

## 106 年成大化熱

### Problem 1

#### **【Solution】**

(1)

For an isothermal process,

$$\underline{\underline{\Delta U = \Delta H = 0}}$$

$$\begin{aligned} Q &= \Delta U - W = -W = \int P dV = \int_{V_1}^{V_2} \frac{nRT}{V} dV \\ &= nRT \ln \frac{V_2}{V_1} = nRT \ln \frac{P_1}{P_2} \\ &= 1 \times 8.314 \times 300 \ln \frac{20}{1} = \underline{\underline{7471.9 \text{ (J)}}} \end{aligned}$$

(2)

For an isothermal process,

$$\underline{\underline{\Delta U = \Delta H = 0}}$$

For free expansion,

$$\underline{\underline{W = 0}}$$

$$\underline{\underline{Q = \Delta U - W = 0}}$$

(3)

For an adiabatic process,

$$\underline{\underline{Q = 0}}$$

By first law of thermodynamics,

$$\Delta U = W$$

$$C_V(T_f - T_i) = -P_{ex} \left( \frac{RT_f}{P_f} - \frac{RT_i}{P_i} \right) \quad (\text{constant pressure})$$

$$\frac{3}{2} \times 8.314(T_f - 300) = -1 \left( \frac{0.08314T_f}{1} - \frac{0.08314 \times 300}{20} \right) \times \frac{8.314}{0.08314}$$

$$T_f = 186(K) \quad , \quad \Delta U = W = \frac{3}{2} \times 8.314(186 - 300) = \underline{\underline{-1421.7 \text{ (J)}}}$$

$$\Delta H = C_p(T_f - T_i) = \frac{5}{2} \times 8.314 \times (186 - 300) = \underline{\underline{-2367.49 \text{ (J)}}}$$

(本題改編自：Smith, J.; Van Ness, H.; Abbott, M. *Introduction to Chemical Engineering*, 7th ed.;

p 114, Problem 3.19.)

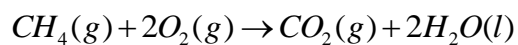
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## Problem 2

### 【Solution】

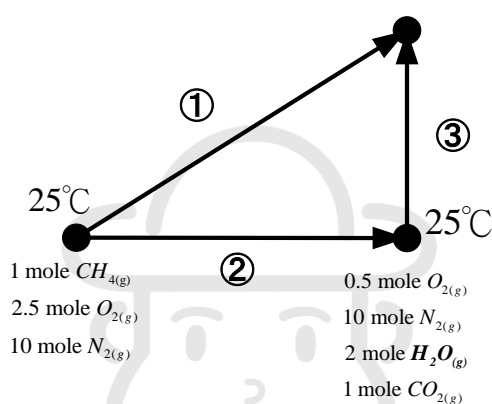
(1)

Reaction :



$$\begin{aligned}\Delta H &= -2\Delta H_f^\circ(\text{H}_2\text{O}_{(\text{l})}) + \Delta H_f^\circ(\text{CO}_{2(\text{g})}) - \Delta H_f^\circ(\text{CH}_{4(\text{g})}) \\ &= 2(-285.83) - 393.51 + 74.81 = \underline{\underline{-890.36 \text{ (kJ / mol)}}}\end{aligned}$$

(2)



By the path diagram,

$$\Delta H_1 = \Delta H_2 + \Delta H_3$$

By the first law of thermodynamics,

$$\Delta H + \cancel{\frac{g}{g_c} \Delta z} + \cancel{\frac{1}{2g_c} \Delta v^2} = Q + \cancel{W}$$

For the temperature to be maximum, the process should be adiabatic (no heat is released),

$$\Delta H = 0, \Delta H_1 = \Delta H_2 + \Delta H_3 = 0$$

$$\Delta H_2 = \Delta H_{\text{combustion}}^{\circ} + 2(\Delta H_{f, H_2O(g)}^{\circ} - \Delta H_{f, H_2O(l)}^{\circ})$$

$$= -890.36 + 44.01 \times 2 = -802.34(kJ) = -802.34 \times 10^3(J)$$

$$\Delta H_3 = (0.5 \times 29.355 + 10 \times 29.125 + 2 \times 33.577 + 37.110 \times 1)(T - 25)$$

$$= 410.1915(T - 25)$$

$$\Delta H_2 + \Delta H_3 = -802.34 \times 10^3 + 410.1915(T - 25) = 0$$

$$\underline{\underline{T = 1981^{\circ}C}}$$

(※注意在計算  $\Delta H_2$  時，預設產物為  $H_2O(g)$ ，因此須加上水的蒸發熱以符合假設)

(本題可參考：Smith, J.; Van Ness, H.; Abbott, M. *Introduction to Chemical Engineering*, 7th ed.;  
p 143~144, Example 4.7.)

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### **Problem 3**

#### **【Solution】**

##### **(1) False**

一個任意之 **reversible cycle** 可以切割成許多無限小之 Carnot cycle 的串聯，然而 Carnot cycle 的串聯不一定是 Carnot cycle。

##### **(2) False**

需還有 **reversible process** 的假設此式才成立，原因為：

For reversible process, entropy balance,

$$\Delta S = \sum \cancel{M_k S_k} + \frac{Q}{T} + \cancel{S_{gen}} = 0$$

$$Q = T\Delta S$$

By the first law of thermodynamics (open system, steady state)

$$\Delta\left[H + \frac{1}{2g_c}v^2 + \frac{g}{g_c}z\right] = Q + W$$

$$W = \Delta\left[H + \frac{1}{2g_c}v^2 + \frac{g}{g_c}z\right] - Q = \Delta\left[H + \frac{1}{2g_c}v^2 + \frac{g}{g_c}z\right] - T\Delta S$$

##### **(3) True**

By mechanical energy balance,

$$\cancel{W} = \frac{1}{2g_c}(v_1^2 - v_2^2) + \cancel{\frac{g}{g_c}(z_1 - z_2)} + \frac{1}{\rho}(P_1 - P_2) - \cancel{h_f}$$

$$\frac{1}{2g_c}(v_1^2 - v_2^2) + \frac{1}{\rho}(P_1 - P_2) = 0$$

$$\because v_1^2 < v_2^2, \quad P_2 < P_1$$

(4) True

For a closed system, reversible phase change,

$$\Delta G = \Delta H - T\Delta S = 0$$

$$\boxed{\Delta H = T\Delta S}$$

((a)~(d)小題可參考：Smith, J.; Van Ness, H.; Abbott, M. *Introduction to Chemical Engineering*, 7th ed.; p 167~168/180/264/169.)

