UNIVERSITY OF SWAZILAND

BACHELOR OF SCIENCE

SUPPLEMENTARY EXAMINATION 2014

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, compressibility and isotherm 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.

[15]

b) Write short notes **on any One** of the following:
   i) Virial equation [10]
   ii) van der waal's equation [10]

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

QUESTION 2 [25 marks]

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

$$P = RT(V_m - \beta)^{-1} - (\alpha / T)V_m^{-2} \quad (1)$$

(i) Derive an expression for $V_{m,c}$, Tc and P_c. [12]

(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: α=1.748 L^2atm mol^{-2}K and β= 0.0345 L mol^{-1}. [2]

(iv) Estimate the radii of real gas molecules using equation (1) for real gases given a critical molar volume of 250 cm^3mol^{-1} [4]

b) Using the critical point expressions for $V_{m,c}$, Tc and P_c find an expression or value for compressibility at the critical point, Z_c [3]

Question 3 [25 Marks]

a) Write short notes on the following
   i) enthalpy change [5]
   ii) Hess's Law [5]

b) Derive Kirrchoff's equation: [6]

$$\Delta H_r(T_2) = \Delta H_r(T_1) + \Delta_r C_{p,m} \Delta T$$

where $C_{p,m}$ is temperature independent.

b) Using the data in the table below calculate
   i) $\Delta_r H^\theta$ at 298 K [4]
   ii) $\Delta_r H$ at 346 K [5]

for the hydrogenation reaction:

$$C_2H_2\,(g) + H_2\,(g) \rightarrow C_2H_4\,(g)$$

	C_2H_4 (g)	H_2 (g)	C_2H_2 (g)
$C_{p,m}$ J/mol/K	43.56	43.93	28.82
$\Delta_f H^\theta$ kJ/mol	+52.30	0	+226.8

Question 4 [25 Marks]

a) Using examples and/or diagrams compare and contrast **any one** pair of the following terms
   i) reversible and irreversible expansion [10]
   ii) path and state functions [10]

b) 4 moles of pentane occupies 25 L at 315 K.
   i) Derive an expression for reversible isothermal expansion. [6]
   ii) Calculate the work done and heat involved when the gas expands isothermally against a constant external pressure of 115 torr until its volume has doubled. [4]
   iii) Calculate the efficiency of the system in 1 b (ii) above. [5]

Question 5 [25 Marks]

a) Define internal energy change [10]

b) To Calibrate a calorimeter a 0.120 g naphthalene, $C_{10}H_8(s)$, 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, $C_6H_5OH(s)$ or ethanol, $CH_3CH_2OH(l)$ whose enthalpies of combustion are $\Delta_C H^\theta$=-3054 $kJmol^{-1}$ and -1368 $kJmol^{-1}$ respectively. [4]

c) Calculate the standard enthalpies of formation of:

   i) $KClO_3(s)$ 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:

$2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$ $\Delta_f H^\theta$=-89.4 kJ/mol

$2NOCl(g) \rightarrow 2NO(g) + Cl_2(g)$ $\Delta_f H^\theta$=+76.5 kJ/mol

Useful information:

	Molecular weights/g mol^{-1}
Benzoic acid	122.12
D-ribose $C_5H_{10}O_5$ (s)	150.13

QUESTION 6 [25 MARKS]

a) Write short notes on any Two of the following: [10]
   i) Eutectic temperature and Congruent melting point
   ii) Zeotrope and Azeotrope
   iii) Lower consulate and upper consulate temperature

b) a) Draw a sketch of the phase diagram of carbon dioxide and explain briefly the slopes and curvature of the liquid-solid and the liquid-gas boundaries, respectively. [5]

c) i) Derive the Clausius-Clapeyron equation for evaporation in the form

$$d(\ln p)/dT .$$ [5]

ii) The triple point of benzene is at 5.5°C and 36 mm Hg. Predict the boiling point of benzene at 0.1 atm pressure. [5]

Useful Relations

$(RT)_{298.15K}$=2.4789 kJ/mol

$(RT/F)_{298.15K}$=0.025 693 V

T/K:	100.15	298.15	500.15	1000.15
T/Cm^{-1}:	69.61	207.22	347.62	695.13

1mmHg=133.222 N m^{-2}

hc/k=1.438 78x10^{-2} m K

1atm	1 cal	1 eV	1cm^{-1}
=1.01325x10^{5} Nm^{-2} **=760torr** **=1 bar**	=4.184 J	=1.602 189x10^{-19} J =96.485 kJ/mol = 8065.5 cm^{-1}	=0.124x10^{-3} eV =1.9864x10^{-23} J

SI-units:

