UNIVERSITI SAINS MALAYSIA

Second Semester Examination
2010/2011 Academic Session

April/May 2011

IEK 309 - CHEMODYNAMICS
[KIMODINAMIK]

Duration: 3 hours
Masa: [3 jam]

Please check that this examination paper consists of ELEVEN pages of printed material before you begin the examination.

[Sila pastikan bahawa kertas peperiksaan ini mengandungi SEBELAS muka surat yang bercetak sebelum anda memulakan peperiksaan ini.]

Instructions: Answer FIVE questions. You may answer the questions either in Bahasa Malaysia or in English. Answer questions from each part in separate answer booklets.

*[**Arahan:** Jawab LIMA soalan. Anda dibenarkan menjawab soalan sama ada dalam Bahasa Malaysia atau Bahasa Inggeris. Jawab soalan-soalan daripada setiap bahagian di dalam buku jawapan yang berasingan.]*

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

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

Answer any FIVE out of SIX questions from Part A and Part B. Answer questions from each part in separate answer booklets.

Part A

1. (a) What are the factors that influence the solubility of oxygen in water?

(20 marks)

(b) Conduct a mass balance on a unit mass of organic chemical X introduced into a stream with constant depth, h. Assume that the chemical X expires as it flow downstream following first order rate equation where k_X is the reaction constant. What are some of the assumptions needed to conduct the above mass balance?

(50 marks)

(c) Using the equation derived in (b), determine the time required for X to deteriorate by 99.99% in the stream and the distance where this would occur. Assume that the time when X is introduced into the stream is t = 0, velocity of the stream is 2.7 m/s and $k_X = 1.2 \times 10^{-3}\ s^{-1}$.

(30 marks)

2. (a) In chemodynamics, what is meant by a solution being ideal?

(25 marks)

(b) Estimate the mole fraction of ethane in water at 30°C if it is present above water as a pure gas at 0.95 atm. Here $\gamma_{A2} = 8.10 \times 10^2$ at 30°C and the estimated vapor pressure of ethane at 30°C is 45.4 atm. Will the mole fraction of ethane in water be higher or lower at temperatures of more than 30°C? Explain.

(40 marks)

(c) A mixture of chloroform and water is exposed to air at 20°C. What is the partition coefficient of chloroform at equilibrium if the solubility of chloroform in water is 0.8 g/100 ml of water? Given $MW_{chloroform}$ = 119.378 g/mol and vapor pressure of chloroform at 20°C = 156.819 mmHg. Explain your answer.

(35 marks)

3. The organic content of the soil strongly affects the partitioning of organic pesticides between soil and water phases. Table 1 contains experimental results of an equilibrium study with soils of organic matter more than 1%. For each test 4 mL of a 1.0 ppm solution was added to each 1.0 g of soil. The pH was adjusted to 2 with HNO_3 and the slurry incubated for 1 hr.

Table 1 Sorption of acidic organic pesticides by soils at pH 2 (wt%)

Soil	**Organic matter content of soil**	**Acid in solution at equilibrium**	**Acid sorbed on soil at equilibrium**
A	1.0	51.0	49
B	2.7	23.0	77
C	4.1	11.0	89
D	10.7	5.8	94
E	32.2	2.0	98

(a) Determine the soil-water partition coefficient, H^*_{A32} (L/kg soil) for each.

(35 marks)

(b) Determine the organic matter-water partition coefficient, H^*_{AC2} (L/kg organic matter) for each.

(40 marks)

(c) Perform simple statistics (average and standard deviation) on each coefficient.

(10 marks)

(d) Which coefficient is nearly constant? Does this suggest anything about the adsorption process?

(15 marks)

Part B

4. The equation below shows the decay rate of organic substance according to first class order

$$S = S_o \exp(-Kt^*)$$

(a) Plot the figures for S versus t on a Cartesian coordinate.
(b) Plot the figures for *ln* S versus t on a semi- log.
(c) Show on the figure that indicates the waste input into a river or a canal with a velocity U using the above equation.
(d) What is meant by the parameter K in the above equation.

(100 marks)

…4/-

5. The time required for a stream to recover from a hypothetical state of no dissolved oxygen to some final degree of saturation gives an indication of the speed of reaeration.

   (a) Calculate the time required for a stream void of oxygen to reach a 50% saturation. This is the oxygen absorption half-life, $\Delta_{O2} = \Delta^{o}_{O2}/2$, for this particular stream. Find the distance downstream and oxygen concentration;

   (b) Calculate the time required to reach 90% saturation. Find the distance and the concentration.
   Stream data: Average velocity v_w = 0.22 m/s; average depth h = 1.9 m, $D_{(O2)W}$ = 1.80 x 10^{-5} cm^2/s at 20 ^oC, temperature of water = 30 ^oC. The temperature coefficient for the system in the temperature range is θ = 1.018.

