UNIVERSITY OF SWAZILAND

SUPPLEMENTARY EXAMINATION 2009-10

TITLE OF PAPER: INTRODUCTORY PHYSICAL CHEMISTRY

COURSE NUMBER: C202

TIME: THREE (3) HOURS

INSTRUCTIONS:

There are **six** questions. Each question is worth 25 marks. Answer **any four** questions.

A data sheet and a periodic table are attached

Non-programmable electronic calculators may be used.

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Question 1(25marks)

(a) Under what conditions are ΔU and ΔH for a reaction involving gases and/or liquids or solids identical. [3]

(b) A sample of liquid methanol weighing 5.27 g was burned in a constant volume bomb calorimeter at 25 °C and 119.5 kJ of heat was evolved.

(i) Calculate the enthalpy of combustion of methanol in kJ/mol. [5]

(ii) The enthalpies of formation of liquid water and carbon dioxide are -285.8 and -393.5 kJ/mol, respectively. Use these data and the result of (i) above to obtain the enthalpy of formation of liquid methanol. [4]

(iii) If the enthalpy of vaporization of methanol is 35.27 kJ/mol, what is the enthalpy of formation of methanol gas? [3]

(c) Consider the reaction

$TiO_2(s) + 2\,C(graphite) + 2Cl_2(g) \rightarrow 2\,CO(g) + TiCl_4(l)$ $\qquad \Delta_r H^\ominus(298\ K) = -80$ kJ/mol

and the following data at 25 °C

Substance	$TiO_2(s)$	$Cl_2(g)$	C(graphite)	CO(g)	$TiCl_4(l)$
$\Delta_f H^\ominus$/kJmol^{-1}	-945			-110.5	
$C_{p,m}$/JK^{-1}mol^{-1}	55.06	33.91	8.53	29.12	145.2

(i) Calculate $\Delta_r H^\ominus$ at 135.8 °C [6]

(ii) Calculate $\Delta_f H^\ominus$ of $TiCl_4$(l) at 25 °C. [4]

Question 2(25 marks)

(a) Explain the thermodynamic meaning of a system, distinguishing among open, closed and isolated systems. Which one of these systems corresponds to

(i) a fish swimming in the sea?

(ii) An egg? [7]

(b) A sample of a perfect gas is initially at 3.0 atm pressure, 25 °C temperature and a volume of 1.5 dm^3. The gas is expanded reversibly and adiabatically until the volume is 5.0 dm^3. The heat capacity of the gas is 28.89 J K^{-1} mol^{-1} and may be assumed to be independent of temperature.

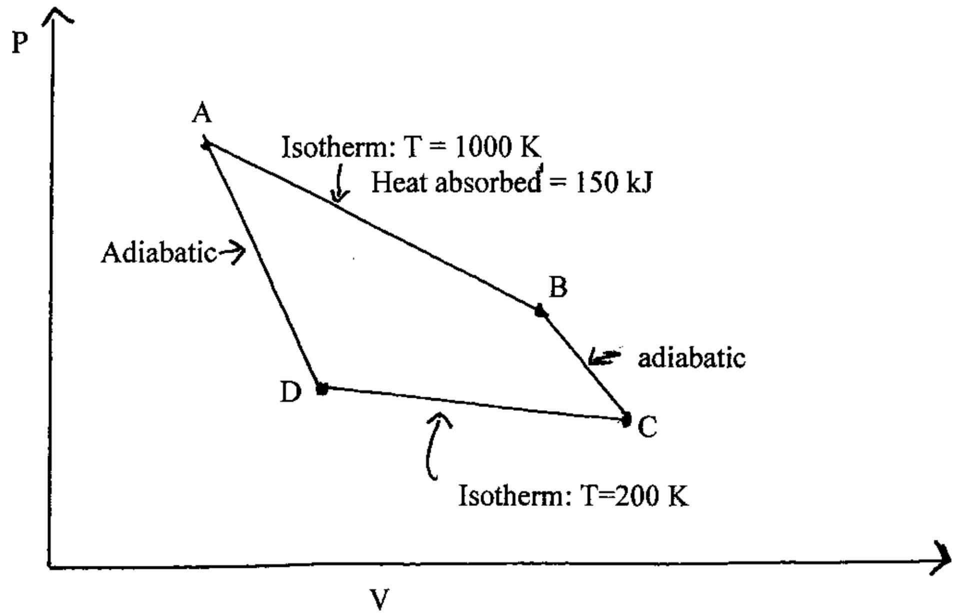
(i) Starting with the first law of thermodynamics show that final temperature of a perfect gas after a reversible adiabatic expansion is given by $T_f = \left(\frac{V_i}{V_f}\right)^{R/C_V} T_i$. [5]

