
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

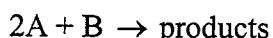
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SECTION A

Answer **ALL** questions.

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



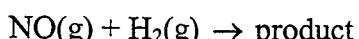
were determined under various initial concentrations of the reactants, $[A]_0$ and $[B]_0$.

Experiment	$[A]_0/\text{mol dm}^{-3}$	$[B]_0/\text{mol dm}^{-3}$	$-\frac{d[B]}{dt}/\text{mol dm}^{-3}\text{s}^{-1}$
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,



The following half-life data were obtained for the initial pressure, P_0 , of each reactant, where $P_0(\text{NO}) = P_0(\text{H}_2)$.

$t_{\frac{1}{2}}/\text{s}$	81	102	140	224
P_0/Torr	354	341	288	202

Determine the overall order of the reaction.

(12 marks)

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

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

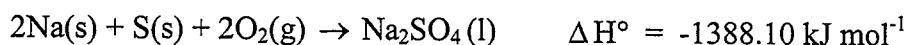
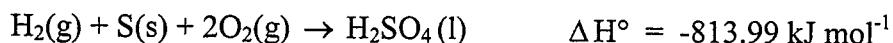
where α , β and γ are constants.

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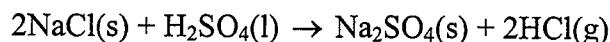
- 3 -

- (i) Obtain an expression for ΔC_p of the reaction as a function of T.
- (ii) Determine the \bar{C}_p of B(g) as a function of T if the \bar{C}_p of A(g) is $20.784 \text{ J K}^{-1} \text{ mol}^{-1}$.
- (10 marks)

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



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



(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 $P_c = 46.5 \text{ atm}$, $T_c = 200.6 \text{ K}$ and $V_c = 148 \text{ cm}^3 \text{ mol}^{-1}$. 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)

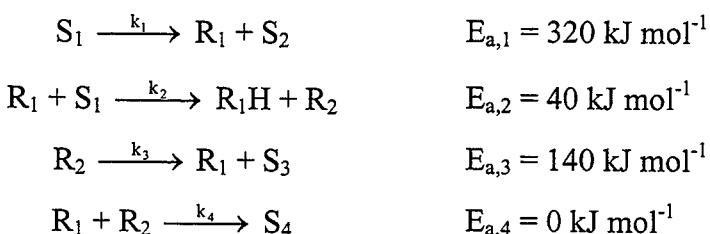
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SECTION B

Answer any **TWO** questions.

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



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

$$-\frac{d[S_1]}{dt} = \left(\frac{k_1 k_2 k_3}{2k_4} \right)^{1/2} [S_1] \quad (12 \text{ marks})$$

- (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

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(ii) work done in the process.

($\gamma = 1.4$)

(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, $M = 83.80 \text{ g mol}^{-1}$, has a vapor pressure of $1 \times 10^5 \text{ Pa}$ 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 $0.0163 \text{ J K}^{-1} \text{ m}^{-1} \text{ s}^{-1}$.

(6 marks)

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

(4 marks)

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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		$\text{J K}^{-1} \text{ mol}^{-1}$
		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}	mol^{-1}
Standard acceleration of free fall	g	9.80665		m s^{-2}

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

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

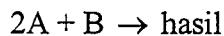
Atomic Weights

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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BAHAGIAN AJawab **SEMUA** soalan

1. (a) Kadar awal bagi tindak balas



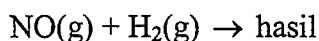
telah ditentukan pada beberapa kepekatan awal bahan tindak balas, $[A]_0$ dan $[B]_0$.

Eksperimen	$[A]_0/\text{mol dm}^{-3}$	$[B]_0/\text{mol dm}^{-3}$	$-\frac{d[B]}{dt}/\text{mol dm}^{-3}\text{s}^{-1}$
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,



data setengah-hayat, $t_{\frac{1}{2}}$, diperoleh untuk tekanan awal, P_0 , bagi setiap bahan tindak balas, $P_0(\text{NO}) = P_0(\text{H}_2)$.

$t_{\frac{1}{2}}/\text{s}$	81	102	140	224
P_0/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:

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

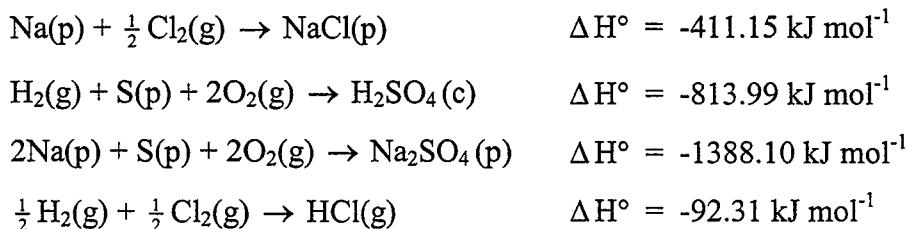
dengan α , β dan γ adalah pemalar.

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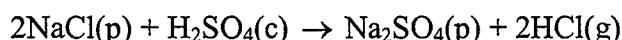
- 9 -

- (i) Dapatkan suatu ungkapan untuk ΔC_p bagi tindak balas ini sebagai fungsi T.
- (ii) Tentukan \bar{C}_p bagi B(g) sebagai fungsi T jika \bar{C}_p bagi A(g) adalah $20.784 \text{ J K}^{-1} \text{ mol}^{-1}$.
- (10 markah)

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



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



(10 markah)

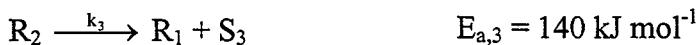
3. (a) Satu gas unggul melalui proses pemampatan isoterma yang mengakibatkan penurunan isipadu sebanyak 2.20 L . Sekiranya tekanan akhir dan isipadu akhir gas tersebut adalah masing-masing $3.78 \times 10^3 \text{ Torr}$ dan 4.65 L , kiralah tekanan asalnya.
- (4 markah)
- (b) Pemalar kritikal metana adalah $P_c = 46.5 \text{ atm}$, $T_c = 200.6 \text{ K}$ dan $V_c = 148 \text{ cm}^3 \text{ mol}^{-1}$. 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)
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BAHAGIAN B

Jawab sebarang DUA soalan

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



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

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

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

(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:

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

$$\text{dengan } \gamma = \frac{C_p}{C_v}$$

(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 berkelakuan sebagai gas unggul, kirakan

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

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- (ii) kerja yang dibuat dalam proses itu.

$(\gamma = 1.4)$

(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 kritis; sekiranya ya, nyatakan pemalar kritis dalam sebutan a dan b . Sekiranya tidak, jelaskan bagaimana anda menentukannya. Apakah implikasinya jika gas tersebut tidak mempunyai takat kritis?

(10 markah)

- (b) Suatu bahan dengan jisim molar, $M = 83.80 \text{ g mol}^{-1}$, mempunyai tekanan wap $1 \times 10^5 \text{ Pa}$ 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

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

(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 $0.0163 \text{ JK}^{-1} \text{ m}^{-1} \text{s}^{-1}$.

(6 markah)

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

(4 markah)

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