

※ 考生請注意：本試題可使用計算機。請於答案卷(卡)作答，於本試題紙上作答者，不予計分。

Problem 1 (33%)

Consider a certain gas whose PVT behavior is governed by the following virial equation of state:

$$\frac{PV}{RT} = 1 + \frac{b - a/RT}{V} + \frac{c}{V^2} \quad (1)$$

where a and b are positive parameters. Please answer the following questions.

- (1) Consider the case of $c = 0$. Suppose that the gas undergoes a *slow* isothermal compression. If the work needed for accomplishing this compression is always greater than that for an ideal gas, a and b must satisfy a certain inequality. What is the inequality? Why? (12%)
- (2) Follow (1). If the compression is *suddenly* performed, will the work here be greater or less than that in (1)? Why? (5%)
- (3) Now let $c = b^2$. Can the gas described by Eq. (1) be condensed into liquid? Why? If this condensation can happen, determine T_c , V_c , and P_c at the critical state as well as the corresponding compressibility factor Z_c . (16%)

Problem 2 (34%)

- (1) (4%) What is the main condition for the equation to establish? $\frac{S^R}{R} = -T \int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - \int_0^P (Z-1) \frac{dP}{P}$
- (2) (4%) Please draw a heat pump which includes constant heat reservoirs of T_H (high temp) and T_C (low temp), work (W), and heat (Q_H and Q_C). [Note] You MUST indicate the directions by arrows.
- (3) (4%) Follow (2), therefore, what is the definition of “coefficient of performance” of a Carnot pump by Carnot’s theorem? (You are only allowed to use those symbols in (2))
- (4) (4%) Please write down the “Carnot efficiency” of a Carnot engine. (Carnot’s theorem is applied again. Again, you are only allowed to use those symbols in (2))
- (5) (4%) Please explain the statement: “For most gases at moderate T and P , a reduction in P at constant H causes a decrease in T .”
- (6) (14%) Please draw the four steps of a Carnot cycle on a P vs. V diagram. (6%) [Note] The shape of the route and the different inclination (斜度) of the curves must be distinguishable (可區分). Please briefly describe each step. (8%) [Note] You MUST indicate the sequence by arrows. Sequence of the path is important.

Problem 3 (16%)

Following are data for the excess Gibbs free energy (G^E) and enthalpy (H^E) for equimolar mixtures of the same organic liquids at different temperatures. Assume the excess isobaric heat capacity, C_p^E , is constant.

T	G^E (J/mol)	H^E (J/mol)
10°C	544.0	932.1
30°C	513.2	893.4
50°C	494.2	845.9

- (1) Please express G^E and H^E , respectively, as a function of temperature T in Kelvin. (8%)
 (2) Please estimate the values of the excess entropy S^E at 25°C. (8%)

Problem 4 (17%)

A single P - x_1 - y_1 data point is available for a binary system at 25°C and shown as follows. The excess Gibbs

free energy of this binary mixture is well modelled with the Margules equation: $\frac{G^E}{x_1 x_2 \cdot RT} = A_{21} x_1 + A_{12} x_2$,

where A_{12} and A_{21} are constants.

Data: At 25°C, $P_1^{\text{Sat}} = 183.4$ kPa, $P_2^{\text{Sat}} = 96.7$ kPa.

For $x_1 = 0.253$, $y_1 = 0.456$ and $P = 139.1$ kPa.

Please estimate the total pressure and the vapor-phase composition at 25°C for the binary mixture with $x_1 = 0.6$.