UNIVERSITI SAINS MALAYSIA

Second Semester Examination
Academic Session 2007/2008

April 2008

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

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

Please check that this examination paper consists of **FOURTEEN** 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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**PART A**
Answer not more than **FOUR** questions.

1. (a) A sample of 6.0 mol $N_2$ is originally confined in 30 $dm^3$ vessel at 273 K and then undergoes adiabatic expansion against a constant pressure of 95 kPa until the volume has increased by a factor of 2.0. Calculate q, w, $\Delta T$, $\Delta U$, and $\Delta H$.

(10 marks)

(b) Derive the following thermodynamic equations of state for an ideal gas

i) $$\left(\frac{\partial H}{\partial T}\right)_S = C_p\left(\frac{\partial\, ln T}{\partial\, ln V}\right)_p$$

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

(10 marks)

2. (a) The constant-pressure heat capacity of a sample of an ideal gas was found to vary with temperature according to the expression

$C_p/(J\ K^{-1}) = 20.17 + 0.03665T - 20.15 \times 10^{-7}T^2$.

Calculate q, w, $\Delta U$, and $\Delta H$ when the temperature is raised from 25 to 300 °C at

i) constant pressure, and

ii) constant volume.

(12 marks)

(b) The partial molar volumes of two liquids A and B in a mixture in which the mole fraction of A is 0.3713 are 188.2 and 176.14 $cm^3\ mol^{-1}$, respectively. The molar masses of A and B are 241.1 and 198.2 g $mol^{-1}$, respectively. What is the volume of the solution of mass 1.000 kg?

(8 marks)

3. (a) Calculate $\Delta S$ (for the system) when the state of 2.50 mol nitrogen, assumed to be an ideal gas, is changed from 25 °C and 2.00 atm to 125 °C and 8.00 atm. Explain the sign of $\Delta S$ obtained?

(12 marks)

(b) i) Show that if the compressibility factor is given by $Z = 1 + Bp/RT$, the fugacity, $f$, is $pe^{Z-1}$.

ii) Estimate the fugacity of nitrogen gas at 25 bar and 298 K. Given Z for $N_2$ gas which follow a van der Waals equation of state is

$$Z = 1 + \left( b - \frac{a}{RT} \right) \frac{p}{RT}$$

where a and b are 0.1408 Pa $m^6$ $mol^{-2}$ and 0.0391 x $10^{-3}$ $m^3$ $mol^{-1}$, respectively.

(8 marks)

4. (a) Consider a container of volume 5.0 $dm^3$ that is divided into two compartments of equal size. In the left compartment there is 1 mol of nitrogen gas at 1.0 atm and 25 °C; in the right compartment is 1 mol of hydrogen gas at the same temperature and pressure. When the partition is removed, calculate the $\Delta G$ and $\Delta S$ of mixing. Assume the gases are ideal.

(8 marks)

(b) The experimental values of the partial molar volume of NaCl(aq) at 298 K are given by the expression

$$V/\ cm^3\ mol^{-1} = 22.380 + 18.216 b^{1/2}$$

where $b$ is the numerical value of the molality of NaCl. Use the Gibbs-Duhem equation to derive an expression for the partial molar volume of water in the solution. At 298 K, the molar volume of pure water is 18.079 $cm^3$ $mol^{-1}$.

(12 marks)

5. (a) For a chemical reaction described below and using the data given, calculate $\Delta G^{o}$, $\Delta H^{o}$ and $\Delta S^{o}$ at 1000 K.

$$\frac{1}{2} N_2(g) + \frac{3}{2} H_2(g) \rightleftharpoons NH_3(g)$$

$$\Delta G^{o}_{298\,K} = -26.65 \text{ kJ mol}^{-1}$$

$$\Delta H^{o}_{T} = (-37500 - 32.8\,T - 12 \times 10^{-3} T^2 - 21.3 \times 10^{-7} T^3) \text{ J mol}^{-1}$$

(12 marks)

(b) Calculate $\Delta G$ when the pressure of 70 g of gas X having a mass density of 0.791 g $cm^{-3}$, when the pressure increases isothermally from 10 to 100 kPa. Given that the compressibility coefficient, $\kappa_T$ is $76.8 \times 10^{-6}$ $atm^{-1}$.

