

**UNIVERSITY OF SWAZILAND**

**SUPPLEMENTARY EXAMINATION 2015**

**TITLE OF PAPER:** **INTRODUCTORY PHYSICAL CHEMISTRY**

**COURSE NUMBER:** **C202**

**TIME:** **3 HOURS**

**INSTRUCTIONS:** **ANSWER ANY FOUR QUESTIONS.**

**BEGIN THE ANSWER TO EACH QUESTION ON  
SEPARATE SHEET OF PAPER.**

**EACH QUESTION IS 25 MARKS**

**DATA SHEETS ARE PROVIDED WITH THIS  
EXAMINATION PAPER**

**DO NOT OPEN THIS PAPER UNTIL THE INVIGILATOR INSTRUCTS YOU TO DO  
SO.**

### **QUESTION 1 (25 Marks)**

a) Many gases show nearly ideal behaviour at room temperature and low pressures. Using a sketch of either an isotherm or the compressibility factor 'z' for a real gas and that of an ideal gas , briefly explain how they compare at high pressure, moderate pressure, and at low pressure. [15]

b) The equation of state of Dieterici is:

$$P = \frac{nRT}{V - nb} e^{-an/VRT}$$

i) Express the equation in a Virial equation form and find expressions for the second and third Virial coefficients. [5]

useful relations: Virial equation states:  $PV_m = RT + B(T)\left(\frac{1}{V_m}\right) + C(T)\left(\frac{1}{V_m}\right)^2 + \dots$

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots \quad \& \quad \frac{1}{1-x} = 1 + x + x^2 + x^3 + \dots$$

ii). Calculate the temperature below which O<sub>2</sub> behaves as a real gas. [5]  
 $a=1.748 \text{ L}^2 \text{ atm. mol}^{-2}$  and  $b=0.0345 \text{ Lmol}^{-1}$

### **QUESTION 2 (25 Marks)**

a) Briefly define any three of the following terms: [15]

- i). Enthalpy
- ii). Internal Energy
- iii). Equipartition principle
- iv). State function

b). Derive an expression for work in an isothermal reversible expansion of an ideal gas. [5]

Useful relation:  $W = - \int_{x_1}^{x_2} F(x)dx$

c). 2.5 mol of Argon is taken from an initial state at  $P_i=10.0$  atm and  $T=27^\circ\text{C}$  to a final state through the following sequence: [5]

- i) isothermal reversible expansion to twice its initial volume.
- iii) Isothermal expansion to 3 times its initial volume against a constant external pressure of 1 atm.

Calculate  $W$  for each step.

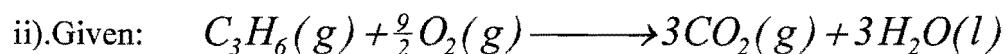
**QUESTION 3 (25 Marks)**

a).

- i). Write short notes on the following: [10]
  - 1) Hess's Law of thermodynamics
  - 2) Kirchoff's Laws of thermodynamics
- ii) Calculate  $\Delta H_m^\theta$  at 298 K for the following reaction: [3]



	N <sub>3</sub> H(l)	NO(g)	H <sub>2</sub> O <sub>2</sub> (l)	N <sub>2</sub> (g)
$\Delta H_f^\theta/\text{kJmol}^{-1}$	+264	90.25	-187.8	0



$$\Delta H_m^\theta(\text{hydrogenation, } C_3H_6(g)) = -124 \text{ kJmol}^{-1}$$

$$\Delta H_m^\theta(\text{combustion, } C_3H_6(g)) = -2220 \text{ kJmol}^{-1}$$

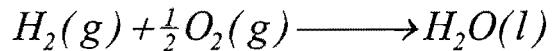
$$\Delta H_m^\theta(\text{formation, } H_2O(l)) = -286 \text{ kJmol}^{-1}$$

Determine  $\Delta H_m^\theta(\text{combustion, } C_3H_6(g))$ . [2]

b). i). To calibrate a calorimeter a 1.00g sample of  $C_6H_{12}(l)$  was burned at constant pressure and it caused the temperature of the calorimeter to rise by  $0.160^\circ\text{C}$ . Then a 1.50 g sample of an unknown liquid was burned in the same calorimeter, causing a temperature rise of  $0.249^\circ\text{C}$ . Is the unknown  $C_6H_{12}(l)$  or  $C_6H_{14}(l)$ ?