**Problem 4**

**【Solution】**

(1)

A Venturi meter is a device or component which is used for measuring the rate of flow of liquid through pipes.

(2)

The Venturi meter is correlated to two equations,

(1) The equation of continuity (mass balance)

$$\rho_1 v_1 A_1 = \rho_2 v_2 A_2$$

(2) Bernoulli's equation (mechanical energy balance)

$$W = \frac{1}{2g_c}(v_1^2 - v_2^2) + \frac{g}{g_c}(z_1 - z_2) + \frac{1}{\rho}(P_1 - P_2) - h_f$$

(3)

Venturi meter is more closer to a nozzle, whose  $dS/dx$  term approaches zero because in a properly designed nozzle the area changes with length in such as a way as to make the flow nearly frictionless, so the answers should **be (3)**

※(1)(2)為 Pipe flow 的關係式

(4)與 nozzle flow 非常相似，但與題目有一點些微不同

(不確定是故意考的還是打字錯誤)

在 Smith 原文書中等號右邊 u 的次方為 1，即

$$\frac{du}{dx} = \frac{-u}{A} \left( \frac{1}{1-M^2} \right) \frac{dA}{dx}$$

(本題可參考：Smith, J.; Van Ness, H.; Abbott, M. *Introduction to Chemical Engineering*, 7th ed.;  
p 258~260.)



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### **Problem 5**

#### **【Solution】**

Assume :

(1) the binary mixture is composed of two species of similar size and energies of interaction

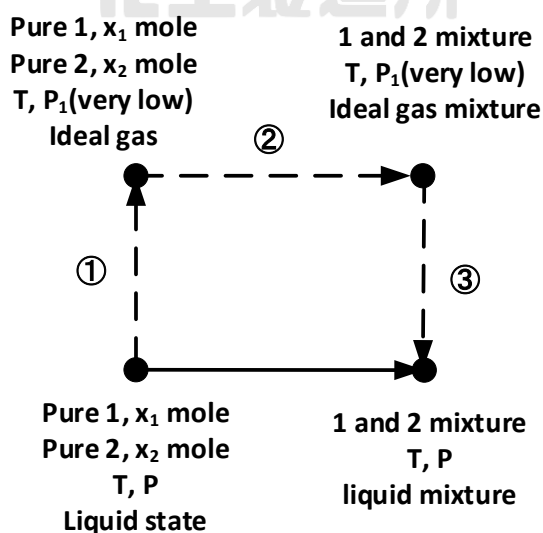
$$S^{ex} = 0 \text{ 、 } V^{ex} = 0$$

(2) the van der Waals equation of state applies to both the pure fluids and the binary mixture.

$$G^E = H^E - T S^E = H^E = U^E + P V^E = U^E$$

Since  $U^{ex}$  is a state function, we can propose a path as follows,

- (1) Start with  $x_1$  moles of pure liquid 1 and  $x_2$  moles of pure liquid 2 at the temperature and pressure of the mixture, and, at constant temperature, lower the pressure so that each of the pure liquids vaporize to an ideal gas
- (2) At constant temperature and pressure, mix the ideal gases to form an ideal gas mixture
- (3) Compress the gas mixture isothermally to a liquid mixture at the final pressure  $P$





$$U^E = \Delta U^1 + \cancel{\Delta U^2} + \Delta U^3 = \underbrace{x_1 \int_{V_1}^{\infty} \left( \frac{\partial U}{\partial V} \right)_T dV \Big|_{pure1} + x_2 \int_{V_2}^{\infty} \left( \frac{\partial U}{\partial V} \right)_T dV \Big|_{pure2}}_{\Delta U^1} + \underbrace{\int_{\infty}^{V_{mix}} \left( \frac{\partial U}{\partial V} \right)_T dV \Big|_{mixture}}_{\Delta U^3}$$

$$\because \left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P \text{ 代入}$$

$$U^E = x_1 \int_{V_1}^{\infty} [T \left( \frac{\partial P}{\partial T} \right)_V - P] dV + x_2 \int_{V_2}^{\infty} [T \left( \frac{\partial P}{\partial T} \right)_V - P] dV + \int_{\infty}^{V_{mix}} [T \left( \frac{\partial P}{\partial T} \right)_V - P] dV$$

$$= x_1 \int_{V_1}^{\infty} \frac{a_1}{V^2} dV + x_2 \int_{V_2}^{\infty} \frac{a_2}{V^2} dV + \int_{\infty}^{V_{mix}} \frac{a_m}{V^2} dV$$

$$= x_1 \frac{a_1}{V_1} + x_2 \frac{a_2}{V_2} - \frac{a_m}{V_{mix}}$$

$$\because \text{液體體積在同溫且不同壓力下趨近於定值：} \left( \frac{\partial P}{\partial V} \right)_T \rightarrow \infty$$

$$\left( \frac{\partial P}{\partial V} \right)_T = \frac{-RT}{(V-b)^2} + \frac{2a}{V^3} \rightarrow \infty, V=b$$

$$U^E = x_1 \frac{a_1}{b_1} + x_2 \frac{a_2}{b_2} - \frac{a_m}{b_m} = \frac{x_1 x_2 b_1 b_2}{x_1 b_1 + x_2 b_2} \left( \frac{\sqrt{a_1}}{b_1} - \frac{\sqrt{a_2}}{b_2} \right)^2$$

(本題為原文書段落說明：Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*, 5th ed.; p 460~462.)

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**Problem 6****【Solution】**

(1) By modified Raoult's law,

$$\begin{cases} x_1 P_1^{sat} r_1 = y_1 P \\ x_2 P_2^{sat} r_2 = y_2 P \end{cases}$$

$$\begin{cases} \ln r_1 = \left[ \frac{\partial(nG^E / RT)}{\partial n_1} \right]_{n_2} = Ax_2^2 \\ \ln r_2 = \left[ \frac{\partial(nG^E / RT)}{\partial n_2} \right]_{n_1} = Ax_1^2 \end{cases} \rightarrow \begin{cases} r_1 = \exp(Ax_2^2) \\ r_2 = \exp(Ax_1^2) \end{cases}, \text{代入數據}$$

$$\begin{cases} 0.389 \times 120.2 e^{0.611^2 A} = y_1 \times 108.6 \\ 0.611 \times 73.9 e^{0.389^2 A} = y_2 \times 108.6 \end{cases}, y_1 + y_2 = 1$$

$$\underline{\underline{A = 0.622}}$$

(2)

