UNIVERSITI SAINS MALAYSIA

Second Semester Examination
Academic Session 2007/2008

April 2008

KFT 131 – Physical Chemistry I
[Kimia Fizik I]

Duration: 3 hours
[Masa : 3 jam]

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

Instructions:

Answer **FIVE** (5) questions. Part A is **COMPULSORY**. Answer any **TWO** (2) questions from Part B. All questions carry the same marks.

Answer to 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

...2/-

SECTION A

Answer **ALL** questions.

1. The number of wall collisions for gas molecule A at 25 °C and 1.0 atm is 2.7×10^{23} $cm^{-2} s^{-1}$.

   (a) Calculate the molar mass of gas molecule A.

   (6 marks)

   (b) The time taken for gas molecule B to strike a hole of C cm^2 is three times longer than gas molecule A at the same temperature and pressure. Determine the molar mass of gas molecule B.

   (4 marks)

   (c) The collision diameter, d, for gas molecule A is 2.4 Å. Calculate the mean free path of gas molecule A.

   (4 marks)

   (d) Will the mean free path of gas molecule A change when the temperature is increased to 596 K at constant volume? Explain.

   (2 marks)

   (e) Use the mean free path value obtained in (d) to calculate the collision density of gas molecule A.

   (4 marks)

2. (a) A reaction obeys the equation

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

The following data are given:

[A] / mol dm^{-3}	[B] / mol dm^{-3}	[C] / mol dm^{-3}	Initial rate/ mol $dm^{-3}s^{-1}$
0.550	0.200	1.15	6.76×10^{-6}
0.210	0.200	1.15	9.82×10^{-7}
0.210	0.333	1.15	1.68×10^{-6}
0.210	0.200	1.77	9.84×10^{-7}

Determine the order with respect to A, B and C and the rate constant of the reaction.

(8 marks)

(b) The following data were obtained for the second order reaction

$$C_3H_7Br + S_2O_3^{2-} \rightarrow C_3H_7S_2O_3^{-} + Br^{-}$$

in aqueous solution at 311 K. The initial concentration of C_3H_7Br was 0.0395 mol dm^{-3}.

t x 10^{-3} / s	0	1.110	2.010	5.052	11.232
[$S_2O_3^{2-}$] / mol dm^{-3}	0.0966	0.0904	0.0863	0.0766	0.0668

Determine the rate constant of this reaction.

Given that:

$$\frac{1}{a[B]_0 - b[A]_0} \ell n \frac{[B]/[B]_0}{[A]/[A]_0} = kt$$

for the reaction

$$aA + bB \rightarrow \text{products}$$

(12 marks)

3. (a) Given the following data at 25 °C,

	$\Delta H°$ (kJ mol^{-1})
$\frac{1}{2}H_2(g) + \frac{1}{2}O_2(g) \rightarrow OH(g)$	38.95
$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$	-241.814
$H_2(g) \rightarrow 2H(g)$	435.994
$O_2(g) \rightarrow 2O(g)$	498.34

Calculate $\Delta H°$ and $\Delta U°$ for the following reactions:

(i) $OH(g) \rightarrow H(g) + O(g)$

(ii) $H_2O(g) \rightarrow 2H(g) + O(g)$

assuming ideal gas behaviour.

(10 marks)

(b) A total of 100 g of CO_2 gas is heated from 300 to 400 K. Calculate the amount of heat required if the process is carried out at

(i) constant pressure, and

(ii) constant volume.

Assume that CO_2 gas behaves as an ideal gas and its heat capacity is given by

$$\overline{C}_p = (29.3 + 3.0 \times 10^{-2} T - 7.78 \times 10^{-6} T^2) \text{ J K}^{-1} \text{mol}^{-1}$$

(10 marks)

SECTION B

Answer any **TWO (2)** questions.

4. (a) Determine $\left(\frac{\partial Z}{\partial P}\right)_T$ for the ideal gas and the virial equations where B and C are the second and third virial coefficients, respectively. Show that not all properties of real gases will give ideal gas values as the pressure approaches zero.

