國立成功大學 105 學年度碩士班招生考試試題

系　　所：化學工程學系

考試科目：物理化學

考試日期：0227，節次：3

※ 考生請注意：本試題可使用計算機。　請於答案卷(卡)作答，於本試題紙上作答者，不予計分。

1. Answer each of the following questions with Y (Yes) or N (No). (14%)
   (a) The internal energy of an isolated system is constant whether it undergoes a reversible or an irreversible process.
   (b) The entropy is conservative for any cyclic process whether it undergoes a reversible or an irreversible process.
   (c) Most substances contract on freezing, and for them the slope for the melting line is positive.
   (d) The dissolution of sodium chloride in water always causes an increase in entropy.
   (e) In a dilute solution, the activity coefficient of an ion species is increased with increasing the ionic strength.
   (f) The activation energy of a reaction is always positive.
   (g) Due to mixing, a simple gas reaction never goes to completion.

2. Two moles of a monatomic ideal gas is expanded isothermally and reversibly at 25 °C from 5 to 1 bar. Calculate q, w, ΔH, ΔU, ΔG, ΔA, and ΔS for the gas. (14%)

3. The following thermodynamic data apply to the complete oxidation of butane at 25 °C.

   $C_4H_{10}(g) + 13/2O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$ $\quad \Delta H^o = -2877\ kJ\ mol^{-1}$

   $\Delta S^o = -432.7\ J\ K^{-1}\ mol^{-1}$

   Suppose that a completely efficient fuel cell could be set up utilizing this reaction. Calculate (a) the maximum electrical work and (b) the standard emf of the cell. (14%)

4. Oxygen at pressures that are not too high obeys the van der Waals' equation

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT.$$

   The constants a and b are 0.1378 Pa m^6 mol^{-1}, and 0.0318 x 10^{-3} m^3 mol^{-1}, respectively.

   (a) Show that the fugacity f can be expressed as $f = P\exp\left[\frac{P}{RT}(b - \frac{a}{RT})\right]$ starting from

$$RT\ln\frac{f}{P} = \int_0^P (V_m - \frac{RT}{P})dP.$$ (8%)

   (b) Calculate ΔG at 25°C if the pressure is raised from 1 bar to 5 bar. (6%)

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5. The standard Gibbs energy of formation of NO_2 and N_2O_4 are 51.31 and 97.89 kJ mol^{-1}, respectively, at 298.15 K. For the reaction $N_2O_4(g) = 2NO_2(g)$, calculate the equilibrium constant K_P and Gibbs energy change ΔG°. If only one mole of NO_2 exists in the reaction system initially, and the total pressure is 2 bar, what is the extent of reaction in equilibrium? (15%)

6. The reaction $2NO + O_2 \rightarrow 2NO_2$ is believed to occur by the mechanism:

$$2NO \xrightarrow{k_1} N_2O_2$$

$$N_2O_2 \xrightarrow{k_{-1}} 2NO$$

$$N_2O_2 + O_2 \xrightarrow{k_2} 2NO_2$$

Assume N_2O_2 to be in a steady state and derive the rate equation. Under what conditions does the rate equation reduce to second-order kinetics in NO and first-order kinetics in O_2 ? (15 %)

7. For the parallel reversible first-order reactions

$$C \underset{k_2}{\overset{k_{-2}}{\rightleftarrows}} A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B, \quad [A] = [A]_0, \text{ and } [B] = [C] = 0 \quad \text{at} \quad t = 0.$$

The equilibrium constants for the formation of B and C from A are given by

$$K_1 = \frac{k_1}{k_{-1}} \quad \text{and} \quad K_2 = \frac{k_2}{k_{-2}}.$$

(a) Derive the equilibrium concentrations of A, B, and C. (6%)

(b) If $k_1 = 1$, $k_{-1} = 0.01$, $k_2 = 0.1$, and $k_{-2} = 0.0005\ s^{-1}$, show that B is formed initially 10 times faster than C (*i.e.*, $[B] = 10[C]$) and, C is twice of B (*i.e.*, $[C] = 2[B]$) at infinite time. (8%)