For  $y_1$

$$\begin{aligned} y_1 &= \frac{x_1 P_1^{sat} r_1}{P} = \frac{x_1 P_1^{sat} \exp[Ax_2^2]}{P} \\ &= \frac{0.389 \times 120.2 \exp[0.622 \times 0.611^2]}{108.6} \\ &= \underline{\underline{0.543}} \end{aligned}$$

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## Problem 1

### **【Solution】**

#### **(1) False**

For example, For an open, steady state system, if

$$\begin{cases} \text{neglegible change of kinetc and potential energies} \\ \text{no shaft work} \end{cases}$$

$$\Delta H + \cancel{\frac{g}{g_c} \Delta z} + \cancel{\frac{1}{2g_c} \Delta v^2} = Q + \cancel{W}$$

$$\Delta H = Q$$

#### **(2) False**

For different signs of  $\left(\frac{\partial T}{\partial P}\right)_H = \mu_H \begin{cases} > 0 \\ = 0 \\ < 0 \end{cases}$ , there will be different relations between

temperature and pressure changes, for  $\mu_H < 0$ , the situation of the problem will be satisfied.

((b)小題可參考：Smith, J.; Van Ness, H.; Abbott, M. *Introduction to Chemical Engineering*, 7th ed.; p 267.)

## **Problem 2**

### **【Solution】**

For a polytropic process,

$$PV^\delta = \text{constant} \begin{cases} \delta = 0 \rightarrow P = \text{constant} \\ \delta = r \rightarrow \text{adiabatic} \\ \delta = \infty \rightarrow P^{\frac{1}{\delta}} V = \text{constant} \rightarrow V = \text{constant} \end{cases}$$

For a constant  $V$  process,  $\delta = \infty$  代入 ,

$$\begin{aligned} Q &= \lim_{\delta \rightarrow \infty} \frac{(\delta - r)RT_1}{(\delta - 1)(r - 1)} \left[ \left( \frac{P_2}{P_1} \right)^{\frac{\delta - 1}{\delta}} - 1 \right] \\ &= \frac{RT_1}{r - 1} \left[ \left( \frac{P_2}{P_1} \right) - 1 \right] \end{aligned}$$

$\therefore$  for ideal gas,  $V = \text{constant}$

$$\frac{P_2}{P_1} = \frac{T_2}{T_1}, \quad r = \frac{C_p}{C_v}, \quad r - 1 = \frac{C_p - C_v}{C_v} = \frac{R}{C_v} \text{ 代入}$$

$$Q = \frac{RT_1}{\left( \frac{R}{C_v} \right)} \left[ \frac{T_2}{T_1} - 1 \right] = \underline{\underline{C_v(T_2 - T_1)}}$$

(本題關於 polytropic process 的觀念可參考：Smith, J.; Van Ness, H.; Abbott, M. *Introduction to Chemical Engineering*, 7th ed.; p 78~79.)

### Problem 3

#### 【Solution】

By the first law of thermodynamics,

$$\cancel{\Delta H} + \cancel{\frac{g}{g_c} \Delta z} + \cancel{\frac{1}{2g_c} \Delta v^2} = Q + W$$

$$\begin{aligned}\Delta H &= \int_{T_1}^{T_2} nC_p dT \\&= \int_{760}^{T_2} 10 \times 1.987 [3.60 + 3.02 \times 10^{-3} T - 0.16 \times 10^5 T^{-2}] dT \\&= 10 \times 1.987 [3.60(T_2 - 760) + 1.51 \times 10^{-3} (T_2^2 - 760^2) + 0.16 \times 10^5 (\frac{1}{T_2} - \frac{1}{760})] \\&= 10 \times 1.987 [3.60 + 1.51 \times 10^{-3} (T_2 + 760) + 0.16 \times 10^5 (\frac{1}{760 T_2})] \cdot (T_2 - 760) \\&\quad \underbrace{\hspace{10em}}_{<C_p>_H} \\ \Delta H &= <C_p>_H (T_2 - 760) = 1.0 \times 10^5\end{aligned}$$

#### 【1<sup>st</sup> try】

For first try, insert  $T_{2,1} = 750 + 460 = 1210 R$  into  $<C_p>_H$  to calculate  $T_2$

$$\begin{aligned}T_2 &= \frac{1.0 \times 10^5}{<C_p>_H} + 760 \\&= \frac{1.0 \times 10^5}{10 \times 1.987 [3.60 + 1.51 \times 10^{-3} (1210 + 760) + 0.16 \times 10^5 (\frac{1}{760 \times 1210})]} + 760 = 1523.4 (R)\end{aligned}$$

#### 【2<sup>nd</sup> try】

Insert  $T_{2,2} = 1523.4 (R)$  into  $<C_p>_H$  to calculate  $T_2$

$$\begin{aligned}T_2 &= \frac{1.0 \times 10^5}{<C_p>_H} + 760 \\&= \frac{1.0 \times 10^5}{10 \times 1.987 [3.60 + 1.51 \times 10^{-3} (1523.4 + 760) + 0.16 \times 10^5 (\frac{1}{760 \times 1523.4})]} + 760 = 1472.3 (R)\end{aligned}$$

【3<sup>rd</sup> try】

Insert  $T_{2,3} = 1472.3(R)$  into  $\langle C_p \rangle_H$  to calculate  $T_2$

$$T_2 = \frac{1.0 \times 10^5}{\langle C_p \rangle_H} + 760$$
$$= \frac{1.0 \times 10^5}{10 \times 1.987 [3.60 + 1.51 \times 10^{-3} (1472.3 + 760) + 0.16 \times 10^5 (\frac{1}{760 \times 1472.3})]} + 760 = 1480.5 (R)$$

【4<sup>th</sup> try】

Insert  $T_{2,4} = 1480.5(R)$  into  $\langle C_p \rangle_H$  to calculate  $T_2$

$$T_2 = \frac{1.0 \times 10^5}{\langle C_p \rangle_H} + 760$$
$$= \frac{1.0 \times 10^5}{10 \times 1.987 [3.60 + 1.51 \times 10^{-3} (1480.5 + 760) + 0.16 \times 10^5 (\frac{1}{760 \times 1480.5})]} + 760 = 1479.2 (R)$$

【5<sup>th</sup> try】

Insert  $T_{2,5} = 1479.2(R)$  into  $\langle C_p \rangle_H$  to calculate  $T_2$

$$T_2 = \frac{1.0 \times 10^5}{\langle C_p \rangle_H} + 760$$
$$= \frac{1.0 \times 10^5}{10 \times 1.987 [3.60 + 1.51 \times 10^{-3} (1479.2 + 760) + 0.16 \times 10^5 (\frac{1}{760 \times 1479.2})]} + 760 = 1479.4 (R)$$

$$\underline{\underline{T_2 = 1479.4 (R)}}$$

若根據計算機 solve 功能做計算，則可得  $T_2 = 1481.9 (R)$ ，相當接近

(關於此類計算 sensible-heat 積分題型，可參考：Smith, J.; Van Ness, H.; Abbott, M.