Explain the basis of your answer. [5]

ii). Using Kirrchoff's Law Calculate  $\Delta H_f$  at 100°C for the reaction: [5]



given:

	H <sub>2</sub> (g)	O <sub>2</sub> (g)	H <sub>2</sub> O(l)
C <sub>p,m</sub> /Jmol <sup>-1</sup> K <sup>-1</sup>	28.82	29.36	33.58

#### QUESTION 4 (25 Marks)

a) Write short notes on the following [10]

- i) Gibbs Free Energy
- ii) HelmHoltz Function

b) The master equation states that:

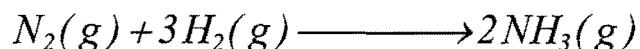
$$dU = TdS - PdV$$

a). Prove that:  $dG = VdP - SdT$  and  $-S = \left(\frac{\partial G}{\partial T}\right)_P$  [3]

b). Derive the Gibbs-Helmholtz equation.

$$\left(\frac{\partial \left(\frac{\Delta G}{T}\right)}{\partial T}\right)_P = -\frac{\Delta H}{T^2} \quad [5]$$

c). The standard enthalpy of the following reaction at 298 K is -92.38 kJ/mol and the standard Gibbs function at the same temperature is -33.26 kJ/mol.



- i) Estimate the Gibbs function at 500 K using the Gibbs-Helmholtz equation. [2]
- ii) Using Kirrchoff's Law calculate the Gibbs function. Comment on the magnitude of the Gibbs function. (Assume C<sub>p</sub> is dependent on temperature and  $\Delta H^\theta$  independent on temperature). [5]

Substance	$\Delta H_f^\theta / \text{kJ mol}^{-1}$	$S^\theta(298 \text{ K}) / \text{J K}^{-1} \text{mol}^{-1}$	$C_p / \text{JK}^{-1} \text{mol}^{-1}$		
			a	b/10 <sup>-3</sup>	c/10 <sup>5</sup>
N <sub>2</sub> (g)	0	192.1	28.58	3.77	-0.50
H <sub>2</sub> (g)	0	130.6	27.28	3.26	0.50
NH <sub>3</sub> (g)	-46.11	192.5	29.75	25.10	-1.55

$$*C_p = a + bT + cT^2 \text{ in the range 273 to 1500 K}$$

### QUESTION 5 (25 Marks)

The Clapeyron equation states that:

$$\frac{dP}{dT} = \frac{\Delta S_m}{\Delta V_m}$$

where P is the vapour pressure of a solid or liquid,  $\Delta S_m$  and  $\Delta V_m$  are the changes in molar entropy and molar volume for phase change respectively.

- a) Derive the Clausius-Clapeyron equation for evaporation. [15]

$$\ln \frac{P_2}{P_1^*} = \frac{\overline{\Delta H}_{vap}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

- b). The railway station at Jungfraujoch is the highest in the world, at 3540 m above sea level. The atmospheric pressure there is 0.662 atm. [10]

- i) At what temperature does the station-master's kettle boil?  
ii). calculate the melting point of ice at the same altitude.

useful information: enthalpy of vaporisation of water is 40.7 kJmol<sup>-1</sup> at 373.15K and the enthalpy of fusion of water is 6.008 kJmol<sup>-1</sup> at 273.15 K

useful relation:

$$\ln \chi_B = \left\{ \frac{-\Delta H_{melt,m}}{R} \left( \frac{1}{T} - \frac{1}{T^*} \right) \right\}$$

