

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

- i) Isothermal reversible expansion [5]
- ii) Isothermally irreversibly against a constant external pressure of 3.0 atm [5]
- iii) Adiabatic irreversible expansion [5]

Question 5 [25 Marks]

- a) Write short notes on any one of the following

- i) enthalpy change [10]
- ii) internal energy change [10]

- b) To Calibrate a calorimeter a 0.8220 g benzoic acid, C₆H₅COOH(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 temperatuue rise of 2.05 K.

- i) Calculate the heat capacity of the calorimeter [3]
- (ii) Is the unknown compound ethanol, CH₃CH₂OH or Methanol, CH₃OH(l) whose enthalpies of combustion are $\Delta_c H^\theta = -1368 \text{ kJ mol}^{-1}$ (CH₃CH₂OH) and -726.1 kJmol⁻¹ (CH₃OH(l)), respectively. [4]

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

- i) NH₃(g) + HCl(g) → NH₄Cl(s) [2]
- ii) Cyclopropane(g) → propene(g) [2]
use table attached

- d) The standard enthalpy of reaction of C₅H₁₀O₅(s) + 5O₂(g) → 5H₂O(l) + 5CO₂(g) is - 2127 kJ/mol. Calculate the standard enthalpy of formation of C₅H₁₀O₅(s). [4]

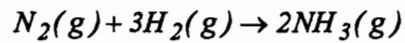
Question 6 [25 Marks]

- 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	
(R/T) _{298.15K}	=2.4789 kJ/mol	speed of light	c
(RT/F) _{298.15K}	=0.025 693 V	charge of proton	e
T/K:	100.15 298.15 500.15 1000.15	Faraday constant	F=1e
T/Cm ⁻¹ :	69.61 207.22 347.62 695.13	Boltzmann constant	k
1mmHg	=133.222 N m ⁻²	Gas constant	R=Lk
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
760torr		96.485 kJ/mol	1.9864x10 ⁻²³ J
		8065.5 cm ⁻¹	
SI-units:			
1 L = 1000 ml = 1000cm ³ = 1 dm ³		Avogadro constant	L or N _{av}
1 dm = 0.1 m		Atomis mass unit	u
1 cal (thermochemical) = 4.184 J		Electron mass	m _e
dipole moment: 1 Debye = 3.335 64x10 ⁻³⁰ C m		Proton mass	m _p
force: IN=IJ m ⁻¹ = 1kgms ⁻² =10 ⁵ dyne	pressure: IPa=INm ⁻² =1Jm ⁻³	Neutron mass	m _n
power: 1W = 1J s ⁻¹	potential: 1V = 1 J C ⁻¹	Vacuum permittivity	$\epsilon_0 = \mu_0^{-1} c^{-2}$
magnetic flux: 1T=1 Vs m ⁻² =1JCsm ⁻²	current: 1A=1Cs ⁻¹	Nuclear magneton	$\mu_N = e\hbar/2m_p$
Prefixes:		Gravitational constant	G
p n m m c d k M G		Gravitational	g
pico nano micro milli centi deci kilo mega giga	acceleration		9.80665 ms ⁻²
10 ⁻¹² 10 ⁻⁹ 10 ⁻⁶ 10 ⁻³ 10 ⁻¹ 10 ³ 10 ⁶ 10 ⁹	Bohr radius		5.291 77x10 ⁻¹¹ m

