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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]*

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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.

**PART A**

Answer not more than **FOUR** questions.

1. In the expansion of 1 mol of an ideal gas from initial volume of  $0.010 \text{ m}^3$  to final volume of  $0.100 \text{ m}^3$  at  $25 \text{ }^\circ\text{C}$ .
- (a) Calculate the work done by the following processes:
- (i) Against a constant external pressure of 1 atm.
- (ii) Change from  $0.010 \text{ m}^3$  to  $0.025 \text{ m}^3$  against a constant external pressure of 0.330 atm, followed by a second expansion from  $0.025 \text{ m}^3$  to  $0.050 \text{ m}^3$  against a constant external pressure of 0.200 atm and a third expansion from  $0.050 \text{ m}^3$  to  $0.100 \text{ m}^3$  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  $\Delta S_{(\text{system})}$  for the above system. If the above process is carried out irreversibly by placing the gas in the oven at 1000 K, calculate  $\Delta S_{(\text{surrounding})}$  and  $\Delta S_{(\text{universe})}$ .

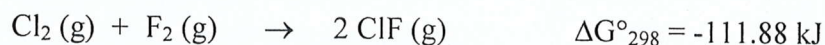
(12 marks)

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



If the pressures for  $P_{(\text{Cl}_2)} = 16.3 \text{ bar}$ ,  $P_{(\text{F}_2)} = 5.2 \text{ bar}$  and  $P_{(\text{ClF})} = 0.063 \text{ bar}$ , determine the free energy change under this condition. Comment.

(10 marks)

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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

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

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

(8 marks)

- (b) At 75 °C, the vapour pressures for HNO<sub>3</sub> and H<sub>2</sub>O are 4,670 and 11,500 Pa, respectively, in a nitric acid solution with a HNO<sub>3</sub> weight fraction of 0.650. Calculate the
- partial vapour pressure of ideal solution,
  - total vapour pressure of ideal and real solutions, and
  - mole fractions of the components for ideal and real solutions.

Given: Vapour pressures of pure HNO<sub>3</sub> and H<sub>2</sub>O are 71,990 and 38,540 Pa, respectively.

(12 marks)