(5 marks)

(c) Describe what is meant by colligative properties.

(3 marks)

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

6. (a) The potential, $\phi$, at a distance r from a selected $i^{th}$ type ion is

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

and

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

where $N_i$ and $Z_i$ represent the number per unit volume and the positive value of the valence of ions of the $i^{th}$-type, respectively. $\in$ is the electronic charge and $\varepsilon$ is the dielectric constant.

The potential on the ion due to the ionic atmosphere when r approaches a, the distance of closest approach, is

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

Show that the mean ionic activity coefficient, $\gamma_\pm$, of an electrolyte dissociating into $\nu_1$ cations of valency $Z_1$ and $\nu_2$ anions of valency $Z_2$, is given by

$$\log \gamma_\pm = -\frac{A|Z_1 Z_2|\sqrt{I}}{1 + Ba\sqrt{I}}$$

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

(12 marks)

(b) The solubility of $BaSO_4$ is $9.2 \times 10^{-11}$ $mol^2\ dm^{-6}$ at 25 °C.

Calculate

(i) the mean activity coefficient of the $Ba^{2+}$ and $SO_4^{2-}$ ions in a solution containing 0.05 M $KNO_3$ and 0.05 M KCl by using the Debye-Hückel limiting law, and

(ii) the solubility of $BaSO_4$ in that solution and in pure water.

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

(8 marks)

7. (a) Consider the cell at 25 °C

$$Cd(s) \mid CdCl_2\ (aq, 0.100\ m) \mid AgCl(s) \mid Ag(s)$$

the mean ionic activity coefficient of $CdCl_2$ in a 0.100 m aqueous solution at 25 °C and 1 atm is 0.228. Calculate the standard emf, E°, and emf, E, of the cell at 25 °C.

Given : $E^\circ_{Cd^{2+}/Cd} = -0.402\ V$

$E^\circ_{AgCl/Cl^-} = +0.2223\ V$

(8 marks)

(b) Consider the cell at 1 atm $H_2$ pressure

$$Pt \mid H_2(g) \mid NaOH(m_1), NaCl(m_2) \mid AgCl(s) \mid Ag(s)$$

(i) show that

$$E = E^\circ - \frac{RT}{F} \ell n \left( \frac{K_w\ m_{Cl^-}\ \gamma_{Cl^-}}{m_{OH^-}\ \gamma_{OH^-}} \right)$$

where $K_w$ is the ionization constant of water.

**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 | $F=N_A e$ | 9.64853 | $10^{4}$ | $C\ mol^{-1}$ |
| Boltzmann constant | $k$ | 1.38065 | $10^{-23}$ | $J\ K^{-1}$ |
| Gas constant | $R=N_A k$ | 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 | | Useful relation | Unit relations | |
|---|---|---|---|---|
| 1 eV | 1.60218 x $10^{-19}$ J<br>96.485 kJ $mol^{-1}$ | 2.303 RT/F<br>= 0.0591 V at 25 °C | Energy | 1 J = 1 kg $m^2$ $s^{-2}$<br>= 1 A V s |
| | 8065.5 $cm^{-1}$ | | Force | 1 N = 1 kg m $s^{-2}$ |
| 1 cal<br><br>1 atm | 4.184 J<br><br>101.325 kPa<br>760 Torr | | Pressure | 1 Pa = 1 N $m^{-2}$<br>= 1 kg $m^{-1}$ $s^{-2}$<br>= 1 J $m^{-3}$ |
| 1 $cm^{-1}$ | 1.9864 x $10^{-23}$ J | | Charge | 1 C = 1 A s |
| 1 Å<br>1 L atm | $10^{-10}$ m<br>101.325 J | | 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 | | |

**TERJEMAHAN**

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**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. (a) Satu sampel 6 mol gas $N_2$ asalnya diletakkan didalam bekas berisipadu 30 $dm^3$ pada suhu 273 K dan kemudiannya melalui proses pengembangan adiabatik melawan tekanan tekanan tetap 95 kPa sehingga isipadunya meningkat 2 kali ganda. Kiralah q, w, $\Delta T$, $\Delta U$, dan $\Delta H$.

