Final Examination
2017/2018 Academic Session

May/June 2018

JIK420 – Advanced Physical Chemistry
[Kimia Fizik Lanjutan]

Duration : 3 hours
[Masa : 3 jam]

Please ensure that this examination paper contains **THIRTEEN** printed pages before you begin the examination.

Answer **FIVE (5)** questions only. Answer the questions in English. You may also answer the questions in Bahasa Malaysia, but not a mix of both languages.

All answers must be written in the answer booklet provided.

Each question is worth 20 marks and the mark for each sub question is given at the end of that question.

In the event of any discrepancies in the exam questions, the English version shall be used.

*Sila pastikan bahawa kertas peperiksaan ini mengandungi **TIGA BELAS** muka surat yang bercetak sebelum anda memulakan peperiksaan ini.*

*Jawab **LIMA (5)** soalan sahaja. Jawab soalan-soalan dalam Bahasa Inggeris. Anda juga dibenarkan menjawab soalan dalam Bahasa Malaysia, tetapi campuran antara kedua-dua bahasa ini tidak dibenarkan.*

Setiap jawapan mesti dijawab di dalam buku jawapan yang disediakan.

Setiap soalan bernilai 20 markah dan markah subsoalan diperlihatkan di penghujung subsoalan itu.

Sekiranya terdapat sebarang percanggahan pada soalan peperiksaan, versi Bahasa Inggeris hendaklah diguna pakai.

Answer **FIVE (5)** questions.
*Jawab **LIMA (5)** soalan.*

1. (a). Max Planck managed to describe the spectrum of the black-body radiation. What are the differences of his proposals as compared to the proposals used by Rayleigh-Jeans?

   Max Planck berjaya memerihalkan spektrum sinaran jasad hitam. Apakah perbezaan-perbezaan di antara cadangan-cadangannya dengan cadangan-cadangan yang digunakan oleh Rayleigh-Jeans?

   (7 marks/*markah*)

   (b). According to de Broglie, every moving object generates matter waves in a relationship given by $\lambda = h/p$ where λ is the wavelength of the matter wave, h is the Planck constant and p is the momentum of the object. Explain why we could not detect matter waves generated by an 80-kg man walking at 1 m s^{-1}?

   Menurut de Broglie, setiap objek yang bergerak akan menjana gelombang jirim dalam suatu perhubungan $\lambda = h/p$ di sini λ ialah panjang gelombang jirim, h ialah pemalar Planck dan p ialah momentum objek. Jelaskan mengapa kita tidak dapat mengesan gelombang jirim yang dijana oleh seorang lelaki 80 kg yang berjalan pada kelajuan 1 m s^{-1}?

   (5 marks/*markah*)

   (c). Explain the meaning of the following terms:

   (i). Hermitian operator
   (ii). eigenvalue
   (iii). expectation value
   (iv). degenerate state

   Jelaskan maksud sebutan-sebutan berikut:

   (i). operator Hermitian
   (ii). nilai eigen
   (iii). nilai jangkaan
   (iv). keadaan degenerat

   (8 marks/*markah*)

2. (a). Discuss the physical origin of the quantisation of energy for a particle confined to move inside a one-dimensional square-well potential.

Bincangkan asal fizik pengkuantuman tenaga bagi suatu zarah yang terkurung untuk bergerak di dalam suatu keupayaan telaga persegi satu dimensi.

(10 marks/*markah*)

(b). Assuming that the vibrations of a $^{14}N_2$ molecule are equivalent to those of a harmonic oscillator with a constant force κ = 2293.8 N m^{-1}, determine the zero-point energy of vibration of this molecule. The mass of a ^{14}N atom is 14.9688 u.

Dengan anggapan bahawa getaran suatu molekul $^{14}N_2$ adalah setara dengan getaran pengayun harmonik dengan pemalar daya κ = 2293.8 N m^{-1}, tentukan tenaga titik sifar getaran molekul ini. Jisim atom ^{14}N ialah 14.9688 u.

(5 marks/*markah*)

(c). The energy of a particle inside a 3-dimensional box of sides *L* where the potential *V* is zero inside the box and is infinity at the wall and outside the box is given by

Tenaga suatu zarah di dalam suatu kotak 3 dimensi dengan sisi L di mana keupayaan V adalah sifar di dalam kotak dan infiniti di dinding dan di luar kotak diberikan oleh

$$E_{n_x n_y n_z} = \frac{h^2}{8mL^2}\left(n_x^2 + n_y^2 + n_z^2\right), \qquad n = 1, 2, 3, ...$$

Show that energy degeneracy exists for this system. Does degeneracy occur in a 1-dimensional system too?

Tunjukkan bahawa tenaga terdegenerat wujud dalam sistem ini. Adakah kedegenaratan juga berlaku dalam sistem 1 dimensi?

