國立臺灣科技大學
九十學年度碩士班招生考試試題

系所組別： 化學工程系
科　目： 化工熱力學與動力學　　本科總分為 100 分

Part I. 化工熱力學

(1) A heat engine is a device, considered a closed system operating in a cyclic manner, that is supplied with heat and performs work. The Carnot engine regulates the maximum efficiency of a heat engine with which heat could be converted into work.

(a) If an ideal gas is chosen as the working fluid, please start from the first law of thermodynamics to show that the net work of a cycle is $R(T_2 - T_1)\ln(V_c / V_b)$, where R is the gas constant and V is the volume. (8%)

(b) Please show that the thermal efficiency of the Carnot engine, which is defined as the ratio of net work output to heat input, to be a function of temperatures. (5%)

(c) Please explain two main reasons why the efficiency of a real heat engine cannot exceed the theoretical value defined in question (b). (6%)

(d) The Carnot engine, when operated in reverse, becomes a heat pump. A heat pump is required to supply 24000BTU/h to a house when the outdoor temperature is 20^0F . If the house is to be kept at 70^0F , what is the minimum power (in kW) demand? (1 J = 9.486×10^{-4} BTU, $T(^\circ R) = 459.67 + t(^\circ F)$) (6%)

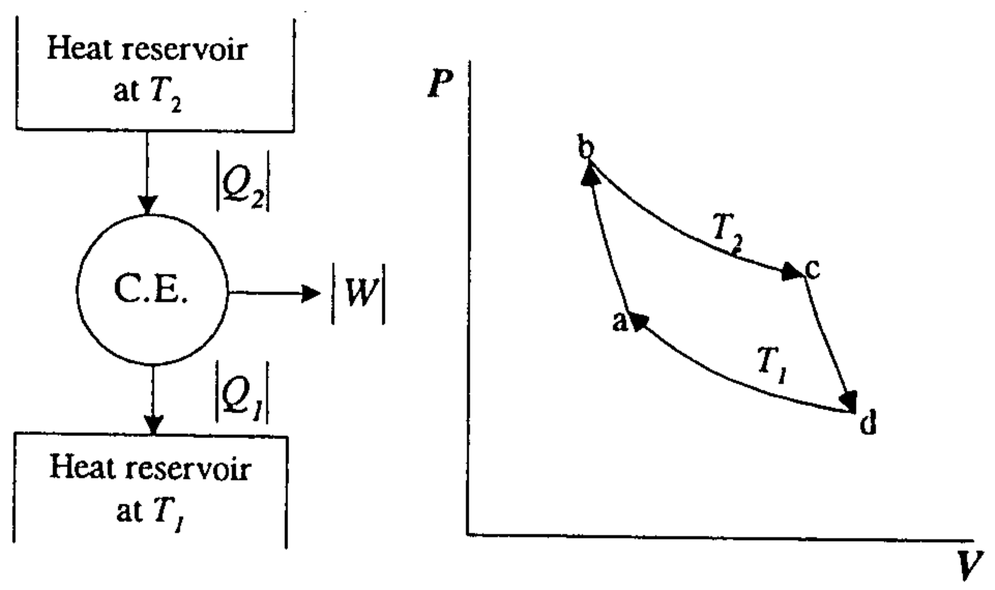

Fig. 1 Carnot engine and its representation in PV diagram.

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(2) (*i*) The fugacity f is defined in terms of the chemical potential (μ), and for a pure substance the relationship is $\mu = \mu_0 + RT \ln f$, where μ_0 is a function only of temperature.

(a) To determine how fugacities are related to measurable properties, please begin with the differential of the chemical potential ($d\mu$) and apply a basic equation of $dg = -sdT + vdP$ (g, s, and v are the molar Gibbs free energy, entropy, and volume, respectively) to show that the fugacity coefficient ($\phi = f/P$, P is the gas pressure) of a pure gas at a constant temperature is given by $\ln \phi = \int_0^P (Z-1)\frac{dP}{P}$ (where Z is the compressibility factor). (6%)

(b) Show the relation between ln ϕ and the residual Gibbs free energy (Δg^*). (4%)

(*ii*) The activity coefficient γ_i is introduced to correct the ideal liquid solution model into the real vapor pressure of species i (p_i) in the gas-liquid equilibrium of a real liquid solution as $\gamma_i = (\frac{p_i}{p_i^0 x_i})$, where $p^0{}_i$ is the vapor pressure of pure liquid species i, and x_i is the molar fraction of species i in the liquid solution.

