系所組別：化學工程學系甲組

考試科目：化工熱力學

考試日期：0223，節次：2

※ 考生請注意：本試題可使用計算機

1. (33%) Consider a certain gas whose PVT behavior is governed by Dieterici equation of state:

$$P(V-b) = RT\exp\left(-\frac{a}{RTV}\right),$$

where *a* and *b* are constant parameters (but not necessarily positive). Please answer the following questions:

(a) Suppose $|b/V| \ll 1$ and $|a/RTV| \ll 1$. Expand the above equation of state as a virial equation of state in the form: $PV/RT = 1 + B/V + C/V^2 + \ldots$. Determine the 2nd virial coefficient, *B*, and the 3rd virial coefficient, *C*. **(10%)**

(b) Now consider the virial equation of state up to the 2nd virial term in (a). Suppose that the gas undergoes *slow* isothermal compression. If the work needed for accomplishing this compression is always greater than that for an ideal gas, the parameters *a* and *b* must satisfy a certain criterion. What is the criterion? Explain your answer physically. **(12%)**

(c) Follow (b). If the compression is *suddenly* performed, will the work here be greater or less than that in (b)? Why? **(3%)**

(d) Suppose that the gas can be condensed into liquid at a sufficiently low temperature. This transition can only happen when *a* and *b* have proper signs (i.e. > 0 or <0). What the signs of *a* and *b* should be? Why? **(8%)**

2. (24%) Answer "True" or "False". If you answer is "false", you MUST explain it.

(1) No process is possible which consists of the transfer of heat from one temperature level to a higher one.

(2) The residual property M^R is defined as $M^R \equiv M - M^{ig}$, where *M* and M^{ig} are the actual and the ideal-gas values of the thermodynamic property at the same *T* and *P*.

(3) The relation $TdS + VdP = -udu$ is valid for the homogeneous phase with change between equilibrium states, which is generated from the energy balance for the adiabatic, steady-state/ steady (one-dimensional; single influent/ single effluent) flow of a fluid in the absence of shaft work and of changes in potential energy.

(4) For one kind of the internal combustion engines, Otto cycle (Otto engine), it is also a traditional four-struck piston-cylinder process. Before combustion, the temperature of the Otto engine is extremely high as to ignite the combustion automatically.

(5) Considering a heat engine as a system, then, the entropy change of the heat engine should not be less than zero.

(6) $< C_P^{ig} >_S = \dfrac{\int_{T_o}^{T} C_P^{ig}\, dT/T}{(T - T_o)}$, where $< C_P^{ig} >_S$ denotes a mean value of specific heat capacity for the calculation of entropy change caused by temperature change.

(背面仍有題目,請繼續作答)

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3. (9%)

$$V\cdot(1-M^2)\cdot\frac{dP}{dx}+T\cdot\left(1+\frac{\beta u^2}{C_p}\right)\cdot\frac{dS}{dx}-\frac{u^2}{A}\cdot\frac{dA}{dx}=0$$

$$u\frac{du}{dx}-T\cdot\left(\frac{\beta u^2/C_P+M^2}{1-M^2}\right)\cdot\frac{dS}{dx}+\left(\frac{1}{1-M^2}\right)\cdot\frac{u^2}{A}\cdot\frac{dA}{dx}=0$$

(a) For the isentropic and subsonic flow in a convergent–divergent nozzle, please analyze $\frac{dP}{dx}$, $\frac{du}{dx}$ along the nozzle (for examples, increasing, decreasing, etc.), respectively. **(6%)**

(b) Where is the place in the nozzle for the maximum obtainable fluid velocity that can be reached? **(3%)**

4. (10%) In a binary mixture, P_A and P_B are the partial vapor pressure of the two constituents, and x_A and x_B are the mole fractions of the liquid. Assume that the vapor mixture could be regarded as an ideal gas.

Please express $\left(\frac{d\ln P_A}{d\ln P_B}\right)_{T,P}$ as a function of x_A and x_B.

5. (24 %) Trichloromethane (1), *aka* chloroform, and ethanol (2) form an azeotrope at ***P= 101.33 kPa***, which contains ***84.10 mol%*** of chloroform (1) and boils at ***332.45K***.

(a) Estimate the van Laar constants, α and β, in the following van Laar equation for the activity coefficients, γ_1 and γ_2. **(12%)**

$$\ln\gamma_1=\frac{\alpha}{\left(1+\frac{\alpha x_1}{\beta x_2}\right)^2}\quad\text{and}\quad\ln\gamma_2=\frac{\beta}{\left(1+\frac{\beta x_2}{\alpha x_1}\right)^2}$$

(b) Find the azeotropic composition and the pressure ***P*** (kPa) if the binary mixture boils at **320 K**. Assume that the van Laar constants are still the same. **(12%)**

The vapor pressures of chloroform (1) and ethanol (2) could be well described by the Antoine Equation, $\log_{10}(P)=A-\frac{B}{T+C}$, where ***P*** is the vapor pressure in ***bar***; ***T*** the temperature in ***K***, and the Antoine Equation parameters (A, B, and C) given as follows.

P (bar)	***T*** (K)	A	B	C
Chloroform (1)	215.0 – 334.4	4.20772	1233.129	-40.953
Ethanol (2)	292.77 – 366.63	5.24677	1598.673	-46.424