*Introduction to Chemical Engineering*, 7th ed.; p 129~130.)

**Problem 4****【Solution】***Reaction,*

	$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$			
<i>I</i>	2.0	2.5	0	0
<i>C</i>	-2.0	-2.0	+2.0	+6.0
-----				
<i>E</i>	0	0.5	2.0	6.0
	$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$			
<i>I</i>	2.0	0.5	0	6.0
<i>C</i>	- <i>x</i>	- <i>x</i>	+ <i>x</i>	+ <i>x</i>
-----				
<i>E</i>	2.0 - <i>x</i>	0.5 - <i>x</i>	<i>x</i>	6.0 + <i>x</i>

$$y_{CO} = 0.2 = \frac{2.0 - x}{2.0 - x + 0.5 - x + x + 6.0 + x}, \quad x = 0.3$$

$$\begin{cases} CO(g) = 1.7 \text{ (mol)} \\ H_2O(g) = 0.2 \text{ (mol)} \\ CO_2(g) = 0.3 \text{ (mol)} \\ H_2(g) = 6.3 \text{ (mol)} \end{cases}$$

(本題改編自：Smith, J.; Van Ness, H.; Abbott, M. *Introduction to Chemical Engineering*, 7th ed.;

p 144~147, Example 4.8.)

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### **Problem 5**

#### **【Solution】**

(1) For two liquid phase coexists, (single phase is unstable)

$$\frac{d^2(\Delta G / RT)}{dx_1^2} < 0$$

又

$$\Delta G = \Delta G_{mix} + G^E$$

$$\frac{\Delta G}{RT} = x_1 \ln x_1 + x_2 \ln x_2 + \frac{G^E}{RT} \text{ 代入}$$

可推得

$$\frac{d^2(G^E / RT)}{dx_1^2} < \frac{-1}{x_1 x_2}$$

$G^E / RT = Ax_1 x_2$  代入，

$$\frac{d^2(G^E / RT)}{dx_1^2} = -2A < \frac{-1}{x_1 x_2}, \quad A > \frac{1}{2x_1 x_2}$$

$\therefore x_1 x_2$  之 maximum 為  $(0.5)^2 = 0.25$  代回

即  $A > 2$  時系統將穩定呈現兩相狀態

(2)

For two liquid phases system to coexist,

$$A = 2.5 > \frac{1}{2x_1 x_2} = \frac{1}{2x_1(1-x_1)}$$

$$5x_1(1-x_1) > 1, \quad \underline{\underline{0.276 < x_1 < 0.724}}$$

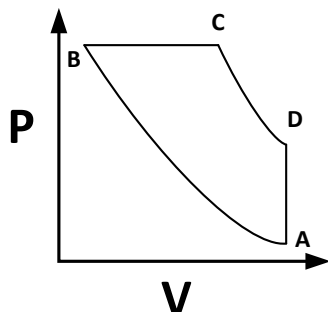
(本題可參考：Smith, J.; Van Ness, H.; Abbott, M. *Introduction to Chemical Engineering*,

7th ed.; p 578~579/589.)



**Problem 6****【Solution】**

(1)



This is the so-called Diesel cycle

(2)

$$\eta = 1 - \frac{|Q_c|}{|Q_H|}, \quad \begin{cases} |Q_c| = |Q_{DA}| = C_V(T_D - T_A) \\ |Q_H| = |Q_{BC}| = C_P(T_C - T_B) \end{cases}$$

 $\because A \rightarrow B$ 、 $C \rightarrow D$  are adiabatic steps,

$$\begin{cases} \frac{T_A}{T_B} = \left(\frac{V_B}{V_A}\right)^{\gamma-1} \rightarrow T_A = T_B \left(\frac{1}{\gamma}\right)^{\gamma-1} \\ \frac{T_C}{T_D} = \left(\frac{V_D}{V_C}\right)^{\gamma-1} \rightarrow T_D = T_C \left(\frac{1}{k}\right)^{\gamma-1} \end{cases}$$

又

$$\frac{T_C}{T_B} = \frac{V_C}{V_B} = \frac{V_C/V_D}{V_B/V_A} = \frac{\gamma}{k}$$

原式：

$$\begin{aligned} \eta &= 1 - \frac{C_V(T_D - T_A)}{C_P(T_C - T_B)} = 1 - \frac{1}{\gamma} \frac{(T_D - T_A)}{(T_C - T_B)} \\ &= 1 - \frac{1}{\gamma} \frac{T_C \left[ \left(\frac{1}{k}\right)^{\gamma-1} - \frac{k}{\gamma} \left(\frac{1}{\gamma}\right)^{\gamma-1} \right]}{T_C \left(1 - \frac{k}{\gamma}\right)} \quad \text{上下同乘 } \frac{1}{k} = 1 - \frac{1}{\gamma} \frac{\left[\left(\frac{1}{k}\right)^{\gamma} - \left(\frac{1}{\gamma}\right)^{\gamma}\right]}{\left(\frac{1}{k} - \frac{1}{\gamma}\right)} \end{aligned}$$

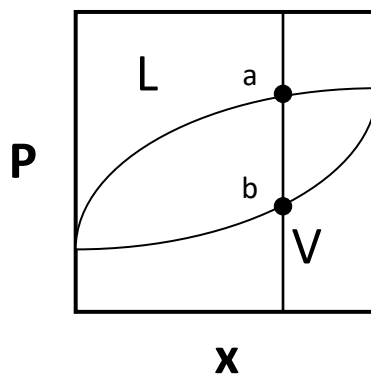
(本題可參考：Smith, J.; Van Ness, H.; Abbott, M. *Introduction to Chemical Engineering*,

7th ed.; p 305~306, Example 8.3.)

