
UNIVERSITI SAINS MALAYSIA

Second Semester Examination
2009/2010 Academic Session

April/May 2010

KFT 232 – Physical Chemistry II
[Kimia Fizik II]

Duration: 3 hours
[Masa : 3 jam]

Please check that this examination paper consists of ELEVEN pages of printed material before you begin the examination

Instructions:

Answer any **FIVE** (5) questions with at least **ONE** (1) question from Part B.

Answer each question on a new page.

You may answer either in Bahasa Malaysia or in English.

If a candidate answers more than five questions, only the answers to the first five questions in the answer sheet will be graded.

In the event of any discrepancies, the English version shall be used.

Appendix: Fundamental constants in physical chemistry.

PART A

Answer not more than **FOUR** questions.

1. (a) A reversible Carnot engine operates between 300 K and a higher temperature, T_h . If the engine produces 10 kJ mol^{-1} of work per cycle and the entropy change in the isothermal expansion at T_h is $100 \text{ J mol}^{-1} \text{ K}^{-1}$. Calculate the values for heat at hot and cold temperatures, q_h and q_c , respectively and the T_h ?

(10 marks)

- (b) One mole of an ideal gas is contained in an insulated piston-cylinder arrangement ($dq = 0$) in an initial state (T_1, p_1, V_1). The gas is allowed to expand adiabatically and irreversibly against a constant external pressure, p_{ex} , until a point is reached when the internal pressure equals to p_{ex} . If $C_{V,m}$ for the gas is equal to $1.5R$, derive an equation giving the final temperature of the gas in terms of p_{ex}, V_1, T_1 and R .

(10 marks)

2. (a) A sample of aluminium is heated from 27 to 700 °C. Given that the melting point of aluminium is 660 °C, the heat of fusion is 393 J g^{-1} and the heat capacities for the solid and liquid aluminium are $31.8 \ln T$ and $34.4 \ln T \text{ J K}^{-1} \text{ mol}^{-1}$, respectively. Calculate the change in molar entropy of aluminium.

(10 marks)

- (b) An ideal gas with $C_{V,m} = 1.5R$ is heated along a path for which the molar heat capacity is $3.5R$. One mole of the gas with an initial volume of 20 L is heated from 300 to 500 K along this path and the process is reversible. Calculate.

- (i) the final volume, V_f , of the gas, and
 (ii) the entropy change, ΔS , for the process.

(10 marks)

3. (a) Derive the following thermodynamics relations

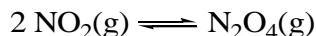
$$(i) \quad \left(\frac{\partial C_p}{\partial p} \right)_T = -T \left(\frac{\partial^2 V}{\partial T^2} \right)_p$$

$$(ii) \quad \left(\frac{\partial T}{\partial p} \right)_S = \left(\frac{\partial V}{\partial S} \right)_p$$

(10 marks)

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- (b) One mole of $\text{NO}_2(\text{g})$ was introduced into a 1 L container at 298 K. The $\text{NO}_2(\text{g})$ spontaneously dimerizes to form $\text{N}_2\text{O}_4(\text{g})$ via the reaction



After the system reaches equilibrium, the number of moles of $\text{NO}_2(\text{g})$ and $\text{N}_2\text{O}_4(\text{g})$ are 0.0530 and 0.4735 mol, respectively. Calculate the Gibbs free energy change, ΔG , for the process and comment how the reaction occurs.

Given: $\mu^\circ_{\text{NO}_2(\text{g})} = 5.131 \times 10^4 \text{ J mol}^{-1}$; $\mu^\circ_{\text{N}_2\text{O}_4(\text{g})} = 9.789 \times 10^4 \text{ J mol}^{-1}$

(10 marks)

4. (a) An ideal solution mixture is composed of 5 mol of benzene and 3.25 mol of toluene. At 298 K, the vapor pressure of the pure benzene and toluene are 96.4 and 28.9 Torr, respectively. Determine

- (i) the total pressure, and
 (ii) the composition of the vapor.

(8 marks)

- (b) What is meant by activity and activity coefficient of a substance?

The activity of a solution consists of two components A and B, can be determined by the following Gibbs-Duhem equation,

$$X_A d \ln a_A + X_B d \ln a_B = 0$$

where X_A and X_B are the mole fractions of A and B, respectively; a_A and a_B are the activities of A and B, respectively. Derive the above equation and justify any assumption made.