(10 markah)

(b) Terbitkan persamaan keadaan termodinamik bagi satu gas unggul berikut

i) $$\left(\frac{\partial H}{\partial T}\right)_S = C_p\left(\frac{\partial \mathit{ln} T}{\partial \mathit{ln} V}\right)_p$$

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

(10 markah)

2. (a) Muatan haba pada tekanan tetap satu gas unggul didapati bergantung kepada suhu melalui persamaan

$$C_p/(J\,K^{-1}) = 20.17 + 0.03665T - 20.15 \times 10^{-7}T^2.$$

Kiralah q, w, $\Delta U$, dan $\Delta H$ apabila suhu ditingkatkan daripada 25 kepada 300 °C pada

i) tekanan tetap, dan

ii) isipadu tetap.

(12 markah)

(b) Pecahan separa isipadu dua cecair, A dan B, dalam satu campuran masing-masing adalah 188.2 dan 176.14 $cm^3\ mol^{-1}$. Pecahan mol A adalah 0.3713. Jisim molar A dan B adalah masing-masing 241.1 dan 198.2 $g\ mol^{-1}$. Berapakah isipadu bagi 1.000 kg larutan tersebut?

(8 markah)

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3. (a) Kira $\Delta S$ (untuk sistem) apabila 2.50 mol nitrogen, dianggap sebagai satu gas unggul, ditukar keadaannya daripada 25 °C dan 2.00 atm kepada 125 °C dan 8.00 atm. Terangkan tanda $\Delta S$ yang diperoleh?

(12 markah)

(b) i) Tunjukkan jika faktor ketermampatan diberikan sebagai $Z = 1 + Bp/RT$, fugasiti, $f$, adalah $pe^{Z-1}$.

ii) Anggarkan fugasiti gas nitrogen pada tekanan 25 bar dan suhu 298 K. Diberikan Z bagi gas $N_2$ yang mematuhi persamaan van der Waals ialah

$$Z = 1 + \left( b - \frac{a}{RT} \right) \frac{p}{RT}$$

dengan $a$ dan $b$ adalah 0.1408 Pa $m^6$ $mol^{-2}$ dan 0.0391 x $10^{-3}$ $m^3$ $mol^{-1}$, masing-masing.

(8 markah)

4. (a) Pertimbangkan satu bekas berisipadu 5.0 $dm^3$ yang dibahagikan kepada dua bahagian yang bersaiz sama. Bahagian di sebelah kiri mengandungi 1 mol gas nitrogen pada 1.0 atm dan 25 °C; bahagian di sebelah kanan pula mengandungi 1 mol gas hidrogen pada suhu dan tekanan yang sama. Apabila pemisah dibuang, kiralah $\Delta G$ dan $\Delta S$ pencampuran. Anggap bahawa kedua-dua gas adalah gas unggul.

(8 markah)

(b) Nilai eksperimen pecahan isipadu molar bagi NaCl(ak) pada 298 K diberikan oleh persamaan

$$V/\ cm^3\ mol^{-1} = 22.380 + 18.216b^{1/2}$$

dengan $b$ ialah nilai numerik kemolalan NaCl. Gunakan persamaan Gibbs-Duhem untuk menerbitkan persamaan bagi isipadu molar air dalam larutan tersebut. Pada suhu 298 K, isipadu molar air tulen ialah 18.079 $cm^3$ $mol^{-1}$.

(12 markah)

5. (a) Bagi satu tindak balas kimia yang ditunjukkan di bawah dan dengan menggunakan data yang diberikan, kiralah $\Delta G^o$, $\Delta H^o$ dan $\Delta S^o$ pada 1000 K.