Standard molar enthalpies of formation at 298.15 K

Temperature dependence of heat capacities, $C_p/m = a + bT + cT^2$

M_f	$\Delta H_f^\theta / \text{kJ/mol}$	M_f	$\Delta H_f^\theta / \text{kJ/mol}$			$a / \text{J K}^{-1} \text{mol}^{-1}$	$b / 10^{-3} \text{K}^2 \text{mol}^{-1}$	$c / 10^5 \text{J K mol}^{-1}$
				Gas (g)	Gases (298–2000 K)			
$\text{H}_2\text{O(g)}$	18.015	-241.8	$\text{O}_3(\text{g})$	47.998	+142.7			
$\text{H}_2\text{O(l)}$	34.015	-187.8	$\text{NO}_2(\text{g})$	30.006	+90.2	$\text{He}, \text{Ne}, \text{Ar}, \text{Kr}, \text{Xe}$	20.78	0
$\text{NH}_3(\text{g})$	17.031	-46.1	$\text{NO}_4(\text{g})$	46.006	+33.2	H_2	27.28	3.26
$\text{NH}_4(\text{l})$	32.045	+50.6	$\text{SO}_2(\text{g})$	92.012	+9.2	O_2	29.96	4.18
$\text{NH}_4(\text{l})$	43.028	+264.1	$\text{H}_2\text{S}(\text{g})$	64.063	-296.8	N_2	28.58	3.77
$\text{NH}_3(\text{g})$	43.028	+294.1	$\text{SF}_6(\text{g})$	34.080	-20.6	Cl_2	37.03	0.67
$\text{HNO}_3(\text{l})$	63.013	-174.1	$\text{HF}(\text{g})$	20.006	-120.9	CO_2	44.23	-2.95
$\text{NH}_3\text{OH}(\text{s})$	33.030	-114.2	$\text{HCl}(\text{g})$	36.461	-271.1	H_2O	30.54	-8.62
$\text{NH}_4\text{Cl}(\text{s})$	53.492	-314.4	$\text{HCl}(\text{aq})$	101.945	-92.3	NH_3	29.75	0
$\text{HgCl}(\text{s})$	271.50	-224.3	$\text{HBr}(\text{g})$	80.917	-167.5	CH_4	23.64	-1.55
$\text{H}_2\text{SO}_4(\text{l})$	98.078	-814.0	$\text{HI}(\text{g})$	127.912	-167.7			-1.92
$\text{H}_2\text{SO}_4(\text{aq})$	98.078	-909.3	$\text{CO}_2(\text{g})$	44.010	-393.5			
$\text{NaCl}(\text{s})$	58.443	-411.0	$\text{CO}(\text{g})$	28.011	-110.5			
$\text{NaOH}(\text{s})$	39.997	-426.7	$\text{Al}_2\text{O}_3(\alpha, \text{s})$	119.975	-178.2			
$\text{KCl}(\text{s})$	74.555	-435.9	$\text{SiO}_2(\text{s})$	60.086	-910.9			
$\text{KBr}(\text{s})$	119.011	-392.2	$\text{FeS}(\text{s})$	87.91	-100.0			
$\text{KI}(\text{s})$	166.006	-327.6	$\text{FeS}_2(\text{s})$	119.975	-178.2			
Diatomics(g)	—	0	$\text{AgCl}(\text{s})$	143.323	-127.1			
Enthalpies of fusion and evaporation $\Delta H_m/KJ/mol$ at the transition temperature								