(6 marks)

(b) In a 3.0-L container, a gas with a mass of 1.2×10^{-12} g molecule^{-1} has a root mean square speed, $\langle v^2 \rangle^{\frac{1}{2}}$ of 200 m s^{-1} at 2.67×10^{17} Pa. What is the number of gas molecules in the container?

(4 marks)

(c) Two unknown gases, X and Y, effuse towards each other from the opposite ends of a 36-cm vacuumed tube. If the ratio of molar mass of gas X to gas Y is 4:1, where is the meeting point of these gases?

(5 marks)

(d) A certain gas obeys the van der Waals equation with $a = 0.76$ m^6 Pa mol^{-2}. It has a volume of 4.00×10^{-4} m^3 mol^{-1} at 273 K and 3.0 MPa. From this information, estimate the radius of the gas molecules (in nm) on the assumption that they are spheres.

(5 marks)

5. (a) Write the Maxwell equation for the distribution of speeds. Based on the equation, explain the effects of temperature and molecular mass on the distribution function (probability density) of gas molecules. Sketch a graph to illustrate your answer.

(8 marks)

(b) The kinetic energy of a molecule is given by:

$$\varepsilon = \frac{1}{2}mv^2$$

Using the Maxwell equation, prove that the probability that a molecule has the kinetic energy in the range ε to $\varepsilon + d\varepsilon$ is

$$F(\varepsilon)d\varepsilon = \frac{2\pi}{(\pi kT)^{3/2}} \varepsilon^{1/2} e^{-\varepsilon/kT} d\varepsilon$$

(5 marks)

(c) What causes the thermal conductivity of gases?

FIGURE 1 shows an iron rod in contact with two heat reservoirs at different temperatures. A steady state will eventually be reached in which there is a uniform temperature gradient in the rod.

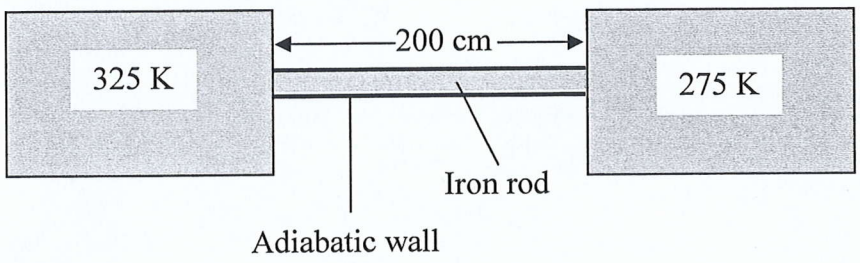


FIGURE 1

If the cross-sectional area of the rod is 24 cm^2 and κ = 0.80 J K^{-1} cm^{-1} s^{-1}, calculate the rate of heat flow across the iron rod and the heat energy conducted in 60 s.

(7 marks)

6. (a) Consider two consecutive first-order reactions with the rate constants, k_1 and k_2,

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

(i) Show that the rate of formation of C is given by

$$[C] = [A]_0 \left(1 + \frac{k_2 e^{-k_1 t} - k_1 e^{-k_2 t}}{k_1 - k_2}\right)$$

where $[A]_0$ is the initial concentration of A.

Given:

The solution of the differential equation

$$\frac{dx}{dt} = abe^{-bt} - cx$$

is

$$x = \frac{ab}{c-b}(e^{-bt} - e^{-ct}) + \theta$$

where a, b, and c are constants.

(ii) Sketch the plots of the concentrations versus time for these two reactions with the rate constants $k_2 = 6k_1$ and $k_2 = \frac{1}{6}k_1$, respectively.

(12 marks)

(b) For the gas-phase reaction

$$N_2O_5 + NO \rightarrow 3NO_2,$$

the following mechanism has been proposed:

$$N_2O_5 \xrightarrow{k_1} NO_2 + NO_3$$

$$NO_2 + NO_3 \xrightarrow{k_2} N_2O_5$$

$$NO + NO_3 \xrightarrow{k_3} 2NO_2$$

Derive an equation for the rate of consumption of N_2O_5 using the steady state approximation

(8 marks)

7. (a) Derive the equation

$$\left(\frac{\partial H}{\partial P}\right)_T = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial P}\right)_T + V$$

Evaluate $\left(\frac{\partial H}{\partial P}\right)_T$ for an ideal gas.

