

UNIVERSITY OF SWAZILAND

BACHELOR OF SCIENCE

FINAL EXAMINATION 2008

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) Write short notes on Van der Waals 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:

$$(P+5an^2/V^2)(V-3nb)=nRT \quad (1)$$

- (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: $a=6.493 \text{ L}^2\text{atmmol}^{-2}$, $b=5.622 \times 10^{-2} \text{ Lmol}^{-1}$ [2]
(iv) Estimate the radii of real gas molecules using equation (1) for real gases given a critical molar volume of $250 \text{ cm}^3\text{mol}^{-1}$ [2]

QUESTION 2 [25 marks]

A sample of 70 mmol Kr(g) expands reversible and isothermally at 373 K from 5.25 cm^3 to 6.79 cm^3 , and the internal energy of the sample is known to increase by 83.5J.

- a) Determine expressions for the critical point P_c , $V_{m,c}$, and T_c . [9]
- b) Assuming perfect gas behaviour calculate
- | | | |
|-------|------------|-----|
| (i) | W | [3] |
| (ii) | Q | [2] |
| (iii) | ΔH | [2] |
- c) Using the virial equation of state up to the second coefficient $B=-28.7\text{cm}^3 \text{ mol}^{-1}$ calculate: [9]
- | | |
|-------|------------|
| (i) | W |
| (ii) | Q |
| (iii) | ΔH |
- for this change of state.

Useful relation:

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

Question 3 [25 Marks]

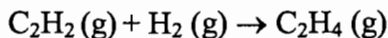
- a) Derive Kirrchoff's equation: [6]

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

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

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

for the hydrogenation reaction:



	$\text{C}_2\text{H}_4(\text{g})$	$\text{H}_2(\text{g})$	$\text{C}_2\text{H}_2(\text{g})$
$C_{p,m} \text{ J/mol/K}$	43.56	43.93	28.82
$\Delta_f H^\ominus \text{ kJ/mol}$	+52.30	0	+226.8

- c) (i) Using an appropriate Master Equation 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 Berthelot's relation:

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

Question 4 [25 Marks]

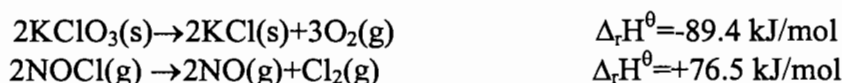
- a) Compare and contrast **Any One Pair** of the following concepts:
- Statistical view and the thermodynamic view of entropy [10]
 - Adiabatic and Isothermal expansion [10]
 - Second and Third law of thermodynamics [10]

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) 1.00 mol of perfect gas at 27°C is expanded isothermally from an initial pressure of 3.00 atm to a final pressure of 1.00 atm. Calculate q , w , ΔS_{sys} , ΔS_{surr} and ΔS_{tot} if the expansion is done:
- reversibly, and [5]
 - against a constant external pressure of 1.00 atm. [5]
 - adiabatically against a constant pressure of 1.00 atm. [5]

Question 5 [25 Marks]

- a) Write short notes on **any two** of the following
- enthalpy change [5]
 - internal energy change [5]
 - Hess's Law [5]
- b) Calculate the standard enthalpies of formation of:
- $\text{KClO}_3(\text{s})$ from the enthalpy of formation of KCl [2]
 - $\text{NOCl}(\text{g})$ from the enthalpy of formation of NO [2]
- Given the attached table and the following information:



- c) A sample of sugar D-ribose ($\text{C}_5\text{H}_{10}\text{O}_5$) of mass 0.727g was placed in a bomb calorimeter and then ignited in the presence of excess oxygen. The temperature rose by 0.910 K. In a separate experiment in the same calorimeter, the combustion

of 0.825g of benzoic acid, for which the internal energy of combustion is $-3251 \text{ kJ mol}^{-1}$, gave a temperature rise of 1.940 K.

Calculate:

- i) the heat capacity at constant volume of the calorimeter in J/K [1]
- ii) the internal energy of combustion of D-ribose in kJ/mol [2]
- iii) the enthalpy of combustion of D-ribose in kJ/mol [2]
- iii) the enthalpy of formation of D-ribose in kJ/mol [2]
- iv) Heat at constant volume and heat at constant pressure in J [2]
- v) Comment on values in ii), iii) and iv) [2]

Useful information:

	Molecular weights/g mol ⁻¹
Benzoic acid	122.12
D-ribose C ₅ H 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

$$\frac{d(\ln p)}{dT} \quad [5]$$
- 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]