   $\rho_{(O2)W} = \rho^*_{(O2)W} - [\rho^*_{(O2)W} - \rho^o_{(O2)W}]\exp[-k_{(O2)W}t/h]$
   $L = tv_w$
   At 30 ^oC, $\rho^*_{(O2)W}$ = 7.53 mg O_2/L
   $k_{(O2)W}/h = [D_{(O2)W}v_w]^{1/2}/h^{3/2}$
   $\Delta_{O2} = \rho^*_{(O2)W} - \rho_{(O2)W}$
   $k_{T1} = k_{T2}\theta^{(T1-T2)}$

$$\frac{\Delta A}{\Delta^0 A} = \exp\left(\frac{-{}^1k'_{A2}\,t}{h}\right); where \Delta_A \equiv \rho^*_{A2} - \rho_{A2} \text{ and } \Delta^0{}_A \equiv \rho^*_{A2} - \rho^0_{A2}$$

$$\frac{{}^1k'_{A2}}{h} = \frac{\wp_{A2}}{h^{3/2}}^{1/2}$$

(100 marks)

6. A natural stream 0.8 m deep flows with an average velocity at 0.10 m/s. At a point where the waste outfall enters the stream after homogeneous mixing the concentration of the oxygen demanding organic materials is 30 mg/L. The oxygen demanding materials decays and utilizes oxygen according to the given equation ρ_{B2} at 0.5 per day;

$$\rho_{B2} = \rho_{B2}^{O} exp(-k_B^{'''} t^*)$$

$$\Delta_A^O = \rho_{A2}^* - \rho_{A2}^O$$

$$\Delta_A = \frac{K_{BB2}^{'''O}}{(^1_{K_{A2}} / h - k_b^{'''}} \left[\exp(-k_b^{'''} t) - \exp\left(\frac{-^1 k_{A2} t}{h} \right) \right] + \Delta_A^o \exp\left(\frac{-^1 k_{A2} t}{h} \right)$$

$$t_c = \frac{1}{(^1 k_{A2}^{'} / h) - k_B^{'''}} \ln \left\{ \frac{^1 k_{A2}^{'}}{h k_B^{'''}} \left[1 - \Delta_A^0 \left(\frac{(^1 k_{A2}^{'} / h) - k_B^{'''}}{k_B^{'''} \rho_{b2}^0} \right) \right] \right\}$$

$$\frac{^1 k_{A2}^{'}}{h} = \frac{\wp_{A2}}{h^{3/2}}^{1/2}$$

ρ_{A2}^* = 8.84 mg/l @ 20 ^oC

ϑ_{A2} =1.8 E-5 cm^2/s

$$t = \frac{L}{v_2}$$

Calculate what is the:

(a) Liquid mass transfer coefficient,

$^1k_{A2} = (\vartheta_{A2} v_x / h)^{1/2}$

(b) The dissolved oxygen concentration at 15 kilometers downstream if the after mixing homogeneous concentration at the outfall ρ_{A2}^O = 6 mg/L. Assume the stream water temperature is 20°C .

(100 marks)

…6/-

Bahagian A

Jawab LIMA daripada ENAM soalan daripada Bahagian A dan Bahagian B. Jawab soalan-soalan daripada setiap bahagian di dalam buku jawapan yang berasingan.

1. *(a) Apakah faktor yang mempengaruhi keterlarutan oksigen ke dalam air?*

(20 markah)

(b) Lakukan imbangan jisim ke atas seunit jisim bahan kimia X yang dimasukkan ke dalam suatu sungai yang mempunyai kedalaman yang malar, h. Anggap bahawa bahan kimia X akan lenyap kerana tindakbalas kimia darjah pertama di mana k_X ialah pemalar tindakbalas. Apakah anggapan-anggapan yang diperlukan untuk melakukan imbangan jisim di atas?

(50 markah)

(c) Dengan menggunakan persamaan yang didapati di (b), tentukan masa yang diperlukan untuk X lenyap sebanyak 99.99% dan jarak di mana ini akan berlaku. Anggap bahawa masa X dimasukkan ke dalam sungai ialah t = 0, halaju sungai tersebut ialah 2.7 m/s dan $k_X = 1.2 \times 10^{-3}\ s^{-1}$.

(30 markah)

2. *(a) Dalam bidang kimodinamik, apakah dimaksudkan dengan larutan unggul?*

(25 markah)

(b) Anggar pecahan mol etana di dalam air pada 30^oC jika etana tersebut hadir sebagai gas tulen pada 0.95 atm. Diberi $\gamma_{A2} = 8.10 \times 10^2$ pada 30^oC dan anggaran tekanan gas etana pada 30^oC ialah 45.4 atm. Adakah pecahan mol etana dalam air akan menjadi lebih tinggi atau rendah pada suhu melebihi 30^oC? Jelaskan.

