UNIVERSITI SAINS MALAYSIA

Second Semester Examination
2011/2012 Academic Session

June 2012

# KFT 232 – Physical Chemistry II
## *[Kimia Fizik II]*

Duration: 3 hours
*[Masa : 3 jam]*

Please check that this examination paper consists of THIRTEEN 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) By giving examples, define the path (non-state) and state functions.

(3 marks)

(b) One mole of a gas at the temperature of 298 K and the pressure of 1 bar is heated and compressed reversibly in a frictionless piston and cylinder to 573 K and 10 bar. Two paths were employed to achieve the final state as illustrated in Figure 1. For this system,

(i) Describe the processes for paths A and B.

(ii) Calculate the heat and work for both paths and comment weather they are state or non-state functions.

Given that $\bar{C}_P = 38\ J\ K^{-1}\ mol^{-1}$.

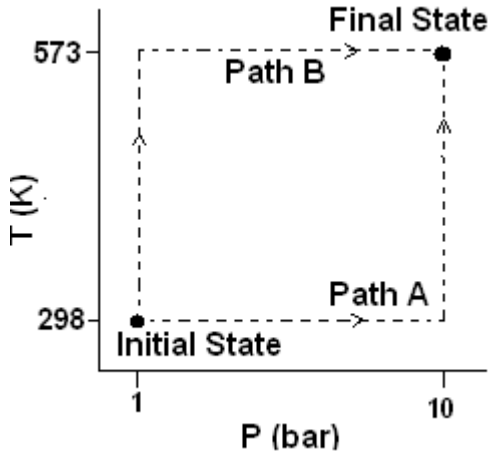



Figure 1

(8 marks)

(c) Using the appropriate relations and thermodynamics laws, prove that:

(i) $\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T$

(ii) $\left(\frac{\partial^2 A}{\partial T^2}\right)_V = -\frac{C_V}{T}$

(9 marks)

2. (a) Describe the term ‘ideal solution’ based on the intermolecular forces of liquids. Explain why a mixture of hexane and heptane forms ideal solutions.

(3 marks)



(b) An ideal mixture of benzene and methylbenzene is formed upon mixing. If the vapour pressures of pure benzene and methylbenzene at 302 K are 32.6 kPa and 30.1 kPa respectively, calculate the total pressure and the composition of the vapour which is in equilibrium with a liquid mixture containing 100 g of benzene and 80 g of methylbenzene at 302 K.

(10 marks)

(c) Derive the expressions for fugacity and fugacity coefficient for a gas which obeys the following equation of state

$$\frac{PV_m}{RT} = 1 + \frac{a}{V_m} + \frac{b}{V_m^2}$$

where a = -21.3 $cm^3\ mol^{-1}$ and b = 1054 $cm^6\ mol^{-2}$. Calculate the fugacity of neon gas at 1 atm and 298 K.

(7 marks)

3. (a) Given that the entropy, S = f(T, P) and S = f(T, V), prove that:

$$C_P - C_V = T\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V$$

(10 marks)

(b) At 27 $^oC$ and 1 bar, the volume of a NaCl solution in 1.0 kg methanol is given by the following equation:

$$V = \left(1008.45 + 12.62\ b + 1.78\ b^{3/2} + 0.12\ b^3\right)\ cm^3$$

where b is the number of mol of NaCl

(i) Derive the expression for partial molar volume for NaCl
(ii) Calculate the partial molar volume for NaCl and methanol in 0.1 m NaCl
(iii) Calculate the density of the 0.1 m NaCl solution

(10 marks)

4. A Carnot cycle uses 1 mol of a monatomic ideal gas as the working substance at an initial state of 5 atm and 500 K. The gas expands isothermally to a pressure of 1 atm (Step 1) and then adiabatically to a final temperature of 300 K (Step 2). This expansion is followed by an isothermal compression (Step 3) and then by an adiabatic compression (Step 4) back to its initial state. Determine the values of q, w, $\Delta H$, $\Delta U$, $\Delta S$, $\Delta G$ for each step and finally the $\Delta S_{tot}$.