**QUESTION 6** (25 Marks)

a) Write short notes on ***Any Two*** of the following: [10]

- i) Upper Consulate Temperature
- ii) Eutectic temperature
- iii) Azeotrope
- iii) Zeotrope
- iv) Phase reaction

Use example and diagrams to illustrate your points.

b) Write short notes on **Any Three** of the following concepts:

- i) Statistical view of entropy [5]
- ii) Clausius inequality [5]
- iii) Second law of thermodynamics [5]
- iv) Third law of thermodynamics [5]

Use example and diagrams to illustrate your points.

Useful Relations				General Data			
$(RT)_{298.15K} = 2.4789 \text{ kJ/mol}$				speed of light	c	$2.997\ 925 \times 10^8 \text{ ms}^{-1}$	
$(RT/F)_{298.15K} = 0.025\ 693 \text{ V}$				charge of proton	e	$1.602\ 19 \times 10^{-19} \text{ C}$	
T/K: 100.15 298.15 500.15 1000.15				Faraday constant	F=Le	$9.648\ 46 \times 10^4 \text{ C mol}^{-1}$	
T/Cm <sup>-1</sup> : 69.61 207.22 347.62 695.13				Boltzmann constant	k	$1.380\ 66 \times 10^{-23} \text{ J K}^{-1}$	
$1\text{mmHg} = 133.222 \text{ N m}^{-2}$				Gas constant	R=Lk	$8.314\ 41 \text{ J K}^{-1} \text{ mol}^{-1}$	
$hc/k = 1.438\ 78 \times 10^{-2} \text{ m K}$						$8.205\ 75 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$	
1atm	1 cal	1 eV	1cm <sup>-1</sup>	Planck constant	h	$6.626\ 13 \times 10^{-34} \text{ Js}$	
$1.01325 \times 10^5 \text{ N m}^{-2}$	4.184 J	$1.602\ 189 \times 10^{-19} \text{ J}$	$0.124 \times 10^{-3} \text{ eV}$		$\hbar = \frac{h}{2\pi}$	$1.054\ 59 \times 10^{-34} \text{ Js}$	
760torr		96.485 kJ/mol	$1.9864 \times 10^{-23} \text{ J}$	Avogadro constant	L or N <sub>av</sub>	$6.022\ 14 \times 10^{23} \text{ mol}^{-1}$	
		8065.5 cm <sup>-1</sup>		Atomis mass unit	$\mu$	$1.660\ 54 \times 10^{-27} \text{ kg}$	
SI-units:				Electron mass	$m_e$	$9.109\ 39 \times 10^{-31} \text{ kg}$	
$1 L = 1000 \text{ ml} = 1000 \text{ cm}^3 = 1 \text{ dm}^3$				Proton mass	$m_p$	$1.672\ 62 \times 10^{-27} \text{ kg}$	
1 dm = 0.1 m				Neutron mass	$m_n$	$1.674\ 93 \times 10^{-27} \text{ kg}$	
1 cal (thermochemical) = 4.184 J				Vacuum permittivity	$\epsilon_0 = \mu_0^{-1} c^{-2}$	$8.854\ 188 \times 10^{-12} \text{ J}^1 \text{ C}^2 \text{ m}^{-1}$	
dipole moment: 1 Debye = $3.335\ 64 \times 10^{-30} \text{ C m}$				Vacuum permeability	$\mu_0$	$4\pi \times 10^{-7} \text{ Js}^2 \text{ C}^{-2} \text{ m}^{-1}$	
force: $1N = 1J \text{ m}^{-1} = 1 \text{ kgms}^{-2} = 10^5 \text{ dyne}$	pressure: $1Pa = 1Nm^{-2} = 1Jm^{-3}$			Bohr magneton	$\mu_B = e\hbar / 2m_e$	$9.274\ 02 \times 10^{-24} \text{ JT}^{-1}$	
$IJ = I \text{ Nm}$				Nuclear magneton	$\mu_N = e\hbar / 2m_p$	$5.05079 \times 10^{-27} \text{ JT}^{-1}$	
power: $1W = 1J \text{ s}^{-1}$	potential: $1V = 1 \text{ JC}^{-1}$			Gravitational constant	G	$6.67259 \times 10^{-11} \text{ Nm}^2 \text{ kg}^{-2}$	
magnetic flux: $1T = 1 \text{ Vs}^{-2} = 1 \text{ JCsm}^{-2}$	current: $1A = 1 \text{ Cs}^{-1}$			Gravitational acceleration	g	$9.80665 \text{ ms}^{-2}$	
Prefixes:				Bohr radius	a <sub>0</sub>	$5.291\ 77 \times 10^{-11} \text{ m}$	
pico	nano	micro	milli				
$10^{-12}$	$10^{-9}$	$10^{-6}$	$10^{-3}$				