1 L = 1000 ml = 1000cm^{3} = 1 dm^{3}

1 dm = 0.1 m

1 cal (thermochemical) = 4.184 J

dipole moment: 1 Debye = 3.335 64x10^{-30} C m

force: ***1N=1J m^{-1}= 1kgms^{-2}***=10^{5} dyne pressure: ***1Pa=1Nm^{-2}***=1Jm^{-3}

1J = 1 Nm

power: 1W = 1J s^{-1} potential: 1V =1 J C^{-1}

magnetic flux: 1T=1Vsm^{-2}=1JCsm^{-2} current: 1A=1Cs^{-1}

Prefixes:

p	n	m	m	c	d	k	M	G
pico	nano	micro	milli	centi	deci	kilo	mega	giga
10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}	10^{3}	10^{6}	10^{9}

General Data		
speed of light	**c**	**2.997 925x10^{8} ms^{-1}**
charge of proton	*e*	1.602 19x10^{-19} C
Faraday constant	F=L*e*	9.648 46x10^{4} C mol^{-1}
Boltzmann constant	**k**	**1.380 66x10^{-23} J K^{-1}**
Gas constant	**R=Lk**	**8.314 41 J K^{-1} mol^{-1}**
		8.205 75x10^{-2} dm^{3} atm K^{-1} mol^{-1}
Planck constant	**h**	**6.626 18x10^{-34} Js**
	$\hbar = \frac{h}{2\pi}$	1.054 59x10^{-34} Js
Avogadro constant	**L or N_{av}**	**6.022 14x10^{23} mol^{-1}**
Atomis mass unit	u	1.660 54x10^{-27} kg
Electron mass	**m_e**	**9.109 39x10^{-31} kg**
Proton mass	m_p	1.672 62x10^{-27} kg
Neutron mass	m_n	1.674 93x10^{-27} kg
Vacuum permittivity	$\varepsilon_o = \mu_o^{-1}c^{-2}$	8.854 188x10^{-12} J^{-1} C^{2} m^{-1}
Vacuum permeability	μ_o	4πx10^{-7} Js^{2}C^{-2} m^{-1}
Bohr magneton	$\mu_B = e\hbar/2m_e$	9.274 02x10^{-24} JT^{-1}
Nuclear magneton	$\mu_N = e\hbar/2m_p$	5.05079x10^{-27} JT^{-1}
Gravitational constant	G	6.67259x10^{-11} Nm^{2}kg^{-2}
Gravitational acceleration	**g**	**9.80665 ms^{-2}**
Bohr radius	a_o	5.291 77x10^{-11} m

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

	M_r	ΔG_f^θ/KJ/mol	S^θ/J K^{-1} mol^{-1}		M_r	ΔG_f^θ/KJ/mol	S^θ/J K^{-1} mol^{-1}
$H_2O(g)$	18.015	-228.57	188.83	$O_3(g)$	47.998	163.2	238.93
$H_2O(l)$	18.015	-120.35	109.6	$NO(g)$	30.006	86.55	210.76
$H_2O_2(l)$	34.015	-120.35	109.6	$NO_2(g)$	46.006	51.31	240.06
$NH_3(g)$	17.031	-16.45	192.45	$N_2O_4(g)$	92.012	97.89	304.29
$N_2H_4(l)$	32.045	149.43	121.21	$SO_2(g)$	64.063	-300.19	248.22
$N_3H(l)$	43.028	327.3	140.6	$H_2S(g)$	34.080	-33.56	205.79
$N_3H(g)$	43.028	328.1	238.97	$SF_6(g)$	146.054	-1105.3	291.82
$HNO_3(l)$	63.013	-80.71	155.60	$HF(g)$	20.006	-273.2	173.78
$NH_2OH(s)$	33.030			$HCl(g)$	36.461	-95.30	186.91
$NH_4Cl(s)$	53.492	-202.87	94.6	$HCl(aq)$	36.461	-131.23	56.5
$HgCl_2(s)$	271.50	-178.6	146.0	$HBr(g)$	80.917	-53.45	198.70
$H_2SO_4(l)$)	98.078	-690.00	156.90	$HI(g)$	127.912	1.70	206.59
$H_2SO_4(aq)$	98.078	-744.53	20.1	$CO_2(g)$	44.010	-394.36	213.74
$NaCl(s)$	58.443	-384.14	72.13	$CO(g)$	28.011	-137.17	197.67
$NaOH(s)$	39.997	-379.49	64.46	Al_2O_3(□,s)	101.945	-1582.3	50.92
$KCl(s)$	74.555	-409.14	82.59	SiO_2	60.09	-856.64	41.84
$KBr(s)$	119.011	-380.66	95.90	$FeS(s)$	87.91	-100.4	60.29
$KI(s)$	166.006	-324.89	106.32	$FeS_2(s)$	119.975	-166.9	52.93
				$AgCl(s)$	143.323	-109.79	96.2
$He(g)$	4.003	0	126.15	$Hg(g)$	200.59	31.82	174.96
$Ar(g)$	39.95	0	154.84	$Hg(l)$	200.59	0	76.02
$H_2(g)$	2.016	0	130.684	$Ag(g)$	107.87	245.65	173.00
$N_2(g)$	28.013	0	191.61	$Ag(s)$	107.87	0	42.55
$O_2(g)$	31.999	0	205.138	$Na(g)$	370.95	76.76	153.71
$O_3(g)$	47.998	163.2	238.93	$Na(s)$	22.99	0	51.21
$Cl_2(g)$	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				