T/K	Fusion ^a	T_b/K	Evaporation ^b			M_f	$\Delta H_f^\theta / \text{kJ/mol}$	$\Delta H_c^\theta / \text{kJ/mol}$
He	3.5	0.021	4.22	0.084	$\text{C}_3\text{He cyclopropane(g)}$	26.038	+226.8	1300
Ar	83.81	1.188	87.29	6.506	$\text{C}_2\text{H}_8(\text{g})$	28.054	+52.30	1411
H_2	13.96	0.117	20.38	0.9163	$\text{C}_2\text{H}_2(\text{g})$	30.070	-84.64	1560
N_2	63.15	0.719	77.35	5.586	$\text{C}_3\text{He propene(g)}$	42.081	53.35	2091
O_2	54.36	0.444	90.18	6.820	$\text{C}_4\text{H}_{10}\text{ n-butane(g)}$	58.124	-126.11	2877
Cl_2	172.12	6.406	239.05	20.410	$\text{C}_5\text{H}_{12}\text{ n-pentane(g)}$	72.151	-146.4	3536
Br_2	265.90	10.573	332.35	29.45	$\text{C}_6\text{H}_{12}\text{ cyclohexane(l)}$	84.163	-156.2	3920
I_2	386.75	15.52	458.39	41.80	$\text{C}_6\text{H}_{14}\text{ n-hexane(l)}$	86.178	-198.7	4163
Hg	234.29	2.292	629.73	59.296	$\text{C}_6\text{H}_6\text{ benzene(l)}$	78.115	+48.99	3268
Ag	123.4	11.30	243.6	250.63	$\text{C}_8\text{H}_{18}\text{ n-octane(l)}$	114.233	-249.8	5471
Na	370.95	2.601	1156	98.01	$\text{C}_{10}\text{H}_8\text{ naphthalene(l)}$	128.175	+78.53	5157
CO_2	217.0	8.33	194.64	25.23 ₁	$\text{CH}_3\text{OH(l)}$	32.042	-239.0	726.1
H_2O	273.15	6.008	373.15	40.656 (44.016 at 298.15 K)	$\text{CH}_3\text{CHO(l)}$	44.054	-166.0	1193
NH_3	195.40	5.652	239.73	23.351	$\text{CH}_3\text{CH}_2\text{OH(l)}$	46.070	-277.0	1368
H_2S	187.61	2.377	212.80	18.673	$\text{CH}_3\text{COOH(l)}$	60.053	-484.2	874.9
CH_4	90.68	0.941	111.66	8.18	$\text{CH}_2(\text{NH}_2)\text{CO}_2\text{H, glycine(s)}$	75.068	-537.2	964.4
CH_6	89.85	2.86	184.55	14.7	$\text{C}_6\text{H}_{12}\text{O}_6, \alpha\text{-D-glucose(s)}$	180.159	-1274	2802
CH_9OH	278.65	10.59	353.25	30.8	$\text{C}_8\text{H}_{22}\text{O}_8, \beta\text{-D-glucose(s)}$	180.159	-1268	2808
	175.25	3.159	337.22	35.27 (37.99 at 298.15 K)	$\text{C}_{12}\text{H}_{22}\text{O}_{11}, \text{sucrose(s)}$	342.303	-2222	5645
					$\text{CH}_3\text{CH(OH)COOH}$	90.079	-694.0	1344
					tactic acid(s)			

