UNIVERSITI SAINS MALAYSIA

Peperiksaan Kursus Semasa Cuti Panjang
Sidang Akademik 2007/2008

June 2008

KFT 232 – Physical Chemistry II
[Kimia Fizik II]

Duration: 3 hours
[Masa : 3 jam]

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

Instructions:

Answer any **FIVE** (5) questions with at least **ONE** question from Part B.

Answer 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/-

PART A
Answer not more than **FOUR** questions.

1. In the expansion of 1 mol of an ideal gas from initial volume of 0.010 m^3 to final volume of 0.100 m^3 at 25 °C.

   (a) Calculate the work done by the following processes:

   (i) Against a constant external pressure of 1 atm.

   (ii) Change from 0.010 m^3 to 0.025 m^3 against a constant external pressure of 0.330 atm, followed by a second expansion from 0.025 m^3 to 0.050 m^3 against a constant external pressure of 0.200 atm and a third expansion from 0.050 m^3 to 0.100 m^3 against a constant pressure of 0.100 atm.

   (iii) A reversible expansion.

   (17 marks)

   (b) Give comment on the work done by the above processes.

   (3 marks)

2. A reversible four-stroke engine uses 1 mol of an ideal gas as a working material. The four strokes are as follows:

   Stroke 1: Expansion from (P_1, V_1, T_1) to (P_1, V_2, T_2)

   Stroke 2: Cooling from (P_1, V_2, T_2) to (P_2, V_2, T_3)

   Stroke 3: Compression from (P_2, V_2, T_3) to (P_2, V_1, T_4)

   Stroke 4: Heating from (P_2, V_1, T_4) to (P_1, V_1, T_1)

   If C_V^m and C_P^m are 1.5 R and 2.5 R, respectively:

   (a) Sketch a complete diagramme of pressure – volume plot for the operational four- stroke engine.

   (5 marks)

   (b) Obtain an expression for the net work per cycle of the engine in terms of various temperatures.

   (8 marks)

(c) Obtain an expression for the total heat given to the engine in one cycle as a function of various temperatures.

(7 marks)

3. (a) From the relevant thermodynamic equation, obtain the criteria required for the equilibrium and spontaneity of a chemical reaction at constant entropy and pressure.

(8 marks)

(b) For a reversible heating of 1 mol ethane from 298 to 1000 K at constant pressure, the C_p value is given as

$$C_p = (5.350 + 186.532 \times 10^{-2} T - 584.12 \times 10^{-6} T^2 + 5.184 \times 10^{-8} T^3) \text{ J K}^{-1} \text{ mol}^{-1}$$

Calculate $\Delta S_{(system)}$ for the above system. If the above process is carried out irreversibly by placing the gas in the oven at 1000 K, calculate $\Delta S_{(surrounding)}$ and $\Delta S_{(universe)}$.

(12 marks)

4. (a) Show that by using the relevant thermodynamic equation, the internal energy for an ideal gas is independent of the constant volume and temperature,

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

(10 marks)

(b) Consider the following chemical reaction

$$Cl_2 (g) + F_2 (g) \rightarrow 2 ClF (g) \qquad \Delta G°_{298} = -111.88 \text{ kJ}$$

If the pressures for $P_{(Cl2)} = 16.3$ bar, $P_{(F2)} = 5.2$ bar and $P_{(ClF)} = 0.063$ bar, determine the free energy change under this condition. Comment.

(10 marks)

5. (a) What is meant by the molar volume and partial molar volume of a substance?

Show that for a specific temperature and pressure, the volume of a solution, V, consisting of two components A and B, is given by the following equation

$$V = n_A \overline{V}_A + n_B \overline{V}_B$$

where n_A and n_B are the number of moles of A and B, respectively; $\overline{V}_A$ and $\overline{V}_B$ are the partial molar volumes of A and B, respectively.

(8 marks)

(b) At 75 °C, the vapour pressures for HNO_3 and H_2O are 4,670 and 11,500 Pa, respectively, in a nitric acid solution with a HNO_3 weight fraction of 0.650. Calculate the

(i) partial vapour pressure of ideal solution,

(ii) total vapour pressure of ideal and real solutions, and

(iii) mole fractions of the components for ideal and real solutions.

Given: Vapour pressures of pure HNO_3 and H_2O are 71,990 and 38,540 Pa, respectively.

(12 marks)