	M_r	ΔG_f^θ/KJ/mol	S^θ/J K^{-1} mol^{-1}
organic compounds			
$CH_4(g)$ methane	16.043	-50.72	186.26
$C_2H_2(g)$ ethyne	26.038	209.20	200.94
$C_2H_4(g)$ ethene	28.05	68.15	219.56
$C_2H_6(g)$ ethane	30.070	-32.82	229.60
C_3H_6 cyclopropane(g)	42.081	104.45	237.55
C_3H_6 propene(g)	42.081	62.78	267.05
C_4H_{10} n-butane (g)	58.124	-17.03	310.23
C_5H_{12} n-pentane(g)	72.151	-8.20	348.40
C_6H_{12} cyclohexane (l)	84.163	26.8	
C_6H_{14} n-hexane (l)	86.178		204.3
C_6H_6 benzene (l)	78.115	124.3	173.3
C_6H_6 benzene (g)	78.115	129.72	269.31
C_8H_{18} n-octane (l)	114.233	6.4	361.1
$C_{10}H_8$ naphthalene (l)	128.175		
CH_3OH (g)	32.042	-161.96	239.81
CH_3OH (l)	32.042	-166.27	126.8
CH_3CHO (g)	44.054	-128.86	250.3
CH_3CH_2OH (l)	46.07	-174.78	160.7
CH_3COOH (l)	60.053	-389.9	159.8
$CH_3COOC_2H_5$ (l)	88.107	-332.7	259.4
C_6H_5OH (s)	94.114	-50.9	146.0
$C_6H_5NH_2$ (l)	93.129		
$CH_2(NH_2)CO_2H$, glycine (s)	75.068	-373.4	103.5
$C_6H_{12}O_6$, □-D-glucose (s)	180.159		
$C_6H_{22}O_6$, □-D-glucose (s)	180.159	-910	212
$C_{12}H_{22}O_{11}$, sucrose (s)	342.303	-1543	360.2
$CH_3CH(OH)COOH$	90.079		
lactic acid (s)			

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

Standard molar enthalpies of formation at 298.15 K

	M_r	ΔH_f^θ/KJ/mol		M_r	ΔH_f^θ/KJ/mol
$H_2O(g)$	18.015	-241.8	$O_3(g)$	47.998	+142.7
$H_2O(l)$	18.015	-285.8	$NO(g)$	30.006	+90.2
$H_2O_2(l)$	34.015	-187.8	$NO_2(g)$	46.006	+33.2
$NH_3(g)$	17.031	-46.1	$N_2O_4(g)$	92.012	+9.2
$N_2H_4(l)$	32.045	+50.6	$SO_2(g)$	64.063	-296.8
$N_3H(l)$	43.028	+264.1	$H_2S(g)$	34.080	-20.6
$N_3H(g)$	43.028	+294.1	$SF_6(g)$	146.054	-1209
$HNO_3(l)$	63.013	-174.1	$HF(g)$	20.006	-271.1
$NH_2OH(s)$	33.030	-114.2	$HCl(g)$	36.461	-92.3
$NH_4Cl(s)$	53.492	-314.4	$HCl(aq)$	36.461	-167.2
$HgCl_2(s)$	271.50	-224.3	$HBr(g)$	80.917	+36.4
$H_2SO_4(l)$)	98.078	-814.0	$HI(g)$	127.912	+26.5
$H_2SO_4(aq)$	98.078	-909.3	$CO_2(g)$	44.010	-393.5
$NaCl(s)$	58.443	-411.0	$CO(g)$	28.011	-110.5
$NaOH(s)$	39.997	-426.7	$Al_2O_3(\alpha,s)$	101.945	-1675.7
$KCl(s)$	74.555	-435.9	SiO2(s)	60.085	-910.9
$KBr(s)$	119.011	-392.2	$FeS(s)$	87.91	-100.0
$KI(s)$	166.006	-327.6	$FeS_2(s)$	119.975	-178.2
DIATOMICS	Eg. N_2, O_2, H_2	0	$AgCl(s)$	143.323	-127.1