^a Sublimation: ^b Various pressures: ^c at 1 atm

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

Third Law entropies at 25°C, Sm⁰/J K⁻¹ mol⁻¹

Solvent	F.P °C	K _f °C kg mol ⁻¹	B.P (°C, 101kNm ⁻³)	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	3.63
Chloroform	-64	61.3	-	-

F.P Depression, B.P. Elevation

Solids	Liquids	Gases
Ag	42.68	Hg
C(g)	5.77	Br ₂
C(d)	2.44	O ₂
Cu	33.4	Cl ₂
Zn	41.6	H ₂ O
I ₂	116.7	70.0
SRU)	31.9	HNO ₃
		155.6
		CO ₂
		HCl
		H ₂ S
AgCl	96.2	C ₂ H ₅ OH
AgBr	104.6	CH ₃ OH
CuSO ₄ ·5H ₂ O	305.4	C ₂ H ₆
HgCl ₂	144	CH ₃ COOH
Sucrose	360.2	C ₆ H ₁₂
		298.2

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

M _r	$\Delta G_f^\theta / \text{kJ/mol}$	S $^\theta_{\text{J}} \text{K}^{-1} \text{mol}^{-1}$	M _r	$\Delta G_f^\theta / \text{kJ/mol}$	S $^\theta_{\text{J}} \text{K}^{-1} \text{mol}^{-1}$
H2O(g)	18.015	-228.57	188.83	03(g)	47.998
H2O(l)	18.015	-120.35	109.6	NO(g)	30.006
H2O2(l)	34.015	-120.35	109.6	NO2(g)	46.006
NH3(g)	17.031	-16.45	192.45	N2O4(g)	92.012
N2H4(l)	32.045	149.43	121.21	SO2(g)	64.063
N3H(l)	43.028	327.3	140.6	H2S(g)	34.080
N3H(g)	43.028	328.1	238.97	SF6(g)	146.054
HNO3(l)	63.013	-80.71	155.60	HF(g)	20.006
NH2OH(s)	33.030			HCl(g)	36.461
NH4Cl(s)	53.492	-202.87	94.6	HCl(aq)	36.461
HgCl2(s)	271.50	-178.6	146.0	HBr(g)	80.917
H2SO4(l))	98.078	-690.00	156.90	Hl(g)	127.912
H2SO4(aq)	98.078	-744.53	20.1	CO2(g)	44.010
NaCl(s)	58.443	-384.14	72.13	CO(g)	28.011
NaOH(s)	39.997	-379.49	64.46	Al2O3(a,s)	101.945
KCl(s)	74.555	-409.14	82.59	SiO2	60.09
KB(s)	119.011	-380.66	95.90	FeS(s)	87.91
KI(s)	166.006	-324.89	106.32	FeS2(s)	119.975
				AgCl(s)	143.323
				Hg(g)	126.15
				Hg(l)	200.59
				Hg(l)	200.59
				Ag(g)	107.87
				Ag(s)	107.87
				O2(g)	31.999
				O3(g)	47.998
				Cl2(g)	70.91
				Br2(g)	159.82
				I2(g)	253.81
				I2(s)	253.81
					0
					116.135

organic compounds	M _r	$\Delta G_f^\theta / \text{kJ/mol}$	S $^\theta_{\text{J}} \text{K}^{-1} \text{mol}^{-1}$
CH4(g) methane	16.043	-50.72	186.26
C2H2(g) ethyne	26.038	209.20	200.94
C2H4(g) ethene	28.05	68.15	219.56
C2H6(g) ethane	30.070	-32.82	229.60
C3H6 cyclopropane(g)	42.081	104.45	237.55
C3H6 propene(g)	42.081	62.78	267.05
C4H10 n-butane(g)	58.124	-17.03	310.23
C5H12 n-pentane(g)	72.151	-8.20	348.40
C6H12 cyclohexane(l)	84.163	26.8	
C6H14 n-hexane(l)	86.178		204.3
C6H6 benzene(l)	78.115	124.3	173.3
C6H6 benzene(g)	78.115	129.72	269.31
C8H18 n-octane(l)	114.233	6.4	361.1
C10H8 naphthalene(l)	128.175		
CH3OH(l)	32.042	-161.96	239.81
CH3OH(l)	32.042	-166.27	126.8
CH3CHO(g)	44.054	-128.86	250.3
CH3CH2OH(l)	46.07	-174.78	160.7
CH3COOH(l)	60.053	-389.9	159.8
CH3COOC2H5(l)	88.107	-332.7	259.4
C6H5OH(l)	94.114	-50.9	146.0
C6H5NH2(l)	93.129		
CH2(NH2)CO2H, glycine(s)	75.068	-373.4	103.5
C6H12O6, α -D-glucose(s)	180.159		
C6H22O6, β -D-glucose(s)	180.159	-910	212
C12H22O11, sucrose(s)	342.303	-1543	360.2
CH3CH(OH)COOH	90.079		
lactic acid(s)			

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

THE PERIODIC TABLE OF ELEMENTS

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period	IA	IIA	IIIB	IVB	VIB	VIB	VIB	VIB	VIB	VIIB	VIIB	VIIB	VIIB	VIIB	VIIB	VIIB	VIIA	VIIA
1	1 H	1.008																
2	3 Li	6.94	4 Be	9.01														
3	11 Na	22.99	12 Mg	24.31														
4	19 K	39.10	20 Ca	40.08	21 Sc	44.96	22 Ti	47.90	23 Cr	50.94	24 Mn	52.01	25 Fe	54.9	26 Co	55.85	27 Ni	58.71
5	37 Rb	85.47	38 Sr	87.62	39 Y	88.91	40 Zr	91.22	41 Nb	95.94	42 Mo	98.9	43 Tc	101.1	44 Ru	102.9	45 Pd	106.4
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
7	87 Fr	223	88 Ra	226.0	103 Lr	257	104 Unq	257	105 Unp	257	106 Unh	257	107 Uno	257	108 Une	257		

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