

UNIVERSITY OF SWAZILAND

BACHELOR OF SCIENCE

SUPPLEMENTARY EXAMINATION 2007

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) Write short notes on Van der Waals 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:

$$(P + 5an^2/V^2)(V - nb) = nRT \quad (1)$$

- (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: $a = 6.493 \text{ L}^2 \text{atmmol}^{-2}$, $b = 5.622 \times 10^{-2} \text{ Lmol}^{-1}$ [2]
- (iv) Estimate the radii of real gas molecules using equation (1) for real gases given a critical molar volume of $250 \text{ cm}^3 \text{mol}^{-1}$ [2]

QUESTION 2 [25 marks]

- a) Using examples and/or diagrams compare and contrast the following terms

- i) reversible and irreversible expansion [5]
- ii) path and state functions [5]
- iii) change in internal energy and change in enthalpy [5]

- b) 4 moles of butane occupies 24 L at 310 K.

- i) Derive an expression for reversible isothermal expansion. [5]
- ii) Calculate the work done and heat involved when the gas expands isothermally against a constant external pressure of 100 torr until its volume has doubled. [2]
- iii) Calculate the efficiency of the system in 1 b (ii) above. [3]

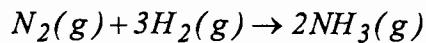
Question 3 [25 Marks]

- a) Derive the integrated Gibbs-Helmholtz equation [3]

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

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)

- (i) Using an appropriate Master Equation 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:

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

Question 4 [25 Marks]

- a) Compare and contrast **Any One Pair** of the following concepts:

- i) Statistical view and the thermodynamic view of entropy [10]
ii) Adiabatic and Isothermal expansion [10]
iii) 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) 1.00 mol of perfect gas at 27°C is expanded isothermally from an initial pressure of 3.00 atm to a final pressure of 1.00 atm. Calculate q , w , ΔS_{sys} , ΔS_{surr} and ΔS_{tot} if the expansion is done:
(1) reversibly, and [5]
(2) against a constant external pressure of 1.00 atm. [5]
(3) adiabatically against a constant pressure of 1.00 atm. [5]

Question 5 [25 Marks]

- a) Write short notes on **any two** of the following

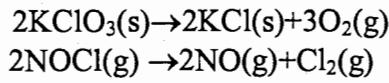
- i) enthalpy change [5]
ii) internal energy change [5]
iii) Hess's Law [5]

- b) To Calibrate a calorimeter a 0.120 g naphthalene, C₁₀H₈(s), was burnt at constant volume and it caused the temperature of the calorimeter to rise by 3.05 K. Then 0.10 g of an unknown compound was burned in the same calorimeter, causing a temperature rise of 2.05 K.
(i) Calculate the heat capacity of the calorimeter [3]
(ii) Is the unknown compound phenol, C₆H₅OH(s) or ethanol, CH₃CH₂OH(l) whose enthalpies of combustion are $\Delta_c H^\theta = -3054 \text{ kJ mol}^{-1}$ and $-1368 \text{ kJ mol}^{-1}$ respectively. [4]

- c) Calculate the standard enthalpies of formation of:

- i) KClO₃(s) from the enthalpy of formation of KCl [4]
ii) NOCl(g) from the enthalpy of formation of NO [4]

Given the attached table and the following information:



$$\begin{aligned} \Delta_f H^\theta &= -89.4 \text{ kJ/mol} \\ \Delta_f H^\theta &= +76.5 \text{ kJ/mol} \end{aligned}$$

QUESTION 6 [25 MARKS]

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

- i) Phase rule
- ii) Eutectic temperature
- iii) Freezing point depression
- iv) Boiling point elevation
- v) Azeotrope

b) i) Using the chemical potential expression:

$$\mu_A = \mu_A^* + RT \ln \chi_A$$

where μ_A^* is the chemical potential of the pure solvent A, derive the expression for the boiling point elevation in terms of the boiling point of the pure solvent T, its enthalpy of evaporation and the molality of the solute m_s . [5]

c) i) What is the approximate relative molecular mass of compound X if 1.00g of X added to 20.0 g benzene leads to a freezing point depression of 1.51°C ? [5]
ii) Why is the freezing point depression preferred to boiling point elevation for the determination of relative molecular masses? [2]
iii) Why would benzene be a better solvent to use than ethanol? [3]

