

UNIVERSITY OF SWAZILAND
BACHELOR OF SCIENCE

SUPPLEMENTARY 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 $V_{m,c}$, 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: $a=1.748 \text{ L}^2\text{atm mol}^{-2}\text{K}$ and $b=0.0345 \text{ L mol}^{-1}$. [2]
(iv) Estimate the radii of real gas molecules using equation (1) for real gases given a critical molar volume of $250 \text{ cm}^3\text{mol}^{-1}$ [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]
- 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 in a series of equilibrium steps . [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) Second law of thermodynamics [5]
iv) Third law of thermodynamics [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) $\text{NH}_3(g) + \text{HCl}(g) \rightarrow \text{NH}_4\text{Cl}$ [5]
ii) $\text{Cyclopropane}(g) \rightarrow \text{propene}(g)$ [5]

Question 4 [25 Marks]

- a) Write short notes on of the following [15]
- 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 $\Delta_c H^\ominus = -3054 \text{ kJmol}^{-1}$ and -1368 kJmol^{-1} respectively. [6]

Question 5 [25 Marks]

- a) Calculate the change in entropies of the system, ΔS_{sys} , the surroundings, ΔS_{surr} , and the total change in entropy, ΔS_{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. [4]
- b) 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? [5]
- c) If 50g water at 80°C is poured into 100g water at 10°C in an insulated vessel given that $C_{p,m} = 75.5 \text{ JK}^{-1}\text{mol}^{-1}$: Calculate:
- i) final temperature of the mixture [4]
 - ii) the entropy change [6]

Question 6 [25 Marks]

- a) i) Define fugacity [5]
ii) Given that fugacity is given by the expression: [5]

$$f = p \exp \int_{p_i}^{p_f} \left\{ \frac{Z(p, T) - 1}{p} \right\} dp$$

- b) Find an expression for the fugacity coefficient of a gas that obeys the equation of state: [5]

$$\frac{PV_m}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots$$

- a) The following are fundamental thermodynamic equations (FTE):

$$dU = TdS - pdV$$

$$dA = -pdV - SdT$$

$$dG = VdP - SdT$$

$$dH = TdS - VdP$$

- (i) Using the appropriate FTE: [5]

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$$

- iii) Find an expression for internal energy change with volume for a van der waals gas. [5]

Useful relation:
$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

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- b) Find an expression for the fugacity coefficient of a gas that obeys the equation of state: [5]

$$\frac{PV_m}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots$$

- a) The following are fundamental thermodynamic equations (FTE):

$$dU = TdS - pdV$$

$$dA = -pdV - SdT$$

$$dG = VdP - SdT$$

$$dH = TdS - VdP$$

- (i) Using the appropriate FTE: [5]

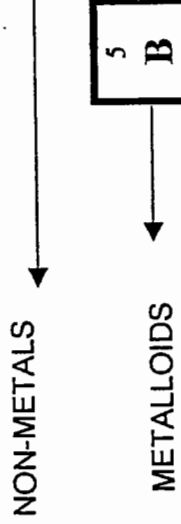
$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$$

- iii) Find an expression for internal energy change with volume for a van der waals gas. [5]

Useful relation:
$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

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	VB	VIB	VIIIB	VIIIB	VIIIB	IB	IIB	IIIB	IIIA	IVA	VA	VIA	VIIA	VIIIA	VIIIA										
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												57 Lu 174.9	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		
7	87 Fr 223	88 Ra 226.0												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
														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	103 Lr 257	



Numbers below the symbol indicates the atomic masses; and the numbers above the symbol indicates the atomic numbers.