(12 marks)

5. (a) The partial molar volume of component 2 in a solution can be written as

$$\begin{aligned} V_2 &= \left(\frac{\partial V}{\partial n_2} \right)_{n_1} \\ &= \frac{M_2}{\rho} - \left(M_1 n_1 + M_2 n_2 \right) \frac{1}{\rho^2} \left(\frac{\partial \rho}{\partial n_2} \right)_{n_1} \end{aligned}$$

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where n_1 and M_1 are the concentration and molar mass of component 1, n_2 and M_2 represent the same meaning for component 2. ρ is the density.

- (i) Rewrite the expression for V_2 in terms of mole fractions X_1 and X_2 .
 (i) Calculate the molar volume of methanol, V_2 , when $X_2 = 0.1$ mol. Given that the density of a water-methanol solution (in g cm^{-3}) at 298 K is

$$\rho = 0.9971 - 0.2893X_2 + 0.2990X_2^2 - 0.6087X_2^3 + 0.5944X_2^4 - 0.2058X_2^5$$

(12 marks)

- (b) Carbon disulfide (CS_2) has vapour pressures of 40 and 100 Torr at 250.65 and 268.05 K, respectively. Calculate

- (i) the enthalpy of vapourisation and the normal boiling point of CS_2 ,
 (ii) the standard partial molar enthalpy of $\text{CS}_2(\text{g})$.

Given: The standard partial molar enthalpy of $\text{CS}_2(\ell)$ is $89.70 \text{ kJ mol}^{-1}$.

(8 marks)

PART B

Answer at least **ONE** question.

6. (a) The potential, ϕ , on the ion due to the ionic atmosphere when the distance from this selected ion, r , approaches the distance of closest approach, a , is given by

$$\phi = -\frac{Z_i \epsilon}{4\pi\epsilon_0\epsilon} \cdot \frac{\kappa}{1 + \kappa a}$$

$$\text{and } \kappa^2 = \frac{\epsilon^2}{\epsilon_0\epsilon kT} \sum_i N_i Z_i^2$$

where N_i and Z_i represent the number per unit volume and the positive value of the valence of the i^{th} -type ion, respectively, ϵ is the electronic charge and ϵ is the dielectric constant. Taking into account the deviations from ideality of the behavior of a single ion of type i , the Gibbs energy could be expressed as:

$$G_i = G_i^0 + kT \ln C_i \gamma_i$$

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where C_i is the concentration of the ion and γ_i is the activity coefficient. Show that the mean ionic activity coefficient, γ_{\pm} , of an electrolyte dissociating into ν_+ cations of valency Z_+ and ν_- anions of valency Z_- , is given by

$$-\log \gamma_{\pm} = \frac{|Z_+ Z_-| A \sqrt{I}}{1 + B a \sqrt{I}}$$

where A and B are the Debye-Hückel constants and I is the ionic strength of the solution.

(10 marks)

- (b) The solubility, S, of a cobalt complex salt, AX, was measured in water at 25 °C as a function of added NaCl concentration, C.

C (NaCl) x 10 ³ / mol dm ⁻³	0	0.3	1.0	2.0	10	20
S x 10 ⁴ / mol dm ⁻³	3.355	3.377	3.405	3.451	3.627	3.790

Calculate the solubility product and the mean ionic activity coefficient, γ_{\pm} for these solutions and compare γ_{\pm} with the values calculated by using Debye-Hückel limiting law.

Given: Debye-Hückel constant, A = 0.5091 kg^{1/2} mol^{-1/2}

(10 marks)

7. (a) The emf of the cell,
Pt | H₂(g, 1 atm) | HCl (aq, m) | AgCl (s) | Ag(s)
has been measured with the following results at 25 °C:

m/mol kg ⁻¹	0.0010	0.0020	0.0050	0.0100	0.0200	0.0500	0.100
E/V	0.57915	0.54425	0.49846	0.46417	0.43024	0.38588	0.31874

Calculate the standard emf of the cell and the mean ionic activity coefficient of HCl at m = 0.0010, 0.0100, and 0.100 mol kg⁻¹.

(10 marks)

- (b) The emf of the cell
Pt | PbSO₄(s) | H₂SO₄ (aq, m) | PbSO₄(s) | PbO₂ (s) | Pt
was measured over a wide range of temperatures and H₂SO₄ concentrations. In 1 mol kg⁻¹ H₂SO₄, the emf was:

$$E/V = 1.91737 + 56.1 \times 10^{-6} T + 108 \times 10^{-8} T^2$$

where T is the temperature in unit °C. Calculate ΔG , ΔH and ΔS for the cell reaction at 0 °C and 25 °C.

(10 marks)

TERJEMAHAN

Arahan:

Jawab **LIMA** (5) soalan sahaja dengan sekurang-kurangnya **SATU** (1) soalan daripada Bahagian B.