(20 marks)

5. (a) For a chemical reaction described below and using the data given:

$$CO_2(g) + O_2(g) \longleftrightarrow 2CO_2(g)$$

$\Delta G^{o}_{298\,K} = -24.65\ kJ\ mol^{-1}$

$\Delta H^{o}_{298\,K} = (-32000 - 12.8\,T - 12 \times 10^{-3}\,T^2 - 21.3 \times 10^{-7}\,T^3)\ J\,mol^{-1}$

Calculate $\Delta G^{o}$, $\ln K_P$ and $\Delta S^{o}$ at 800 K.

(12 marks)

(b) Gas A forms an ideal solution with liquid B. At 350 K and the pressure above the solution 760 Torr, a saturated solution formed and is found to have a mole fraction of A, $x_A = 0.3017$. At 200 K, gas A condensed to a liquid form and is found to have an equilibrium vapour pressure of 11.47 Torr. Assume that the vapour behaves ideally and that the heat capacity of the liquid and the gas are the same at all temperatures. Compute the partial molar enthalpy of vaporization and the normal boiling point of A.

(8 marks)

**PART B**

Answer at least **ONE** question.

6. (a) Write the overall cell reaction and calculate $\Delta G^{\circ}$ and the equilibrium constant K at 25 °C for the reaction occurring in the following cells,

$Zn(s) \mid ZnCl_2\,(aq) \parallel CdSO_4\,(aq) \mid Cd\,(s)$

Given the standard reduction potentials:

$E^{\circ}_{Zn^{2+}/Zn} = -0.7618$ V
$E^{\circ}_{Cd^{2+}/Cd} = -0.403$ V

(4 marks)

(b) For the following cell,

Pt, $H_2$ (g, 1 atm) | HCl (m) | AgCl (s) | Ag (s)

prove that

$$E + \frac{2RT}{F} ln\, m = E^{\circ} - \frac{2RT}{F} ln\, \gamma_{\pm}$$

where m is the molality and $\gamma_{\pm}$ is the mean ionic activity coefficient.

(6 marks)

(c) For the following concentration cell with transference.

$H_2$ (g,1 atm) | HCl (m = 0.02) || HCl (m = 1.00) | $H_2$ (g,1 atm)

(i) Show that the equation of the cell potential is:

$$E_{cell} = -\frac{2t_{-}RT}{F} ln \frac{m_1 \gamma_{\pm 1}}{m_2 \gamma_{\pm 2}}$$

(ii) Calculate the cell potential, given the mean activity coefficient, $\gamma_{\pm}$, of the left and right side of the cell, 0.88 and 0.81, respectively, and the transport number, $t_{-}$=0.178.

(10 marks)

7. (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

$$\phi = -\frac{Z_i \in}{4\pi\varepsilon_o \varepsilon} \cdot \frac{\kappa}{1 + \kappa a}$$

and $$\kappa^2 = \frac{\in^2}{\varepsilon_o \varepsilon kT} \sum_i N_i Z_i^{\,2}$$

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, $\in$ 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:

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

where $C_i$ is the concentration of the ion and $\gamma_i$ is the activity coefficient.
Show that the mean ionic activity coefficient, $\gamma_\pm$ , of an electrolyte dissociating into $\nu_+$ cations of valency $Z_+$ and $\nu_-$ anions of valency $Z_-$, is given by

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

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

(10 marks)

(b) The following rate constants were obtained for the reaction between $[CoBr(NH_3)_5]^{2+}$ ion (present in the form of $Br^-$) and $OH^-$ ion (present as NaOH):

$$[CoBr(NH_3)_5]^{2+} + OH^- \rightarrow [Co(NH_3)_5OH]^{2+} + Br^-$$

under the following conditions:

| Concentration / mol $dm^{-3}$ | | | Rate Constants, |
|---|---|---|---|
| $[CoBr(NH_3)_5]^{2+} \times 10^4$ | NaOH x $10^4$ | NaCl | k / $dm^3$ $mol^{-1}$ $s^{-1}$ |
| 5.0 | 7.95 | 0 | 1.52 |
| 5.96 | 10.04 | 0 | 1.45 |
| 6.00 | 6.96 | 0.005 | 1.23 |
| 6.00 | 6.96 | 0.020 | 0.97 |
| 6.00 | 6.91 | 0.030 | 0.91 |

Make an estimate of the rate constant of the reaction at zero ionic strength and the value of the product of the charge numbers.