(40 markah)

(c) Satu larutan kloroform dan air didedahkan ke udara pada 20^oC. Apakah pemalar pemisah kloroform pada keseimbangan jika keterlarutan kloroform di dalam air ialah 0.8 g / 100 ml air? Diberi $MW_{kloroform}$ = 119.378 g/mol dan tekanan gas kloroform pada 20^oC = 156.819 mmHg. Jelaskan jawapan anda.

(35 markah)

3. *Kandungan organik di dalam tanah dipengaruhi oleh pemisahan racun serangga antara fasa tanah dan air. Jadual 1 menunjukkan keputusan eksperimen keseimbangan ke atas tanah yang mempunyai kandungan organik melebihi 1%. Untuk setiap ujikaji, 4 mL daripada larutan 1.0 ppm ditambah kepada 1.0 g tanah. pH dikekalkan pada 2 dengan menggunakan HNO_3 and campuran tersebut diperam selama 1 jam.*

Jadual 1 Jerapan racun serangga organic oleh tanah pada pH 2 (% jisim)

Tanah	***Kandungan organik di dalam tanah***	***Racun serangga di dalam fasa cecair pada keseimbangan***	***Racun serangga di dalam tanah pada keseimbangan***
A	*1.0*	*51.0*	*49*
B	*2.7*	*23.0*	*77*
C	*4.1*	*11.0*	*89*
D	*10.7*	*5.8*	*94*
E	*32.2*	*2.0*	*98*

(a) Tentukan pemalar pemisah tanah-air, H^*_{A32} (L/kg tanah) untuk setiap jenis tanah.

(35 markah)

(b) Tentukan pemalar pemisah bahan organik-air, H^*_{AC2} (L/kg bahan organik) untuk setiap jenis tanah.

(40 markah)

(c) Hitungkan purata dan sisihan piawai untuk setiap pemalar.

(10 markah)

(c) Di mana antara pemalar adalah malar? Adakah ini mencadangkan apa-apa mengenai proses penjerapan ini?

(15 markah)

Bahagian B

4. *Persamaan dibawah menunjukkan kadar bahan organik mereput mengikut tindak balas tertib pertama.*

$$S = S_o \exp(-Kt^*)$$

(a) Plotkan rajah pembolehubah S lawan t pada koordinat Cartesan.
(b) Plotkan rajah ln S lawan t pada kertas semi- log.
(c) Tunjukkan dengan rajah yang menggambarkan input suatu lepasan air sisa yang mengalir masuk ke dalam sungai atau alur pada halaju U berhubung dengan persamaan di atas.
(d) Apakah yang dimaksudkan dengan pembolehubah K dalam persamaan di atas.

(100 markah)

5. *Masa yang diperlukan untuk satu arus memulih daripada keadaan hipotetikal tanpa oksigen terlarut ke hatap akhir ketepuan tertentu memberikan penunjuk mengenai kecepatan pengudaraan semula.*

   (a) Hitungkan masa yang diperlukan bagi satu arus tanpa oksigen untuk mencapai 50% ketepuan. Ini merupakan penyerapan oksigen separuh-hayat, $\Delta_{O2} = \Delta^{o}_{O2}/2$ bagi arus ini. Carikan jarak di hilir dan kepekatan oksigen.

   (b) Hitungkan masa yang diperlukan untuk mencapai 90% ketepuan. Carikan jarak dan kepekatan.
   Data arus: Halaju purata, v_w = 0.22 m/s; purata kedalaman h = 1.9 m; $D_{(O2)W}$ = 1.80 x 10^{-5} cm^2/s pada 20 ^oC; suhu air = 30 ^oC; koefisien suhu bagi sistem dalam julat suhu ialah θ = 1.018.

   $\rho_{(O2)W} = \rho^*_{(O2)W} - [\rho^*_{(O2)W} - \rho^o_{(O2)W}]exp[-k_{(O2)W}t/h]$
   $L = tv_w$
   Pada 30^oC, $\rho^*_{(O2)W}$ = 7.53 mg O_2/L
   $k_{(O2)W}/h = [D_{(O2)W}v_w]^{1/2}/h^{3/2}$
   $\Delta_{O2} = \rho^*_{(O2)W} - \rho_{(O2)W}$
   $k_{T1} = k_{T2}\theta^{(T1-T2)}$

$$\frac{\Delta A}{\Delta^0 A} = \exp\left(\frac{-{}^1k'_{A2}\,t}{h}\right); where \Delta_A \equiv \rho^*_{A2} - \rho_{A2} \; and \; \Delta^0{}_A \equiv \rho^*_{A2} - \rho^0_{A2}$$

$$\frac{{}^1k'_{A2}}{h} = \frac{\wp_{A2}}{h^{3/2}}^{1/2}$$

(100 markah)

