

UNIVERSITY OF SWAZILAND

BACHELOR OF SCIENCE

SUPPLEMENTARY EXAMINATION 2006

TITLE OF PAPER : PHYSICAL CHEMISTRY

COURSE NUMBER : C202

TIME : 3 HOURS

INSTRUCTIONS : THERE ARE SIX QUESTIONS

: ANSWER ANY FOUR QUESTIONS

: BEGIN THE ANSWER TO EACH QUESTION ON
A SEPARATE SHEET OF PAPER

: 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) Define the variable, compressibility factor, z . With the aid of Lennard-Jones potential plot and compressibility plots, compare and contrast real and ideal gases.

Your account should make mention of interactions, equations and any necessary theories to help clarify your discussion.

[10]

- b) A mixture of butane (C_4H_{10}) and ethene (C_2H_4) occupied 35.5 L at 1.000 bar and 405 K. This mixture reacted completely with 220.6 g of O_2 to produce CO_2 and H_2O .
- i) What was the composition of the original mixture? Assume ideal gas behaviour. MW (O_2)=32 g/mol [12]
- ii) Calculate the partial pressure, mole fraction of CO_2 in the final mixture. [3]

Question 2 [25 Marks]

- a) Write short notes on the van der waal's equation [10]

Use diagrams, equations or plots to clarify your notes where necessary.

- b) A real gas equation of state for a gas is given by:

$$(P+an^2/V^2)(V-nb)=nRT \quad (1)$$

- (i) Derive an expression for $V_{m,c}$, T_c and P_c . [6]
- (ii) Find an expression for the Boyle's temperature, T_B . [4]
- (iii) Estimate the temperature at which oxygen behaves as an ideal gas, T_B given the constants: $a=6.493 \text{ L}^2\text{atmmol}^{-2}$ and $b=5.622 \times 10^{-2} \text{ Lmol}^{-1}$ [2]
- (iv) Estimate the radii of real gas molecules using equation (1) given that the critical molar volume is $250 \text{ cm}^3\text{mol}^{-1}$ [3]

Question 3 [25 MARKS]

- a) Derive an expression for an isothermal reversible expansion of an ideal gas. [10]

$$W = - \int_{x_i}^{x_f} f(x) dx$$

- b) 2.5 mol of Argon is at an initial state at $P_i=10.0 \text{ atm}$ and 27°C . Calculate
- i) work done when the system expands to twice its initial volume through isothermal reversible. [5]
- ii) The efficiency of the system on expansion against a constant external pressure of 5 atm to twice its initial volume. [5]
- c) State and explain the equipartition principle. Using H_2 as an example show how the principle could be used to evaluate the heat capacity ratio: $\gamma=C_{p,m}/C_{v,m}$ [5]

Question 4 [25 Marks]

- a) Compare and contrast between Second and Third law of thermodynamics [10]

For each concept include the origin or a short derivation showing its origin, an example where applicable and the role or implication of each of the concepts in thermodynamics.

- b) Calculate the change entropy of the system, surroundings and the total change in entropy when 32 g of oxygen gas at 25 °C is expanded from an initial pressure of 6.00 atm to a final pressure of 3 atm in
- Isothermal reversible expansion [5]
 - Isothermally irreversibly against a constant external pressure of 3.0 atm [5]
 - Adiabatic irreversible expansion [5]

Question 5 [25 Marks]

- a) Write short notes on **any one** of the following
- enthalpy change [10]
 - internal energy change [10]

b) To Calibrate a calorimeter a 0.8220 g benzoic acid, $C_6H_5COOH(s)$ whose enthalpy of combustion is -3251 kJ/mol , was burned at constant volume and it caused the temperature of the calorimeter to rise by 3.05 K. Then 0.727 g of an unknown compound was burned in the same calorimeter, causing a temperature rise of 2.05 K.