Useful Relations		General Data	
$(RT)_{298.15K} = 2.4789 \text{ kJ/mol}$		speed of light	c $2.997\ 925 \times 10^8 \text{ m s}^{-1}$
$(RT/F)_{298.15K} = 0.025 \text{ } 693 \text{ V}$		charge of proton	e $1.602\ 19 \times 10^{-19} \text{ C}$
T/K: 100.15 298.15 500.15 1000.15		Faraday constant	$F=L e$ $9.648\ 46 \times 10^4 \text{ C mol}^{-1}$
T/Cm ⁻¹ : 69.61 207.22 347.62 695.13		Boltzmann constant	k $1.380\ 66 \times 10^{-23} \text{ J K}^{-1}$
1mmHg=133.222 N m ⁻²		Gas constant	R=Lk $8.314\ 41 \text{ J K}^{-1} \text{ mol}^{-1}$
$\text{hc}/k=1.438\ 78 \times 10^{-2} \text{ m K}$			$8.205\ 75 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$
1atm	1 cal	1 eV	1cm⁻¹
=1.01325x10⁵ Nm⁻²	=4.184 J	=1.602 189x10⁻¹⁹ J	=0.124x10⁻³ eV
=760torr		=96.485 kJ/mol	=1.9864x10⁻²³ J
=1 bar		=8065.5 cm⁻¹	
SI-units:			
I L = I 000 ml = 1000cm³ = 1 dm³			
1 dm = 0.1 m			
1 cal (thermochemical) = 4.184 J			
dipole moment: 1 Debye = $3.335\ 64 \times 10^{-30} \text{ C m}$			
force: $IN=IJ\ m^{-1}=1kgms^{-2}=10^5 \text{ dyne}$ pressure: $IPa=INm^{-2}=1Jm^{-3}$			
power: 1W = $1J\ s^{-1}$			
magnetic flux: 1T=1Vs m ⁻² =1JCsm ⁻²		potential: 1V=1 J C ⁻¹	
current: 1A=1Cs ⁻¹			
Prefixes:			
p n m m c d k M G		Gravitational constant	G $6.67259 \times 10^{-11} \text{ Nm}^2 \text{ kg}^{-2}$
pico nano micro milli centi deci kilo mega giga		Gravitational acceleration	g 9.80665 ms^{-2}
10^{-12} 10^{-9} 10^{-6} 10^{-3} 10^{-2} 10^{-1} 10^3 10^6 10^9		Bohr radius	a₀ $5.291\ 77 \times 10^{-11} \text{ m}$

M_f	$\Delta H_f^\theta / \text{kJ/mol}$	M_r	$\Delta H_r^\theta / \text{kJ/mol}$	$a / \text{J K}^{-1} \text{mol}^{-1}$	$b \times 10^{-3} \text{ J K}^2 \text{mol}^{-1}$	$c \times 10^5 \text{ J Kmol}^{-1}$
$\text{H}_2\text{O}(g)$	18.015	-241.8	$\text{O}_3(g)$	47.998	+142.7	Gases (298-2000K)
$\text{H}_2\text{O}(l)$	18.015	-285.8	$\text{NO}(g)$	30.008	+80.2	$\text{He}, \text{Ne}, \text{Ar}, \text{Kr}, \text{Xe}$
$\text{H}_2\text{O}_2(l)$	34.015	-187.8	$\text{NO}_2(g)$	48.008	+33.2	H_2
$\text{NH}_3(g)$	17.031	-48.1	$\text{N}_2\text{O}_4(g)$	92.012	+9.2	O_2
$\text{N}_2\text{H}_4(l)$	32.045	+60.8	$\text{SO}_2(g)$	64.003	-268.8	N_2
$\text{N}_3\text{H}(l)$	43.028	+284.1	$\text{H}_2\text{S}(g)$	34.080	-20.6	Cl_2