Temperature dependence of heat capacities, $C_{p,m} = a+bT+cT^{-2}$

	a/J K^{-1} mol^{-1}	$b/10^{-3}$ J K^{-2} mol^{-1}	$c/10^5$ J K mol^{-1}
Gases (298-2000K)			
He, Ne, Ar, Kr, Xe	20.78	0	0
H_2	27.28	3.26	0.50
O_2	29.96	4.18	-1.67
N_2	28.58	3.77	-0.50
Cl_2	37.03	0.67	-2.85
CO_2	44.23	8.79	-8.62
H_2O	30.54	10.29	0
NH_3	29.75	25.10	-1.55
CH_4	23.64	47.86	-1.92
C(S)	16.86	4.77	-8.54

Enthalpies of fusion and evaporation ΔH_m/KJ/mol at the transition temperature

	T_f/K	Fusion[a]	T_b/K	Evaporation[b]	
He	3.5	0.021	4.22	0 084	
Ar	83.81	1.188	87.29	6.506	
H_2	13.96	0.117	20.38	0.9163	
N_2	63.15	0.719	77.35	5.586	
O_2	54.36	0.444	90.18	6.820	
Cl_2	172.12	6.406	239.05	20.410	
Br_2	265.90	10.573	332.35	29.45	
I_2	386.75	15.52	458.39	41.80	
Hg	234.29	2.292	629.73	59.296	
Ag	1234	11.30	2436	250.63	
Na	370.95	2.601	1156	98.01	
CO_2	217.0	8.33	194.64	25.23⊥	
H_2O	273.15	6.008	373.15	40.656	(44.016 at 298.15 K)
NH_3	195.40	5.652	239.73	23.351	
H_2S	187.61	2.377	212.80	18.673	
CH_4	90.68	0.941	111.66	8.18	
C_2H_6	89.85	2.86	184.55	14.7	
C_6H_6	278.65	10.59	353.25	30.8	
CH_3OH	175.25	3.159	337.22	35.27	(37.99 at 298.15K)

Standard molar enthalpies of formation and combustion at 298.15 K.

	M_r	ΔH_f^θ/KJ/mol	ΔH_c^θ/KJ/mol
$CH_4(g)$	16.043	-74.81	
$C_2H_2(g)$	26.038	+226.8	-1300
$C_2H_4(g)$	28.054	+52.30	-1411
$C_2H_6(g)$	30.070	-84.64	-1560
C_3H_6 cyclopropane(g)	42.081	53.35	-2091
C_3H_6 (propene(g)	42.081	20.5	-2058
C_4H_{10} n-butane (g)	58.124	-126.11	-2877
C_5H_{12} n-pentane(g)	72.151	-146.4	-3536
C_6H_{12} cyclohexane (l)	84.163	-156.2	-3920
C_6H_{14} n-hexane (l)	86.178	-198.7	-4163
C_6H_6 benzene (l)	78.115	+48.99	-3268
C_8H_{18} n-octane (l)	114.233	-249.8	-5471
$C_{10}H_8$ naphthalene (l)	128.175	+78.53	-5157
CH_3OH (l)	32.042	-239.0	-726.1
CH_3CHO (g)	44.054	-166.0	-1193
CH_3CH_2OH (l)	46.070	-277.0	-1368
CH_3COOH (l)	60.053	-484.2	-874.5
$CH_3COOC_2H_5$ (l)	88.107	-486.6	-2231
C_6H_5OH (s)	94.114	-165.0	-3054
$C_6H_5NH_2$ (l)	93.129	-31.1	-3393
$NH_2CO.NH$, urea(s)	60.056	-333.0	-632.2
$CH_2(NH_2)CO_2H$, glycine (s)	75.068	-537.2	-964.4
$C_6H_{12}O_6$, α-D-glucose (s)	180.159	-1274	-2802
$C_6H_{22}O_6$, β-D-glucose (s)	180.159	-1268	-2808
$C_{12}H_{22}O_{11}$, sucrose (s)	342.303	-2222	-5645
$CH_3CH(OH)COOH$ lactic acid (s)	90.079	-694.0	-1344

⊥ Sublimation: [a]various pressures: [b]at 1atm

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_2O_4		77.28
NO_2		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, S_m^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_2O	70.0	CO	197.67
I_2	116.7			CO_2	213.7
S(Rh)	31.9	HNO_3	155.6	HCl	186.8
				H_2S	205.6
AgCl	96.2	C_2H_5OH	161.0	NH_3	192.5
AgBr	104.6	CH_3OH	126.7	CH_4	186.1
$CuSO_45H_2O$	305.4	C_6H_6	49.03	C_2H_6	229.4
$HgCl_2$	144	CH_3COOH	159.8	CH_3CHO	265.7
Sucrose	360.2	C_6H_{12}	298.2		