UNIVERSITI SAINS MALAYSIA

Peperiksaan Kursus Semasa Cuti Panjang
Sidang Akademik 2006/2007

June 2007

KFT 131 – Physical Chemistry I
[Kimia Fizik I]

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 **FIVE** (5) questions. Section A is **COMPULSORY**. Answer any **TWO** (2) questions from Section B. All questions carry the same marks. You may answer a question either in Bahasa Malaysia or in English.

Appendix: Fundamental Constants in Physical Chemistry

...2/-

SECTION A

Answer **ALL** questions.

1. (a) The initial rates of the following reaction

$$2A + B \rightarrow \text{products}$$

were determined under various initial concentrations of the reactants, $[A]_o$ and $[B]_o$.

Experiment	$[A]_o$/mol dm^{-3}	$[B]_o$/mol dm^{-3}	$-\frac{d[B]}{dt}$ / mol dm^{-3}s^{-1}
1	0.10	0.10	0.25
2	0.20	0.10	0.50
3	0.10	0.20	0.25

Determine the order of the reaction for each reactant.

(8 marks)

(b) For the following reaction at 1100 K,

$$NO(g) + H_2(g) \rightarrow \text{product}$$

The following half-life data were obtained for the initial pressure, P_o, of each reactant, where P_o (NO) = P_o (H_2).

$t_{½}$/s	81	102	140	224
P_o/Torr	354	341	288	202

Determine the overall order of the reaction.

(12 marks)

2. (a) Consider a dimerization reaction in the gaseous phase, $2A(g) \rightarrow B(g)$. Given that the enthalpy change of the reaction can be represented by the following quadratic function of temperature:

$$\Delta H = \alpha T^2 + \beta T + \gamma \text{ kJ mol}^{-1}$$

where α, β and γ are constants.

...3/-

(i) Obtain an expression for ΔC_p of the reaction as a function of T.

(ii) Determine the $\overline{C}_p$ of B(g) as a function of T if the $\overline{C}_p$ of A(g) is 20.784 J K^{-1} mol^{-1}.

(10 marks)

(b) The enthalpy changes of the following reactions at 25 °C are:

$Na(s) + \frac{1}{2} Cl_2(g) \rightarrow NaCl(s)$ $\quad \Delta H° = -411.15$ kJ mol^{-1}

$H_2(g) + S(s) + 2O_2(g) \rightarrow H_2SO_4(l)$ $\quad \Delta H° = -813.99$ kJ mol^{-1}

$2Na(s) + S(s) + 2O_2(g) \rightarrow Na_2SO_4(l)$ $\quad \Delta H° = -1388.10$ kJ mol^{-1}

$\frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g) \rightarrow HCl(g)$ $\quad \Delta H° = -92.31$ kJ mol^{-1}

From these data, find the heat of reaction at constant volume at 25 °C for the process.

$$2NaCl(s) + H_2SO_4(l) \rightarrow Na_2SO_4(s) + 2HCl(g)$$

(10 marks)

3. (a) A perfect gas undergoes isothermal compression, which reduces its volume by 2.20 L. If the final pressure and volume of the gas are 3.78×10^3 Torr and 4.65 L, respectively, calculate the original pressure.

(3 marks)

(b) The critical constants of methane are $P_c = 46.5$ atm, $T_c = 200.6$ K and $V_c = 148$ cm^3 mol^{-1}. Calculate the van der Waals parameters and estimate the radius of the methane molecules.

(7 marks)

(c) A vessel of volume 2.0 dm^3 contains 2.0 mol H_2 and 1.0 mol N_2 at 273.15 K. Calculate;

(i) the mole fraction of each component,

(ii) the partial pressure,

(iii) numbers of molecules present, and

(iv) the relative speed of the gas molecules.

(10 marks)

...4/-

SECTION B

Answer any **TWO** questions.

4. A chain mechanism for the thermal decomposition of an organic compound is

$$S_1 \xrightarrow{k_1} R_1 + S_2 \qquad E_{a,1} = 320 \text{ kJ mol}^{-1}$$

$$R_1 + S_1 \xrightarrow{k_2} R_1H + R_2 \qquad E_{a,2} = 40 \text{ kJ mol}^{-1}$$

$$R_2 \xrightarrow{k_3} R_1 + S_3 \qquad E_{a,3} = 140 \text{ kJ mol}^{-1}$$

$$R_1 + R_2 \xrightarrow{k_4} S_4 \qquad E_{a,4} = 0 \text{ kJ mol}^{-1}$$

where R represents a highly reactive radical and S represents a stable molecule.

(a) Prove that the rate equation for this long-chain organic compound is

$$-\frac{d[S_1]}{dt} = \left(\frac{k_1 k_2 k_3}{2k_4}\right)^{1/2} [S_1]$$

(12 marks)

(b) What is the value of the activation energy for the overall reaction?