(8 marks)

(b) Calculate w, q, ΔH and ΔU for the process in which 1 mol of water undergoes the transition $H_2O(\ell, 373\ K) \rightarrow H_2O(g, 460\ K)$ at 1 atm pressure. Given that the volume of water at 373 K is $1.89 \times 10^{-5}\ m^3$ and the volume of steam at 373 and 460 K is 3.03×10^{-2} and $3.74 \times 10^{-2}\ m^3$, respectively. For steam, the molar heat capacity, $\overline{C}_p$, can be considered constant at 33.58 J K^{-1} mol^{-1} over the temperature range of interest. The enthalpy of vaporization of water at 1 atm and 373 K is 40.66 kJ mol^{-1}.

(12 marks)

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 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 1 atm	4.184 J 101.325 kPa 760 Torr		Pressure	1 Pa = 1 N m^{-2} = 1 kg m^{-1} s^{-2} = 1 J m^{-3}
1 cm^{-1}	1.9864 x 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		

TERJEMAHAN

Arahan:

Jawab **LIMA** (5) soalan. Bahagian A **WAJIB** dijawab. Pilih sebarang **DUA** (2) soalan sahaja bagi Bahagian B. Semua soalan membawa jumlah markah yang sama.

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 **SEMUA** soalan

1. Bilangan pelanggaran pada dinding bagi molekul gas A pada 25 °C dan 1.0 atm adalah 2.7×10^{23} cm^{-2} s^{-1}.

   (a) Hitung jisim molar molekul gas A.

   (6 markah)

   (b) Masa yang diambil bagi molekul gas B menghentam permukaan satu lubang kecil berkeluasan C cm^2 adalah tiga kali lebih panjang dari molekul gas A pada suhu dan tekanan yang sama. Tentukan jisim molar molekul gas B.

   (4 markah)

   (c) Diameter pelanggaran , d, bagi molekul gas A adalah 2.4 Å. Hitung laluan bebas min bagi molekul gas A.

   (4 markah)

   (d) Adakah laluan bebas min bagi molekul gas A akan berubah jika suhu ditingkatkan kepada 596 K pada isipadu tetap? Jelaskan.

   (2 markah)

   (e) Dengan menggunakan nilai laluan bebas min yang diperoleh dari (d) hitung ketumpatan pelanggaran bagi molekul gas A.

   (4 markah)

2. (a) Suatu tindak balas mematuhi persamaan

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

Data berikut diberi:

[A] / mol dm^{-3}	[B] / mol dm^{-3}	[C] / mol dm^{-3}	Kadar awal / mol $dm^{-3}s^{-1}$
0.550	0.200	1.15	6.76×10^{-6}
0.210	0.200	1.15	9.82×10^{-7}
0.210	0.333	1.15	1.68×10^{-6}
0.210	0.200	1.77	9.84×10^{-7}

Tentukan tertib terhadap A, B dan C dan pemalar kadar bagi tindak balas ini.

(8 markah)

(b) Data berikut diperoleh untuk tindak balas bertertib kedua

$$C_3H_7Br + S_2O_3^{2-} \rightarrow C_3H_7S_2O_3^- + Br^-$$

di dalam larutan akueus pada 311 K. Kepekatan awal bagi C_3H_7Br ialah 0.0395 mol dm^{-3}.

t x 10^{-3} / s	0	1.110	2.010	5.052	11.232
[$S_2O_3^{2-}$] / mol dm^{-3}	0.0966	0.0904	0.0863	0.0766	0.0668

Tentukan pemalar kadar tindak balas.