(10 marks)

**TERJEMAHAN**

Sila pastikan kertas peperiksaan ini mengandungi TIGA BELAS muka surat bahan bercetak.

**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.

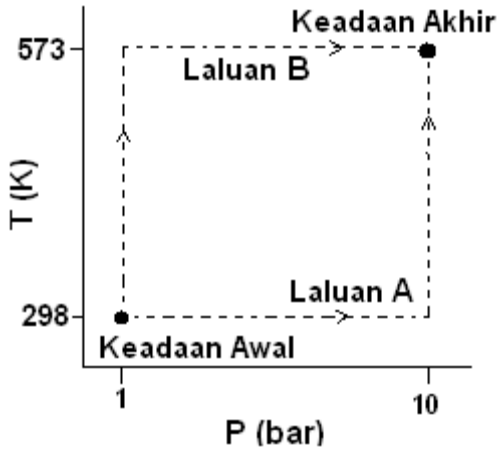
1. (a) Dengan memberikan contoh, takrifkan fungsi laluan (bukan fungsi keadaan) dan fungsi keadaan.

(3 markah)

(b) Satu mol gas pada suhu 298 K dan tekanan 1 bar dipanaskan dan dimampatkan secara berbalik di dalam omboh tanpa geseran dan silinder kepada 573 K dan 10 bar. Dua laluan digunakan untuk mencapai keadaan akhir seperti ditunjukkan dalam Gambarajah 1. Bagi sistem ini,

(i) Huraikan proses laluan A dan B.
(ii) Kirakan haba dan kerja bagi kedua–dua laluan dan ulaskan sama ada haba dan kerja adalah fungsi keadaan.

Diberikan $\bar{C}_P = 38\ J\ K^{-1}\ mol^{-1}$




Gambarajah 1

(8 markah)

(c) Dengan menggunakan hubungan dan hukum termodinamik yang berkaitan, buktikan bahawa:

(i) $\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T$

(ii) $\left(\frac{\partial^2 A}{\partial T^2}\right)_V = -\frac{C_V}{T}$

(9 markah)

2. (a) Huraikan istilah ‘larutan unggul’ berdasarkan daya antara molekul bagi cecair. Terangkan mengapa campuran heksana dan heptana membentuk larutan unggul?

(3 markah)

(b) Campuran unggul benzena dan metilbenzena terbentuk melalui proses pencampuran. Jika tekanan wap tulen benzena dan metilbenzena pada suhu 302 K masing–masing adalah 32.6 kPa dan 30.1 kPa, kirakan jumlah tekanan dan komposisi wap yang berada pada keseimbangan dengan campuran cecair yang mengandungi 100 g benzena dan 80 g metilbenzena pada 302 K.

(10 markah)

(c) Terbitkan sebutan bagi fugasiti dan pekali fugasiti bagi gas yang mematuhi persamaan keadaan berikut

$$\frac{PV_m}{RT} = 1 + \frac{a}{V_m} + \frac{b}{V_m^2}$$

dengan a = -21.3 $cm^3\ mol^{-1}$ dan b = 1054 $cm^6\ mol^{-2}$. Kira nilai fugasiti bagi gas neon pada 1 atm dan 298 K.

