國立成功大學
114學年度碩士班招生考試試題

編　號：61

系　所：化學工程學系

科　目：物理化學

日　期：0210

節　次：第 3 節

注　意：1.可使用計算機
　　　　2.請於答案卷(卡)作答，於
　　　　　試題上作答，不予計分。

Useful constants:

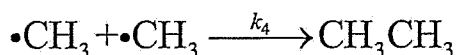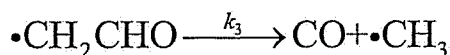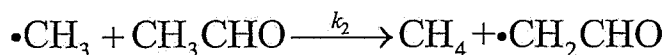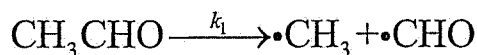F=96485 C mol^{-1}

R= 8.315 J K^{-1} mol^{-1}

1. Derive the following relationships:

   (a) The entropy of a perfect gas depends on the volume, $S \propto R\ln(V)$ (8%)

   (b)

   $$\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

   (8%)

2. A layer of certain liquid (density 0.9 g·cm^{-3}) is floating on water with density 1.0 g·cm^{-3}, and a vertical tube of internal diameter 0.1 mm is inserted at the interface. It is observed that there is a capillary rise of 3.0 cm and that the contact angle is 45°. Calculate the interfacial tension between water and this liquid. (10%)

3. A certain solid sample adsorbs 0.63 mg of CO when the pressure of the gas is 36.0 kPa and the temperature is 300 K. The mass of gas adsorbed at 4.0 kPa and 300 K is 0.21 mg. The Langmuir isotherm is known to describe the adsorption. Find the fraction coverage of the surface at the two pressures. (10%)

4. In some catalytic reactions, the products may adsorb more strongly than the reacting gas. For example, the catalytic decomposition of ammonia on platinum at 1000 °C (NH$_3$ → 1/2N$_2$+3/2H$_2$).

   (a) Show that the rate of ammonia decomposition should follow $\frac{dP_{NH_3}}{dt} = -k_c \frac{P_{NH_3}}{P_{H_2}}$ (10%)

   (b) Solve the rate equation for the catalytic decomposition of NH$_3$ on platinum and show that $F(t) = (1/t)\ln(P/P_0)$ against $G(t) = (P - P_0)/t$, should give a straight line from which k_c can be determined. (P is the pressure of ammonia. P_0 is the initial pressure of ammonia.) (10%)

5. The following free-radical mechanism has been proposed for the thermal decomposition of acetaldehyde (CH$_3$CHO) to methane (CH$_4$) and ethane (CH$_3$CH$_3$). Find an expression for the formation rate of methane and the disappearance rate of acetaldehyde. (14%)

$$CH_3CHO \xrightarrow{k_1} \cdot CH_3 + \cdot CHO$$

$$\cdot CH_3 + CH_3CHO \xrightarrow{k_2} CH_4 + \cdot CH_2CHO$$

$$\cdot CH_2CHO \xrightarrow{k_3} CO + \cdot CH_3$$

$$\cdot CH_3 + \cdot CH_3 \xrightarrow{k_4} CH_3CH_3$$

6. 1.00 mol of perfect gas molecules at 27 °C is expanded isothermally from an initial pressure of 3.00 atm to a final pressure of 1.00 atm in two ways: (a) reversibly and (b) against a constant external pressure of 1.00 atm. Calculate the values of q, w, ΔU, ΔH, ΔS, ΔS_{sur}, ΔS_{tot} for each path.   (12%)

7. Consider the following cell:

$$Pt, H_2(1 \text{ bar})|HCl(aq)|AgCl(s)|Ag$$
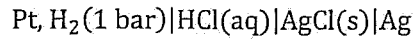
The cell reaction is $2AgCl(s)+H_2(g) \rightarrow 2Ag(s)+2HCl(aq)$, at 25 °C and a molality of HCl of 0.01 mol/kg, $E^O=+0.2223V$.

(a) Calculate the emf of this cell, neglecting the correction of the activity coefficient.   (6%)

(b) Write the Nernst equation that includes activity coefficients for the cell reaction.   (6%)

(c) Assuming that the Debye-Hückel limiting law holds at this concentration, calculate the emf again.   (6%)