Diberi:

$$\frac{1}{a[B]_0 - b[A]_0} \ell n \frac{[B]/[B]_0}{[A]/[A]_0} = kt$$

untuk tindak balas

$$aA + bB \rightarrow \text{hasil}$$

(12 markah)

3. (a) Diberikan data pada 25 °C yang berikut:

	$\Delta H°$ (kJ mol^{-1})
$\frac{1}{2}H_2(g) + \frac{1}{2}O_2(g) \rightarrow OH(g)$	38.95
$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$	-241.814
$H_2(g) \rightarrow 2H(g)$	435.994
$O_2(g) \rightarrow 2O(g)$	498.34

Kirakan $\Delta H°$ and $\Delta U°$ bagi tindak balas yang berikut:

(i) $OH(g) \rightarrow H(g) + O(g)$

(ii) $H_2O(g) \rightarrow 2H(g) + O(g)$

dengan menganggap gas berkelakuan unggul.

(10 markah)

(b) Sejumlah 100 g gas CO_2 dipanaskan daripada 300 hingga 400 K. Kirakan jumlah haba yang diperlukan jika proses ini dilakukan pada

(i) tekanan tetap, dan

(ii) isipadu tetap.

Andaikan bahawa gas CO_2 berkelakuan sebagai gas unggul dan muatan habanya diberikan sebagai

$$\overline{C}_p = (29.3 + 3.0 \times 10^{-2} T - 7.78 \times 10^{-6} T^2) \text{ J K}^{-1} \text{ mol}^{-1}$$

(10 markah)

BAHAGIAN B

Jawab sebarang **DUA** (2) soalan sahaja.

4. (a) Tentukan $\left(\frac{\partial Z}{\partial P}\right)_T$ bagi persamaan-persamaan gas unggul dan virial dengan B dan C masing-masing sebagai pekali virial kedua dan ketiga. Tunjukkan bahawa tidak semua sifat gas sejati akan memberi nilai gas unggul apabila tekanan menghampiri kosong.

(6 markah)

(b) Didalam satu bekas berukuran 3.0 L, suatu gas dengan jisim 1.2×10^{-12} g molekul $^{-1}$ mempunyai halaju punca kuasa dua, $\langle v^2 \rangle^{\frac{1}{2}}$ sejumlah 200 m s^{-1} pada 2.67×10^{17} Pa. Berapakah bilangan molekul gas di dalam bekas tersebut?

(4 markah)

(c) Dua jenis gas yang tidak diketahui, X dan Y, mengefusi ke arah satu sama lain daripada hujung-hujung yang bertentangan pada satu tiub sepanjang 36 cm yang telah divakum. Jika nisbah jisim molar X terhadap gas Y ialah 4:1, dimanakah titik pertemuan gas-gas tersebut?

(5 markah)

(d) Suatu gas mematuhi persamaan van der Waals dengan $a = 0.76$ m^6 Pa mol^{-2}. Ia mempunyai isipadu 4.00×10^{-4} m^3 mol^{-1} pada 273 K dan 3.0 MPa. Daripada maklumat ini, anggarkan jejari molekul gas tersebut (dalam nm) dengan menganggap ia berupa sfera.

(5 markah)

5. (a) Tuliskan persamaan Maxwell bagi taburan laju. Berdasarkan persamaan ini, terangkan kesan suhu dan jisim molekul terhadap fungsi taburan (ketumpatan kebarangkalian) molekul-molekul gas. Lakarkan satu graf bagi menerangkan jawapan anda.

(8 markah)