(7 markah)

3. (a) Diberi entropi S = f(T, P) dan S = f(T, V), buktikan bahawa:

$$C_P - C_V = T\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V$$

(8 markah)

(b) Pada 27 $^oC$ dan 1 bar, isipadu larutan NaCl dalam 1.0 kg metanol diberikan oleh persamaan berikut:

$$V = \left(1008.45 + 12.62\ b + 1.78 b^{3/2} + 0.12\ b^3\right)\ cm^3$$

dengan b adalah bilangan mol NaCl

(i) Terbitkan sebutan bagi isipadu molar separa bagi NaCl
(ii) Kirakan isipadu molar separa bagi NaCl dan metanol dalam larutan 0.1 m NaCl
(iii) Kirakan ketumpatan larutan 0.1 m NaCl itu.

(10 markah)

4. Suatu kitaran Carnot menggunakan 1 mol gas monoatom yang bersifat unggul sebagai bahan asas dengan keadaan awal 5 atm dan 500 K. Gas tersebut mengembang secara isotermal pada tekanan 1 atm (Langkah 1) dan kemudiannya mengembang secara adiabatik kepada suhu akhir 300 K (Langkah 2). Proses pengembangan ini diikuti dengan proses pemampatan secara isotermal (Langkah 3) dan balik kepada keadaan asalnya melalui proses pemampatan adiabatik (Langkah 4). Tentukan nilai bagi q, w, $\Delta H$, $\Delta U$, $\Delta S$, $\Delta G$ pada setiap langkah dan akhirnya $\Delta S_{tot}$.

(20 markah)

5. (a) Bagi tindak balas kimia yang ditunjukkan di bawah dan dengan menggunakan data berikut:-

$$CO_2(g) + O_2(g) \longleftrightarrow 2CO_2(g)$$

$$\Delta G^o_{298\,K} = -24.65 \text{ kJ mol}^{-1}$$

$$\Delta H^o_{298\,K} = (-32000 - 12.8\,T - 12 \times 10^{-3}\,T^2 - 21.3 \times 10^{-7}\,T^3)\,\text{J mol}^{-1}$$

Kirakan $\Delta G^o$, ln $K_P$ dan $\Delta S^o$ pada 800 K.

(12 markah)

(b) Gas A membentuk larutan unggul dengan cecair B. Pada suhu 350 K dan tekanan atas permukaan 760 Torr, suatu larutan tepu terbentuk dan didapati pecahan mol A, $x_A = 0.3017$. Pada suhu 200 K, gas A terkondensasi kepada bentuk cecair dan didapati mempunyai tekanan wap keseimbangan 11.47 Torr. Anggapkan wap tersebut bersifat unggul dan muatan haba bagi cecair tersebut adalah sama pada semua suhu. Kira entalpi molar separa pengewapan dan takat didih normal bagi A.

(8 markah)

**BAHAGIAN B**

Jawab sekurang-kurangnya **SATU** soalan.

6. (a) Tulislah tindak balas sel keseluruhan dan kiralah $\Delta G^o$ dan pemalar keseimbangan, K pada 25°C bagi tindak balas yang berlaku dalam sel yang berikut:

$Zn(p) \mid ZnCl_2\,(ak) \parallel CdSO_4\,(ak) \mid Cd\,(p)$

Diberi keupayaan penurunan piawai:

$E^{\circ}_{Zn^{2+}/Zn} = -0.7618$ V
$E^{\circ}_{Cd^{2+}/Cd} = -0.403$ V

(4 markah)

(b) Bagi sel yang berikut

$Pt, H_2\,(g, 1\ atm) \mid HCl\,(m) \mid AgCl\,(p) \mid Ag\,(p)$.

Buktikan bahawa

$$E + \frac{2RT}{F} ln\, m = E^{\circ} - \frac{2RT}{F} ln\, \gamma_{\pm}$$

Dengan m ialah kemolaran dan $\gamma_{\pm}$ ialah pekali keaktifan ion min.