(8 marks)

5. (a) For an ideal gas undergoing a reversible adiabatic process, derive the following equation:

$$\frac{T_1}{T_2} = \left(\frac{P_1}{P_2}\right)^{(\gamma-1)/\gamma}$$

where $\gamma = C_p / C_v$

(10 marks)

(b) Five moles of hydrogen gas at 273 K and 1 atm are compressed adiabatically and reversibly to 10 L. Assuming that hydrogen behaves as an ideal gas, calculate

(i) the final pressure and temperature of the gas, and

...5/-

(ii) work done in the process.

(γ = 1.4)

(10 marks)

6. (a) A gas is found to obey the following equation of state:

$$P = \frac{RT}{V-b} - \frac{a}{V}$$

where a and b are constants. Determine whether this gas has a critical point; if it does, express the critical constants in terms of a and b. If it does not, explain how you determine this. What is the implication if the gas does not have a critical point?

(10 marks)

(b) A substance of molar mass, M = 83.80 g mol^{-1}, has a vapor pressure of 1 x 10^5 Pa at 25 °C. Determine the mass of the substance that will effuse from a Knudsen cell in 2 hours through a hole of 0.1 cm diameter.

(10 marks)

7. (a) Prove that the coefficient of thermal conductivity, κ, is equal to

$$\frac{1}{3}\lambda v\, C_{v,m}[A]$$

(10 marks)

(b) Two sheets of copper of area 1.25 m^2 are separated by 10 cm. What is the rate of transfer of heat from the warm sheet (45 °C) to the cold sheet (-10 °C)? The experimental value for κ is 0.0163 J K^{-1} m^{-1} s^{-1}.

(6 marks)

(c) Differentiate diffusion from effusion and state the laws associated with each of these processes.

(4 marks)

...6/-

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

...7/-

BAHAGIAN A

Jawab **SEMUA** soalan

1. (a) Kadar awal bagi tindak balas

$$2A + B \rightarrow \text{hasil}$$

telah ditentukan pada beberapa kepekatan awal bahan tindak balas, $[A]_o$ dan $[B]_o$.

Eksperimen	$[A]_o$/mol dm^{-3}	$[B]_o$/mol dm^{-3}	$-\frac{d[B]}{dt}$ / mol dm^{-3}s^{-1}
1	0.10	0.10	0.25
2	0.20	0.10	0.50
3	0.10	0.20	0.25

Tentukan tertib tindak balas bagi setiap bahan tindak balas

(8 markah)

(b) Bagi tindak balas yang berikut pada 1100 K,

$$NO(g) + H_2(g) \rightarrow \text{hasil}$$

data setengah-hayat, $t_{1/2}$, diperoleh untuk tekanan awal, P_o, bagi setiap bahan tindak balas, P_o (NO) = P_o (H_2).

$t_{1/2}$/s	81	102	140	224
P_o/Torr	354	341	288	202

Tentukan tertib keseluruhan bagi tindak balas tersebut.

(12 markah)

2. (a) Pertimbangkan suatu tindak balas pendimeran fasa gas, $2A(g) \rightarrow B(g)$. Diberikan bahawa perubahan entalpi bagi tindak balas tersebut dapat diwakili dengan fungsi kuadratik suhu yang berikut:

$$\Delta H = \alpha T^2 + \beta T + \gamma \text{ kJ mol}^{-1}$$

dengan α, β dan γ adalah pemalar.

...9/-

(i) Dapatkan suatu ungkapan untuk ΔC_p bagi tindak balas ini sebagai fungsi T.

(ii) Tentukan $\overline{C}_p$ bagi B(g) sebagai fungsi T jika $\overline{C}_p$ bagi A(g) adalah 20.784 J K^{-1} mol^{-1}.

(10 markah)

(b) Perubahan entalpi bagi tindak balas yang berikut pada 25 °C adalah:

$Na(p) + \frac{1}{2} Cl_2(g) \rightarrow NaCl(p)$ $\Delta H° = -411.15$ kJ mol^{-1}

$H_2(g) + S(p) + 2O_2(g) \rightarrow H_2SO_4(c)$ $\Delta H° = -813.99$ kJ mol^{-1}

$2Na(p) + S(p) + 2O_2(g) \rightarrow Na_2SO_4(p)$ $\Delta H° = -1388.10$ kJ mol^{-1}

$\frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g) \rightarrow HCl(g)$ $\Delta H° = -92.31$ kJ mol^{-1}

Berdasarkan data ini, kirakan haba tindak balas pada isipadu tetap pada 25 °C bagi tindak balas.

$$2NaCl(p) + H_2SO_4(c) \rightarrow Na_2SO_4(p) + 2HCl(g)$$

(10 markah)

3. (a) Satu gas unggul melalui proses pemampatan isoterma yang mengakibatkan penurunan isipadu sebanyak 2.20 L. Sekiranya tekanan akhir dan isipadu akhir gas tersebut adalah masing-masing 3.78×10^3 Torr dan 4.65 L, kiralah tekanan asalnya.

