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UNIVERSITI SAINS MALAYSIA

Second Semester Examination  
Academic Session 2008/2009

April/May 2009

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

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

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Please check that this examination paper consists of **THIRTEEN** printed pages before you begin the examination.

**Instructions:**

Answer any **FIVE** (5) questions with at least **ONE** 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.

**Appendix:** Fundamental constants in physical chemistry.

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- 2 -

**PART A**Answer not more than **FOUR** questions.

1. Assume  $C_{p,m}$  is constant at  $3.5R$  for  $N_2(g)$  in the temperature range of 100 to 400 K and at low pressure and behaves as ideal gas.
- (a) Calculate  $q$ ,  $w$ ,  $\Delta U$  and  $\Delta H$  for the reversible adiabatic compression of 1.12 g  $N_2(g)$  from 53.3 kPa and  $1000 \text{ cm}^3$  to a final volume of  $250 \text{ cm}^3$ .  
(10 marks)
- (b) If a sample of  $N_2(g)$  at room temperature and pressure ( $25 \text{ }^\circ\text{C}$  and 101 kPa) is cooled to 100 K in a reversible adiabatic expansion, what is the final pressure?  
(10 marks)
2. (a) Consider 2.00 mol of argon undergoing a reversible isothermal expansion from  $0.01$  to  $0.1 \text{ m}^3$  at  $25 \text{ }^\circ\text{C}$ .
- (i) Derive an equation for  $\Delta S$  (system) for a van der Waals gas.
- (ii) Compare the value with  $\Delta S$  (system) for ideal gas.

Given: the van der Waals equation is

$$p = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

where  $a$  and  $b$  are  $1.337 \text{ atm dm}^6 \text{ mol}^{-2}$  and  $0.03219 \text{ dm}^3 \text{ mol}^{-1}$ , respectively.

(12 marks)

- (b) (i) Derive the following Gibbs-Helmholtz equation:

$$\left[ \frac{\partial(G/T)}{\partial T} \right]_p = -\frac{H}{T^2}$$

- (ii) Prove the Maxwell relation

$$\left( \frac{\partial S}{\partial p} \right)_T = - \left( \frac{\partial V}{\partial T} \right)_p$$

(8 marks)

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3. (a) Prove the following equation:

$$\left(\frac{\partial H}{\partial S}\right)_p \left(\frac{\partial U}{\partial S}\right)_v = T^2$$

(6 marks)

- (b) (i) Derive the following Clausius-Clapeyron equation:

$$\frac{d \ln p}{dT} = \frac{\Delta H_{\text{vap}}}{RT^2}$$

- (ii) The vapour pressure of propane at 200 K is 198 Torr and at 250 K is 2074 Torr. Calculate the heat of vaporization and the vapour pressure at 225 K.

(14 marks)

4. (a) Briefly explain the partial molar quantity of a system consisting of components 1 and 2.

According to the definition of apparent molar quantity,  $\phi_1$ , for component 1,

$$\phi_1 = \frac{M - X_2 M_2}{X_1}$$

where  $X$  is the mole fraction,  $M$  the molar properties of mixture and  $M_2$  the molar properties of pure components 2 at the solution temperature and pressure. Derive the equations to determine the partial molar properties of  $\bar{M}_1$  and  $\bar{M}_2$  with  $\phi_1$  as a function of  $X_1$  at constant temperature  $T$  and pressure  $p$ . The equation must contain only quantities of  $X_1$ ,  $M_2$ ,  $\phi_1$  and  $\frac{d\phi_1}{dX_1}$ .

(12 marks)

- (b) Consider a container of volume 250 mL that is divided into two compartments of equal size. The left compartment contains argon at 100 kPa and 0 °C whereas in the right compartment contains neon at the same temperature and pressure. Calculate the entropy and Gibbs energy of mixing when the partition is removed. Assume that the gases are ideal.

(8 marks)

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- 4 -

5. (a) What are meant by the molar volume and partial molar volume of a substance?

Show that for a specific temperature and pressure, the volume of solution,  $V$ , consisting of two components A and B, is given by the following equation

$$V = n_A \bar{V}_A + n_B \bar{V}_B$$

where  $n_A$  and  $n_B$  are the number of moles of A and B, respectively;  $\bar{V}_A$  and  $\bar{V}_B$  are partial molar volume of A and B, respectively.

