UNIVERSITI SAINS MALAYSIA

First Semester Examination
Academic Session 2008/2009

November 2008

KFE 331 – Special Topics in Physical Chemistry
[Tajuk Khusus dalam Kimia Fizik]

Duration : 3 hours
[Masa : 3 jam]

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

Instruction

Answer any **FIVE** (5) questions.

You may answer the questions 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.

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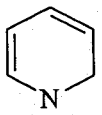
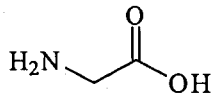
Answer any **FIVE** questions.

1. (a) Write molecular specification for one of the following structures below using Z-matriks format or Cartesian coordinates.





Given the bond distances: C-C = 1.32 Å, C-H = 1.07 Å, CO = 1.20-1.25 Å, C-N = 1.47 Å and N-H = 1.00 Å.

(12 marks)

(b) Calculate the number of basis functions for calcium dihydrogen phosphate, $Ca(H_2PO_4)_2$ using the minimal, split valence 3-21G* and 6-31G** basis sets.

(8 marks)

2. Discuss the difference between molecular modeling methods, Quantum Mechanics *ab initio* Hartree Fock and Density Functional Theory namely

(i) the basic theory for total energy,
(ii) the procedures to solve the total energy,
(iii) the advantages and disadvantages of these methods, and
(iv) two examples of problems that can be solved by the method.

(20 marks)

3. (a) Ferric-catechin complex, Fe(III)-$C_{15}O_6H_{14}$ has been reported to be a good corrosion inhibitor. If you are asked to perform a molecular modeling study on this system, give

(i) the method that will be used,
(ii) the reasons why the method is chosen,
(iii) the types of calculation that can be done, and
(iv) the possible values for spin multiplicity.

(12 marks)

(b) Describe the differences between geometry optimization algorithm Newton Raphson compared to Steepest Descent.

(8 marks)

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4. (a) Explain the effect of Born-Oppenheimer approximation to the solution of Schrödinger equation.

Give the meaning of all the five terms in the Hamiltonian operator below:

$$\hat{\mathbf{H}} = \sum_{i}^{electrons} \frac{-\hbar^2}{2m_e}\nabla_i^2 + \sum_{A}^{nuclei} \frac{-\hbar^2}{2m_A}\nabla_A^2 + \sum_{i}^{electrons}\sum_{A}^{nuclei} \frac{-e^2 Z_A}{r_{iA}} + \sum_{i>j}^{electrons} \frac{e^2}{r_{ij}} + \sum_{A>B}^{nuclei} \frac{e^2 Z_A Z_B}{r_{AB}}$$

(10 marks)

(b) Explain the differences between light and heavy crude oils with respect to their 'API' gravity and viscosity.

(5 marks)

(c) Name three additives in lubricating oil and explain their functions.

(5 marks)

5. The most important refinery product from crude oil is gasoline, a blend of hydrocarbons with boiling points ranging from ambient temperature to about 260 °C.

(a) Describe and discuss refinery processes for the production of gasoline components.

(10 marks)

(b) Define 'octane number' and explain its relation to 'knocking'.

(5 marks)

(c) Discuss the volatility of gasoline with respect to its components.

(5 marks)

6. Zeolites are a well-defined class of crystalline hydrated aluminosilicates. They have three-dimensional structures arising from a framework of $(SiO_4)^{4-}$ and $(AlO_4)^{5-}$ coordination polyhedra linked by all their corners.The frameworks generally are very open and contain channels and cavities in which are located cations and water molecules.

(a) Describe and discuss the special properties of zeolite ZSM-5.

(7 marks)

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(b) Briefly explain five attributes/properties that make zeolites important catalysts.

(8 marks)

(c) The silicon/aluminium ratio in zeolite structures is variable, ranging from the values of one to several hundreds. Discuss the acidity and shape selectivity of zeolite structures.

(5 marks)

7. Langmuir visualized adsorption equilibrium as a dynamic process. At equilibrium the amount adsorbed has a definite value; the rate of adsorption must therefore be equal to the rate of desorption.

(a) Derive the Langmuir equation ;

$$x = \frac{x_{\circ} bp}{1 + bp}$$

where x is the monolayer capacity, $x_{\circ}$ the completed monolayer capacity, b a constant and p the pressure. Explain the main assumptions.

(12 marks)

(b) Describe the treatment of the equation at low and high pressures.

(4 marks)

(c) Discuss briefly the significance of the constant *b*.

(4 marks)

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TERJEMAHAN

Arahan :

Jawab **LIMA** soalan.

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.

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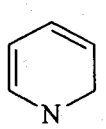
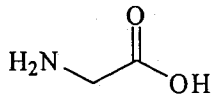
Jawab hanya **LIMA** soalan.

1. (a) Tulis spesifikasi molekul bagi salah satu struktur di bawah menggunakan format Z-matriks ataupun Cartesian coodinates.