### Problem 7

#### 【Solution】

(1)



By modified Raoult's law,

$$y_i P = r_i x_i P_i^{sat}$$

For point b, (bubble point)

$$x_1 = 0.65, \quad x_2 = 0.35 \quad (z_i = x_i) \text{ 代入}$$

$$\begin{cases} y_1 P_b = \exp[0.67(1-0.65)^2] \cdot 0.65 \cdot 32.27 \text{-----(1)} \\ y_2 P_b = \exp[0.67 \times 0.65^2] \cdot (1-0.65) \cdot 73.14 \text{-----(2)} \end{cases}$$

$$(1) + (2) = P_b = 56.745 \text{ (kPa)}$$

For point a, (dew point)

$$y_1 = 0.65, \quad y_2 = 0.35 \quad (z_i = y_i) \text{ 代入}$$

$$\begin{cases} 0.65 P_a = \exp[0.67(1-x_1)^2] \cdot x_1 \cdot 32.27 \text{-----(3)} \\ 0.35 P_a = \exp[0.67 \times x_1^2] \cdot (1-x_1) \cdot 73.14 \text{-----(4)} \end{cases}$$

$$\frac{(3)}{(4)} = \frac{0.65}{0.35} = \frac{\exp[0.67(1-x_1)^2] x_1 \times 32.27}{\exp[0.67(x_1)^2] (1-x_1) \times 73.14}$$

$$x_1 = 0.874, \quad \text{代入(3)}$$

$$P_a = 43.86 \text{ (kPa)}$$

For the pressure range,

$43.86 < P < 56.74$  (kPa), the binary system can coexist

(2)

$$\begin{cases} y_1 P = \exp[0.67(0.25)^2] \cdot 0.75 \cdot 32.27 \text{ --- (5)} \\ y_2 P = \exp[0.67(0.75)^2] \cdot 0.25 \cdot 73.14 \text{ --- (6)} \end{cases}$$

$$(5) + (6) = \underline{\underline{P = 51.89 \text{ (kPa)}}}$$

(本題改編自：Smith, J.; Van Ness, H.; Abbott, M. *Introduction to Chemical Engineering*,  
7th ed.; p 373, Problem 10.19.)



# 108 年成大化熱

## Problem 1

### **【Solution】**

(1)

假設從  $V_1$  壓縮到  $V_2$

For ideal gas,

$$W = -\int_{V_1}^{V_2} P dV = -RT \ln \frac{V_2}{V_1} = RT \ln \frac{V_1}{V_2}$$

For non-ideal gas,

$$W_{irrev} = -\int_{V_1}^{V_2} P dV = -\int_{V_1}^{V_2} \left( \frac{RT}{V} + \frac{bRT - a}{V^2} \right) dV = RT \left[ \ln \frac{V_1}{V_2} + \left( b - \frac{a}{RT} \right) \left( \frac{1}{V_2} - \frac{1}{V_1} \right) \right]$$

Compare the result, if the work needed for the certain gas is always greater than that for an ideal gas, the relation will be as following

$$\begin{aligned} & \underline{\underline{W_{rev} < W_{irrev}}} \\ & RT \ln \frac{V_1}{V_2} < \underbrace{RT \ln \frac{V_1}{V_2}}_{>0} + \underbrace{\left( b - \frac{a}{RT} \right) \left( \frac{1}{V_2} - \frac{1}{V_1} \right)}_{>0}, \quad \underline{\underline{\left( b - \frac{a}{RT} \right) > 0}} \end{aligned}$$

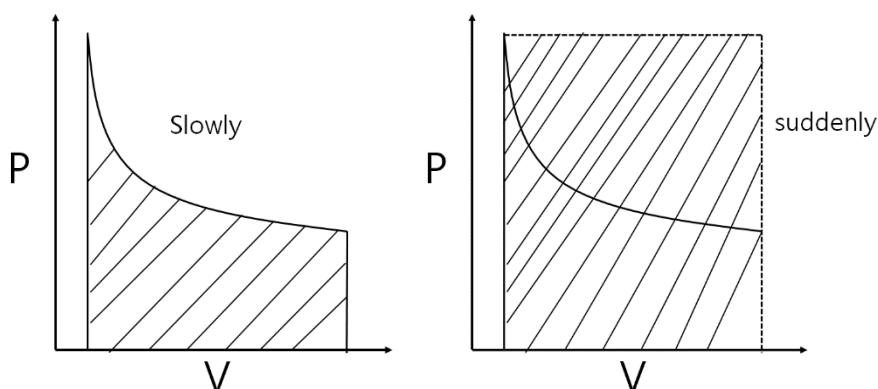
Because  $b - \frac{a}{RT}$  is the second-virial coefficient of the virial form of the Van der Waals equation, which represents the interactions between two molecules. When second virial coefficient is larger than zero, we have,

$$Z = 1 + \frac{B}{V} + \frac{C}{V^2} \dots \approx 1 + \frac{B}{V} > 1$$

which means the repulsive force between two molecules is obvious. Therefore, the compression work should be larger than that of an ideal gas, whose interaction should be zero.

(2)

By the area of the PV diagram, work suddenly performed is higher



(3)

To determine the critical properties, set  $V_c$  is the triple root of

$$(V - V_c)^3 = V^3 - 3V^2V_c + 3VV_c^2 - V_c^3 = 0$$

For this equation of state at critical point,

$$\frac{P_c V}{RT_c} = 1 + \frac{B}{V} + \frac{C}{V^2} \quad (B = b - \frac{a}{RT_c})$$

$$V^3 - \frac{RT_c}{P_c} V^2 - \frac{BRT_c}{P_c} V - \frac{CRT_c}{P_c} = 0$$

對照兩式：

$$\left\{ \begin{array}{l} \frac{-RT_c}{P_c} = -3V_c \rightarrow Z_c = \frac{P_c V_c}{RT_c} = \frac{1}{3} \\ \frac{-BRT_c}{P_c} = 3V_c^2 \rightarrow P_c = \frac{-BRT_c}{3V_c^2} = \frac{-BRV_c}{3RC} \\ \frac{-CRT_c}{P_c} = -V_c^3 \rightarrow T_c = \frac{P_c V_c^3}{RC} \end{array} \right.$$

因為此 Equation of state model 之  $Z_c$ 、 $P_c$ 、 $T_c$  三者皆存在，能被液化

## Problem 2

### 【Solution】

(1)

For this fundamental residual-property relation applies to fluids of constant composition, and at constant temperature.

