UNIVERSITY OF SWAZILAND

BACHELOR OF SCIENCE

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

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Question 1(25 marks)

The compressibility factor, Z, for a.real gas is given by

$$Z = PV / nRT$$

and is a measure of the ideal behaviour of the gas.

(a) Use the following data to plot Z versus P for O_2 at 273 K.

P/(atm)	1	100	200	300	500	700	900
V_m/L.mol^{-1})	22.4138	0.2077	0.1024	0.0719	0.0518	0.0444	0.0403

Where V_m is the molar volume.
[5]

(b) Using the data in "a" compare and contrast real gases and ideal gases. [10]

(c) The mass composition of air at 1.00 atm is N_2 0.755g, O_2 .232g and Ar 0.013g.

(i) Find the partial pressures of each gas.
[5]

The relative atomic and molecular weights for the gases are: N_2 28 g/mol, O_2 32 g/mol and Ar 39.95 g/mol.

(ii) The density of gaseous compound was found to be 1.23 g/L at 330K and 150 torr. Find the Molar mass of the compound.
[5]

Question 2 (25Marks)

The Dieterici equation state

$$P = \frac{nRT}{V - nb}\exp\left(-an/VRT\right)$$

(a) Write short notes on Virial equation. [5]

(b) Express Dieterici's equation in a Virial equation from and find expressions for the second and third Virial coefficients. [10]

Useful Formulae:

Virial equation state:

$$PVm = RT + B(T)\left(\frac{1}{Vm}\right) + C(T)\left(\frac{1}{Vm}\right)^2 + D(T)\left(\frac{1}{Vm}\right)^3 + \bullet\bullet\bullet$$

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x}{3!} + \bullet\bullet\bullet; \frac{1}{1-x} = 1 + x + x^2 + x^3 + \bullet\bullet\bullet;$$ use the first two terms.

c) Derive an expression for Boyles temperature, T_B. [5]

d) Estimate the temperature at which Oxygen behaves as an ideal gas given the constants: a=1.748 L^2 atm mol^{-2} and b = 0.0345 L mol^{-1}. [5]

QUESTION 3 [25 marks]

Adiabatic expansion of an ideal gas is quite different from isothermal expansion.

a) Explain what is meant by adiabatic expansion, draw an adiabat and an isotherm on a P versus V graph and compare them. [5]

b) Derive the expression for the change in temperature of an adiabatic expansion of an ideal gas against constant external pressure from V_i to V_f. [5]

c) A sample of argon at 1.0 atm pressure and 25°C expands reversibly and adiabatically from 0.50 L to 1.00 L. calculate: [15]
   i) final temperature
   ii) work done
   iii) change in internal energy.

Question 4 [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:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

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

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

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

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

QUESTION 5 [25 MARKS]

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. [10]

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

$$d(\ln p)/dT .$$ [10]

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

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:

$$\mu_A = \mu_A^{\bullet} + RT \ln \chi_A$$

where $\mu_A^{\bullet}$ 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 1.51ºC ? [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

$(RT)_{298.15K}$=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}	=4.184 J	=1.602 189x10^{-19} J	=0.124x10^{-3} eV
=760torr **=1 bar**		=96.485 kJ/mol = 8065.5 cm^{-1}	=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 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

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

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)	84.183	-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	-488.6	-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^{-}
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		
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
$CuSO_4 5H_2O$	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		

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	SiO2	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.

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	3 **Li** 6.94	4 **Be** 9.01											5 **B** 10.81					
3	11 **Na** 22.99	12 **Mg** 24.31											13 **Al** 26.9	14 **Si** 28.09				
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			
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		
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	
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.*

SOURCE: International Union of Pure and Applied Chemistry, I mills, ed., Quantities, Units, and symbols in Physical Chemistry, Blackwell Scientific publications, Boston, 1988, pp 86-98.