(ii) Calculate the final temperature in the above expansion [3]

(iii) Calculate the final pressure [3]

(iv) Calculate ΔU and ΔH for the above process. [7]

Question 3 (25 marks)



(a) The above diagram shows a reversible Carnot cycle in the form of a p-V. Sketch the corresponding entropy – temperature, (S-T), clearly labelling all the steps. [7]

(b) What is the thermodynamic efficiency of the engine? [3]

(c) How much heat is deposited at the lower temperature, 200 K, during the isothermal compression? [3]

(d) What is the entropy increase during the isothermal expansion at 1000 K? [2]

(e) What is the entropy decrease during the isothermal compression at 200 K? [2]

(f) What is the entropy change during the adiabatic expansion B→ C? [2]

(g) What is the overall entropy change for the entire cycle? [1]

(h) What is the change in the Gibbs function during the process A → B? [2]

(i) If C_p=200 J K^{-1} mol^{-1}, what is the increase in the Gibbs function in the process D→A? [3]

Question 4(25 marks)

(a) Define the terms degree of freedom, component and phase and then derive the phase rule. [12]

(b) State the number of components, phases and degrees of freedom in the following systems:
  (i) Liquid water in equilibrium with both ice and its vapour.
  (ii) A saturated aqueous solution of sodium chloride in a closed vessel. [6]

(c) Sketch a phase diagram for a mixture of two liquids which are completely mixed in all proportions at low and high but not intermediate temperatures. Deduce what would be observed if a liquid mixture initially at low temperature is slowly heated. [7]

Question 5 (25 marks)

One mole of a gas obeys the equation of state $pV = RT + Bp$ in which B is a constant at constant temperature, p, V, T and R have their usual meaning.

(a) Use the thermodynamic equation of state, $(\partial U/\partial V)_T = T(\partial p/\partial T)_V - p$, to show that the internal energy of the gas is a function of temperature only. [6]

(b) If the gas is expanded isothermally and reversibly to double its initial volume, derive the expressions for w, ΔU, q, ΔH, ΔS, and ΔG [10]

(c) If the expansion in (b) is carried out isothermally but irreversibly, which of the properties calculated in (b) would have different values and which would remain unchanged? Explain. [3]

(d) If the expansion in (b) is carried out adiabatically and reversibly, derive the expression for all the properties mentioned in (b). [6]

Question 6 (25 marks)

Toluene and xylene form an ideal solution. At 25 °C the vapour pressure of pure toluene is 22 Torr and that of pure xylene is 5 Torr.

(a) Define an ideal solution, briefly explaining its characteristics. [5]

(b) Sketch a graph, showing how the vapour pressure of a solution of toluene and xylene should vary with composition. Show on the same graph the approximate appearance of the plot of the equilibrium vapour composition. [6]

(c) Calculate the composition of the vapour in equilibrium with a solution in which the mole fraction of toluene is 0.2. [6]

(d) If the force of attraction between a toluene and a xylene molecule were less than in an ideal solution i.e. the toluene-xylene pair were less strongly attracted than the toluene-toluene and xylene-xylene pairs, show graphically the changes to be expected in the plot in (b) above. Briefly explain the reasons for these changes. [8]

General data and fundamental constants

Quantity	Symbol	Value
Speed of light	c	$2.997\,924\,58 \times 10^{8}$ m s^{-1}
Elementary charge	e	$1.602\,177 \times 10^{-19}$ C
Faraday constant	$F = N_A e$	9.6485×10^{4} C mol^{-1}
Boltzmann constant	k	$1.380\,66 \times 10^{-23}$ J K^{-1}
Gas constant	$R = N_A k$	$8.314\,51$ J K^{-1} mol^{-1}
		$8.205\,78 \times 10^{-2}$ dm^{3} atm K^{-1} mol^{-1}
		6.2364×10 L Torr K^{-1} mol^{-1}
Planck constant	h	$6.626\,08 \times 10^{-34}$ J s
	$\hbar = h/2\pi$	$1.054\,57 \times 10^{-34}$ J s
Avogadro constant	N_A	$6.022\,14 \times 10^{23}$ mol^{-1}
Atomic mass unit	u	$1.660\,54 \times 10^{-27}$ Kg
Mass		
electron	m_e	$9.109\,39 \times 10^{-31}$ Kg
proton	m_p	$1.672\,62 \times 10^{-27}$ Kg
neutron	m_n	$1.674\,93 \times 10^{-27}$ Kg
Vacuum permittivity	$\varepsilon_o = 1/c^2\mu_o$	$8.854\,19 \times 10^{-12}$ J^{-1} C^{2} m^{-1}
	$4\pi\varepsilon_o$	$1.112\,65 \times 10^{-10}$ J^{-1} C^{2} m^{-1}
Vacuum permeability	μ_o	$4\pi \times 10^{-7}$ J s^{2} C^{-2} m^{-1}
		$4\pi \times 10^{-7}$ T^{2} J^{-1} m^{3}
Magneton		
Bohr	$\mu_B = e\hbar/2m_e$	$9.274\,02 \times 10^{-24}$ J T^{-1}
nuclear	$\mu_N = e\hbar/2m_p$	$5.050\,79 \times 10^{-27}$ J T^{-1}
g value	g_e	2.002 32
Bohr radius	$a_o = 4\pi\varepsilon_o\hbar/m_e e^2$	$5.291\,77 \times 10^{-11}$ m
Fine-structure constant	$\alpha = \mu_o e^2 c/2h$	$7.297\,35 \times 10^{-3}$
Rydberg constant	$R_\infty = m_e e^4/8h^3 c\varepsilon_o^{\,2}$	$1.097\,37 \times 10^{7}$ m^{-1}
Standard acceleration of free fall	g	$9.806\,65$ m s^{-2}
Gravitational constant	G	$6.672\,59 \times 10^{-11}$ N m^{2} Kg^{-2}