If we begin from,

$$\frac{V^R}{RT} = \left[ -\frac{\partial(\frac{G^R}{RT})}{\partial P} \right]_T$$

(constant temperature)

$$d\left(\frac{G^R}{RT}\right) = \frac{V^R}{RT} dP, \quad \frac{G^R}{RT} = \underbrace{\left(\frac{G^R}{RT}\right)_{P=0}}_{\text{constant, set}=0} + \int_0^P \frac{V^R}{RT} dP = \int_0^P \frac{V^R}{RT} dP$$

$$\frac{G^R}{RT} = \int_0^P (Z-1) \frac{dP}{P}$$

For that of enthalpy, we may have,

$$\frac{H^R}{RT} = -T \left[ \frac{\partial(\frac{G^R}{RT})}{\partial T} \right]_P = -T \int_0^P \left( \frac{\partial Z}{\partial T} \right)_P \frac{dP}{P}$$

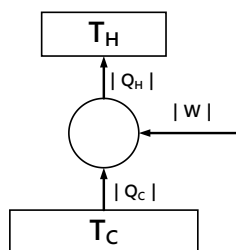
Therefore,

$$\frac{S^R}{R} = \frac{H^R}{RT} - \frac{G^R}{RT} = -T \int_0^P \left( \frac{\partial Z}{\partial T} \right)_P \frac{dP}{P} - \int_0^P (Z-1) \frac{dP}{P}$$

(本題可參考：Smith, J.; Van Ness, H.; Abbott, M. *Introduction to Chemical Engineering*, 7th ed.;

p 208-210.)

(2)



(3)

$$\text{COP(Coefficient of performance)} \equiv \frac{|Q_C|}{|W|} = \frac{T_C}{T_H - T_C}$$

(4)

$$\text{Efficiency, } \eta \equiv \frac{|W|}{|Q_H|}$$

(5)

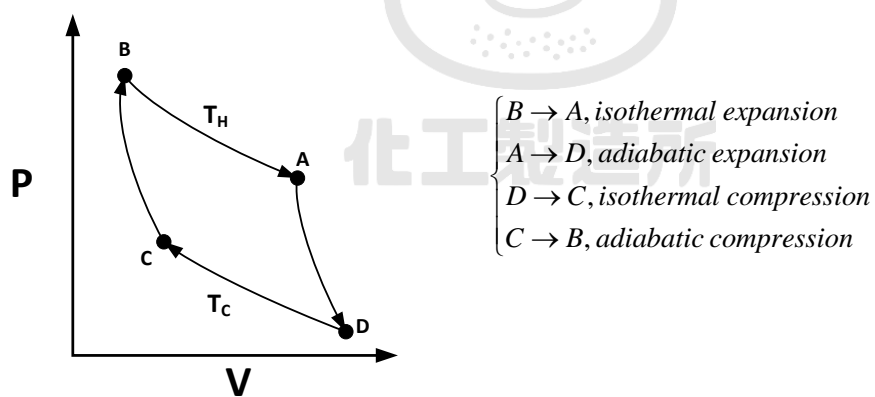
For most gases, at moderate T, and P, the Joule-Thompson coefficient,

$$\mu \equiv \left( \frac{\partial T}{\partial P} \right)_H > 0$$

Therefore, a reduction in P at constant H will causes a decrease in T.

(本題可參考：Smith, J.; Van Ness, H.; Abbott, M. *Introduction to Chemical Engineering*, 7th ed.; p 167, Figure 7.2.)

(6)



### Problem 3

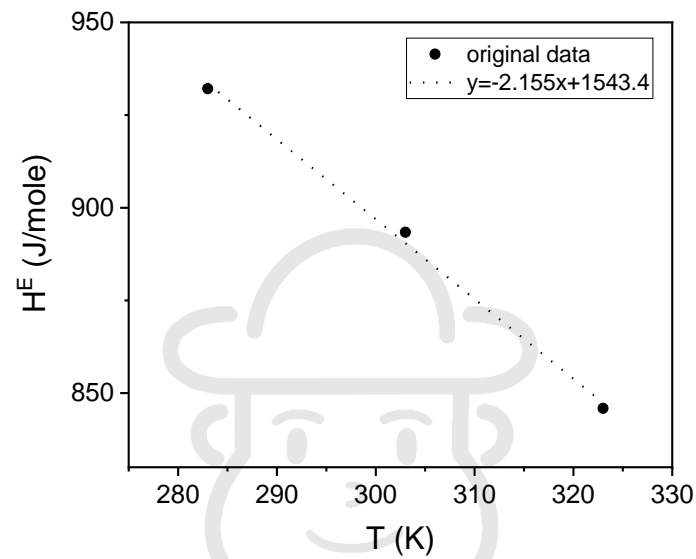
#### 【Solution】

(1)

For  $C_p^E$  to be constant,  $H^E$  can be assumed to be,

$$H^E = a + \int_{T_R}^T C_p^E dT = a + C_p^E (T - T_R) = a + bT$$

Plot  $H^E - T$  diagram,



$$\begin{cases} \text{slope} = b = -2.155 \\ \text{interception} = a = 1543.43 \end{cases}, \underline{\underline{H^E = 1543.43 - 2.155T}}$$

For  $G^E$  :

$$G^E = H^E - TS^E = H^E + T\left(\frac{\partial G^E}{\partial T}\right)_P = (a + bT) + T \frac{dG^E}{dT}$$

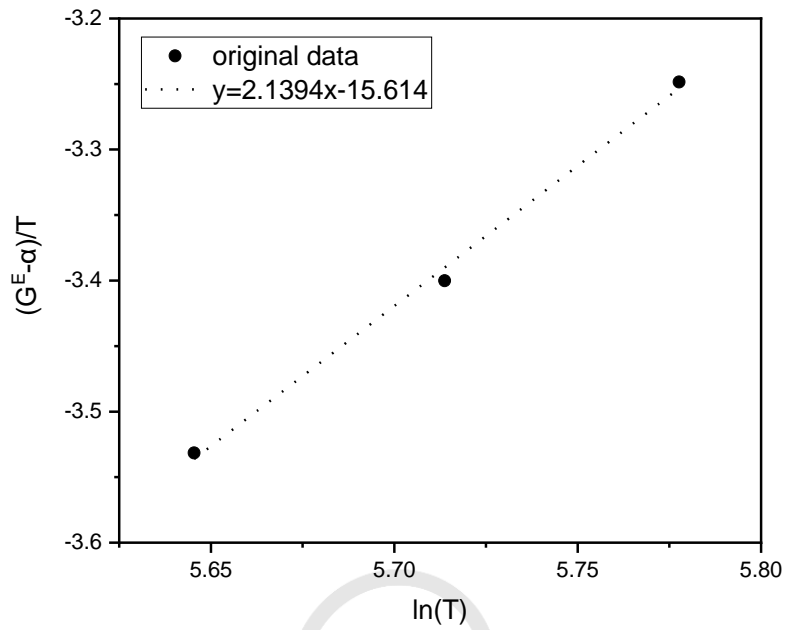
移項並解微分方程

$$G^E = a - bT \ln T + cT$$

$$\frac{G^E - a}{T} = -b \ln T + c$$



For  $c$ , plot  $G^E - \ln T$  diagram



$$c = -15.614, \quad G^E = 1543.43 + 2.155T \ln T - 15.614T$$

(2)

At 25°C,

$$\begin{cases} H^E = 901.24 \text{ (J/mol)} \\ G^E = 548.897 \text{ (J/mol)} \\ S^E = \frac{H^E - G^E}{T} = 1.1814 \text{ (J/mol} \cdot \text{K)} \end{cases}$$

(本題改編自：Smith, J.; Van Ness, H.; Abbott, M. *Introduction to Chemical Engineering*, 7th ed.; p 429, Problem 11.50.)