(4 markah)

(b) Pemalar kritikal metana adalah $P_c = 46.5$ atm, $T_c = 200.6$ K dan $V_c = 148$ cm^3 mol^{-1}. Kiralah parameter van der Waals dan anggarkan jejari bagi molekul metana.

(6 markah)

(c) Suatu bekas dengan isipadu 2.0 dm^3 mengandungi 2.0 mol H_2 dan 1.0 mol N_2 pada suhu 273.15 K. Kira;

(i) pecahan mol setiap komponen,

(ii) tekanan separa,

(iii) bilangan molekul yang ada, dan

(iv) halaju purata molekul gas tersebut .

(10 markah)

...10/-

BAHAGIAN B

Jawab sebarang **DUA** soalan

4. Suatu mekanisme berantai untuk penguraian termal bagi sebatian organik ialah

$$S_1 \xrightarrow{k_1} R_1 + S_2 \qquad E_{a,1} = 320 \text{ kJ mol}^{-1}$$

$$R_1 + S_1 \xrightarrow{k_2} R_1H + R_2 \qquad E_{a,2} = 40 \text{ kJ mol}^{-1}$$

$$R_2 \xrightarrow{k_3} R_1 + S_3 \qquad E_{a,3} = 140 \text{ kJ mol}^{-1}$$

$$R_1 + R_2 \xrightarrow{k_4} S_4 \qquad E_{a,4} = 0 \text{ kJ mol}^{-1}$$

Simbol R mewakili suatu radikal yang sangat reaktif dan S ialah molekul stabil.

(a) Tunjukkan bahawa persamaan kadar bagi sebatian organik berantai panjang ialah

$$-\frac{d[S_1]}{dt} = \left(\frac{k_1 k_2 k_3}{2k_4}\right)^{1/2} [S_1]$$

(12 markah)

(b) Berapakah nilai tenaga pengaktifan keseluruhan bagi tindak balas tersebut?

(8 markah)

5. (a) Bagi suatu gas unggul yang mengalami suatu proses adiabatik berbalik, terbitkan persamaan berikut:

$$\frac{T_1}{T_2} = \left(\frac{P_1}{P_2}\right)^{\frac{(\gamma-1)}{\gamma}}$$

dengan $\gamma = \dfrac{C_p}{C_v}$

(10 markah)

(b) Lima mol gas hidrogen pada 273 K dan 1 atm dimampatkan secara adiabatik dan berbalik ke isipadu 10 L. Dengan menganggap bahawa hidrogen berkelakukan sebagai gas unggul, kirakan

(i) tekanan dan suhu akhir bagi gas itu, dan

...11/-

(ii) kerja yang dibuat dalam proses itu.

(γ = 1.4)

(10 markah)

6. (a) Suatu gas didapati mematuhi persamaan keadaan berikut;

$$P = \frac{RT}{V-b} - \frac{a}{V}$$

dimana *a* dan *b* adalah pemalar. Tentukan sama ada gas ini mempunyai takat kritikal; sekiranya ya, nyatakan pemalar kritikal dalam sebutan *a* dan *b*. Sekiranya tidak, jelaskan bagaimana anda menentukannya. Apakah implikasinya jika gas tersebut tidak mempunyai takat kritikal?

(10 markah)

(b) Suatu bahan dengan jisim molar, M = 83.80 g mol^{-1}, mempunyai tekanan wap 1 x 10^5 Pa pada 25 °C. Tentukan jisim bahan yang akan mengefusi dari satu sel Knudsen dalam masa 2 jam melalui suatu lubang berdiameter 0.1 cm.

(10 markah)

7. (a) Buktikan koefisien kekonduksian termal, κ, adalah bersamaan dengan

$$\frac{1}{3}\lambda\nu\, C_{v,m}[A]$$

(10 markah)

(b) Dua lapisan kuprum dengan luas permukaan 1.25 m^2 dipisahkan dengan jarak 10 cm. Berapakah kadar pemindahan haba dari lapisan panas (45 °C) ke lapisan sejuk (-10°C)? Nilai eksperimen bagi κ adalah 0.0163 $JK^{-1}\, m^{-1}s^{-1}$.

(6 markah)

(c) Bezakan pembauran dari efusi dan nyatakan hukum-hukum yang berkaitan dengan proses tersebut.

(4 markah)

-oooOooo-