- Calculate the heat capacity of the calorimeter [3]
- Is the unknown compound ethanol, CH_3CH_2OH or Methanol, $CH_3OH(l)$ whose enthalpies of combustion are $\Delta_c H^\ominus = -1368 \text{ kJmol}^{-1}$ (CH_3CH_2OH) and $-726.1 \text{ kJmol}^{-1}$ ($CH_3OH(l)$), respectively. [4]

c) Using Hess's Law calculate the standard enthalpies of the following reactions

- $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$ [2]
- $Cyclopropane(g) \rightarrow propene(g)$ [2]

use table attached

d) The standard enthalpy of reaction of $C_5H_{10}O_5(s) + 5O_2(g) \rightarrow 5H_2O(l) + 5CO_2(g)$ is -2127 kJ/mol . Calculate the standard enthalpy of formation of $C_5H_{10}O_5(s)$. [4]

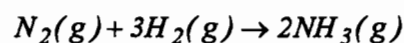
Question 6 [25 Marks]

a) Derive the integrated Gibbs-Helmholtz equation [5]

$$\frac{\Delta G_2}{T_2} - \frac{\Delta G_1}{T_1} = \Delta H \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

from the fundamental thermodynamic equation $dG = VdP - SdT$

b) Given the reaction:



Calculate the change in Gibbs free energy ΔG^θ

- i) at 298K [5]
- ii) at 500K [5]
- iii) Comment on the significance of the values obtained in (i) and (ii). [2]

c) The Master Equation states that $dU = TdS - PdV$.

(i) Using the Master Equation above derive the Maxwell's relation

$$(\delta S / \delta V)_T = (\delta P / \delta T)_V \quad [5]$$

(ii) Using the Maxwell's relation in (i) find the expression for internal energy change with volume under isothermal conditions for real gases using Van der Waal's relation:

$$(P + an^2/V^2)(V - nb) = nRT \quad [5]$$

PHYSICAL CHEMISTRY
GENERAL DATA SHEETS

5 PAGES

THIS LEAFLET CONSISTS OF:

- ◆ GENERAL CONSTANTS
- ◆ STANDARD MOLAR ENTHALPIES
- ◆ STANDARD MOLAR ENTROPIES
- ◆ STANDARD MOLAR GIBBS FREE ENERGIES
- ◆ HEAT CAPACITIES
- ◆ PERIODIC TABLE

Useful Relations	General Data		
$(RT)_{298.15K} = 2.4789 \text{ kJ/mol}$	speed of light	c	$2.997925 \times 10^8 \text{ m s}^{-1}$
$(RT/F)_{298.15K} = 0.025693 \text{ V}$	charge of proton	e	$1.60219 \times 10^{-19} \text{ C}$
T/K: 100.15 298.15 500.15 1000.15	Faraday constant	$F = Le$	$9.64846 \times 10^4 \text{ C mol}^{-1}$
T/Cm ⁻¹ : 69.61 207.22 347.62 695.13	Boltzmann constant	k	$1.38066 \times 10^{-23} \text{ J K}^{-1}$
1mmHg = 133.222 N m^{-2}	Gas constant	$R = Lk$	$8.31441 \text{ J K}^{-1} \text{ mol}^{-1}$
hc/k = $1.43878 \times 10^{-2} \text{ m K}$			$8.20575 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$
1atm	1 cal	1 eV	1cm ⁻¹
$1.01325 \times 10^5 \text{ Nm}^{-2}$	4.184 J	$1.602189 \times 10^{-19} \text{ J}$	$0.124 \times 10^{-3} \text{ eV}$
760 torr	96.485 kJ/mol	$1.9864 \times 10^{23} \text{ J}$	
	8065.5 cm ⁻¹		
SI-units:	Avogadro constant	L or N_{av}	$6.02214 \times 10^{23} \text{ mol}^{-1}$
$1 L = 1000 \text{ ml} = 1000 \text{ cm}^3 = 1 \text{ dm}^3$	Atomis mass unit	u	$1.66054 \times 10^{-27} \text{ kg}$
1 dm = 0.1 m	Electron mass	m_e	$9.10939 \times 10^{-31} \text{ kg}$
1 cal (thermochemical) = 4.184 J	Proton mass	m_p	$1.67262 \times 10^{-27} \text{ kg}$
dipole moment: 1 Debye = $3.33564 \times 10^{-30} \text{ C m}$	Neutron mass	m_n	$1.67493 \times 10^{-27} \text{ kg}$
force: $1N = 1J \text{ m}^{-1} = 1kgms^{-2} = 10^5 \text{ dyne}$	Vacuum permittivity	$\epsilon_0 = \mu_0^{-1} c^{-2}$	$8.854188 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$
$1Pa = 1Nm^{-2} = 1Jm^{-3}$	Vacuum permeability	μ_0	$4\pi \times 10^{-7} \text{ Js}^2 \text{ C}^{-2} \text{ m}^{-1}$
$1J = 1Nm$	Bohr magneton	$\mu_B = e\hbar/2m_p$	$9.27402 \times 10^{-24} \text{ JT}^{-1}$
power: $1W = 1J \text{ s}^{-1}$	Nuclear magneton	$\mu_N = e\hbar/2m_p$	$5.05079 \times 10^{-27} \text{ JT}^{-1}$
magnetic flux: $1T = 1Vsm^{-2} = 1JCs^{-1}$	current: $1A = 1Cs^{-1}$		
Prefixes:	Gravitational constant	G	$6.67259 \times 10^{-11} \text{ Nm}^2 \text{ kg}^{-2}$
p nano	Gravitational acceleration	g	9.80665 ms^{-2}
10 ⁻¹² pico	Bohr radius	a_0	$5.29177 \times 10^{-11} \text{ m}$

