系所組別： 化學工程學系甲組

考試科目： 化工熱力學

※ 考生請注意：本試題可使用計算機，並限「考選部核定之國家考試電子計算器」機型

一、

(14%) Please list the conditions that satisfy $Q = \Delta H$. **(list all the possible cases)**

二、

(19%) The dehydrogenation of butene to butadiene is an endothermic reaction:

$$C_4H_8(g) \rightarrow C_4H_6(g) + H_2(g).$$

This reaction is to be carried out at atmospheric pressure and to minimize the temperature drop, the reactor feed will consist of 10 mol of steam per mol of butene. The steam is nonreactive. The mixture enters the reactors at 900 K and at atmospheric pressure. What will be the maximum reactor effluent temperature when 20% of the butene has been converted? **[Note] Please do trial & error EXACTLY three times to obtain the answer.** The following are the data you might need.

$C_P^{ig}/R = A + BT + CT^2 + DT^{-2}$ T (K) from 298 to T_{max}

Chemical species		T_{max}	$C_{P,298}^{ig}/R$	A	$10^3 \cdot B$	$10^6 \cdot C$	$10^{-5} \cdot D$	ΔH_{f298}^{o} (J/mol)
Butene	$C_4H_8(g)$	1,500	10.520	1.967	31.630	–9.873	–	–540
Butadiene	$C_4H_6(g)$	1,500	10.720	2.734	26.783	–8.882	–	109,240
Hydrogen	$H_2(g)$	3,000	3.468	3.249	0.422	–	0.083	—
Water	$H_2O(g)$	2,000	4.038	3.470	1.450	–	0.121	–241,818

三、

(33%) Consider a pure fluid whose equation of state is given by $\frac{PV}{RT} = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2}$,

where B and C are the second and the third virial coefficients. Please answer the following questions.

(a) Determine the Helmholtz free energy A at constant T. **(6%)**

(b) Suppose C is a positive constant. Also assume that B varies with T according to $B = v_2(1 - T_0/T)$, where v_2 is a positive constant and T_0 is the Boyle temperature at which B vanishes. The objective here is to see how A behaves as a function of the molar density $\rho \equiv 1/V$ when decreasing T from $T >> T_0$ to $T << T_0$. You expect to get a family of curves whose shapes vary with T. Sketch these curves in the A-ρ plane. **(6%).**

(c) You might observe in (b) that A can vary monotonically with ρ for some range of T and exhibit maximum/minimum for the other. In the latter case, what does it imply? What would happen to the fluid? Provide your physical explanations. **(9%)**

(d) There exists a critical temperature T_c that separates the monotonic and non-monotonic free energy profiles. Determine T_c in terms of C, v_2, and T_0. What is the corresponding molar density ρ_c? For $T > T_c$, what state would the fluid be situated at? Explain your answer physically. **(12%)**

(背面仍有題目,請繼續作答)

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四、

(10%) Please derive the fugacity of a pure liquid, $f_i^{(l)}$. Please specify clearly all variables used in your derivation and expression for $f_i^{(l)}$.

五、

(12%) Consider a binary solution. Let x_i and γ_i be the mole fraction and the activity coefficient of component i, respectively. Please estimate the integral:

$$\int_{x_1=0}^{x_1=1} \ln\left(\frac{\gamma_1}{\gamma_2}\right) \cdot dx_1 .$$

六、

(12%) Toluene (1) and water (2) are essentially immiscible as liquids. Determine the dew-point temperature and the composition of the first drop of liquid, when vapor mixture of these species with mole fraction z_1 = 0.7 is cooled at the constant pressure of 101.33 kPa. The Antoine Equations for vapor pressures of toluene (1) and water (2) are

$$\ln P_{(1)}^{sat} = 13.9320 - \frac{3056.96}{T + 217.625} \quad \text{and} \quad \ln P_{(2)}^{sat} = 16.3872 - \frac{3885.70}{T + 230.170},$$

where the units of pressure $P_{(i)}^{sat}$ and temperature T are given in kPa and °C, respectively.