Conversion factors

1 cal	=	4.184 joules (J)	1 erg	=	1×10^{-7} J
1 eV	=	$1.602\,2 \times 10^{-19}$ J	1 eV/molecule	=	96 485 kJ mol^{-1}

Prefixes

f	p	n	μ	m	c	d	k	M	G
femto	pico	nano	micro	milli	centi	deci	kilo	mega	giga
10^{-15}	10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}	10^{3}	10^{6}	10^{9}

PERIODIC TABLE OF ELEMENTS

GROUPS

PERIODS	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
1	1.008 H 1																	4.003 He 2
2	6.941 Li 3	9.012 Be 4											10.811 B 5	12.011 C 6	14.007 N 7	15.999 O 8	18.998 F 9	20.180 Ne 10
3	22.990 Na 11	24.305 Mg 12					TRANSITION ELEMENTS						26.982 Al 13	28.086 Si 14	30.974 P 15	32.06 S 16	35.453 Cl 17	39.948 Ar 18
4	39.098 K 19	40.078 Ca 20	44.956 Sc 21	47.88 Ti 22	50.942 V 23	51.996 Cr 24	54.938 Mn 25	55.847 Fe 26	58.933 Co 27	58.69 Ni 28	63.546 Cu 29	65.39 Zn 30	69.723 Ga 31	72.61 Ge 32	74.922 As 33	78.96 Se 34	79.904 Br 35	83.80 Kr 36
5	85.468 Rb 37	87.62 Sr 38	88.906 Y 39	91.224 Zr 40	92.906 Nb 41	95.94 Mo 42	98.907 Tc 43	101.07 Ru 44	102.91 Rh 45	106.42 Pd 46	107.87 Ag 47	112.41 Cd 48	114.82 In 49	118.71 Sn 50	121.75 Sb 51	127.60 Te 52	126.90 I 53	131.29 Xe 54
6	132.91 Cs 55	137.33 Ba 56	138.91 *La 57	178.49 Hf 72	180.95 Ta 73	183.85 W 74	186.21 Re 75	190.2 Os 76	192.22 Ir 77	195.08 Pt 78	196.97 Au 79	200.59 Hg 80	204.38 Tl 81	207.2 Pb 82	208.98 Bi 83	(209) Po 84	(210) At 85	(222) Rn 86
7	223 Fr 87	226.03 Ra 88	(227) **Ac 89	(261) Rf 104	(262) Ha 105	(263) Unh 106	(262) Uns 107	(265) Uno 108	(266) Une 109	(267) Uun 110								

Atomic mass →
Symbol →
Atomic No. →

*Lanthanide Series	140.12 Ce 58	140.91 Pr 59	144.24 Nd 60	(145) Pm 61	150.36 Sm 62	151.96 Eu 63	157.25 Gd 64	158.93 Tb 65	162.50 Dy 66	164.93 Ho 67	167.26 Er 68	168.93 Tm 69	173.04 Yb 70	174.97 Lu 71
**Actinide Series	232.04 Th 90	231.04 Pa 91	238.03 U 92	237.05 Np 93	(244) Pu 94	(243) Am 95	(247) Cm 96	(247) Bk 97	(251) Cf 98	(252) Es 99	(257) Fm 100	(258) Md 101	(259) No 102	(260) Lr 103

( ) indicates the mass number of the isotope with the longest half-life.