(5 marks/*markah*)

3. (a). Explain in terms of constructive and destructive interference how we obtain diffraction peaks and no peaks in X-ray diffraction patterns. In addition to your explanation, include illustrations.

Terangkan dari segi interferens membina dan interferens memusnah, bagaimanakah kita mendapat puncak dan tanpa puncak belauan dalam corak pembelauan sinar-X. Selain penjelasan anda, sertakan ilustrasi.

(8 marks/*markah*)

(b). Why are X-rays used, rather than any other part of the electromagnetic spectrum, for crystal structure determination?

Mengapakah sinar-X digunakan, dan bukannya mana-mana bahagian spektrum elektromagnet lain, untuk penentuan struktur hablur?

(2 marks/*markah*)

(c). Why is it not possible to build and use an X-ray microscope to observe molecules directly?

Mengapakah mikroskop sinar-X tidak mungkin dibina dan digunakan untuk memerhatikan molekul-molekul secara langsung?

(3 marks/*markah*)

(d). Why is a single crystal used in the X-ray structure determination?

Mengapa hablur tunggal digunakan dalam penentuan struktur sinar-X?

(3 marks/*markah*)

(e). Why must a crystal be rotated in the X-ray beam during data collection:

(i). in order to obtain the complete diffraction pattern;

(ii). in the measurement of a single reflection with a serial diffractometer?

Mengapa hablur mesti diputar dalam sinar-X semasa pengumpulan data:

(i). untuk mendapatkan corak pembelauan yang lengkap;

(ii). dalam pengukuran pantulan tunggal dengan difraktometer bersiri?

(4 marks/*markah*)

4. (a). For the cubic crystal system, many calculations are easier than in lower-symmetry systems. For example, the spacing of lattice planes d_{hkl} is simply $a/\sqrt{(h^2 + k^2 + l^2)}$. For a cubic unit cell with a = 10 Å, calculate the d spacings for the lattice planes (1 0 0), (2 0 0), (0 2 0) and (1 1 1). Using the Bragg equation, calculate the Bragg angle θ for the reflections from these lattice planes, with an X-ray wavelength λ = 0.7 Å.

Bagi sistem hablur kubik, pengiraan adalah lebih mudah daripada sistem simetri rendah. Contohnya, jarak satah kekisi d_{hkl} hanyalah $a / \sqrt{(h^2 + k^2 + l^2)}$. Untuk sel unit kubik dengan a = 10 Å, kirakan jarak d untuk satah kekisi (1 0 0), (2 0 0), (0 2 0) dan (1 1 1). Dengan menggunakan persamaan Bragg, hitung sudut Bragg θ untuk pantulan dari satah kekisi ini, dengan panjang gelombang sinar-X, λ = 0.7 Å.

(10 marks/*markah*)

(b). Inter planar distance between two layers is 4.0 Å in a crystal. Calculate the angle of reflection for first order reflection. X-rays of wavelength 1.54 Å are diffracted by the crystal.

Jarak antara satah di antara dua lapisan dalam hablur adalah 4.0 Å. Kirakan sudut pantulan untuk pantulan tertib pertama. Panjang gelombang sinar-X yang 1.54 Å telah terbelau oleh hablur.

(4 marks/*markah*)

(c). A beam of X-rays of wavelength 0.071 nm is diffracted by (110) plane of rock salt with lattice constant of 0.28 nm. Find the glancing angle for the second-order diffraction.

Suatu alur sinar-X yang mempunyai panjang gelombang 0.071 nm dibelau oleh satah (110) garam batu dengan pemalar kekisi 0.28 nm. Cari sudut lekapan untuk pembelahan tertib kedua.

(6 marks/*markah*)

5. (a). GPC is a common technique to determine the molecular weight of a polymer.

   (i). What does GPC stand for?

   (ii). Give two other names for this instrument and explain what each of these names has to do with the functioning of this instrument.

   GPC adalah teknik umum untuk menentukan berat molekul polimer.

   (i). Apakah yang dimaksudkan dengan GPC?

   (ii). Berikan dua nama lain untuk instrumen ini dan terangkan apakah kaitan setiap nama ini dengan fungsi instrumen ini.

   (6 marks/*markah*)

   (b). The number-average molecular weight of a poly(styrene-butadiene) alternating copolymer is 1,350,000 g mol^{-1}, determine the average number of styrene and butadiene repeat units per molecule.

   Berat molekul nombor-purata kopolimer selang-seli poli(stirena-butadiena) ialah 1,350,000 g mol^{-1}, tentukan nombor purata unit ulangan per molekul stirena dan butadiena.

   (8 marks/*markah*)

   (c). Compute repeat unit molecular weights for the following:

   (i). poly(vinyl chloride),

   (ii). poly(ethylene terephthalate),

   (iii). polycarbonate.