(6 markah)

(c) Bagi sel kepekatan dengan pindahan yang berikut:

$H_2\,(g,1\ atm) \mid HCl\,(m = 0.02) \mid HCl\,(m = 1.00) \mid H_2\,(g,1\ atm)$

(i) Tunjukkan persamaan bagi keupayaan sel ialah:

$$E_{sel} = -\frac{2t_{-}RT}{F} ln\, \frac{m_1 \gamma_{\pm 1}}{m_2 \gamma_{\pm 2}}$$

(ii) Kiralah keupayaan sel. Diberi pekali keaktifan min, $\gamma_{\pm}$, bagi sel setengah kiri dan kanan masing-masing ialah 0.88 dan 0.81, dan nombor pindahan, $t_{-}$=0.178.

(10 markah)

7. (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

$$\phi = -\frac{Z_i \in}{4\pi\varepsilon_o\varepsilon} \cdot \frac{\kappa}{1+\kappa a}$$

$$\text{dan} \quad \kappa^2 = \frac{\in^2}{\varepsilon_o \varepsilon kT} \sum_i N_i Z_i^{\,2}$$

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

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

dengan $C_i$ ialah kepekatan ion dan $\gamma_i$ ialah pekali keaktifan.Tunjukkan bahawa pekali keaktifan ion min, $\gamma_\pm$ , bagi suatu elektrolit yang bercerai kepada $\nu_+$ kation bervalensi $Z_+$ dan $\nu_-$ anion bervalensi $Z_-$, diberi dengan:

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

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

(10 markah)

(b) Pemalar kadar yang berikut diperoleh bagi tindak balas antara ion $[CoBr(NH_3)_5]^{2+}$ (wujud dalam bentuk $Br^-$) dan ion $OH^-$ (wujud sebagai NaOH)

$$[CoBr(NH_3)_5]^{2+} + OH^- \rightarrow [Co(NH_3)_5OH]^{2+} + Br^-$$

di bawah keadaan yang berikut:

| Kepekatan / mol $dm^{-3}$ | | | Pemalar kadar |
|---|---|---|---|
| $[CoBr(NH_3)_5]^{2+} \times 10^4$ | NaOH x $10^4$ | NaCl | k / $dm^3\ mol^{-1}\ s^{-1}$ |
| 5.0 | 7.95 | 0 | 1.52 |
| 5.96 | 10.04 | 0 | 1.45 |
| 6.0 | 6.96 | 0.005 | 1.23 |
| 6.0 | 6.96 | 0.020 | 0.97 |
| 6.0 | 6.96 | 0.030 | 0.97 |

Kiralah pemalar kadar bagi tindak balas ini pada kekuatan ion bernilai sifar dan nilai hasil darab nombor cas.

(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 | | $J\ K^{-1}\ mol^{-1}$ |
| | | 8.31447 | $10^{-2}$ | $L\ bar\ K^{-1}\ mol^{-1}$ |
| | | 8.20574 | $10^{-2}$ | $L\ atm\ K^{-1}\ mol^{-1}$ |
| | | 6.23637 | 10 | $LTorr\ K^{-1}\ mol^{-1}$ |
| 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

| | |
|---|---|
| 1 eV | 1.60218 x $10^{-19}$ J<br>96.485 kJ $mol^{-1}$ |
| | 8065.5 $cm^{-1}$ |
| 1 cal | 4.184 J |
| 1 atm | 101.325 kPa<br>760 Torr |
| 1 $cm^{-1}$ | 1.9864 x $10^{-23}$ J |
| 1 Å | $10^{-10}$ m |
| 1 L atm | 101.325 J |

### Useful relation

2.303 RT/F
= 0.0591 V at 25 $^{o}$C

### Unit relations

| | |
|---|---|
| Energy | 1 J = 1 kg $m^2$ $s^{-2}$<br>= 1 A V s |
| Force | 1 N = 1 kg m $s^{-2}$ |
| Pressure | 1 Pa = 1 N $m^{-2}$<br>= 1 kg $m^{-1}$ $s^{-2}$<br>= 1 J $m^{-3}$ |
| Charge | 1 C = 1 A s |
| Potential difference | 1 V = 1 J $C^{-1}$<br>= 1 kg $m^2$ $s^{-3}$ $A^{-1}$ |

### 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 | | |

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