# 國立清華大學 102 學年度碩士班考試入學試題

系所班組別：化學工程學系

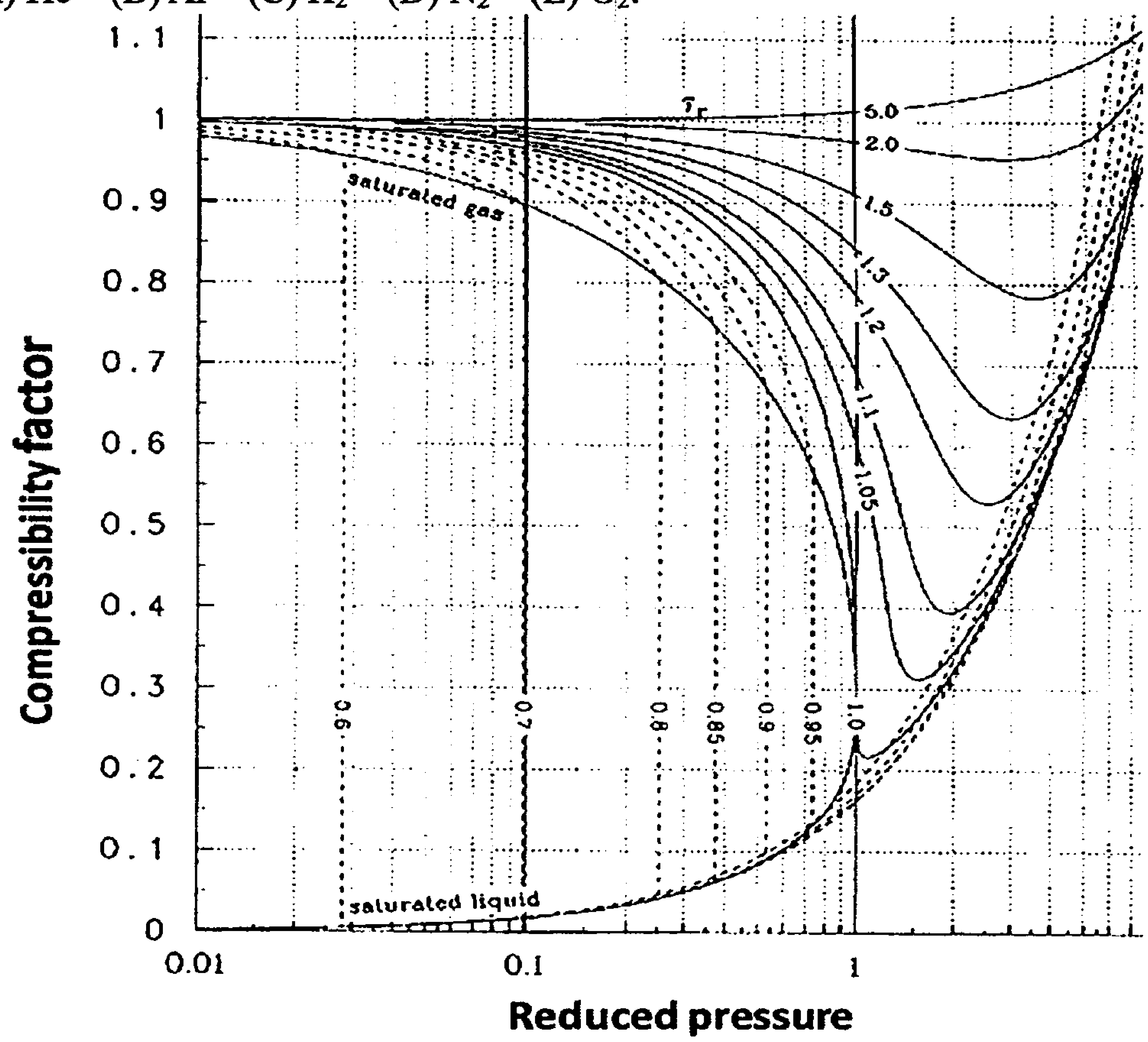
考試科目（代碼）：化工熱力學及化學反應工程(0902)

　　*請在【答案卡】作答

選擇題 4 題，每題 5 分，答錯不倒扣（請在答案卡上面作答，違者不計分）

Multiple choices.