(10 marks)

- (b) The vapour pressure of a pure liquid A at 293 K is 68.8 kPa and that of a pure liquid B is 82.1 kPa. These two compounds form ideal liquid and gaseous mixture. Consider the equilibrium composition of a mixture in which the mole fraction of A in the vapour is 0.612, calculate the total pressure of the vapour and the composition of the liquid mixture.

(10 marks)

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**PART B**Answer at least **ONE** question.

6. (a) The activity,  $a_i$ , of species  $i$  is defined as

$$\mu_i = \mu_i^\circ + RT \ln a_i$$

and  $a_i = \gamma_i m_i$

where  $\mu_i$  is the chemical potential of species  $i$  and  $\mu_i^\circ$ , the chemical potential of species  $i$  in its chosen standard state. For the strong electrolyte,  $M_{v_+} X_{v_-}$ , where  $v_+$  and  $v_-$  are the number of cations and anions, respectively, show that the mean ionic activity,  $a_\pm$ , and the mean ionic activity coefficients,  $\gamma_\pm$ , are

$$(a_\pm)^v = (a_+)^{v_+} (a_-)^{v_-}$$

and  $(\gamma_\pm)^v = (\gamma_+)^{v_+} (\gamma_-)^{v_-}$

(10 marks)

- (b) The rate constant,  $k$ , for the reaction between persulphate ions and iodide ions varies with the ionic strength,  $I$ , as follows:

|   |      |      |      |      |      |       |
|---|------|------|------|------|------|-------|
| $I/10^{-3} \text{ mol dm}^{-3}$                 | 2.45 | 3.65 | 4.45 | 6.45 | 8.45 | 12.45 |
| $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ | 1.05 | 1.12 | 1.16 | 1.18 | 1.26 | 1.39  |

- (i) Derive the Brønsted – Bjerrum relation.
- (ii) Estimate the value of  $Z_A Z_B$ , the product of the charge number.

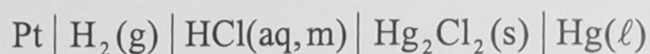
Given: Debye-Hückel constant,  $A = 0.5091 \text{ kg}^{\frac{1}{2}} \text{ mol}^{-\frac{1}{2}}$

(10 marks)

...6/-

- 6 -

7. (a) The emf of the cell



has been measured with the following results at 25 °C:

|                         |         |         |         |         |         |
|-------------------------|---------|---------|---------|---------|---------|
| $m/\text{mmol kg}^{-1}$ | 1.6077  | 3.0769  | 5.0403  | 7.6938  | 10.9474 |
| $E/\text{V}$            | 0.60080 | 0.56825 | 0.54366 | 0.52267 | 0.50532 |

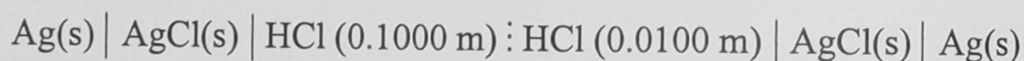
Determine the standard emf of the cell and the mean activity coefficient of HCl at these molalities.

(10 marks)

- (b) Compare the cell potentials at 25 °C for the cells without and with liquid junction:



and



Given:  $\gamma_{\pm} = 0.798$  and  $t(\text{H}^+) = 0.8314$  for 0.1000 m HCl;  
 $\gamma_{\pm} = 0.906$  and  $t(\text{H}^+) = 0.8251$  for 0.0100 m HCl.

(10 marks)

...7/-

**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 | $10^8$       | $\text{m s}^{-1}$                     |
| Elementary charge                  | $e$              | 1.602176   | $10^{-19}$   | C                                     |
| Faraday constant                   | $F=N_Ae$         | 9.64853    | $10^4$       | $\text{C mol}^{-1}$                   |
| Boltzmann constant                 | $k$              | 1.38065    | $10^{-23}$   | $\text{J K}^{-1}$                     |
| 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    | $10^{23}$    | $\text{mol}^{-1}$                     |
| Standard acceleration of free fall | $g$              | 9.80665    |              | $\text{m s}^{-2}$                     |

**Conversion factors****Useful relation****Unit relations**

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

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**TERJEMAHAN****Arahan:**

Jawab **LIMA** (5) soalan sahaja dengan sekurang-kurangnya **SATU** 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.

**Lampiran:** Pemalar asas dalam kimia fizik.



**BAHAGIAN A**

Jawab tidak lebih daripada **EMPAT** soalan.