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$$

$$\Delta G^o_{298\,K} = -26.65 \text{ kJ mol}^{-1}$$

$$\Delta H^o_T = (-37500 - 32.8\,T - 12 \times 10^{-3}T^2 - 21.3 \times 10^{-7}T^3) \text{ J mol}^{-1}$$

(12 markah)

(b) Kiralah $\Delta G$ apabila tekanan bagi 70 g gas X yang mempunyai ketumpatan 0.791 g cm$^{-3}$ ditambah daripada 10 kepada 100 kPa secara isotermal. Diberi pekali ketermampatan, $\kappa_T$ ialah 76.8 x 10$^{-6}$ atm$^{-1}$.

(5 markah)

(c) Terangkan apakah yang dimaksudkan dengan sifat koligatif.

(3 markah)

**BAHAGIAN B**
Jawab sekurang-kurangnya **SATU** soalan.

6. (a) Keupayaan, $\phi$, pada suatu jarak r daripada suatu ion i terpilih ialah

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

dan

$$\kappa^2 = \frac{\in^2}{\varepsilon_o \varepsilon kT} \Sigma N_i Z_i^2$$

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 medium itu.

Keupayaan pada ion yang disumbangkan oleh atmosfera ion apabila r menghampiri a, jarak penghampiran yang terdekat, ialah

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

Tunjukkan bahawa pekali keaktifan ion min, $\gamma_\pm$, bagi suatu elektrolit yang bercerai kepada $\nu_1$ kation bervalensi $Z_1$ dan $\nu_2$ anion bervalensi $Z_2$, diberi dengan

$$\log \gamma_\pm = -\frac{A|Z_1 Z_2|\sqrt{I}}{1 + Ba\sqrt{I}}$$

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

(12 markah)

(b) Keterlarutan $BaSO_4$ ialah $9.2 \times 10^{-11}$ $mol^2\ dm^{-6}$ pada 25 °C.

Kirakan

(i) pekali keaktifan min bagi ion $Ba^{2+}$ dan $SO_4^{2-}$ di dalam suatu larutan yang mengandungi 0.05 M $KNO_3$ dan 0.05 M KCl dengan menggunakan hukum penghadan Debye- Hückel, dan

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(ii) keterlarutan $BaSO_4$ di dalam larutan ini dan juga di dalam air tulen.

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

(8 markah)

7. (a) Pertimbangkan sel berikut pada 25 °C,

$$Cd(p) \mid CdCl_2\ (ak, 0.100\ m) \mid AgCl(p) \mid Ag(p)$$

pekali keaktifan ion min bagi $CdCl_2$ di dalam 0.100 m larutan akueus pada 25 °C dan 1 atm ialah 0.228. Kirakan emf piawai, E°, dan emf, E, bagi sel ini pada 25 °C.

Diberi : $E^\circ_{Cd^{2+}/Cd} = -0.402\ V$

$E^\circ_{AgCl/Cl^-} = +0.2223\ V$

(8 markah)

(b) Pertimbangkan sel berikut pada tekanan $H_2$, 1 atm

$$Pt \mid H_2(g) \mid NaOH(m_1), NaCl(m_2) \mid AgCl(p) \mid Ag(p)$$

(i) Tunjukkan bahawa

$$E = E^\circ - \frac{RT}{F} \ell n \left( \frac{K_w\, m_{Cl^-}\, \gamma_{Cl^-}}{m_{OH^-}\, \gamma_{OH^-}} \right)$$

dengan $K_w$ ialah pemalar pengionan air.

(ii) Bagi sel ini pada 25 °C, di dapati bahawa sebutan

$$E - E^\circ + \frac{RT}{F} \ell n \left( \frac{m_{Cl^-}}{m_{OH^-}} \right)$$

menghampiri had 0.8279 V apabila kekuatan ion menjadi sifar. Kirakan $K_w$ pada 25 °C.

(12 markah)

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