1. By definition, a van der Waals gas obeys the equation of state $p = RT(V-b)^{-1} - aV^{-2}$ where $p$ is the pressure, $T$ the absolute temperature in K, $V$ the molar volume, and $R$ the gas constant. Given below is a generalized compressibility diagram of simple fluids, along with a table of critical parameters and van der Waals coefficients for five gases. Based on these, which two of the five gases are higher in Boyle temperature as compared to the other three? [5%]
(A) He (B) Ar (C) $H_2$ (D) $N_2$ (E) $O_2$.




| | Critical parameters | | | Van der Waals coefficients | |
|---|---|---|---|---|---|
| | $p_c$ (atm) | $V_c$ (mL mol$^{-1}$) | $T_c$ (K) | $a$ (atm L$^2$ mol$^{-2}$) | $b$ (L mol$^{-1}$) |
| He | 2.3 | 58 | 5.2 | 0.027 | 0.024 |
| Ar | 48 | 75 | 151 | 1.34 | 0.032 |
| $H_2$ | 13 | 65 | 33 | 0.24 | 0.027 |
| $N_2$ | 34 | 90 | 126 | 1.35 | 0.039 |
| $O_2$ | 50 | 78 | 155 | 1.36 | 0.032 |

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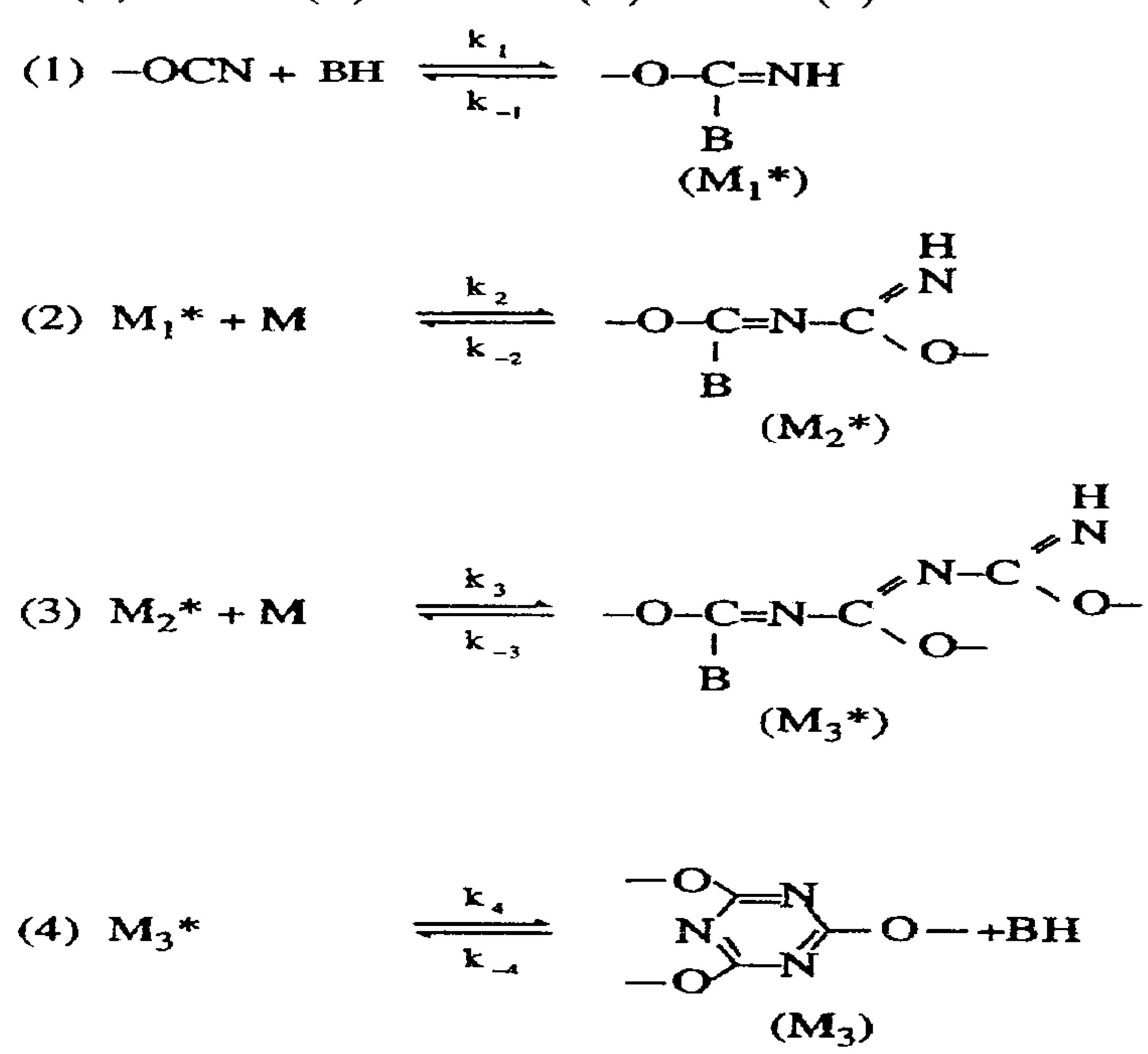
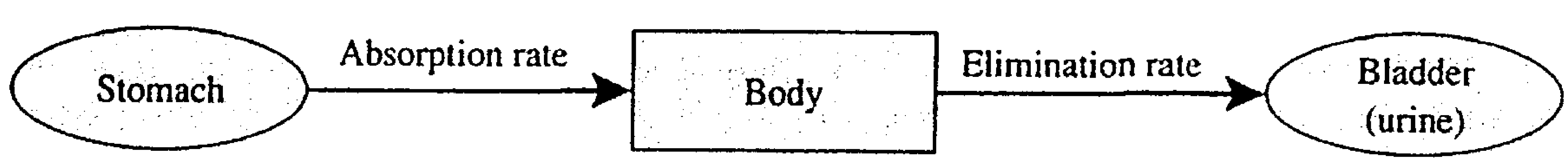
2. Continued from the preceding question, which of the 5 gases are of *negative* Joule-Thomson coefficient $\mu \equiv (\partial T/\partial p)_H$ in an adiabatic process near room temperature? [5%]
(A) He (B) Ar (C) $H_2$ (D) $N_2$ (E) $O_2$.
3. Given below are proposed elementary steps in the cyclotrimerization (catalyzed by a Lewis acid BH) of three cyanate groups to give *sym*-triazene ring structure. On the basis of this mechanism, what may be the possible kinetic order $n$ (in terms of the cyanate concentration) if the rate-determining step is either the first or the second elementary step? [5%]
(A) $n = 1/2$ (B) $n = 1$ (C) $n = 3/2$ (D) $n = 2$ (E) $n = 5/2$



