國立中正大學八十二學年度碩士班考試試題

所　別：化學工程研究所　　科　目：化工熱力學與化工動力學

Thermodynamics

1. For a reversible adiabatic process of an ideal gas with constant heat capacities, please derive an equation relating temperature and volume. (6%)

2. Calculate the entropy change of the following system:
   (a) One mole idea gas A occupied a volume of 1 liter is mixed with 2 moles of idea gas B occupied a volume of 1 liter, and the mixture is occupied a volume of 2 liters. (4%)
   (b) Repeat (a) but the mixture is brought to a volume of 1 liter. (4%)

3. Determine the number of degrees of freedom F for each of the following system:
   (a) A system prepared by partially decomposing $CaCO_3$ into an evacuated space at 350 °C. (4%)
   (b) A gaseous system consisting of CO, CO_2, H_2, H_2O, and CH_4 in chemical equilibrium at one atmosphere. (4%)

4. Figure 1 shows a PT diagram of a binary mixture, where point C indicates the mixture critical point. Please describe what is going to happen if an isothermal process occurs from A to B. (6%)

5. Derive an expression of fugacity, Φ, for a gas whose PVT behavior is given by the virial equation, (6%)

$$Z = 1 + \frac{B\,P}{R\,T}$$

6. A gas that is at a temperature T_o is flowing in a pipe (Fig. 2). A small amount of gas flow into an evacuated cylinder. The flow continues until the pressure in the cylinder is equal to P_o, the pressure in the pipe. If the cylinder is perfectly insulated and the gas is ideal (with C_p and C_v independent of temperature and pressure), find the temperature, T, which exists in the cylinder at the end of the process, in terms of T_o, C_p, C_v, and P_o alone. (8%)

7. Estimate the demand of cooling-water for a 1 million-kW nuclear-powered thermal power station, if the heat engine is approximated by a Carnot cycle operating between 327 and 87 °C and the maximum temperature rise in the cooling is restricted to 20 °C. Express the amount of water in terms of liters/s and use a heat capacity of water of 1 cal/g. (8%)

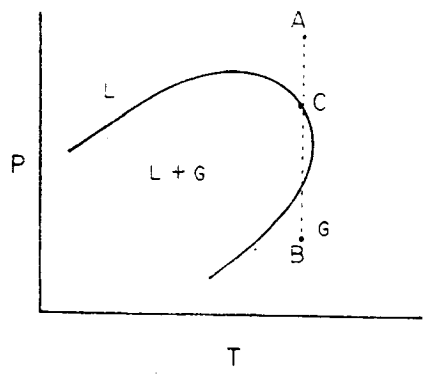


FIG 1

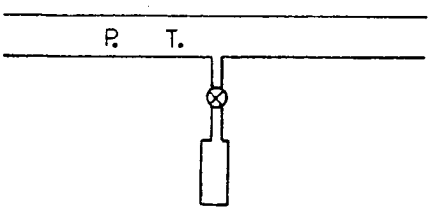
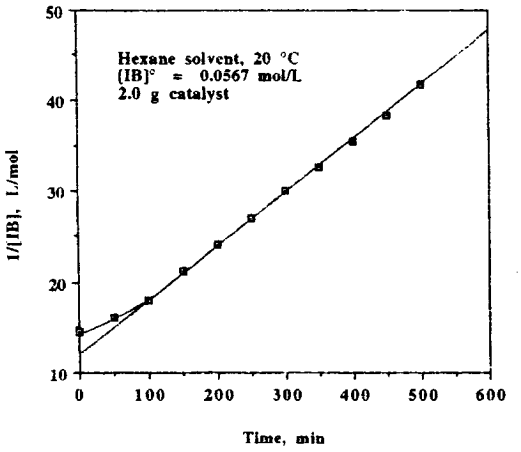
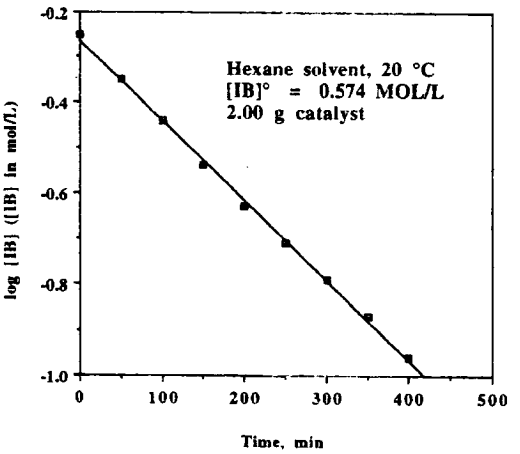


FIG 2

化工動力學 50%

1. Haag, W.O., Chem. Eng. Prog. Symp., Ser., 63, No. 73, 140 (1967)





上圖爲異丁烯 [IB] 以 Poly(Styrenesulfonic acid)爲觸媒生成 dimer $[IB_2]$之反應動力學數據

5% (a). 根據以上數據證明在異丁烯[IB]濃度低時爲二次反應而在高濃度時爲一次反應,並求出其反應速率常數.

$r = k[IB]^2$, $[IB]^\circ < 0.1$ mol/L

$r = k[IB]$, $[IB]^\circ > 0.4$ mol/L

$[IB]^\circ$ 爲反應之初濃度

10% (b). 下式的反應機構能否滿足上述實驗數據?請詳細推導並證明之.

$IB + S \rightleftharpoons IBS^*$ (快)

$IBS^* + IB \rightarrow IB + S$ (慢)

上式 S 爲觸媒之活化基(Active Site),且活化基的總數不變

$[S]^\circ = [S] + [IBS^*]$

2. 請以公式及文字解釋下列各名詞的物理意義.

3% (a). Space time

3% (b). autocatalytic reaction

3% (c). effctiveness factor

3% (d). transition state

3% (e). Thiele modulus

P.2

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3. 請簡答下列問題

5% (a). 說明Plug flow reactor (PFR) 與 Continuous-stirred tank reactor (CSTR) 之不同點，並以圖示法表示如何計算理想之CSTR及PFR之反應器大小.

5% (b). 如何由實驗方法證實一在固定床中之觸媒反應存在內在質傳限制 (Internal Mass Transfer Limitation).

5% (c). 請由觸媒物化性及反應性的觀點分別討論在什麼情況下選擇(1)固定床，(2)移動床，及(3)流體化床反應器.

5% (d). 試比較以微分法 (differential method) 或積分法 (integral method)分析反應動力數據之優缺點?