UNIVERSITI SAINS MALAYSIA

Second Semester Examination
Academic Session 2006/2007

April 2007

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 Only **FIVE** (5) questions with at least **ONE** question from Section B. If candidate answers more than five questions, only the answers to the first five questions will be graded. You may answer a question either in Bahasa Malaysia or in English

Appendix: Fundamental Constants in Physical Chemistry

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SECTION A
(Answer not more than **FOUR** questions)

1. (a) Based on the first law of thermodynamic and other relevant definitions, derive the following equations for an ideal gas.

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

(8 marks)

(b) A sample consisting of 1.00 mol argon (Ar) is expanded isothermally at O°C from 22.4 L to 44.8 L (i) reversibly, (ii) against a constant external pressure equal to the final pressure of the gas, and (iii) freely (against zero external pressure). For the three processes, calculate heat (q), work (w), the change in internal energy (ΔU), and the change in enthalpy (ΔH).

(12 marks)

2. (a) Show that, if entropy (S) is regarded as a function of temperature, T, and pressure, p, then

$$TdS = C_V dT + T\left(\frac{\partial p}{\partial T}\right)_V dV$$

(10 marks)

(b) Consider a system consisting of 2.0 mol CO_2 (g), initially at 25 °C and 10 atm and confined to a cylinder of a cross-section 10.0 cm^2. It is allowed to expand adiabatically against an external pressure of 1.0 atm until the piston has moved outwards through 20 cm. Assume that carbon dioxide may be considered a prefect gas with $C_V^m = 28.8\ J\ K^{-1}\ mol^{-1}$. Calculate

(i) heat, q
(ii) work, w
(iii) change in internal energy, ΔU
(iv) change in temperature, ΔT, and
(v) change in entropy, ΔS

(10 marks)

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3. (a) Show that the relations between Gibbs free energy with temperature and pressure are given as follows:

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

(10 marks)

(b) A sample of 2.0 mol perfect gas at 30 °C is expanded isothermally from an initial pressure of 3.00 atm to a final pressure of 1.00 atm against a constant external pressure of 1.00 atm. Determine the values of q, w, ΔU, ΔH, ΔS, ΔU_{surr}, and ΔS_{univ} of the process.

(10 marks)

4. (a) What is meant by fugacity and fugacity coefficient of a gas? A specific gas follows the following state equation:

$$p\overline{V} = RT + bp$$

where $\overline{V}$ is the molar volume and b is a constant. Derive the equations for the fugacity and fugacity coefficient of the gas.

(10 marks)

(b) A dilute solution of bromine (Br_2) in carbon tetrachloride (CCl_4) behaves as an ideal-dilute solution. The vapour pressure of pure CCl_4 is 33.85 Torr at 298 K. The Henry's law constant is 122.36 Torr when the concentration of Br_2 is expressed as a mole fraction. Calculate

(i) the vapour pressure of each component,
(ii) the total pressure, and
(iii) the composition of the vapour phase when the mole fraction of Br_2 is 0.050.

Assume that the conditions of the ideal-dilute solution are satisfied at this concentration.

(10 marks)

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5. (a) Given that a volatile solvent (component A) and a non volatile solute (component B) in a solution are in equilibrium at temperature, T, and pressure, p. Starting with the Gibbs free energy (G) equation of the solution,

$$G = n_A \mu_A + n_B \mu_B$$

where n and μ are the number of moles and the chemical potential, respectively, show how you could determine of the activity of the non volatile solute (component B)

(10 marks)

(b) Naphthalene ($C_{10} H_8$) melts at 80.2 °C. If the vapour pressure of the liquid is 10 Torr at 85.8 °C and 40 Torr at 119.3 °C, calculate

(i) the enthalpy of vaporization,
(ii) the normal boiling point, and
(iii) the enthalpy of vaporization at the boiling point.

(10 marks)

SECTION B
(Answer at least **ONE** question)

6. (a) The solubility product of $BaSO_4$ is 9.2×10^{-11} mol^2 dm^{-6}. Assuming the Debye – Hückel limiting law applies, calculate

(i) the mean activity coefficients for the Ba^{2+} and SO_4^{2-} ions in a saturated solution of $BaSO_4$ in 0.2 M K_2SO_4,

(ii) the solubility of $BaSO_4$ in a solution consisting 0.10 M $NaNO_3$ and 0.20 M Zn $(NO_3)_2$.

(8 marks)

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(b) The following values for the rate constants (k) were obtained for the reaction between $[CoBr(NH_3)_5]^{2+}$ ion (present in the form of the bromide) and OH^- ion (present as sodium hydroxide),

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

under the following conditions:

Concentration / mol dm^{-3}			k / $dm^3\ mol^{-1}\ s^{-1}$
$[CoBr(NH_3)_5]^{2+}$	NaOH	NaCl	
5.0×10^{-4}	7.95×10^{-4}	0	1.52
5.96×10^{-4}	1.004×10^{-3}	0	1.45
6.00×10^{-4}	0.696×10^{-3}	0.005	1.23
6.00×10^{-4}	0.696×10^{-3}	0.020	0.97
6.00×10^{-4}	0.696×10^{-3}	0.030	0.91

Calculate the rate constant at zero ionic strength. Are the results consistent with the product of the charge numbers, $Z_A Z_B = -2$?