4. A simplified kinetic model of metabolic consumption of ethanol in human body can be represented by the single compartmental model given below. A man 60 kg in body weight has quickly consumed two cans of beer (each 400 g, containing 5 wt% of ethanol) at $t = 0$. If $k_{absorption}/k_{elimination} = 5$ and $k_{elimination} = 0.5\ hr^{-1}$, what would be the time $t_{max}$ that his alcohol level in the blood stream reaches the maximum level? [5%]
(A) $t_{max} \le 0.6$ hr (B) 0.3 hr $\le t_{max} \le 0.9$ hr (C) 0.6 hr $\le t_{max} \le 1.2$ hr (D) 0.9 hr $\le t_{max} \le 1.5$ hr (E) 1.2 hr $\le t_{max} \le 1.8$ hr



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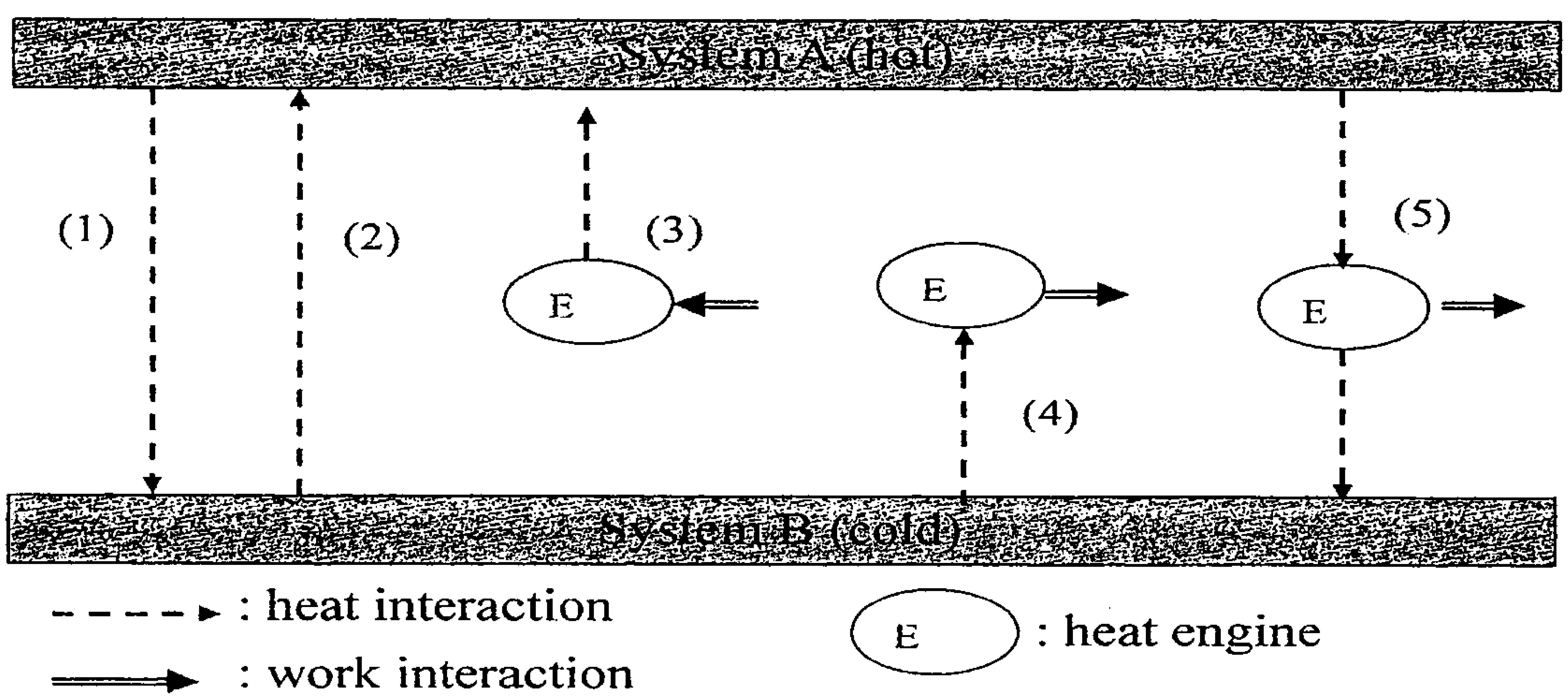
以下四題，請在答案卷作答。

**Problem 2(A)** To apply an equation of state to a mixture of gases, additional information is needed beyond what is required for the pure gases. The second virial coefficient for an N-component gaseous mixture is given by $B = \sum_{i=1}^{N} \sum_{j=1}^{N} y_i y_j B_{ij}$ .

Please give the physical meaning/reasons for this equation and how to evaluate $B_{ij}$? (10%)

**Problem 2(B)** Please explain and discuss the possibility of the following 5 processes based on the second law of thermodynamics. (10%)



**Problem 3(A)** At 313.15 K, the excess volume of mixing propionic acid with oxane is $V^E=x_1x_2\{a_0+a_1(x_1-x_2)\}$, where $x_1$ is the mole fraction of propionic acid, $x_2$ that of oxane, $a_0$=-2.47 cm$^3$mol$^{-1}$, and $a_1$=0.0608 cm$^3$mol$^{-1}$. The density of propionic acid at this temperature is 0.972 g cm$^{-3}$; that of oxane is 0.864 g cm$^{-3}$.

(1) Derive an expression for the partial molar volume of each component at this temperature. (8%)

(2) Compute the partial molar volume for each component in an equimolar mixture. (6%)

**Problem 3(B)** For the calculation of the solubility c of a gas in a solvent, it is often convenient to use the expression c=Kp, where K is the Henry's law constant. Breathing air at high pressure, such as in scuba diving, results in an increased concentration of dissolved nitrogen. The Henry's law constant for the solubility of nitrogen is 0.36 $\mu$ g/(g $H_2O$ atm).