6. *Sebatang sungai semulajadi kedalamannya 0.8 m mengalir dengan kelajuan purata 0.10 m/s. Pada satu titik dimana terdapat satu titik punca yang mendiscas sisa kedalam sungai dimana didapati bahawa kepekatan oksigen setelah air bercampur secara homogen ialah 30 mg/L. Jika kadar reputan bahan sisa ialah 0.5 per hari dan keperluan oksigen bagi bahan sisa mereput mengikut persamaan seperti ρ_{B2} yang diberikan ;*

$$\rho_{B2} = \rho_{B2}^{O} \exp(-k_B''' t^*)$$

$$\Delta_A^O = \rho_{A2}^* - \rho_{A2}^O$$

$$\Delta_A = \frac{K_{B\,B2}'''^{O}}{(^1K_{A2}/h - k_b''')} \left[\exp(-k_b''' t) - \exp\left(\frac{-^1k_{A2} t}{h}\right) \right] + \Delta_A^o \exp\left(\frac{-^1k_{A2} t}{h}\right)$$

$$t_c = \frac{1}{(^1k'_{A2}/h) - k_B'''} \ln\left\{ \frac{^1k'_{A2}}{h k_B'''} \left[1 - \Delta_A^0 \left(\frac{(^1k'_{A2}/h) - k_B'''}{k_B''' \rho_{b2}^0} \right) \right] \right\}$$

$$\frac{^1k'_{A2}}{h} = \frac{\vartheta_{A2}}{h^{3/2}}^{1/2}$$

ρ_{A2}^* = 8.84 mg/l @ 20 ^oC

ϑ_{A2} =1.8 E-5 cm^2/s

$$t = \frac{L}{v_2}$$

Kirakan berapakah:

(a) Koefisien pemindahan jisim fasa cecair

$^1k_{A2} = (\vartheta_{A2} v_x/h)^{1/2}$

(b) Kepekatan oksigen pada jarak 15 kilometer dari titek punca jika kepekatan oksigen pada titek punca percampuran ialah ρ_{A2}^O = 6 mg/L. Anggapkan bahawa suhu air sungai ialah pada 20^oC .

(100 markah)

…11/-

Table C.2. Dissolved-Oxygen Solubility Data
(dissolved oxygen mg/L)

Tempera-ture (°C)	Chloride Concentration (mg/L)				
	0[a]	5,000[b]	10,000[b]	15,000[b]	20,000[b]
0	14.16	13.79	12.97	12.14	11.32
1	13.77	13.41	12.61	11.82	11.03
2	13.40	13.05	12.28	11.52	10.76
3	13.05	12.72	11.98	11.24	10.50
4	12.70	12.41	11.69	10.97	10.25
5	12.37	12.09	11.39	10.70	10.01
6	12.06	11.79	11.12	10.45	9.78
7	11.76	11.51	10.85	10.21	9.57
8	11.47	11.24	10.61	9.98	9.36
9	11.19	10.97	10.36	9.76	9.17
10	10.92	10.73	10.13	9.55	8.98
11	10.67	10.49	9.92	9.35	8.80
12	10.43	10.28	9.72	9.17	8.62
13	10.20	10.05	9.52	8.98	8.46
14	9.98	9.85	9.32	8.80	8.30
15	9.76	9.65	9.14	8.63	8.14
16	9.56	9.46	8.96	8.47	7.99
17	9.37	9.26	8.78	8.30	7.84
18	9.18	9.07	8.62	8.15	7.70
19	9.01	8.89	8.45	8.00	7.56
20	8.84	8.73	8.30	7.86	7.42
21	8.68	8.57	8.14	7.71	7.28
22	8.53	8.42	7.99	7.57	7.14
23	8.38	8.27	7.85	7.43	7.00
24	8.25	8.12	7.71	7.30	6.87
25	8.11	7.96	7.56	7.15	6.74
26	7.99	7.81	7.42	7.02	6.61
27	7.86	7.67	7.28	6.88	6.49
28	7.75	7.53	7.14	6.75	6.37
29	7.64	7.39	7.00	6.62	6.25
30	7.53	7.25	6.86	6.49	6.13

[a]Solubility of oxygen from a wet atmosphere at a pressure of 760 mm Hg.
Source. G. E. Hutchinson, *A Treatise on Limnology*, Wiley, New York, 1957.

* Saturation values of dissolved oxygen in fresh and seawater exposed to dry air containin% 20.90% oxygen under a total pressure of 760 mm of mercury.

Source: G. C. Whipple and M. C. Whipple, "Solubility of Oxygen in Sea Water," *J. Am.Chem. Soc*,33, (1911), 362.