$\text{N}_4\text{H}(l)$	43.028	+284.1	$\text{SF}_6(g)$	148.054	-1209	CO_2
$\text{HNO}_3(l)$	63.013	-174.1	$\text{HF}(g)$	20.008	-27.1	H_2O
$\text{NH}_2\text{OH}(l)$	33.030	-114.2	$\text{HC}(g)$	36.461	-92.3	NH_3
$\text{NH}_4\text{Cl}(s)$	53.482	-314.4	$\text{HCl}(aq)$	36.481	-167.2	CH_4
$\text{HgCl}_4(s)$	271.50	-284.3	$\text{HBr}(g)$	80.917	+38.4	$\text{C}(s)$
$\text{H}_2\text{SO}_4(l)$	98.078	-814.0	$\text{HCl}(g)$	127.912	+26.5	
$\text{H}_2\text{SO}_4(aq)$	98.078	-988.3	$\text{CO}_2(g)$	44.010	-393.5	
$\text{NaCl}(s)$	58.443	-411.0	$\text{CO}(g)$	28.011	-110.5	
$\text{NaOH}(s)$	39.987	-428.7	$\text{Al}_2\text{O}_3(\alpha, s)$	101.945	-167.7	
$\text{KCl}(s)$	74.555	-435.9	$\text{SiO}_2(s)$	80.085	-910.9	Standard molar enthalpies of formation and combustion at 298.15 K.
$\text{KBr}(s)$	119.011	-392.2	$\text{FeS}(s)$	87.91	-100.0	
$\text{KI}(s)$	166.008	-327.8	$\text{FeS}_2(s)$	119.975	-178.2	
DIATOMICS	$E_g, \text{N}_2, \text{O}_2, \text{H}_2$	0	$\text{AgCl}(s)$	143.323	-127.1	
			$\text{CH}_4(g)$		26.038	+228.8
			$\text{C}_2\text{H}_4(g)$		28.054	+62.30
			$\text{C}_2\text{H}_6(g)$		30.070	-84.84
			$\text{C}_3\text{H}_8(g)$		42.081	-20.91
			C_3H_6 cyclopropane(g)			
			C_3H_6 (propene)(g)		42.081	20.5
			C_4H_{10} n-butane(g)		58.124	-128.11
			C_5H_{12} n-pentane(g)		72.151	-148.4
			C_6H_{12} cyclohexane(g)		84.163	-158.2
			C_6H_{14} n-hexane(g)		86.178	-198.7
			C_6H_6 benzene(g)		76.115	+48.99
			C_7H_{18} n-octane(g)		114.293	-248.8
			C_10H_8 naphthalene(g)		128.176	-478.53
			C_13OH (l)		32.042	-728.1
			CH_3CHO (g)		44.054	-188.0
			$\text{CH}_3\text{CH}_2\text{OH}$ (g)		46.070	-277.0
			CH_3COOH (l)		80.053	-484.2
			$\text{CH}_3\text{COOC}_2\text{H}_5(\text{l})$		86.107	-488.8
			CH_3OH (s)		64.114	-2231
			$\text{C}_6\text{H}_5\text{OH}$ (s)			-3054
			$\text{C}_6\text{H}_5\text{NH}_2(\text{l})$		83.129	-3383
			$\text{NH}_2\text{CO}_2\text{NH}_2(\text{s})$		60.058	-333.0
			$\text{CH}_2(\text{NH}_2)\text{CO}_2\text{H}$, glycine(s)		75.088	-637.2
			$\text{C}_6\text{H}_10\text{O}_6$, α -D-glucose(s)		180.159	-1274
			$\text{C}_6\text{H}_{12}\text{O}_6$, β -D-glucose(s)		180.159	-1288
			$\text{C}_2\text{H}_2\text{O}_1$, sucrose(s)		342.303	-2808
			$\text{CH}_3\text{CHOHCOOH}$		80.079	-5845
			lactic acid(s)		18.88	-8.54

