UNIVERSITY OF SWAZILAND
BACHELOR OF SCIENCE

FINAL EXAMINATION 2011

TITLE OF PAPER	:	INTRODUCTORY PHYSICAL CHEMISTRY
COURSE NUMBER	:	C202
INSTRUCTOR	:	Dr. J. M. Thwala (ext.2176/2133/6036616)
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 any One** of the following: [10]
   i) Virial equation
   ii) van der waal's equation

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

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

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

(i) Derive an expression for $V_{m,c}$, Tc 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=1.748 L^2atm mol^{-2}K and b= 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} [3]

Question 2 [25 MARKS]

a) Using examples and/or diagrams compare and contrast ***Any Two*** of the following terms
   i) reversible and irreversible expansion [5]
   ii) path and state functions [5]
   iii) work and heat [5]
   iv) change in internal energy and change in enthalpy [5]

b) 2 moles of methane occupies 12 L at 310 K.
   i) Derive an expression for reversible isothermal expansion. [5]
   ii) Calculate the work done when the gas expands isothermally against a constant external pressure of 200 torr until its volume has tripled. [5]
   iii) Calculate the work that would be done if the same expansion in b(ii) occurred reversibly . [5]

Question 3 [25 Marks]

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

i)	Statistical view of entropy	[5]
ii)	Clausius inequality	[5]
iii)	Gibbs Free Energy	[5]
iv)	Helmholtz function	[5]

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) Find $\Delta_r H^\theta$ for the following reactions from standard enthalpies of formation:
   i) $NH_3(g) + HCl(g) \rightarrow NH_4Cl$ [2]
   ii) $Cyclopropane(g) \rightarrow propene(g)$ [3]

c) 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) Write short notes on of the following [15]
   i) enthalpy change
   ii) internal energy change
   iii) Hess's Law

b) To Calibrate a calorimeter a 0.120 g naphthalene, $C_{10}H_8$(s), was burned 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 [4]
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. [6]

Question 5 [25 Marks]

a) Write Short notes on the following terms
   i) Second Law of Thermodynamics [6]
   ii) Third Law of Thermodymanics [8]

b) Calculate the change in entropies of the system, $\Delta S_{sys,}$ the surroundings, $\Delta S_{surr,}$ and the total change in entropy, $\Delta S_{tot,}$, when a sample of nitrogen gas of mass 14 g at 298 K and 1.00 bar doubles its volume in:
   i) an isothermal reversible expansion [6]
   ii) an irreversible isothermal expansion against an external pressure of 0.5 bar. [2]

c) What would the change in entropy be if the gas in (a) was compressed to half its volume and simultaneously heated to twice its initial temperature? [3]

QUESTION 6 [25 MARKS]

a) Draw a sketch of the phase diagrams for carbon dioxide and water; and explain briefly the slopes and curvature of the liquid-solid and the liquid-gas boundaries, respectively. [10]

b) i) Derive the Clausius-Clapeyron equation for evaporation in the form. [10]
   ii) The triple point of benzene is at 5.5 ^{o}C and 36 mm Hg. Predict the boiling point of benzene at 0.1 atm pressure. [5]

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

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(α,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

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)

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

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/10^5J $Kmol^{-1}$
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

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

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

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^{-}
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(α,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
$C_6H_{12}O_6$, α-D-glucose (s)	180.159		
$C_6H_{22}O_6$, β-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.

THE PERIODIC TABLE OF ELEMENTS

NON-METALS

METALLOIDS

METALS

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	VIIB	VIIIB			IB	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	55 **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**	105 **Unp**	106 **Unh**	107 **Uns**	108 **Uno**	109 **Une**									

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.*