Useful Relations				General Data			
(RT) <sub>298.15K</sub> =2.4789 kJ/mol				speed of light	c	2.997 925x10 <sup>8</sup> ms <sup>-1</sup>	
(RT/F) <sub>298.15K</sub> =0.025 693 V				charge of proton	e	1.602 19x10 <sup>-19</sup> C	
T/K: 100.15 298.15 500.15 1000.15				Faraday constant	F=Le	9.648 46x10 <sup>4</sup> C mol <sup>-1</sup>	
T/Cm <sup>-1</sup> : 69.61 207.22 347.62 695.13				Boltzmann constant	k	1.380 66x10 <sup>-23</sup> J K <sup>-1</sup>	
1mmHg=133.222 N m <sup>-2</sup>				Gas constant	R=Lk	8.314 41 J K <sup>-1</sup> mol <sup>-1</sup>	
hc/k=1.438 78x10 <sup>-2</sup> m K						8.205 75x10 <sup>-2</sup> dm <sup>3</sup> atm K <sup>-1</sup> mol <sup>-1</sup>	
1atm	1 cal	1 eV	1cm <sup>-1</sup>				
=1.01325x10 <sup>5</sup> Nm <sup>-2</sup>	=4.184 J	=1.602 189x10 <sup>-19</sup> J	=0.124x10 <sup>-3</sup> eV	Planck constant	h	6.626 18x10 <sup>-34</sup> Js	
=760torr		=96.485 kJ/mol	=1.9864x10 <sup>-23</sup> J		$\hbar = \frac{h}{2\pi}$	1.054 59x10 <sup>-34</sup> Js	
=1 bar		= 8065.5 cm <sup>-1</sup>					
<b>SI-units:</b>				Avogadro constant	L or N <sub>av</sub>	6.022 14x10 <sup>23</sup> mol <sup>-1</sup>	
1 L = 1000 ml = 1000cm <sup>3</sup> = 1 dm <sup>3</sup>				Atomis mass unit	u	1.660 54x10 <sup>-27</sup> kg	
1 dm = 0.1 m				Electron mass	m <sub>e</sub>	9.109 39x10 <sup>-31</sup> kg	
1 cal (thermochemical) = 4.184 J				Proton mass	m <sub>p</sub>	1.672 62x10 <sup>-27</sup> kg	
dipole moment: 1 Debye = 3.335 64x10 <sup>-30</sup> C m				Neutron mass	m <sub>n</sub>	1.674 93x10 <sup>-27</sup> kg	
force: 1N=1J m <sup>-1</sup> = 1kgms <sup>-2</sup> =10 <sup>5</sup> dyne pressure: 1Pa=1Nm <sup>-2</sup> =1Jm <sup>-3</sup>				Vacuum permittivity	$\epsilon_0 = \mu_0^{-1} c^{-2}$	8.854 188x10 <sup>-12</sup> J <sup>1</sup> C <sup>2</sup> m <sup>-1</sup>	
1J = 1 Nm				Vacuum permeability	$\mu_0$	4πx10 <sup>-7</sup> Js <sup>2</sup> C <sup>-2</sup> m <sup>-1</sup>	
power: 1W = 1J s <sup>-1</sup>			potential: 1V =1 J C <sup>-1</sup>	Bohr magneton	$\mu_B = \frac{e\hbar}{2m_e}$	9.274 02x10 <sup>-24</sup> JT <sup>-1</sup>	
magnetic flux: 1T=1Vs m <sup>-2</sup> =1JCsm <sup>-2</sup>			current: 1A=1Cs <sup>-1</sup>	Nuclear magneton	$\mu_N = \frac{e\hbar}{2m_p}$	5.05079x10 <sup>-27</sup> JT <sup>-1</sup>	
<b>Prefixes:</b>				Gravitational constant	G	6.67259x10 <sup>-11</sup> Nm <sup>2</sup> kg <sup>-2</sup>	
p n m m c d k M G				Gravitational acceleration	g	9.80665 ms <sup>-2</sup>	
pico nano micro milli centi deci kilo mega giga				Bohr radius	a <sub>0</sub>	5.291 77x10 <sup>-11</sup> m	
10 <sup>-12</sup> 10 <sup>-9</sup> 10 <sup>-6</sup> 10 <sup>-3</sup> 10 <sup>-2</sup> 10 <sup>-1</sup> 10 <sup>3</sup> 10 <sup>6</sup> 10 <sup>9</sup>							