   Kirakan berat molekul unit ulangan untuk yang berikut:

   (i). poli(vinil klorida),

   (ii). poli(etilena tereftalat),

   (iii). polikarbonat.

   (6 marks/*markah*)

6. (a). How are polymers classified on the basis of structure?
Bagaimanakah polimer diklasifikasikan berdasarkan struktur?
(4 marks/*markah*)

(b). Explain the difference between a step growth and a chain growth polymerisation. Draw the structures of monomers that can be polymerised by both processes.
Terangkan perbezaan antara pempolimeran pertumbuhan berperingkat dan pertumbuhan rantaian. Lukiskan struktur monomer-monomer yang boleh dipolimerisasi oleh kedua-dua proses.
(8 marks/*markah*)

(c). Write the free radical mechanism for the polymerisation of ethene.
Tuliskan mekanisme radikal bebas untuk pempolimeran etena.
(8 marks/*markah*)

Constants:

Speed of light $c = 3.0 \times 10^{8}$ m s^{-1}

Avogadro's number $N_A = 6.02 \times 10^{23}$ mol^{-1}

Planck constant $h = 6.63 \times 10^{-34}$ J s

Boltzmann constant $k = 1.38 \times 10^{-23}$ J K^{-1}

Permittivity of free space $\varepsilon_o = 8.85 \times 10^{-12}$ F m^{-1}

Permeability of free space $\mu_o = 4\pi \times 10^{-7}$ H m^{-1}

Basic charge $e = 1.6 \times 10^{-19}$ C

Electron rest-mass $m_e = 9.1 \times 10^{-31}$ kg

Proton rest-mass $m_p = 1.6725 \times 10^{-27}$ kg $\equiv$ 1.0072766 u

Neutron rest-mass $m_n = 1.6748 \times 10^{-27}$ kg $\equiv$ 1.0086654 u

Bohr's radius $a = 5.3 \times 10^{-11}$ m

1 eV = 1.6×10^{-19} J

1 u $\equiv$ 931 MeV c^{-2}

1 barn = 10^{-28} m^2

1 fm = 10^{-15} m

1 Ci = 3.7×10^{10} s^{-1}

USEFUL MATHEMATICS IN QUANTUM MECHANICS

Exponential series

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \frac{x^4}{4!} + \cdots + \frac{x^n}{n!}$$

$$e^{ix} = \cos x + i \sin x$$

$$e^{-ix} = \cos x - i \sin x$$

Trigonometric series

$$\sin x = x - \frac{x^3}{3!} + \frac{x^5}{5!} - \frac{x^7}{7!} + \cdots$$

$$\cos x = 1 - \frac{x^2}{2!} + \frac{x^4}{4!} - \frac{x^6}{6!} + \cdots$$

$$\tan x = x + \frac{x^3}{3} + \frac{2x^5}{15} + \cdots$$

Binomial expansion

$$(1 + x)^n = 1 + nx + \frac{n(n-1)}{2!} x^2 + \frac{n(n-1)(n-2)}{3!} x^3 + \cdots$$

Differentiation and integration (Standard forms)

Differentiation	Integration
$\frac{d}{dx}x^n = nx^{n-1}$ $\frac{d}{dx}(ax+b)^n = na(ax+b)^{n-1}$	$\int x^n dx = \frac{x^{n+1}}{n+1} + c$ $\int (ax+b)^n dx = \frac{(ax+b)^{n+1}}{a(n+1)} + c$
$\frac{d}{dx}\log x = \frac{1}{x}$ $\frac{d}{dx}\log(ax+b) = \frac{a}{ax+b}$	$\int \frac{dx}{x} = \log x + c$ $\int \frac{dx}{ax+b} = \frac{1}{a}\log(ax+b) + c$
$\frac{d}{dx}e^x = e^x$ $\frac{d}{dx}e^{mx} = me^{mx}$	$\int e^x dx = e^x + c$ $\int e^{mx} dx = \frac{e^{mx}}{m} + c$
$\frac{d}{dx}\sin x = \cos x$ $\frac{d}{dx}\sin mx = m\cos mx$	$\int \cos x\, dx = \sin x + c$ $\int \cos mx\, dx = \frac{\sin mx}{m} + c$
$\frac{d}{dx}\cos x = -\sin x$ $\frac{d}{dx}\cos mx = -m\sin mx$	$\int \sin x\, dx = -\cos x + c$ $\int \sin mx\, dx = -\frac{\cos mx}{m} + c$
$\frac{d}{dx}\tan x = \sec^2 x$ $\frac{d}{dx}\tan mx = m\sec^2 mx$	$\int \sec^2 x\, dx = \tan x + c$ $\int \sec^2 mx\, dx = \frac{\tan mx}{m} + c$
$\frac{d}{dx}\cot x = -\mathrm{cosec}^2 x$ $\frac{d}{dx}\cot mx = -m\ \mathrm{cosec}^2 mx$	$\int \mathrm{cosec}^2 x\, dx = -\cot x + c$ $\int \mathrm{cosec}^2 mx\, dx = -\frac{\cot mx}{m} + c$
$\frac{d}{dx}\sinh x = \cosh x$	$\int \cosh x\, dx = \sinh x + c$
$\frac{d}{dx}\cosh x = \sinh x$	$\int \sinh x\, dx = \cosh x + c$