Heat capacities at 25°C

	$C_{v,m}$ JK ⁻¹ mol ⁻¹	$C_{p,m}$ JK ⁻¹ mol ⁻¹
He, Ne, Ar, Kr, Xe	12.47	20.78
H ₂	20.50	28.81
O ₂	21.01	29.33
N ₂	20.83	29.14
CO ₂	28.83	37.14
NH ₃	27.17	35.48
CH ₄	27.43	35.74

F.P. Depression, B.P. Elevation

Solvent	F.P. °C	K_f °C kg mol ⁻¹	B.P. (°C, 101kNm ⁻²)	K_b °C kg mol ⁻¹
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, Sm⁰/J K⁻¹ mol⁻¹

Solids		Liquids		Gases	
Ag	42.68	Hg	76.02	H ₂	130.6
C(gr)	5.77	Br ₂	152.3	N ₂	192.1
C(d)	2.44			O ₂	205.1
Cu	33.4			Cl ₂	223.0
Zn	41.6	H ₂ O	70.0		
I ₂	116.7			CO ₂	213.7
S(Rh)	31.9	HNO ₃	155.6	HCl	186.8
				H ₂ S	205.6
AgCl	96.2	C ₂ H ₅ OH	161.0	NH ₃	192.5
AgBr	104.6	CH ₃ OH	126.7	CH ₄	186.1
CuSO ₄ ·5H ₂ O	305.4	C ₆ H ₆	49.03	C ₂ H ₆	229.4
HgCl ₂	144	CH ₃ COOH	159.8	CH ₃ CHO	265.7
Sucrose	360.2	C ₆ H ₁₂	298.2		

THE PERIODIC TABLE OF ELEMENTS

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
	IA	IIA	IIIB	IVB	VB	VIB	VIIIB	VIIIB	VIIIB	IB	IIB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA	
Period 1	1 H 1.008																	2 He 4.003	
2	3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18	
3	11 Na 22.99	12 Mg 24.31											13 Al 26.9	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95	
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.01	25 Mn 54.9	26 Fe 55.85	27 Co 58.71	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.7	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.91	36 Kr 83.80	
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 91.22	42 Mo 95.94	43 Tc 98.9	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3	
6	56 Cs 132.9	56 Ba 137.3	71 Lu 174.9	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 196.9	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 208.9	84 Po 210	85 At 210	86 Rn 222	
7	87 Fr 223	88 Ra 226.0	103 Lr 257	104 Unq 257	105 Unp 257	106 Unh 257	107 Uns 257	108 Uno 257	109 Une 257										

Lanthanides	57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm 146.9	62 Sm 150.9	63 Eu 151.3	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0
Actinides	89 Ac 227.0	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.1	94 Pu 239.1	95 Am 241.1	96 Cm 247.1	97 Bk 249.1	98 Cf 251.1	99 Es 254.1	100 Fm 257.1	101 Md 258.1	102 No 255

Numbers below the symbol indicates the atomic masses; and the numbers above the symbol indicates the atomic numbers.
 SOURCE: International Union of Pure and Applied Chemistry, I mills, ed., Quantities, Units, and symbols in Physical Chemistry, Blackwell Scientific publications, Boston.