Heat capacities at 25°C

	C <sub>v,m</sub>	C <sub>p,m</sub>
	JK <sup>-1</sup> mol <sup>-1</sup>	JK <sup>-1</sup> mol <sup>-1</sup>
He, Ne, Ar, Kr, Xe	12.47	20.78
H <sub>2</sub>	20.50	28.81
O <sub>2</sub>	21.01	29.33
N <sub>2</sub>	20.83	29.14
CO <sub>2</sub>	28.83	37.14
NH <sub>3</sub>	27.17	35.48
CH <sub>4</sub>	27.43	35.74
N <sub>2</sub> O <sub>4</sub>		77.28
NO <sub>2</sub>		37.20

F.P Depression, B.P. Elevation

Solvent	F.P °C	K <sub>f</sub> °C kg mol <sup>-1</sup>	B.P (°C, 101kNm <sup>-2</sup> )	K <sub>b</sub> °C kg mol <sup>-1</sup>
Water	0	1.86	100.0	0.52
Benzene	5.51	5.10	80.1	2.60
Acetic Acid	16.6	3.90	118.1	3.10
Cyclohexane	6.5	20.2	81.4	2.79
Camphor	177.7	40.0	205	
Nitrobenzene	5.7	6.9	210.9	5.24
Ethanol	-177		78.5	1.22
Chloroform	-64		61.3	3.63

Third Law entropies at 25°C, Sm<sup>θ</sup>/J K<sup>-1</sup> mol<sup>-1</sup>

Solids	Liquids	Gases
Ag	42.68	H <sub>2</sub>
C(gr)	5.77	N <sub>2</sub>
C(d)	2.44	O <sub>2</sub>
Cu	33.4	Cl <sub>2</sub>
Zn	41.6	
I <sub>2</sub>	116.7	CO <sub>2</sub>
S(Rh)	31.9	HCl
		H <sub>2</sub> S
AgCl	96.2	NH <sub>3</sub>
AgBr	104.6	CH <sub>4</sub>
CuSO <sub>4</sub> ·5H <sub>2</sub> O	305.4	C <sub>2</sub> H <sub>6</sub>
HgCl <sub>2</sub>	144	CH <sub>3</sub> CHO
Sucrose	360.2	
	C <sub>6</sub> H <sub>12</sub>	