Diberi jarak ikatan: C-C = 1.32 Å, C-H = 1.07 Å, CO =1-20 -1.25 Å, C-N = 1.47 Å dan N-H = 1.00 Å.

(12 markah)

(b) Kira bilangan fungsi basis bagi kalsium dihidrogen fosfat, $Ca(H_2PO_4)_2$ menggunakan set asas minimal, split valens 3-21G* dan 6-31G**.

(8 markah)

2. Bincangkan perbezaan kaedah permodelan molekul, Mekanik Kuantum *ab initio* Hartree Fock dan Teori Fungsi Ketumpatan iaitu

(i) teori asas bagi tenaga total,
(ii) prosedur penyelesaian tenaga total,
(iii) kelebihan atau kekurangan kaedah ini, dan
(iv) dua contoh permasalahan yang boleh diselesaikan menggunakan kaedah tersebut.

(20 markah)

3. (a) Kompleks ferik-katecin, Fe(III)-$C_{15}O_6H_{14}$ telah dilaporkan sebagai satu agen perencat karat yang baik. Sekiranya anda diminta menjalankan kajian permodelan ke atas sistem ini, berikan

(i) kaedah permodelan yang akan digunakan,
(ii) alasan mengapa kaedah tersebut dipilih,
(iii) jenis pengiraan yang boleh dilakukan, dan
(iv) nilai kegandaan spin yang mungkin.

(12 markah)

(b) Terangkan perbezaan algoritma pengoptimuman geometri Newton Raphson berbanding Steepest Descent.

(8 markah)

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4. (a) Terangkan kesan penghampiran Born-Oppenheimer dalam penyelesaian persamaan Schrödinger.

Berikan makna kesemua lima sebutan dalam operator Hamiltonian yang diberikan di bawah:

$$\hat{\mathbf{H}} = \sum_{i}^{elektron} \frac{-\hbar^2}{2m_e}\nabla_i^2 + \sum_{A}^{nuklei} \frac{-\hbar^2}{2m_A}\nabla_A^2 + \sum_{i}^{elektron}\sum_{A}^{nuklei} \frac{-e^2 Z_A}{r_{iA}} + \sum_{i>j}^{elektron} \frac{e^2}{r_{ij}} + \sum_{A>B}^{nuclei} \frac{e^2 Z_A Z_B}{r_{AB}}$$

(10 markah)

(b) Jelaskan perbezaan diantara minyak mentah ringan dan berat dengan merujuk kepada 'API' graviti dan kelikatan.

(5 markah)

(c) Namakan tiga jenis bahan tambahan didalam minyak pelincir dan jelaskan fungsinya.

(5 markah)

5. Hasilan yang penting daripada proses penapisan adalah gasolina, adunan dari hidrokarbon yang mempunyai takat didih dalam julat suhu ambien hingga 260 °C.

(a) Beri penjelasan dan bincangkan proses-proses penapisan untuk menghasilkan komponen gasolina.

(10 markah)

(b) Apakah yang dimaksudkan dengan 'nombor oktana' dan jelaskan kaitannya dengan 'ketukan'.

(5 markah)

(c) Bincangkan pemeruapan gasolina dengan merujuk kepada kandungannya

(5 markah)

6. Zeolit adalah struktur aluminosilikit terhidrat yang istimewa. Ia mempunyai struktur tiga dimensi yang terbentuk dari kerangka $(SiO_4)^{4-}$ dan $(AlO_4)^{5-}$ dan bersambung melalui koordinasi polihidra oleh semua penjurunya.

(a) Jelas dan bincangkan apakah sifat-sifat khusus zeolit ZSM-5.

(7 markah)

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(b) Secara ringkas, jelaskan lima sifat yang menyebabkan zeolit sebagai pemangkin yang penting.

(8 markah)

(c) Nisbah silika/alumina didalam struktur zeolit adalah berubah, dalam julat satu hingga ratus. Bincangkan keasidan dan bentuk kepilihan bentuk struktur zeolit.

(5 markah)

7. Langmuir menggambarkan penjerapan keseimbangan sebagai suatu proses dinamik. Pada keseimbangan jumlah yang terjerap merupakan suatu nilai tertentu; kadar penjerapan mestilah sama dengan kadar penyahjerapan.

(a) Terbitkan persamaan Langmuir;

$$x = \frac{x_{\circ} bp}{1 + bp}$$

dimana x adalah kapasiti lapisan mono, $x_{\circ}$ adalah kapasiti lapisan mono lengkap, b adalah angkatap dan p adalah tekanan. Jelaskan andaian yang utama.

(12 markah)

(b) Jelaskan pengolahan persamaan tersebut pada tekanan rendah dan tinggi.

(4 markah)

(c) Bincangkan secara ringkas kepentingan angkatap *b*.

(4 markah)

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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 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}	1.9864×10^{-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		

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