(c) Fig. 2 is the partial pressures of water-ethanol solutions at 40 ℃. Please find the activity coefficients for water and ethanol when the molar fraction of ethanol is 0.1. The same question when the molar fraction of ethanol is 0.9. (8%)

(d) In a binary A-B system, the vapor-liquid equilibrium data at 350 K shows that component B follows Henry's law in the range $0 < x_B \le 0.05$. At this temperature the following data point has been reported as $x_A = 0.975, y_A = 0.942, P = 1035$ mmHg, where y is the gas molar fraction and P is the total pressure. Also the vapor pressures are known to be $p_A^0 = 1000$ mmHg, $p_B^0 = 800$ mmHg. Calculate the Henry's constant of this system, and y_B and P when $x_B = 0.04$. (7%)

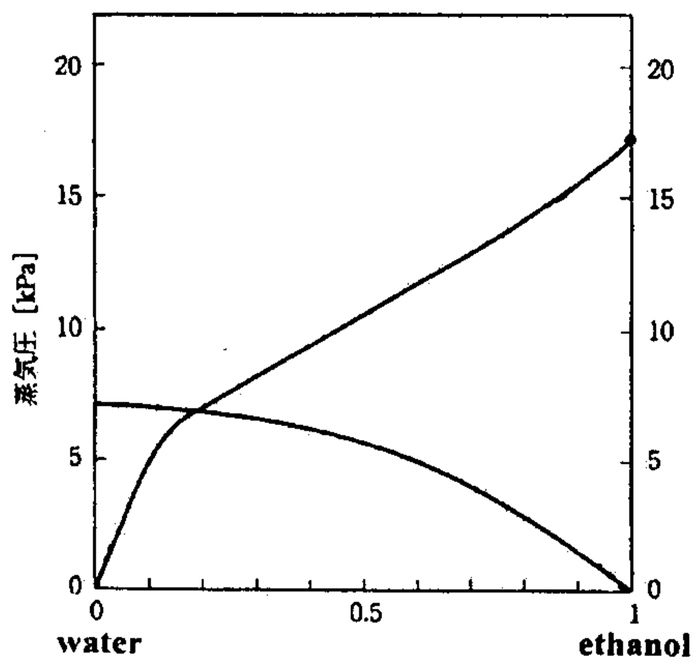

Fig. 2 Equilibrium vapor pressures of water-ethanol binary system at 40 ℃

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Part II. 化工動力學

(3) 氣相反應 A⟶R 的速率式爲 $-r_A = kP_A^2$，其中 $k = 17.3$，$-r_A$ 的單位爲 lb-mol/ft^{3}h，P_A 的單位爲 atm，若反應在 1 atm、72°F(532°R)下進行，
(a) 試問 k 的單位爲何？(5%)
(b) 若速率式寫成 $-r_A = k'C_A^2$，C_A 的單位爲 lb-mol/ft^3，試計算 k' 值並標示其單位。[假設氣體爲理想氣體，理想氣體常數 R = 1.314 atm-ft^3/lb-mol°R] (10%)

(4) 三氧甲烷(trioxane)可在硫酸的存在下分解爲甲醛(formaldehyde)，今以 8 N 的硫酸在 20°C 的批式反應器中液相分解三氧甲烷，得到以下的數據：

反應時間(day)	0	0.51	3.4	6.8
轉化率	0	0.10	0.50	0.75

假設反應爲不可逆，三氧甲烷的初濃度 C_{A0} = 1 mol/dm^3，試決定此反應的反應級數(reaction order)並計算其反應速率常數。(15%)

(5) 今有液相接續反應(consecutive reaction)， $A \xrightarrow{k_1} B \xrightarrow{k_2} C$，於 CSTR 中進行，若進料爲純 A，其濃度爲 C_{A0}，兩階段的反應皆爲一級(first order)，且速率常數 $k_1=k_2$ (min^{-1})，反應器中反應液的體積爲 V，試計算穩態時產物 B 可達成的最大濃度及達成此濃度所需的進料體積流率。(20%)

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