1. (16%)

A piston/cylinder arrangement is placed in a constant-temperature bath. The piston slides in the cylinder with negligible friction, and an external force holds it in place against an initial pressure of 10,000 Pa. The cylinder contains 1mole ideal gas with the initial volume of 0.5 m^3. The gas constant R = 8.314 Joule $mole^{-1}$ K^{-1}.

(a) The external force on the piston is reduced gradually, and the gas expands isothermally as its volume doubles. What is the work done by the gas? (4%)

(b) How much work would be done if the gas were suddenly expanded to double of its initial value instead of being gradually expanded? (4%)

(c) In comparison with (a) and (b), which case has a greater work done? Explain why. (4%)

(d) For real gases, would the conclusion in (c) be also true? Explain why. (4%)

2. (17%)

One mole of gas in a closed system undergoes an adiabatic expansion. At the initial state, the pressure and the temperature are V_1 and T_1, respectively. The final volume of the gas is $2V_1$. The gas obeys the following equation of state:

$$\frac{PV}{RT} = 1 + B'P,$$

where the coefficient B' is assumed to be a constant. The heat capacity at constant volume is given by $Cv = 3R/2$.

(a) Is the final temperature T_2 expected to be lower or higher than T_1? Explain why without solving the problem in detail. (4%)

(b) Determine T_2. (5%)

(c) If $B' < 0$, would the answer to (b) be lower or higher than that of ideal gas? (4%)

(d) Provide a plausible explanation for (c). (4%) (背面仍有題目,請繼續作答)

3. (16%)

Consider a reversible cycle traversed by an ideal gas as the working fluid. It consists of four following reversible steps:

1. a → b: adiabatic compression from a to b
2. b → c: isothermal expansion from b to c
3. c → d: adiabatic expansion from c to d
4. d → a: isothermal compression from d to a

(a) Please sketch the complete cycle on a *P*–*V* diagram according to the above statements, where *P* and *V* stand for pressure and volume. **(5%)**

(b) What is the entropy change from a to c? That is, to estimate the entropy change from a → b → c. **(5%)**

For your convenience, you can assume there is only one mole of ideal gas in the system. Use T_j for temperature of the ideal gas at state *j*. Please label all variables used clearly and describe them precisely.

(c) What is the entropy change of the whole cycle? **(3%)**

(d) How much work in maximum can the working fluid perform in a complete cycle? **(3%)**

4. (17%)

If John conducts a series of thermodynamic experiments for a homogeneous fluid of constant composition at different temperature *T* and pressure *P*, he measures and records *T* and *P* only. Certainly, he gets the Gibbs free energy G. However, he tries to obtain other thermodynamic quantities, such as volume *V*, enthalpy *H*, entropy *S* and internal energy *U*.

(a) Please advise him how to find all of them. **(6%)**

(b) Meanwhile, if John can get the residual Gibbs free energy from his experimental data, can you help him obtain the residual enthalpy and entropy under a constant-*T* condition? Please make your suggestion. **(6%)**

(c) If Tom challenges John on the consistency of his experimental data, could you advise him how to respond it? Please briefly describe your strategy only. **(5%)**

5. (20%)

Please explain the following rules and write down the respective equations. **(9%)**

(a) Raoult's law; (b) Henry's law; (c) Lewis/Randall rule

Please plot Fig. 1 on your answer sheet, and draw Henry's law and Lewis/Randall rule on the figure. **(4%)**

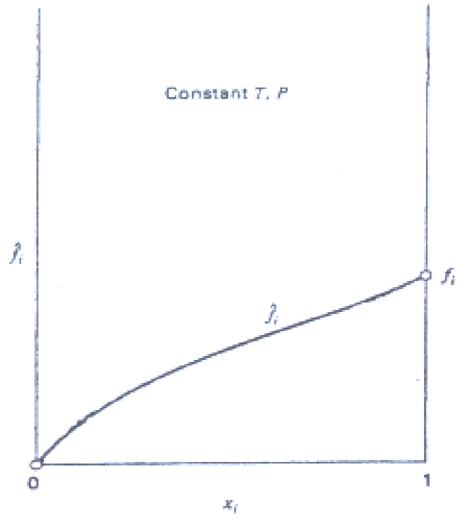

Figure 1 Composition dependence of fugacity for species *i* in a binary solution.

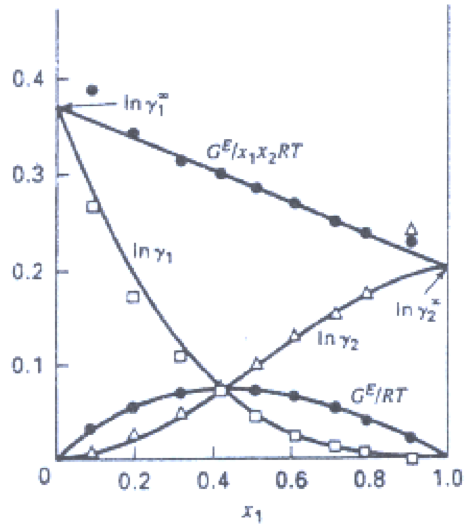

Figure 2 The methyl ethyl ketone(1)/toluene(2) system at 50°C.

Describe the characteristics of the following curves:

G^E/RT **(2%)**; $ln\gamma_1$ **(3%)**; the relation between $d\,ln\gamma_1/dx_1$ and $d\,ln\gamma_2/dx_1$ **(2%)**

6. (14%)

The volume change of mixing ($cm^3\ mol^{-1}$) for the system ethanol(1)/methyl butyl ether(2) at 25°C is given by the equation:

$$\Delta V = x_1 x_2 \cdot [-1.026 + 0.220 \cdot (x_1 - x_2)]$$

Given that $V_1 = 58.63$ and $V_2 = 118.46\ cm^3\ mol^{-1}$, what volume of mixture is formed when 600 cm^3 of pure species 1 is mixed with 1,200 cm^3 of species 2 at 25°C? What would be the volume if any idea solution were formed?