodynamic data for the sublimation of mono-, di-, and trihydrates to nitric acid and water vapors, $\text{HNO}_3 \cdot n\text{H}_2\text{O}(\text{s}) \rightarrow \text{HNO}_3(\text{g}) + n\text{H}_2\text{O}(\text{g})$, for $n = 1, 2$, and 3 . Given $\Delta_r G^\circ$ and $\Delta_r H^\circ$ for these reactions at 220 K, use the Gibbs–Helmholtz equation to compute $\Delta_r G^\circ$ at 190 K. [3 marks]

n	1	2	3
$\Delta_r G^\circ / (\text{kJ mol}^{-1})$	46.2	69.4	93.2
$\Delta_r H^\circ / (\text{kJ mol}^{-1})$	127	188	237

ii) To calculate the work required to lower the temperature of an object, we need to consider how the coefficient of performance changes with the temperature of the object.

(I) Find an expression for the work of cooling an object from T_i to T_f when the refrigerator is in a room at a temperature T_h . *Hint.* Write $dw = dq/c(T)$, relate dq to dT through the heat capacity C_p , and integrate the resulting expression. Assume that the heat capacity is independent of temperature in the range of interest. [1 mark]

(II) Use the result in part (I) to calculate the work needed to freeze 250 g of water in a refrigerator at 293 K. How long will it take when the refrigerator operates at 100 W? [3 mark]

d i) The vapor pressure, p , of nitric acid varies with temperature as follows:

$\theta / ^\circ\text{C}$	0	20	40	50	70	80	90	100
p / kPa	1.92	6.38	17.7	27.7	62.3	89.3	124.9	170.9

What are (I) the normal boiling point and (II) the enthalpy of vaporization of nitric acid?

[3 marks]

ii) The change in enthalpy is given by $dH = C_p dT + V dp$. The Clapeyron equation relates dp and dT at equilibrium, and so in combination, the two equations can be used to find how the enthalpy changes along a phase boundary as the temperature changes and the two phases remain in equilibrium. Show that $d(\Delta H/T) = \Delta C_p d \ln T$. [3 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}

PERIODIC TABLE OF THE ELEMENTS

IA 1												VIIA 17				0 18				
1												13	14	15	16	1	2			
H 1.008												B 10.81	C 12.011	N 14.007	O 15.999	F 18.9984	He 4.0026			
2												3	4	5	6	7	8	9	10	
Li 6.941		Be 9.0122											Al 26.9815	Si 28.085	P 30.9738	S 32.06	Cl 35.453	Ar 39.948		
3		4											11	12	13	14	15	16	17	18
Na 22.9898		Mg 24.3050	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18		
4		5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	
K 39.0983		Ca 40.078	Sc 44.9559	Ti 47.867	V 50.9415	Cr 51.9961	Mn 54.9380	Fe 55.845	Co 58.9332	Ni 58.6934	Cu 63.546	Zn 65.38	Ga 69.723	Ge 72.63	As 74.9216	Se 78.96	Br 79.904	Kr 83.798		
5		6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22		
Rb 85.4678		Sr 87.62	Y 88.9058	Zr 91.224	Nb 92.9064	Mo 95.96	Tc (98)	Ru 101.07	Rh 102.9055	Pd 106.42	Ag 107.8682	Cd 112.411	In 114.818	Sn 118.710	Sb 121.760	Te 127.60	I 126.9045	Xe 131.293		
6		7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22			
Cs 132.9055		Ba 137.327	La 138.9055	Hf 178.49	Ta 180.9479	W 183.84	Re 186.207	Os 190.23	Ir 192.217	Pt 195.084	Au 196.9666	Hg 200.59	Tl 204.38	Pb 207.2	Bi 208.9804	Po (209)	At (210)	Rn (222)		
7		8	9	10	11	12	13	14	15	16	17	18	19	20	21	22				
Fr (223)		Ra (226)	Ac (227)	Rf (261)	Db (268)	Sg (271)	Bh (270)	Hs (277)	Mt (276)	Ds (281)	Rg (280)	Cn (285)	Uut (284)	Fl (289)	Uup (288)	Lv (293)	Uus (294)	Uuo (294)		

*Lanthanide Series

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
140.116	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

** Actinide Series

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

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.