Jawab setiap soalan pada muka surat yang baru.

Anda dibenarkan menjawab soalan ini sama ada dalam Bahasa Malaysia atau Bahasa Inggeris.

Jika calon menjawab lebih daripada lima soalan, hanya lima soalan pertama mengikut susunan dalam skrip jawapan akan diberi markah.

Sekiranya terdapat sebarang percanggahan pada soalan peperiksaan, versi Bahasa Inggeris hendaklah diguna pakai.

Lampiran: Pemalar asas dalam kimia fizik.

BAHAGIAN A

Jawab tidak lebih daripada **EMPAT** soalan.

1. (a) Satu enjin Carnot berbalik berfungsi antara suhu 300 K dan suhu yang lebih tinggi, T_h . Sekiranya enjin tersebut menghasilkan 10 kJ mol^{-1} kerja perpusingan dan perubahan entropi sebanyak $100 \text{ J mol}^{-1} \text{ K}^{-1}$ melalui proses pengembangan isothermal pada T_h , Kiralah nilai haba pada suhu panas dan sejuk, q_h dan q_c , masing-masing dan T_h ?

(10 markah)

- (b) Satu mol suatu gas unggul di dalam suatu susunan silinder-ombok bertebat ($dq = 0$) pada keadaan awalnya (T_1, p_1, V_1). Gas dibenarkan mengembang secara adiabatik dan tak berbalik melawan suatu tekanan luar malar, p_{ex} , sehingga suatu titik tercapai apabila tekanan dalam menjadi sama dengan p_{ex} . Jika $C_{V,m}$ bagi gas adalah sama dengan $1.5R$, terbitkan suatu persamaan yang memberikan suhu akhir gas di dalam sebutan p_{ex}, V_1, T_1 dan R .

(10 markah)

2. (a) Satu sampel aluminium yang dipanaskan dari 27 kepada $700 \text{ }^\circ\text{C}$. Diberikan takat didih bagi aluminium adalah $660 \text{ }^\circ\text{C}$, haba pelakuran adalah 393 J g^{-1} dan muatan haba pada tekanan tetap bagi pepejal dan cecair aluminium masing-masing adalah $31.8 \ln T$ dan $34.4 \ln T \text{ J K}^{-1} \text{ mol}^{-1}$. Kiralah perubahan entropi molar bagi aluminium.

(10 markah)

- (b) Suatu gas unggul dengan $C_{V,m} = 1.5R$ dipanaskan sepanjang laluan dengan muatan haba molar adalah $3.5R$. Satu mol gas dengan isipadu awal 20 L dipanaskan daripada 300 kepada 500 K sepanjang laluan ini dan proses adalah berbalik, Hitunglah.

- (i) isipadu akhir, V_f , gas, dan
(ii) perubahan entropi, ΔS , bagi proses tersebut.

(10 markah)

3. (a) Terbitkan persamaan termodinamik berikut;

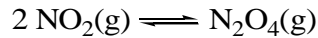
$$(i) \quad \left(\frac{\partial C_p}{\partial p} \right)_T = -T \left(\frac{\partial^2 V}{\partial T^2} \right)_p$$

$$(ii) \quad \left(\frac{\partial T}{\partial p} \right)_S = \left(\frac{\partial V}{\partial S} \right)_p$$

(10 markah)

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- (b) Satu mol $\text{NO}_2(\text{g})$ diisikan ke dalam 1 L bekas pada 298K. $\text{NO}_2(\text{g})$ mendimer secara spontan untuk membentuk $\text{N}_2\text{O}_4(\text{g})$ melalui tindak balas.



Apabila sistem mencapai keseimbangan, bilangan mol $\text{NO}_2(\text{g})$ dan $\text{N}_2\text{O}_4(\text{g})$ masing-masing adalah 0.0530 dan 0.4735 mol. Hitunglah perubahan tenaga bebas Gibbs, ΔG , bagi proses dan ulaskan bagaimana tindak balas berlaku.

Diberi : $\mu^\circ_{\text{NO}_2(\text{g})} = 5.131 \times 10^4 \text{ J mol}^{-1}$; $\mu^\circ_{\text{N}_2\text{O}_4(\text{g})} = 9.789 \times 10^4 \text{ J mol}^{-1}$

(10 markah)

4. (a) Suatu larutan campuran unggul terdiri daripada 5 mol benzena dan 3.25 mol toluena. Pada suhu 298 K, tekanan wap bagi benzena dan toluena tulen, p^* , masing - masing adalah 96.4 dan 28.9 Torr. Tentukan

- (i) tekanan total dan
(ii) komposisi wap tersebut.