1. Anggap  $C_{p,m}$  adalah malar pada  $3.5R$  bagi  $N_2(g)$  pada julat suhu 100 hingga 400 K dan tekanan rendah dan berkelakuan unggul.
  - (a) Kiralah  $q$ ,  $w$ ,  $\Delta U$  dan  $\Delta H$  untuk proses pemampatan adiabatik berbalik bagi 1.12 g  $N_2(g)$  dari 53.3 kPa dan  $1000 \text{ cm}^3$  kepada isipadu akhir  $250 \text{ cm}^3$ .  
(10 markah)
  - (b) Sekiranya sampel  $N_2(g)$  disejukkan dari suhu dan tekanan bilik ( $25 \text{ }^\circ\text{C}$  dan 101 kPa) kepada 100 K menggunakan proses pengembangan adiabatik berbalik, berapakah tekanan akhir?  
(10 markah)
2. (a) Pertimbangkan 2.00 mol argon melalui proses pengembangan isothermal berbalik daripada 0.01 kepada  $0.1 \text{ m}^3$  pada  $25 \text{ }^\circ\text{C}$ .
  - (i) Terbitkan persamaan  $\Delta S$  (sistem) bagi gas van der Waals.
  - (ii) Bandingkan nilai tersebut dengan nilai  $\Delta S$  (sistem) bagi gas unggul.

Diberikan: persamaan van der Waals adalah

$$p = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

dengan  $a$  dan  $b$  adalah  $1.337 \text{ atm dm}^6 \text{ mol}^{-2}$  and  $0.03219 \text{ dm}^3 \text{ mol}^{-1}$ , masing-masing.

(12 markah)

- (b) (i) Terbitkan persamaan Gibbs-Helmholtz berikut:

$$\left[ \frac{\partial(G/T)}{\partial T} \right]_p = -\frac{H}{T^2}$$

- (ii) Buktikan kaitan Maxwell

$$\left( \frac{\partial S}{\partial p} \right)_T = - \left( \frac{\partial V}{\partial T} \right)_p$$

(8 markah)

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3. (a) Buktikan persamaan berikut:

$$\left(\frac{\partial H}{\partial S}\right)_p \left(\frac{\partial U}{\partial S}\right)_v = T^2$$

(6 markah)

- (b) (i) Terbitkan persamaan Clausius-Clapeyron berikut:

$$\frac{d \ln p}{dT} = \frac{\Delta H_{\text{vap}}}{RT^2}$$

- (ii) Tekanan wap propana pada 200 K adalah 198 Torr dan pada 250 K adalah 2074 Torr. Hitunglah haba pengwapan dan tekanan wap pada 225 K.

(14 markah)

4. (a) Terangkan dengan ringkas maksud kuantiti molar separa untuk suatu sistem yang terdiri daripada komponen 1 dan 2. Sifat molar ketara,  $\phi_1$ , bagi komponen 1 ditakrifkan sebagai,

$$\phi_1 = \frac{M - X_2 M_2}{X_1}$$

bagi  $X$  ialah pecahan mol,  $M$  ialah sifat molar campuran, dan  $M_2$  ialah sifat molar komponen tulen 2 pada suhu dan tekanan larutan tersebut. Terbitkan persamaan untuk menentukan sifat molar separa  $\bar{M}_1$  dan  $\bar{M}_2$  dengan  $\phi_1$  ialah suatu fungsi  $X_1$  pada suhu  $T$  dan tekanan  $p$  tetap. Persamaan tersebut mestilah hanya mengandungi kuantiti  $X_1$ ,  $M_2$ ,  $\phi_1$  dan  $\frac{d\phi_1}{dX_1}$ .

(12 markah)

- (b) Pertimbangkan suatu bekas berisipadu 250 mL dibahagikan kepada dua ruang bersaiz sama. Ruang kiri mengandungi argon pada 100 kPa dan 0 °C manakala ruang kanan mengandungi neon pada suhu dan tekanan yang sama. Hitunglah entropi dan tenaga Gibbs campuran apabila pemisahannya disingkirkan. Anggapkan gas adalah unggul.

(8 markah)

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5. (a) Apakah yang dimaksudkan dengan isipadu molar dan isipadu molar separa suatu zat?