^a Sublimation; ^b various pressures; ^c at 1 atm

Source: American Institute of Physics handbook, McGraw-Hill.

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
N ₂ O		77.28
N ₂ O ₅		37.20

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, Sm^θ/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 ·H 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		

Standard molar Gibbs free energy and molar entropy of formation at 298.15 K

M _T	ΔG _f ^θ /KJ/mol	S ^θ /J K ⁻¹ mol ⁻¹	M _T	ΔG _f ^θ /KJ/mol	S ^θ /J K ⁻¹ mol ⁻¹
H ₂ O(g)	18.015	-228.57	188.83	O ₃ (g)	47.998
H ₂ O(l)	18.015	-120.35	109.6	NO(g)	30.006
H ₂ O ₂ (l)	34.015	-120.35	109.6	NO ₂ (g)	46.006
NH ₃ (g)	17.031	-16.45	192.45	NO ₂ (g)	92.012
N ₂ H ₄ (l)	32.045	149.43	121.21	SO ₂ (g)	64.063
N ₃ H(l)	43.028	327.3	140.6	H ₂ S(g)	34.080
NH(g)	43.028	328.1	218.97	SF ₆ (g)	146.054
HNO ₃ (l)	63.013	-80.71	155.60	HFF(g)	20.006
NH ₂ OH(s)	33.030			HCl(g)	36.461
NH ₄ Cl(s)	53.492	-202.87	94.6	HCl(aq)	36.461
HgCl ₂ (s)	271.50	-178.6	146.0	HBr(g)	80.917
H ₂ SO ₄ (l)	98.078	-690.00	156.90	HBr(g)	127.912
H ₂ SO ₄ (aq)	98.078	-744.53	20.1	CO ₂ (g)	44.010
NaCl(s)	58.443	-384.14	72.13	CO(g)	28.011
NaOH(s)	39.997	-379.49	64.46	Al ₂ O ₃ (l,s)	101.945
KCl(s)	74.555	-409.14	82.59	SiO ₂	60.09
KBr(s)	119.011	-380.66	95.90	Fes ₂ (s)	87.91
KI(s)	166.006	-324.89	106.32	Fes ₂ (s)	119.975
				AgCl(s)	143.323
					-109.79
					96.2
He(g)	4.003	0	126.15	Hg(g)	200.59
Ar(g)	39.95	0	154.84	Hg(l)	200.59
H ₂ (g)	2.016	0	130.684	Ag(g)	107.87
N ₂ (g)	28.013	0	191.61	Ag(s)	107.87
O ₂ (g)	31.999	0	205.138	Na(g)	370.95
O ₃ (g)	47.998	163.2	218.93	Na(s)	22.99
Cl ₂ (g)	70.91	0	223.07		
Br ₂ (g)	159.82	3.110	245.46		
Br ₂ (l)	159.82	0	152.23		
I ₂ (g)	253.81	19.33	260.69		
I ₂ (s)	253.81	0	116.135		
organic compounds					
CH ₄ (g) methane				16.043	-50.72
C ₂ H ₂ (g) ethyne				26.038	209.20
C ₂ H ₄ (g) ethene				28.05	68.15
C ₂ H ₆ (g) ethane				30.070	-32.82
C ₃ H ₆ cyclopropane(g)				42.081	104.45
C ₃ H ₆ propene(g)				42.081	237.55
C ₄ H ₁₀ n-butane(g)				58.124	-17.03
C ₅ H ₁₂ n-pentane(g)				72.151	-8.20
C ₆ H ₁₂ cyclohexane(l)				84.163	26.8
C ₆ H ₁₄ n-hexane(l)				86.178	204.3
C ₆ H ₆ benzene(l)				78.115	173.3
C ₆ H ₆ benzene(g)				78.115	129.72
C ₈ H ₁₈ n-octane(l)				114.233	6.4
C ₁₀ H ₈ naphthalene(l)				128.175	
CH ₃ OH(g)				32.042	-161.96
CH ₃ OH(l)				32.042	239.81
CH ₃ CHO(g)				44.054	-128.86
CH ₃ CHO(l)				46.07	250.3
CH ₃ CH ₂ OH(l)				-174.78	160.7
CH ₃ COOH(l)				60.053	-389.9
CH ₃ COOC ₂ H ₅ (l)				88.107	159.8
C ₆ H ₅ OH(s)				94.114	-332.7
C ₆ H ₅ NH ₂ (l)				93.129	259.4
CH ₂ (NH ₂)CO ₂ H, glycine(s)				75.068	-373.4
C ₆ H ₁₂ O ₆ □-D-glucose(s)				180.159	103.5
C ₆ H ₂₂ O ₆ □-D-glucose(s)				180.159	-9.10
C ₁₂ H ₂₂ O ₁₁ , sucrose(s)				342.303	212
CH ₃ CH(OH)COOH				90.079	360.2
lactic acid(s)					

Source: American Institute of Physics handbook, McGraw-Hill.

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period	IA	IIA	IIIB	IVB	VB	VIIB	VIB	VIB	VIB	VIB	IB	IB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1	H 1.008																	
2	Li 6.94	Be 9.01																
3	Na 22.99	Mg 24.31																
4	K 39.10	Ca 40.08	Sc 44.96	Ti 47.90	V 50.94	Cr 52.01	Mn 54.9	Fe 55.85	Co 58.71	Ni 58.71	Cu 63.54	Zn 65.37	Ga 69.7	Ge 72.59	As 74.92			
5	Rb 85.47	Sr 87.62	Y 88.91	Zr 91.22	Nb 91.22	Mo 95.94	Tc 98.9	Ru 101.1	Rh 102.9	Pd 106.4	Ag 107.9	Cd 112.4	In 114.8	Sn 118.7	Sb 121.8	Te 127.6		
6	Cs 132.9	Ba 137.3	Lu 174.9	Hf 178.5	Ta 180.9	W 183.8	Re 186.2	Os 190.2	Ir 192.2	Pt 195.1	Au 196.9	Hg 200.6	Tl 204.4	Pb 207.2	Bi 208.9	Po 210	At 210	
7	Fr 223	Ra 226.0	Lr 257	Unq	Unp	Unh	Uno	Une										
Lanthanides			La 138.9	Ce 140.1	Pr 140.9	Nd 144.2	Pm 146.9	Sm 150.9	Eu 151.3	Gd 157.3	Tb 158.9	Dy 162.5	Ho 164.9	Er 167.3	Tm 168.9	Yb 173.0		
Actinides			Ac 227.0	Th 232.0	Pa 231.0	U 238.0	Np 237.1	Pu 239.1	Am 241.1	Cm 247.1	Bk 249.1	Cf 251.1	Es 254.1	Fm 257.1	Md 258.1	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, 1 mils, ed., Quantities, Units, and symbols in Physical Chemistry, Blackwell Scientific publications, Boston, 1988, pp 86-98.