(8 markah)

- (b) Apakah yang dimaksudkan dengan keaktifan dan pekali keaktifan sesuatu zat?

Keaktifan suatu larutan yang mengandungi dua komponen A dan B, dapat ditentukan dengan menggunakan persamaan Gibbs-Duhem berikut,

$$X_A d \ln a_A + X_B d \ln a_B = 0$$

bagi X_A dan X_B , masing-masing adalah pecahan mol A dan B; a_A dan a_B masing-masing adalah keaktifan A dan B. Terbitkan persamaan diatas dan berikan justifikasi bagi andaian yang dibuat.

(12 markah)

5. (a) Isipadu molar separa komponen 2 dalam suatu larutan boleh ditulis sebagai

$$\begin{aligned} V_2 &= \left(\frac{\partial V}{\partial n_2} \right)_{n_1} \\ &= \frac{M_2}{\rho} - \left(M_1 n_1 + M_2 n_2 \right) \frac{1}{\rho^2} \left(\frac{\partial \rho}{\partial n_2} \right)_{n_1} \end{aligned}$$

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Dengan n_1 dan M_1 masing-masing adalah kepekatan dan jisim molar komponen 1 sementara n_2 dan M_2 mewakili makna yang sama bagi komponen 2. ρ adalah ketumpatan.

- (i) Tuliskan semula ungkapan bagi V_2 tersebut dalam sebutan pecahan mol X_1 dan X_2 .
- (ii) Kiralah isipadu molar bagi metanol, V_2 , bila $X_2 = 0.1$ mol. Diberikan ketumpatan larutan air-metanol (dalam g cm^{-3}) pada 298 K adalah
- $$\rho = 0.9971 - 0.2893X_2 + 0.2990X_2^2 - 0.6087X_2^3 + 0.5944X_2^4 - 0.2058X_2^5$$

Kiralah isipadu molar bagi metanol, V_2 , bila $X_2 = 0.1$ mol.

(12 markah)

- (b) Karbon disulfida (CS_2) memiliki tekanan wap 40 dan 100 Torr masing-masing pada 250.65 dan 268.05 K. Hitunglah
- (i) entalpi pengwapan dan takat didih normal CS_2 .
- (ii) entalpi molar separa piawai $\text{CS}_2(\text{g})$.

Diberi: Entalpi molar separa piawai $\text{CS}_2(\ell)$ ialah $89.70 \text{ kJ mol}^{-1}$.

(8 markah)

BAHAGIAN B

Jawab sekurang-kurangnya **SATU** soalan.

6. (a) Keupayaan, ϕ , pada ion yang disebabkan oleh atmosfera ion, apabila suatu jarak daripada ion terpilih ini, r , menghampiri jarak penghampiran yang terdekat, a , diberi oleh

$$\phi = - \frac{Z_i \epsilon}{4\pi\epsilon_0\epsilon} \cdot \frac{\kappa}{1 + \kappa a}$$

$$\text{dan } \kappa^2 = \frac{\epsilon^2}{\epsilon_0\epsilon kT} \sum_i N_i Z_i^2$$

dengan N_i dan Z_i masing-masing mewakili bilangan per unit isipadu dan nilai positif valensi ion berjenis i , ϵ ialah cas elektron dan ϵ ialah pemalar dielektrik. Dengan mengambil kira penyimpangan daripada keunggulan bagi kelakuan ion tunggal berjenis i , tenaga Gibbs boleh diungkapkan sebagai:

$$G_i = G_i^0 + kT \ln C_i \gamma_i$$

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dengan C_i ialah kepekatan ion dan γ_i ialah pekali keaktifan.

Tunjukkan bahawa pekali keaktifan ion min, γ_{\pm} , bagi suatu elektrolit yang bercerai kepada ν_+ kation bervalensi Z_+ dan ν_- anion bervalensi Z_- , diberi dengan:

$$-\log \gamma_{\pm} = \frac{|Z_+ Z_-| A \sqrt{I}}{1 + B a \sqrt{I}}$$

A dan B ialah pemalar Debye-Hückel dan I ialah kekuatan ion bagi larutan ini.

(10 markah)

- (b) Keterlarutan, S, bagi garam kompleks kobalt, AX, disukat dalam air pada 25 °C sebagai fungsi kepekatan NaCl yang ditambahkan, C.