### Problem 4

#### 【Solution】

$$\frac{G^E}{RT} = A_{21}x_1^2x_2 + A_{12}x_1x_2^2$$

$$\begin{cases} \ln r_1 = \frac{\partial[nG^E / RT]_{T,P,n_2}}{\partial n_1} = 2A_{21}x_1x_2^2 + A_{12}x_2^2(x_2 - x_1) \\ \ln r_2 = \frac{\partial[nG^E / RT]_{T,P,n_1}}{\partial n_2} = 2A_{12}x_1^2x_2 + A_{21}x_1^2(x_1 - x_2) \end{cases}$$

By modified Raoult's law,

$$y_i P = x_i r_i P_i^{sat} \text{ 代入數據}$$

$$\begin{cases} 0.456 \times 139.1 = 183.4 \times 0.253 r_1 \\ 0.544 \times 139.1 = 96.7 \times 0.747 r_2 \end{cases}, \begin{cases} r_1 = 1.367 \\ r_2 = 1.047 \end{cases}$$

代回

$$\begin{cases} \ln(1.367) = 2A_{21} \times 0.253 \times 0.747^2 + A_{12} \times 0.747^2(0.747 - 0.253) \\ \ln(1.047) = A_{21} \times 0.253^2(0.253 - 0.747) + 2A_{12} \times 0.253^2 \times 0.747 \end{cases}$$
$$\begin{cases} A_{12} = 0.644 \\ A_{21} = 0.478 \end{cases}$$

若  $x_1 = 0.6$ ，則此時 activity coefficient 為：

$$r_1 = e^{2A_{21}x_1x_2^2 + A_{12}x_2^2(x_2 - x_1)} = e^{2 \times 0.478 \times 0.6 \times 0.4^2 + 0.644 \times 0.4^2(0.4 - 0.6)} = 1.074$$

$$r_2 = e^{2A_{12}x_2x_1^2 + A_{21}x_1^2(x_1 - x_2)} = e^{2 \times 0.644 \times 0.4 \times 0.6^2 + 0.478 \times 0.6^2(0.6 - 0.4)} = 1.246$$

代入：

$$\begin{cases} y_1 P = 0.6 \times r_1 \times 183.4 = 0.6 \times 1.074 \times 183.4 = 117.998 \\ y_2 P = 0.4 \times r_2 \times 96.7 = 0.4 \times 1.246 \times 96.7 = 48.195 \end{cases}, \frac{y_1}{y_2} = \frac{117.998}{48.195} \rightarrow \begin{cases} y_1 = 0.710 \\ y_2 = 0.289 \end{cases}$$

$$\underline{\underline{P = 166.2 \text{ (kPa)}}}$$

(關於 Margules equation 推導 activity coefficient 之過程，可參考：Smith, J.; Van Ness, H.; Abbott,

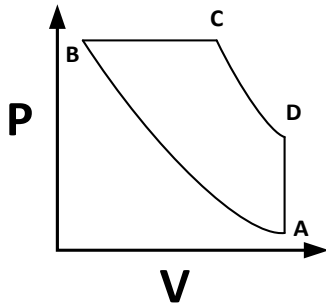
M. *Introduction to Chemical Engineering*, 7th ed.; p 437~438.)

# 109 年成大化熱

## Problem 1

### 【Solution】

(1) False



$A \rightarrow B = \text{reversible adiabatic compression}$

$B \rightarrow C = \text{constant pressure expansion (heating)}$

$C \rightarrow D = \text{reversible adiabatic expansion}$

$D \rightarrow A = \text{constant pressure compression (cooling)}$

The Diesel engine, and Otto engine, direct use the energy of high temperature, high pressure gases to act on a piston within a cylinder, and no heat transfer with an external source is required.

(本小題可參考：Smith, J.; Van Ness, H.; Abbott, M. *Introduction to Chemical Engineering*, 7th ed.; p 305~306, Example 8.3.)

(2) False

The entropy change of the system can be negative.

In the contrast, if one process is spontaneous, the total entropy change should always be larger or equal to zero.

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{sur} + S_{gen} \geq 0$$

(3) True

For a closed system, reversible phase change

$$\Delta G = \Delta H - T\Delta S = 0$$

$$\boxed{\Delta H = T\Delta S}$$

(本題與 106 成大化熱 Problem3-(4)雷同)

(4) True

For an ideal solution, its partial molar volume and enthalpy equals to its pure state, that is,

$$\begin{cases} \overline{V}_i^{id} = V_i \\ \overline{H}_i^{id} = H_i \end{cases}$$

(5)

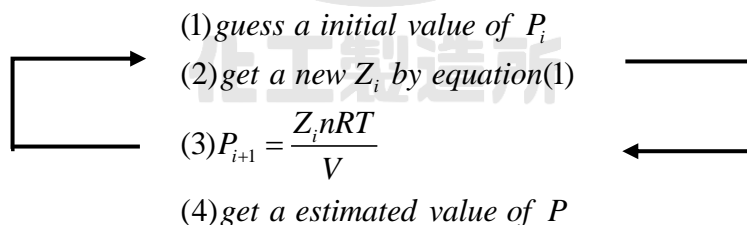
Pitzer correlation can be represented as follows,

$$Z = \frac{BP}{RT} = 1 + \hat{B} \frac{P_r}{T_r} \quad , \quad \hat{B} = \frac{BP_c}{RT_c} = B^\circ + wB^1$$

$$Z = 1 + B^\circ \frac{P_r}{T_r} + wB^1 \frac{P_r}{T_r} \begin{cases} B^\circ = 0.083 - \frac{0.422}{T_r^{1.6}} \\ B^1 = 0.139 - \frac{0.718}{T_r^{4.2}} \end{cases} \text{----- (1)}$$

The correlation has validity only at low to moderate pressures where Z is linear in pressure.