(12 marks)

7 (a) At 25 °C, the potential of the cell with transference

$$Pt, H_2\ (1\ bar)\ |\ HCl\ (a_\pm)_1\ :\ HCl\ (a_\pm)_2\ |\ H_2\ (1\ bar)\ |\ Pt$$

is 0.02802 V when the mean ionic activities of HCl, $(a_\pm)_1 = 0.009048$ and $(a_\pm)_2 = 0.01751$. The corresponding cell without transference has a potential of 0.01696 V.

(i) Derive an expression for the emf of this cell with transference.

(ii) Calculate the transference number of H^+ ion and the value of the liquid junction potential.

(10 marks)

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BAHAGIAN A
(Jawab tidak lebih daripada **EMPAT** soalan)

1. (a) Berdasarkan hukum pertama termodinamik dan takrifan yang sesuai, terbitkan persamaan berikut untuk gas unggul

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

(8 markah)

(b) Suatu sampel terdiri daripada 1.00 mol argon (Ar) dikembangkan secara isotermal pada O°C daripada 22.4 L ke 44.8 L (i) secara berbalik, (ii) melawan suatu tekanan luar tetap sama dengan tekanan akhir gas, dan (iii) secara bebas (melawan tekanan luar sifar). Bagi ketiga-tiga proses ini, hitunglah haba (q), kerja (w), perubahan tenaga dalam (ΔU), dan perubahan entalpi (ΔH),

(12 markah)

2. (a) Tunjukkan, jika entropi (S) dianggap sebagai suatu fungsi suhu, T, dan tekanan, p, maka

$$TdS = C_V dT + T\left(\frac{\partial p}{\partial T}\right)_v dV$$

(10 markah)

(b) Pertimbangkan suatu sistem terdiri daripada 2.0 mol $CO_2(g)$, mulanya pada 25 °C dan 10 atm dan ditempatkan dalam suatu silinder keratan rentas 10.0 cm^2. Ia dibiarkan mengembang secara adiabatik melawan suatu tekanan luar 1.0 atm sehingga omboh bergerak keluar sejauh 20 cm. Anggapkan karbon dioksida sebagai suatu gas unggul dengan $C_V{}^m = 28.8$ $J\,K^{-1}\,mol^{-1}$. Hitunglah,

(i) haba, q
(ii) kerja, w
(iii) perubahan tenaga dalam, ΔU
(iv) perubahan suhu, ΔT, dan
(v) perubahan entropi, ΔS.

(10 markah)

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3. (a) Tunjukkan bahawa hubungan di antara tenaga bebas Gibbs dengan suhu dan tekanan diberikan oleh persamaan berikut:-

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

(10 markah)

(b) Sejumlah 2.0 mol gas unggul pada 30 °C di kembangkan secara isothermal daripada suatu tekanan awal 3.00 atm kepada tekanan akhir 1.00 atm melawan suatu tekanan luar malar 1.00 atm. Tentukan nilai q,w, ΔU, ΔH, ΔS, ΔU_{sek}, and ΔS_{sem} bagi proses tersebut.

(10 markah)

4. (a) Apakah yang dimaksudkan dengan fugasiti dan pekali fugasiti sesuatu gas? Suatu gas tertentu mengikuti persamaan keadaan berikut:

$$p\overline{V} = RT + bp$$

dengan $\overline{V}$ ialah isipadu molar dan b ialah pemalar. Terbitkan persamaan untuk menyatakan fugasiti dan pekali fugasiti gas tersebut.

(10 markah)

(b) Suatu larutan cair bromine (Br_2) di dalam karbon tetraklorida (CCl_4) berkelakuan seperti suata larutan cair-unggul. Tekanan wap CCl_4 tulen ialah 33.85 Torr pada 298 K. Pemalar hukum Henry ialah 122.36 Torr apabila kepekatan Br_2 dinyatakan sebagai suatu pecahan mol. Hitunglah,

(i) tekanan wap setiap komponen,
(ii) tekanan jumlah, dan
(iii) komposisi fasa wap apabila pecahan mol Br_2 ialah 0.050.

Anggapkan keadaan larutan cair-unggul dipatuhi pada kepekatan tersebut

(10 markah)

...10/-

5. (a) Diberi suatu pelarut meruap (komponen A) dan zat terlarut tak meruap (komponen B) dalam suatu larutan adalah dalam keseimbangan pada suhu T, dan tekanan p. Bermula dengan persamaan tenaga bebas Gibbs (G) bagi larutan

$$G = n_A \mu_A + n_B \mu_B$$

dengan n dan μ masing-masing adalah bilangan mol dan keupayaan kimia, tunjukkan bagaimana anda dapat menentukan keaktifan zat terlarut tak meruap (komponen B).