(b) Tenaga kinetik bagi suatu molekul diberi sebagai:

$$\varepsilon = \frac{1}{2}mv^2$$

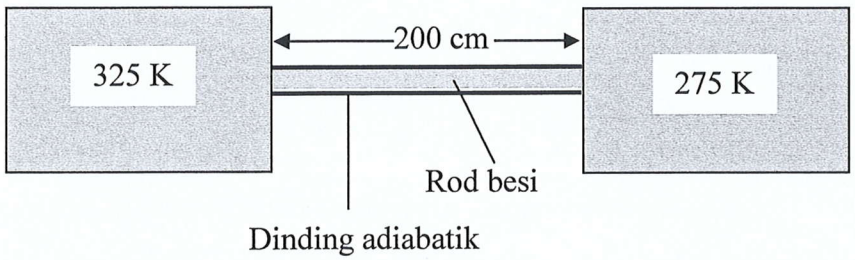
Dengan menggunakan persamaan Maxwell, buktikan bahawa kebarangkalian suatu molekul mempunyai tenaga kinetik dalam julat ε ke $\varepsilon + d\varepsilon$ adalah

$$F(\varepsilon)d\varepsilon = \frac{2\pi}{(\pi kT)^{3/2}} \varepsilon^{1/2} e^{-\varepsilon/kT} d\varepsilon$$

(5 markah)

(c) Apakah yang menyebabkan konduktiviti terma gas-gas?

RAJAH 1 menunjukkan sebatang rod besi yang bersentuhan dengan dua takungan haba pada suhu yang berlainan. Suatu keadaan mantap akan tercapai dengan kecerunan suhu yang seragam dalam rod itu.



RAJAH 1

Jika luas keratan rentas rod itu ialah 24 cm^2 dan κ = 0.80 J K^{-1} cm^{-1} s^{-1}, kiralah kadar pengaliran haba merentasi rod besi itu dan tenaga haba yang dialirkan dalam masa 60 s.

(7 markah)

6. (a) Pertimbangkan dua tindak balas tertib pertama berturutan dengan pemalar kadar, k_1 dan k_2,

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

(i) Tunjukkan bahawa kadar pembentukan C diberi dengan

$$[C] = [A]_0 \ (1 + \frac{k_2 e^{-k_1 t} - k_1 e^{-k_2 t}}{k_1 - k_2})$$

$[A]_0$ ialah kepekatan awal bagi bahan A

Diberi:

Penyelesaian bagi persamaan pembezaan

$$\frac{dx}{dt} = abe^{-bt} - cx$$

ialah

$$x = \frac{ab}{c-b}(e^{-bt} - e^{-ct}) + \theta$$

dengan a, b, dan c adalah pemalar.

(ii) Lakarkan rajah bagi kepekatan melawan masa untuk tindak balas itu masing-masing dengan pemalar kadar $k_2 = 6k_1$ dan $k_2 = \frac{1}{6}k_1$.

(12 markah)

(b) Bagi tindak balas fasa gas

$$N_2O_5 + NO \rightarrow 3NO_2,$$

mekanisme yang berikut telah dicadangkan

$$N_2O_5 \xrightarrow{k_1} NO_2 + NO_3$$

$$NO_2 + NO_3 \xrightarrow{k_2} N_2O_5$$

$$NO + NO_3 \xrightarrow{k_3} 2NO_2$$

Dengan menggunakan kaedah penghampiran keadaan mantap, terbitkan satu persamaan bagi kadar pengurangan N_2O_5.

(8 markah)

7. (a) Terbitkan persamaan

$$\left(\frac{\partial H}{\partial P}\right)_T = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial P}\right)_T + V$$

Nilaikan $\left(\frac{\partial H}{\partial P}\right)_T$ bagi suatu gas unggul.

(8 markah)

(b) Kirakan w, q, ΔH dan ΔU bagi proses dengan 1 mol air mengalami peralihan $H_2O(\ell, 373\,K) \rightarrow H_2O(g, 460\,K)$ pada tekanan 1 atm. Diberikan bahawa isipadu air pada 373 K adalah 1.89×10^{-5} m^3 dan isipadu stim pada 373 dan 460 K masing-masing adalah 3.03×10^{-2} dan 3.74×10^{-2} m^3. Bagi stim, muatan haba molar, $\overline{C}_p$, dapat dianggap tetap pada 33.58 $J\,K^{-1}\,mol^{-1}$ dalam julat suhu yang dikaji. Entalpi pengwapan air pada 1 atm dan 373 K adalah 40.66 $kJ\,mol^{-1}$.

(12 markah)

-oooOooo-