Tunjukkan bahawa pada nilai suhu dan tekanan tertentu, isipadu suatu larutan,  $V$ , yang mengandungi dua komponen A dan B diberikan oleh persamaan

$$V = n_A \bar{V}_A + n_B \bar{V}_B$$

bagi  $n_A$  dan  $n_B$  masing-masing adalah bilangan mol A dan B;  $\bar{V}_A$  dan  $\bar{V}_B$  masing-masing adalah isipadu molar separa A dan B.

(10 markah)

- (b) Tekanan wap cecair tulen A pada 293 K adalah 68.8 kPa dan bagi cecair tulen B adalah 82.1 kPa. Kedua-dua sebatian ini membentuk campuran cecair dan gas unggul. Pertimbangkan komposisi keseimbangan suatu campuran di mana pecahan mol A dalam wap adalah 0.612, hitunglah tekanan total wap dan komposisi campuran cecair.

(10 markah)

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**BAHAGIAN B**

Jawab sekurang-kurangnya **SATU** soalan.

6. (a) Keaktifan,  $a_i$ , bagi spesies  $i$  diaktifkan sebagai

$$\mu_i = \mu_i^\circ + RT \ln a_i$$

dan  $a_i = \gamma_i m_i$

dengan  $\mu_i$  ialah keupayaan kimi bagi spesies  $i$  dan  $\mu_i^\circ$ , keupayaan kimia bagi spesies  $i$  dalam keadaan piawai terpilihnya. Bagi elektrolit kuat,  $M_{v+} X_{v-}$ , dengan  $v_+$  dan  $v_-$  masing-masing ialah bilangan kation dan anion, tunjukkan bahawa keaktifan ion min,  $a_{\pm}$ , dan pekali keaktifan ion min,  $\gamma_{\pm}$ , ialah

$$(a_{\pm})^v = (a_+)^{v_+} (a_-)^{v_-}$$

dan  $(\gamma_{\pm})^v = (\gamma_+)^{v_+} (\gamma_-)^{v_-}$

(10 markah)

- (b) Pemalar kadar,  $k$ , untuk tindak balas di antara ion persulfat dan ion iodida berubah dengan kekuatan ion,  $I$ , seperti berikut:

|   |      |      |      |      |      |       |
|---|------|------|------|------|------|-------|
| $I/10^{-3} \text{ mol dm}^{-3}$                 | 2.45 | 3.65 | 4.45 | 6.45 | 8.45 | 12.45 |
| $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ | 1.05 | 1.12 | 1.16 | 1.18 | 1.26 | 1.39  |

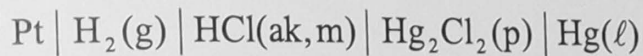
- (i) Terbitkan hubungan Brønsted – Bjerrum.  
 (ii) Anggarkan nilai  $Z_A Z_B$ , iaitu hasil darab nombor cas

Diberi: Pemalar Debye-Hückel,  $A = 0.5091 \text{ kg}^{\frac{1}{2}} \text{ mol}^{-\frac{1}{2}}$

(10 markah)

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7. (a) Emf bagi sel,



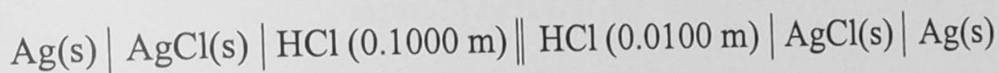
disukat pada 25 °C dengan keputusan yang berikut:

|                                |         |         |         |         |         |
|--------------------------------|---------|---------|---------|---------|---------|
| $\text{m}/\text{mmol kg}^{-1}$ | 1.6077  | 3.0769  | 5.0403  | 7.6938  | 10.9474 |
| E/V                            | 0.60080 | 0.56825 | 0.54366 | 0.52267 | 0.50532 |

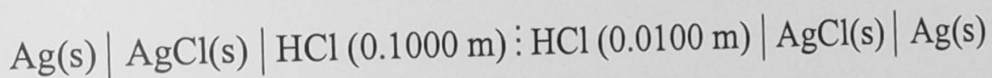
Tentukan emf piawai sel itu dan pekali keaktifan min HCl pada kemolalan itu.

(10 markah)

(b) Bandingkan keupayaan sel pada 25 °C untuk sel tanpa dan dengan simpangan cecair:



dan



Diberi:  $\gamma_{\pm} = 0.798$  and  $t(\text{H}^+) = 0.8314$  untuk 0.1000 m HCl;  
 $\gamma_{\pm} = 0.906$  and  $t(\text{H}^+) = 0.8251$  untuk 0.0100 m HCl.

(10 markah)