(10 markah)

(b) Naftalena ($C_{10}H_8$) melebur pada 80.2 °C. Jika tekanan wap cecair ialah 10 Torr pada 85.8 °C dan 40 Torr pada 119.3 °C, hitunglah

(i) entalpi pengwapan,
(ii) takat didih normal, dan
(iii) entalpi pengwapan pada takat didih.

(10 markah)

BAHAGIAN B
(Jawab sekurang-kurangnya **SATU** soalan)

6 (a) Hasil darab keterlarutan $BaSO_4$ ialah 9.2×10^{-11} mol^2 dm^{-6}.
Dengan menggunakan hukum pembatasan Debye – Hückel, kirakan

(i) pekali keaktifan min untuk ion Ba^{2+} dan ion SO_4^{2-} di dalam suatu larutan $BaSO_4$ tepu dalam 0.2 M K_2SO_4,

(ii) keterlarutan $BaSO_4$ di dalam larutan yang mengandungi 0.10 M $NaNO_3$ dan 0.20 M Zn $(NO_3)_2$

(8 markah)

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(b) Nilai pemalar kadar (k) yang berikut diperoleh bagi tindak balas di antara ion $[CoBr(NH_3)_5]^{2+}$ (wujud dalam bentuk bromida) dan ion OH^- (wujud sebagai natrium hidroksida),

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

di bawah keadaan yang berikut:

Kepekatan / mol dm^{-3}			k/ $dm^3\ mol^{-1}\ s^{-1}$
$[CoBr(NH_3)_5]^{2+}$	NaOH	NaCl	
5.0×10^{-4}	7.95×10^{-4}	0	1.52
5.96×10^{-4}	1.004×10^{-3}	0	1.45
6.00×10^{-4}	0.696×10^{-3}	0.005	1.23
6.00×10^{-4}	0.696×10^{-3}	0.020	0.97
6.00×10^{-4}	0.696×10^{-3}	0.030	0.91

Kirakan pemalar kadar pada kekuatan ion bernilai sifar. Adakah keputusan selaras dengan hasil darab nombor cas, $Z_AZ_B = -2$?

(12 markah)

7 (a) Pada 25 °C, keupayaan bagi sel dengan pindahan

$$Pt, H_2\,(1\ bar)\ |\ HCl\,(a_{\pm})_1\ :\ HCl\,(a_{\pm})_2\ |\ H_2\,(1\ bar)\ |\ Pt$$

ialah 0.02802 V apabila keaktifan ion min bagi HCl, $(a_{\pm})_1 = 0.009048$ dan $(a_{\pm})_2 = 0.01751$. Keupayaan bagi sel tanpa pindaan yang bersepadan ialah 0.01696 V.

(i) Terbitkan satu persamaan untuk emf bagi sel dengan pindaan.

(ii) Kirakan nombor pindaan ion H^+ dan nilai bagi keupayaan simpangan cecair.

(10 markah)

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Pusat Pengajian Sains Kimia

Pemalar Asas dalam Kimia Fizik

Simbol	Keterangan	Nilai
N_A	Nombor Avogadro	6.022×10^{23} mol^{-1}
F	Pemalar Faraday	96,500 C mol^{-1}, atau coulomb per mol, elektron
e	Cas elektron	4.80×10^{-10} esu 1.60×10^{-19} C atau coulomb
m_e	Jisim elektron	9.11×10^{-28} g 9.11×10^{-31} kg
m_p	Jisim proton	1.67×10^{-24} g 1.67×10^{-27} kg
h	Pemalar Planck	6.626×10^{-27} erg s 6.626×10^{-34} J s
c	Halaju cahaya	3.0×10^{10} cm s^{-1} 3.0×10^{8} m s^{-1}
R	Pemalar gas	8.314×10^{7} erg K^{-1} mol^{-1} 8.314 J K^{-1} mol^{-1} 0.082 *l* atm K^{-1} mol^{-1} 1.987 cal K^{-1} mol^{-1}
k	Pemalar Boltzmann	1.380×10^{-16} erg K^{-1} molekul^{-1} 1.380×10^{-23} J K^{-1} molekul^{-1}
g		981 cm s^{-2} 9.81 m s^{-2}
1 atm		76 cmHg 1.013×10^{6} dyne cm^{-2} 101,325 N m^{-2}
$2.303 \frac{RT}{F}$		0.0591 V, atau volt, pada 25 °C

Berat Atom yang Berguna

H = 1.0	C = 12.0	I = 126.9	Fe = 55.8	As = 74.9
Br = 79.9	Cl = 35.5	Ag = 107.9	Pb = 207.0	Xe = 131.1
Na = 23.0	K = 39.1	N = 14.0	Cu = 63.5	F = 19.0
O = 16.0	S = 32.0	P = 31.0	Ca = 40.1	Mg = 24.0
Sn = 118.7	Cs = 132.9	W = 183.85	He = 2.016	

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