國立高雄科技大學 109 學年度碩士班 招生考試 試題紙

系 所 別：化學工程與材料工程系碩士班　　組　別：乙組

考科代碼：1014　　考　科：物理化學

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注意事項：

1、各考科一律可使用本校提供之電子計算器，**考生不得使用自備計算器**，違者該科不予計分。

2、請於答案卷上規定之範圍作答，違者該題不予計分。

本試題共六題，共 100 分。

Given: 1 atm = 1.013 bar = 760 torr, 1 bar = 10^5 Pa

ln (0.1) = −2.303, ln (0.64) = −0.446, $(1/10)^{0.4}$ = 0.398

1. Methanol, a fuel for direction methanol fuel cells, can be synthesized by the following reaction:

$$CO(g) + 2H_2(g) = CH_3OH(g)$$

The reaction was carried out at 523 K and the equilibrium constant K is $6.5*10^{-3}$. Calculate the total pressure (bar) required for an 80% conversion to methanol if CO(g) and H_2(g) are initially in a 1:2 molar ratio. (**5 points**)

2. Benzene and toluene form very nearly ideal solutions. At 333 K, the vapor pressures of benzene and toluene are 51.3 and 18.5 kPa, respectively.
   (a) As the pressure reduced, at what pressure the equimolar mixture of benzene and toluene begins to boiling and what will be the composition of the first bubble of vapor? (**8 points**)
   (b) What composition of solution would boil at 333 K under reduced pressure of 190 torr ? (**4 points**)

3. One mole of monoatomic ideal gas was initially at 10 bar and 300 K, please calculate *w*, *q*, ΔU and ΔS when the gas is allowed to expands according to the following processes:
   (a) Isothermally, reversible to 1.0 bar (*w*, *q*, ΔU and ΔS=?) (**12 points**)
   (b) Adiabatically, reversible to 1.0 bar (*w*, *q*, ΔU and ΔS=?) (**12 points**)
   (c) Adiabatically against a constant pressure of 1.0 bar until the final pressure is 1.0 bar (*w*, *q*, ΔU and ΔS=?) (**14 points**)

   Note: *w*=work, *q*=heat, ΔU=internal energy change and ΔS= entropy change

   C_v = (3/2)R and C_p = (5/2)R for monoatomic ideal gas, R=8.314 J K^{-1} mol^{-1}

4. Derive (a) the internal energy change (ΔU) and (b) the entropy change (ΔS) of the system undergoes an isothermal, reversible expansion from initial volume V_1 to final volume V_2 for gas following the equation of state of van der Waals gas as below. (**10 points**)

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

5. Effect of temperature on the Gibbs energy:
   (a) Please derive the Gibbs-Helmholtz equation (**5 points**)

$$H = -T^2\left[\frac{\partial G/T}{\partial T}\right]_P$$

   (b) If the Gibbs energy varies with temperature according to

$$G/T = a + b/T + c/T^2$$

   Where *a* and *b* are constants, how will the enthalpy and entropy vary with temperature? (**10 points**)
   (c) Integrate the Gibbs-Helmholtz equation to obtain an expression for ΔG_2 at temperature T_2 in terms of ΔG_1 and T_1, assuming that ΔH is independent of temperature. (**5 points**)

6. A gas follows the virial equation

$$Z = \frac{P\overline{V}}{RT} = 1 + \left(b - \frac{a}{RT}\right)\frac{P}{RT}$$

   (a) What is the expression for fugacity, *f ?* you can start from the equation below (5 **points**)

$$\ln\left(\frac{f}{P}\right) = \frac{1}{RT}\int_0^P (\overline{V} - \overline{V}^{\mathrm{id}})\,\mathrm{d}P$$

   where $\overline{V}$ is molar volume, $\overline{V}^{\mathrm{id}}$ is molar volume of ideal gas

   (b) What is the expression for Joule-Thomson coefficient? (**10 points**)