Standard molar enthalpies of formation at 298.15 K

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

M_r	$\Delta H_f^\ominus / \text{kJ/mol}$	M_r	$\Delta H_f^\ominus / \text{kJ/mol}$	$a / \text{J K}^{-1} \text{mol}^{-1}$	$b / 10^{-3} \text{J K}^{-2} \text{mol}^{-1}$	$c / 10^5 \text{J K mol}^{-1}$
$\text{H}_2\text{O(g)}$	18.015	$\text{O}_3(\text{g})$	-241.8	47.998		
$\text{H}_2\text{O(l)}$	-285.8	NO(g)	+90.2	30.006		0
$\text{H}_2\text{O}_2(\text{l})$	-187.8	$\text{NO}_2(\text{g})$	+33.2	46.006		0.50
$\text{NH}_3(\text{g})$	-46.1	$\text{N}_2\text{O}_4(\text{g})$	+9.2	92.012		-1.67
$\text{N}_2\text{H}_4(\text{l})$	+50.6	$\text{SO}_2(\text{g})$	-296.8	64.063		-0.50
$\text{N}_2\text{H}_4(\text{g})$	+264.1	$\text{H}_2\text{S(g)}$	-20.6	34.080		-2.85
$\text{N}_3\text{H(g)}$	+294.1	$\text{SF}_6(\text{g})$	-1209	146.054		-8.62
$\text{HNO}_3(\text{l})$	-174.1	HF(g)	-271.1	20.006		0
$\text{NH}_2\text{OH(s)}$	-114.2	HCl(g)	-92.3	36.461		-1.55
$\text{NH}_4\text{Cl(s)}$	-314.4	HCl(aq)	-167.2	36.461		-1.92
$\text{HgCl}_2(\text{s})$	-224.3	HBr(g)	+36.4	80.917		
$\text{H}_2\text{SO}_4(\text{l})$	-814.0	HI(g)	+26.5	127.912		
$\text{H}_2\text{SO}_4(\text{aq})$	-909.3	$\text{CO}_2(\text{g})$	-393.5	44.010		
NaCl(s)	-411.0	CO(g)	-110.5	28.011		
NaOH(s)	-426.7	$\text{Al}_2\text{O}_3(\text{s})$	-1675.7	101.945		
KCl(s)	-435.9	$\text{SiO}_2(\text{s})$	-910.9	60.085		
KBr(s)	-392.2	FeS(s)	-100.0	87.91		
K(s)	-327.6	$\text{FeS}_2(\text{s})$	-178.2	119.975		
Diatomics(g)	0	AgCl(s)	-127.1	143.323		
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	M_r	$\Delta H_c^\ominus / \text{kJ/mol}$
He	3.5	0.021	4.22	0.084	16.043	-74.81
Ar	83.81	1.188	87.29	6.506	26.038	+226.8
H ₂	13.96	0.117	20.38	0.9163	28.054	+52.30
N ₂	63.15	0.719	77.35	5.586	30.070	-84.64
O ₂	54.36	0.444	90.18	6.820	42.081	53.35
Cl ₂	172.12	6.406	239.05	20.410	42.081	20.5
Br ₂	265.90	10.573	332.35	29.45	58.124	-126.11
I ₂	386.75	15.52	458.39	41.80	72.151	-146.4
Hg	234.29	2.292	629.73	59.296	84.163	-156.2
Ag	1234	11.30	2436	250.63	86.178	-198.7
Na	370.95	2.601	1156	98.01	78.115	+48.99
CO ₂	217.0	8.33	194.64	25.23	114.233	-249.8
H ₂ O	273.15	6.008	373.15	40.656 (44.016 at 298.15 K)	128.175	+78.53
NH ₃	195.40	5.652	239.73	23.351	32.042	-239.0
H ₂ S	187.61	2.377	212.80	18.673	44.054	-166.0
CH ₄	90.68	0.941	111.66	8.18	46.070	-277.0
C ₂ H ₆	89.85	2.86	184.55	14.7	60.053	-484.2
C ₆ H ₆	278.65	10.59	353.25	30.8	88.107	-486.6
CH ₃ OH	175.25	3.159	337.22	35.27 (37.99 at 298.15K)	94.114	-165.0
Gases (298-2000K)						
He, Ne, Ar, Kr, Xe						
H ₂						
O ₂						
N ₂						
Cl ₂						
CO ₂						
H ₂ O						
NH ₃						
CH ₄						
Standard molar enthalpies of formation and combustion at 298.15 K.						
CH ₄ (g)						
C ₂ H ₂ (g)						
C ₂ H ₄ (g)						
C ₂ H ₆ (g)						
C ₃ H ₆ cyclopropane(g)						
C ₃ H ₆ (propene)(g)						
C ₄ H ₁₀ n-butane(g)						
C ₅ H ₁₂ n-pentane(g)						
C ₆ H ₁₂ cyclohexane (l)						
C ₆ H ₁₄ n-hexane (l)						
C ₆ H ₆ benzene (l)						
C ₈ H ₁₈ n-octane (l)						
C ₁₀ H ₈ naphthalene (l)						
C ₉ H ₉ OH (l)						
CH ₃ CHO (g)						
CH ₃ CH ₂ OH (l)						
CH ₃ COOH (l)						
CH ₃ COOC ₂ H ₅ (l)						
C ₆ H ₅ OH (s)						
C ₆ H ₅ NH ₂ (l)						
NH ₂ CO.NH ₂ urea(s)						
CH ₂ (NH ₂)CO ₂ H, glycine (s)						
C ₆ H ₁₂ O ₆ , α-D-glucose (s)						
C ₆ H ₁₂ O ₆ , β-D-glucose (s)						
C ₁₂ H ₂₂ O ₁₁ , sucrose (s)						
CH ₃ CH(OH)COOH lactic acid (s)						

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

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