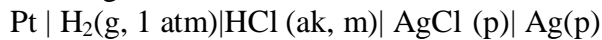
C (NaCl) x 10 ³ /mol dm ⁻³	0	0.3	1.0	2.0	10	20
S x 10 ⁴ /mol dm ⁻³	3.355	3.377	3.405	3.451	3.627	3.790

Kirakan hasil darab keterlarutan dan pekali keaktifan ion min, γ_{\pm} untuk setiap larutan ini dan bandingkan γ_{\pm} dengan nilai yang dikira daripada hukum penghadan Debye-Hückel.

Diberi: pemalar Debye-Hückel, A = 0.5091 kg^{1/2} mol^{-1/2}

(10 markah)

7. (a) Emf bagi sel:



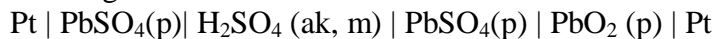
telah disukat pada 25 °C dengan keputusan yang berikut:

m/mol kg ⁻¹	0.001	0.002	0.005	0.010	0.020	0.050	0.100
E/V	0.57915	0.54425	0.49846	0.46417	0.43024	0.38588	0.31874

Kirakan emf piawai sel itu dan pekali keaktifan min HCl pada m = 0.0010, 0.0100, dan 0.100 mol kg⁻¹.

(10 markah)

- (b) Emf bagi sel:



telah disukat pada suatu julat suhu yang luas dan kepekatan H₂SO₄. Dalam 1 mol kg⁻¹ H₂SO₄, emf ialah:

$$E/V = 1.91737 + 56.1 \times 10^{-6} T + 108 \times 10^{-8} T^2$$

T ialah suhu dalam unit °C. Kirakan ΔG , ΔH and ΔS untuk tindak balas sel pada 0 °C dan 25 °C.

(10 markah)

APPENDIX

UNIVERSITI SAINS MALAYSIA
School of Chemical Sciences

General data and fundamental constants

Quantity	Symbol	Value	Power of ten	Units
Speed of light	c	2.99792458	10^8	m s^{-1}
Elementary charge	e	1.602176	10^{-19}	C
Faraday constant	$F=N_Ae$	9.64853	10^4	C mol^{-1}
Boltzmann constant	k	1.38065	10^{-23}	J K^{-1}
Gas constant	$R=N_Ak$	8.31447		$\text{J K}^{-1} \text{mol}^{-1}$
		8.31447	10^{-2}	$\text{L bar K}^{-1} \text{mol}^{-1}$
		8.20574	10^{-2}	$\text{L atm K}^{-1} \text{mol}^{-1}$
		6.23637	10	$\text{LTorr K}^{-1} \text{mol}^{-1}$
Planck constant	h	6.62608	10^{-34}	J s
	$\hbar = h/2\pi$	1.05457	10^{-34}	J s
Avogadro constant	N_A	6.02214	10^{23}	mol^{-1}
Standard acceleration of free fall	g	9.80665		m s^{-2}

Conversion factors

Useful relation

Unit relations

1 eV	$1.60218 \times 10^{-19} \text{ J}$ $96.485 \text{ kJ mol}^{-1}$	2.303 RT/F $= 0.0591 \text{ V at } 25^\circ \text{C}$	Energy	$1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$ $= 1 \text{ A V s}$
	8065.5 cm^{-1}		Force	$1 \text{ N} = 1 \text{ kg m s}^{-2}$
1 cal	4.184 J		Pressure	$1 \text{ Pa} = 1 \text{ N m}^{-2}$ $= 1 \text{ kg m}^{-1} \text{ s}^{-2}$ $= 1 \text{ J m}^{-3}$
1 atm	101.325 kPa 760 Torr			
1 cm^{-1}	$1.9864 \times 10^{-23} \text{ J}$		Charge	$1 \text{ C} = 1 \text{ A s}$
1 \AA	10^{-10} m		Potential difference	$1 \text{ V} = 1 \text{ J C}^{-1}$ $= 1 \text{ kg m}^2 \text{ s}^{-3} \text{ A}^{-1}$
1 L atm	101.325 J			

Atomic Weights

Al	26.98	C	12.01	Fe	55.85	P	30.97
Sb	121.76	Cs	132.92	Kr	83.80	K	39.098
Ar	39.95	Cl	35.45	Pb	207.2	Ag	107.87
As	74.92	Cr	51.996	Li	6.941	Na	22.99
Ba	137.33	Co	58.93	Mg	24.31	S	32.066
Be	9.012	Cu	63.55	Mn	54.94	Sn	118.71
Bi	208.98	F	18.998	Hg	200.59	W	183.84
B	10.81	Au	196.97	Ne	20.18	Xe	131.29
Br	79.90	He	4.002	Ni	58.69	Zn	65.39
Cd	112.41	H	1.008	N	14.01		
Ca	40.078	I	126.90	O	15.999		