Standard molar enthalpies of formation at 298.15 K

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

M_f	$\Delta H_f^\circ / \text{kJ/mol}$	M_f	$\Delta H_f^\circ / \text{kJ/mol}$	$a / \text{J K}^{-1} \text{mol}^{-1}$	$b / 10^{-3} \text{J K}^{-2} \text{mol}^{-1}$	$c / 10^5 \text{J K mol}^{-1}$
$\text{H}_2\text{O}(g)$	18.015	$\text{O}_3(g)$	+142.7	20.78	0	0
$\text{H}_2\text{O}(l)$	-285.8	$\text{NO}(g)$	+90.2	27.28	3.26	0.50
$\text{H}_2\text{O}_2(l)$	-187.8	$\text{NO}_2(g)$	+33.2	29.96	4.18	-1.67
$\text{NH}_3(g)$	-46.1	$\text{N}_2\text{O}_4(g)$	+9.2	37.58	3.77	-0.50
$\text{N}_2\text{H}_4(l)$	+50.5	$\text{SO}_2(g)$	-296.8	28.03	0.67	-2.85
$\text{N}_2\text{H}_4(g)$	+264.1	$\text{H}_2\text{S}(g)$	-20.6	44.23	8.79	-8.62
$\text{N}_2\text{H}(g)$	+294.1	$\text{SF}_6(g)$	-1209	30.54	10.29	0
$\text{HNO}_3(l)$	-174.1	$\text{HF}(g)$	-271.1	29.75	25.10	-1.55
$\text{NH}_2\text{OH}(s)$	-114.2	$\text{HCl}(g)$	-92.3	23.64	47.86	-1.92
$\text{NH}_4\text{Cl}(s)$	-314.4	$\text{HCl}(aq)$	-167.2			
$\text{HgCl}_2(s)$	-224.3	$\text{HBr}(g)$	+36.4			
$\text{H}_2\text{SO}_4(l)$	-814.0	$\text{HI}(g)$	+26.5			
$\text{H}_2\text{SO}_4(aq)$	-909.3	$\text{CO}_2(g)$	-393.5			
$\text{NaCl}(s)$	-411.0	$\text{CO}(g)$	-110.5			
$\text{NaOH}(s)$	-426.7	$\text{Al}_2\text{O}_3(\alpha, s)$	-1675.7			
$\text{KCl}(s)$	-435.9	$\text{SiO}_2(s)$	-910.9			
$\text{KBr}(s)$	-392.2	$\text{Fe}(s)$	-100.9			
$\text{KI}(s)$	-327.6	$\text{FeS}_2(s)$	-176.2			
Diatomics(g)	—	$\text{AgCl}(s)$	-127.1			
				M_f	$\Delta H_f^\circ / \text{kJ/mol}$	$\Delta H_c^\circ / \text{kJ/mol}$
				16.043	-74.81	
				26.038	+226.8	1300
				28.054	+52.30	1411
				30.070	-84.84	1560
				42.081	53.35	2091
				42.081	20.5	2058
				58.124	-126.11	2877
				72.151	-146.4	3536
				84.163	-156.2	3920
				86.178	-198.7	4163
				78.115	+48.99	3268
				114.233	-249.8	5471
				128.175	+78.53	5157
				32.042	-239.0	726.1
				44.054	-166.0	1193
				46.070	-277.0	1368
				60.053	-484.2	874.5
				88.107	-486.6	2231
				94.114	-165.0	3054
				93.129	-31.1	3393
				60.056	-333.0	632.2
				75.068	-537.2	964.4
				180.159	-1274	2802
				180.159	-1268	2808
				342.303	-2222	5645
				90.079	-694.0	1344

Standard molar enthalpies of formation and combustion at 298.15 K.

Enthalpies of fusion and evaporation $\Delta H_m / \text{kJ/mol}$ at the transition temperature

T_f / K	Fusion ^a	T_b / K	Evaporation ^b
3.5	0.021	4.22	0.084
83.81	1.188	87.29	6.506
13.96	0.117	20.38	0.9163
63.15	0.719	77.35	5.586
54.36	0.444	90.18	6.820
172.12	6.406	239.05	20.410
265.90	10.573	332.35	29.45
386.75	15.52	458.39	41.80
234.29	2.292	629.73	59.296
1234	11.30	2436	250.63
370.95	2.601	1156	98.01
217.0	8.33	194.64	25.23
273.15	6.008	373.15	40.656 (44.016 at 298.15 K)
195.40	5.652	239.73	23.351
187.61	2.377	212.80	18.673
90.68	0.941	111.66	8.18
89.85	2.86	184.55	14.7
278.65	10.59	353.25	30.8
175.25	3.159	337.22	35.27 (37.99 at 298.15K)