Integration by parts

$$\int u\upsilon\,dx = u\int \upsilon\,dx - \int\left\{\int \upsilon\,dx\right\}\frac{du}{dx}\,dx$$

Integration common in Quantum Mechanics

$$f(x) = \int_0^{\infty} x^n e^{-ax^2}\,dx$$

n	$f(n)$	*n*	$f(n)$
0	$\frac{1}{2}\sqrt{\frac{\pi}{a}}$	1	$\frac{1}{2a}$
2	$\frac{1}{4}\sqrt{\frac{\pi}{a^3}}$	3	$\frac{1}{2a^2}$
4	$\frac{3}{8}\sqrt{\frac{\pi}{a^5}}$	5	$\frac{1}{a^3}$
6	$\frac{15}{16}\sqrt{\frac{\pi}{a^7}}$	7	$\frac{3}{a^4}$

If *n* is even, $\int_{-\infty}^{\infty} x^n e^{-ax^2}\,dx = 2f(x)$

If *n* is odd, $\int_{-\infty}^{\infty} x^n e^{-ax^2}\,dx = 0$

Other standard integrals

$$\int_{-\infty}^{\infty} e^{-x^2}\,dx = \sqrt{\pi}$$

$$\int_0^{\infty} \frac{x}{\left(e^x - 1\right)}\,dx = \frac{\pi^2}{6}$$

$$\int_0^{\infty} \frac{x^3}{\left(e^x - 1\right)}\,dx = \frac{\pi^4}{15}$$

…12/-

Pythagorean identities

$$\sin^2 u + \cos^2 u = 1$$
$$1 + \tan^2 u = \sec^2 u$$
$$1 + \cot^2 u = \csc^2 u$$

Sum & difference formulas

$$\sin(u \pm \upsilon) = \sin u \cos \upsilon \pm \cos u \sin \upsilon$$
$$\cos(u \pm \upsilon) = \cos u \cos \upsilon \mp \sin u \sin \upsilon$$
$$\tan(u \pm \upsilon) = \frac{\tan u \pm \tan \upsilon}{1 \mp \tan u \tan \upsilon}$$

Double angle formulas

$$\sin(2u) = 2 \sin u \cos u$$
$$\cos(2u) = \cos^2 u - \sin^2 u$$
$$= 2\cos^2 u - 1$$
$$= 1 - 2\sin^2 u$$
$$\tan(2u) = \frac{2 \tan u}{1 - \tan^2 u}$$

Power reducing/half angle formulas

$$\sin^2 u = \frac{1 - \cos(2u)}{2}$$
$$\cos^2 u = \frac{1 + \cos(2u)}{2}$$
$$\tan^2 u = \frac{1 - \cos(2u)}{1 + \cos(2u)}$$

Sum-to-product formulas

$$\sin u + \sin \upsilon = 2\sin\left(\frac{u+\upsilon}{2}\right)\cos\left(\frac{u-\upsilon}{2}\right)$$
$$\sin u - \sin \upsilon = 2\cos\left(\frac{u+\upsilon}{2}\right)\sin\left(\frac{u-\upsilon}{2}\right)$$
$$\cos u + \cos \upsilon = 2\cos\left(\frac{u+\upsilon}{2}\right)\cos\left(\frac{u-\upsilon}{2}\right)$$
$$\cos u - \cos \upsilon = -2\sin\left(\frac{u+\upsilon}{2}\right)\sin\left(\frac{u-\upsilon}{2}\right)$$

Product-to-sum formulas

$$\sin u \sin \upsilon = \frac{1}{2}\left[\cos(u-\upsilon) - \cos(u+\upsilon)\right]$$
$$\cos u \cos \upsilon = \frac{1}{2}\left[\cos(u-\upsilon) + \cos(u+\upsilon)\right]$$
$$\sin u \cos \upsilon = \frac{1}{2}\left[\sin(u+\upsilon) + \sin(u-\upsilon)\right]$$
$$\cos u \sin \upsilon = \frac{1}{2}\left[\sin(u+\upsilon) - \sin(u-\upsilon)\right]$$

- oooOooo -