(1) What mass of nitrogen is dissolved in 100 g of water saturated with air at 4.0 atm and 20 °C? (3%)

(2) If nitrogen is four times as soluble in fatty tissues as in water, what is the increase in nitrogen concentration in fatty tissue in going from 1 atm to 4.0 atm? (3%)

**Problem 4(A)**

For an irreversible, second order elementary reaction A+B→C+D, the reaction is carried out in liquid phase in a batch reactor, demonstrate that in any instant

$$ln\frac{C_A}{C_B}=(C_{Ao}-C_{Bo})kt+ln\frac{C_{Ao}}{C_{Bo}}$$

where $C_{Ao}$ and $C_{Bo}$ represent the initial concentrations of A and B, t is the reaction time and k is the rate constant. (10%)

**Problem 4(B)**

Suppose the initial concentrations of A and B are 0.1 and 0.2 moles/liter, respectively, calculate the rate constant based on the following experimental data. (10%)

| t (min) | 10 | 20 | 30 | 40 |
|---|---|---|---|---|
| Conversion of A (%) | 17.05 | 30.17 | 40.55 | 48.91 |

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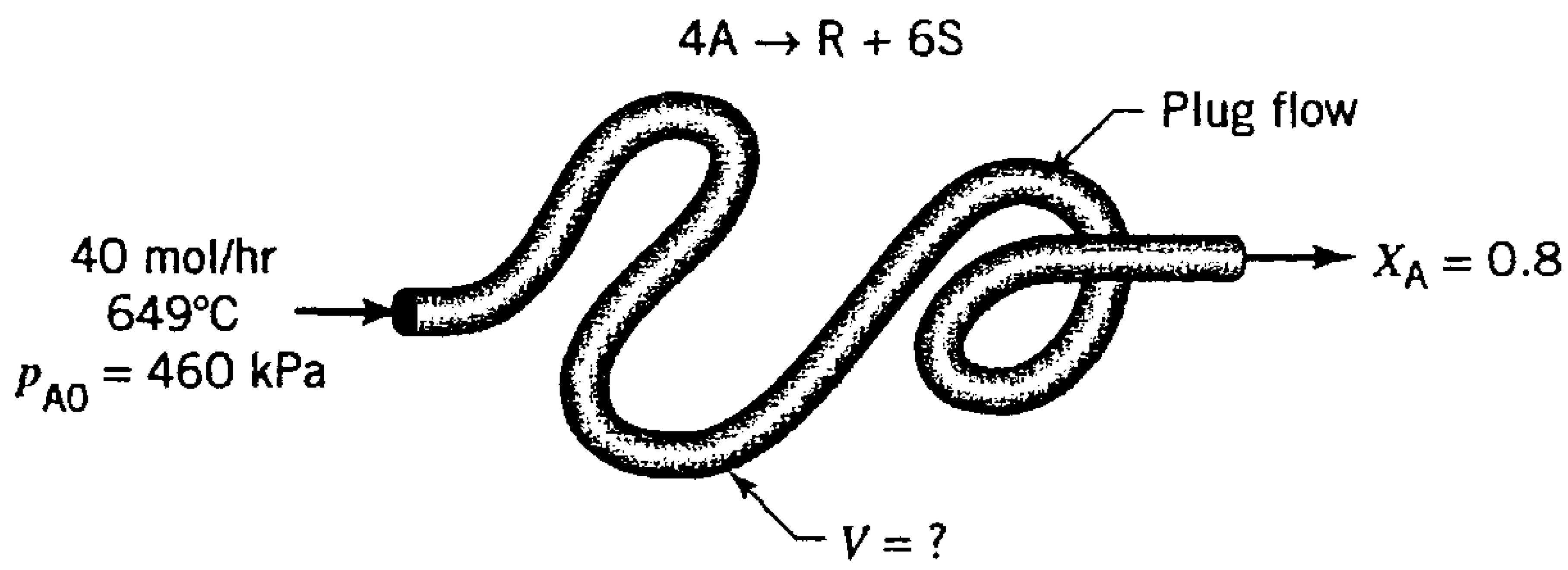
**Problem 5**　The homogeneous gas decomposition of phosphine:

$$4PH_3(g) \rightarrow P_4(g) + 6H_2$$

proceeds at 649 °C with the first-order rate law as:

$$-r_{PH3} = (10/hr)C_{PH3}$$

**5(A)** What size of a PFR operating isothermally at 649 °C and isobarically at 460 kPa can produce 85% conversion of a feed consisting of 40 mol of pure phophine per hour? (10%)




**5(B)** If the PFR is no longer operated at constant pressure. Given the pressure drop inside the tube as a function of tube volume as:

$$(P/P_0) = 1 - 0.0005V$$

What will be the PFR size if we still want to achieve 85% conversion? (10%)