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

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

	M_r	$\Delta G_f^\ominus / \text{kJ/mol}$	$S^\ominus / \text{J K}^{-1} \text{mol}^{-1}$	M_r	$\Delta G_f^\ominus / \text{kJ/mol}$	$S^\ominus / \text{J K}^{-1} \text{mol}^{-1}$
H ₂ O(g)	18.015	-228.57	188.83	O ₃ (g)	163.2	238.93
H ₂ O(l)	18.015	-120.35	109.6	NO(g)	86.55	210.76
H ₂ O ₂ (l)	34.015	-120.35	109.6	NO ₂ (g)	51.31	240.06
NH ₃ (g)	17.031	-16.45	192.45	N ₂ O ₄ (g)	97.89	304.29
N ₂ H ₄ (l)	32.045	149.43	121.21	SO ₂ (g)	-300.19	248.22
N ₃ H(l)	43.028	327.3	140.6	H ₂ S(g)	-33.56	205.79
N ₃ H(g)	43.028	328.1	238.97	SF ₆ (g)	-1105.3	291.92
HNO ₃ (l)	63.013	-80.71	155.60	HF(g)	-273.2	173.78
NH ₂ OH(s)	33.030			HCl(g)	-95.30	186.91
NH ₄ Cl(s)	53.492	-202.87	94.6	HCl(aq)	-131.23	56.5
HgCl ₂ (s)	271.50	-178.6	146.0	HBr(g)	-53.45	198.70
H ₂ SO ₄ (l)	98.078	-690.00	156.90	HI(g)	1.70	206.59
H ₂ SO ₄ (aq)	98.078	-744.53	20.1	CO ₂ (g)	-394.36	213.74
NaCl(s)	58.443	-384.14	72.13	CO(g)	-137.17	197.67
NaOH(s)	39.997	-379.49	64.46	Al ₂ O ₃ (α ,s)	-1582.3	50.92
KCl(s)	74.555	-409.14	82.59	SiO ₂	-856.64	41.84
KBr(s)	119.011	-380.66	95.90	FeS(s)	-100.4	60.29
KI(s)	166.006	-324.89	106.32	FeS ₂ (s)	-166.9	52.93
				AgCl(s)	-109.79	96.2
He(g)	4.003	0	126.15	Hg(g)	31.82	174.96
Ar(g)	39.95	0	154.84	Hg(l)	0	76.02
H ₂ (g)	2.016	0	130.684	Ag(g)	107.87	173.00
N ₂ (g)	28.013	0	191.61	Ag(s)	0	42.55
O ₂ (g)	31.999	0	205.138	Na(g)	370.95	153.71
O ₃ (g)	47.998	163.2	238.93	Na(s)	22.99	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			
organic compounds						
CH ₄ (g) methane	16.043	-50.72	186.26			
C ₂ H ₂ (g) ethyne	26.038	209.20	200.94			
C ₂ H ₄ (g) ethene	28.05	68.15	219.56			
C ₂ H ₆ (g) ethane	30.070	-32.82	229.60			
C ₃ H ₆ cyclopropane(g)	42.081	104.45	237.55			
C ₃ H ₆ propene(g)	42.081	62.78	267.05			
C ₄ H ₁₀ n-butane (g)	58.124	-17.03	310.23			
C ₅ H ₁₂ n-pentane(g)	72.151	-8.20	348.40			
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	124.3	173.3			
C ₆ H ₆ benzene (g)	78.115	129.72	269.31			
C ₈ H ₁₈ n-octane (l)	114.233	6.4	361.1			
C ₁₀ H ₈ naphthalene (l)	128.175					
CH ₃ OH (g)	32.042	-161.96	239.81			
CH ₃ CHO (g)	32.042	-166.27	126.8			
CH ₃ CH ₂ OH (l)	46.07	-174.78	160.7			
CH ₃ COOH (l)	60.053	-389.9	159.8			
CH ₃ COOC ₂ H ₅ (l)	88.107	-332.7	259.4			
C ₆ H ₅ OH (s)	94.114	-50.9	146.0			
C ₆ H ₅ NH ₂ (s)	93.129					
CH ₂ (NH ₂)CO ₂ H, glycine (s)	75.068	-373.4	103.5			
C ₆ H ₁₂ O ₆ , α -D-glucose (s)	180.159					
C ₆ H ₁₂ O ₆ , β -D-glucose (s)	180.159	-910	212			
C ₁₂ H ₂₂ O ₁₁ , sucrose (s)	342.303	-1543	360.2			
CH ₃ CH(OH)COOH lactic acid (s)	90.079					

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

Heat capacities at 25°C

	$C_{v,m}$	$C_{p,m}$
	$\text{JK}^{-1} \text{mol}^{-1}$	$\text{JK}^{-1} \text{mol}^{-1}$
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

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, $\text{Sm}^{\circ} / \text{J K}^{-1} \text{mol}^{-1}$

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