The iteration step is shown below,



(※更詳細之代值步驟可參考 104 成大化熱 Problem 2)

(6)

<ex> by the first law of thermodynamics, (open system, steady state)

$$\Delta H + \cancel{\frac{g}{g_c} \Delta z} + \cancel{\frac{1}{2g_c} \Delta v^2} = Q + \cancel{W}$$

If  $\begin{cases} (1) \text{no shaft work} \\ (2) \text{changes of kinetic and potential energies can be neglected} \end{cases}$

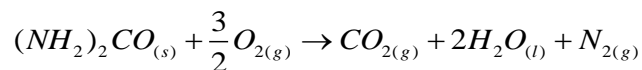
$\Delta H = Q$  is applicable

## **Problem 2**

### **【Solution】**

(2)

Reaction with stoichiometric coefficients,



(1)

$$\Delta H_{comb,298}^{\circ} = -631660 \text{ (J / mol)} = \Delta H_{rxn,298}^{\circ}$$

$$\Delta H_{rxn,298}^{\circ} = \sum_P v_i \Delta H_{f,298,i}^{\circ} - \sum_R v_i \Delta H_{f,298,i}^{\circ}$$

$$= (\Delta H_{f,298,CO_2}^{\circ} + 2\Delta H_{f,298,H_2O}^{\circ} + \Delta H_{f,298,N_2}^{\circ}) - (\Delta H_{f,298,urea}^{\circ} + \frac{3}{2}\Delta H_{f,298,O_2}^{\circ})$$

$$= (-393509 - 2 \times 285830) - \Delta H_{f,298,urea}^{\circ} = -631660$$

$$\underline{\underline{\Delta H_{f,298,urea}^{\circ} = -333509 \text{ (J / mol)}}}$$

(本題改編自：Smith, J.; Van Ness, H.; Abbott, M. *Introduction to Chemical Engineering*, 7th ed.;

p 154, Problem 4.26.)

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### **Problem 3**

#### **【Solution】**

$$\begin{cases} \frac{dP}{P} = \frac{d\rho}{\rho} + \frac{dZ}{Z} \text{----- (1)} \\ \frac{G^R}{RT} = \int_0^P (Z-1) \frac{dP}{P} \text{---- (2)} \end{cases}$$

將(1)代入(2) ,

$$\begin{aligned} \frac{G^R}{RT} &= \int_0^P (Z-1) \left( \frac{d\rho}{\rho} + \frac{dZ}{Z} \right) \\ &= \int_0^P (Z-1) \frac{d\rho}{\rho} + \int_1^Z (Z-1) \frac{dZ}{Z} \\ &= \int_0^P (Z-1) \frac{d\rho}{\rho} + \int_1^Z \left( 1 - \frac{1}{Z} \right) dZ \\ &= \int_0^P (Z-1) \frac{d\rho}{\rho} + Z - 1 + \ln Z \end{aligned}$$

(本題可參考：Smith, J.; Van Ness, H.; Abbott, M. *Introduction to Chemical Engineering*,

7th ed.; p 209-210/p 216.)

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#### **Problem 4**

#### **【Solution】**

For an isentropic expansion process with ideal gas as working fluid, there are some limits,

$$\begin{cases} (1) \text{ reversible} \\ (2) \text{ adiabatic} \\ (3) \text{ ideal gas} \end{cases}$$

Moreover, the whole process obeys the following relation

$$PV^\gamma = \text{constant} = K, \quad \gamma = \frac{C_p}{C_v}$$

整理：

$$V = K^{\frac{1}{\gamma}} P^{-\frac{1}{\gamma}}$$

<法(1)>：

The isentropic work from fundamental thermodynamic relations give,

$$\underbrace{dH = TdS + VdP}_{\text{thermodynamic relation}} = \underbrace{dW}_{\text{energy balance in open system}}$$

(neglect kinetic and potential energy differences)

$$W = \int_{P_1}^{P_2} VdP = \int_{P_1}^{P_2} \left(\frac{K}{P}\right)^{\frac{1}{\gamma}} dP = \sqrt[\gamma]{K} \int_{P_1}^{P_2} P^{-\frac{1}{\gamma}} dP = \frac{\gamma \sqrt[\gamma]{K}}{\gamma-1} (P_2^{\frac{\gamma-1}{\gamma}} - P_1^{\frac{\gamma-1}{\gamma}})$$

$$W = \frac{\gamma \sqrt[\gamma]{K}}{\gamma-1} (P_2^{\frac{\gamma-1}{\gamma}} - P_1^{\frac{\gamma-1}{\gamma}}) = \frac{\gamma}{\gamma-1} \cdot (K^{\frac{1}{\gamma}} P_2^{\frac{\gamma-1}{\gamma}}) [1 - (\frac{P_1}{P_2})^{\frac{\gamma-1}{\gamma}}] = \frac{\gamma}{\gamma-1} \cdot [(K^{\frac{1}{\gamma}} P_2^{\frac{\gamma-1}{\gamma}}) P_2] [1 - (\frac{P_1}{P_2})^{\frac{\gamma-1}{\gamma}}]$$

$$W = \frac{\gamma}{\gamma-1} \cdot [(K^{\frac{1}{\gamma}} P_2^{\frac{\gamma-1}{\gamma}}) P_2] [1 - (\frac{P_1}{P_2})^{\frac{\gamma-1}{\gamma}}] = \frac{\gamma}{\gamma-1} \cdot [V_2 P_2] [1 - (\frac{P_1}{P_2})^{\frac{\gamma-1}{\gamma}}] = \frac{\gamma RT_2}{\gamma-1} [1 - (\frac{P_1}{P_2})^{\frac{\gamma-1}{\gamma}}]$$

For ideal gas,

$$W = \frac{\gamma RT_2}{\gamma-1} [1 - (\frac{P_1}{P_2})^{\frac{\gamma-1}{\gamma}}] = \frac{\frac{C_p}{C_v} RT_2}{\frac{(C_p - C_v)}{C_v}} [1 - (\frac{P_1}{P_2})^{\frac{\gamma-1}{\gamma}}] = \frac{C_p RT_2}{R} [1 - (\frac{P_1}{P_2})^{\frac{\gamma-1}{\gamma}}] = \underline{\underline{C_p T_2 [1 - (\frac{P_1}{P_2})^{\frac{\gamma-1}{\gamma}}]}}$$

<法(2)> :

By isentropic process with ideal gas,

$$\frac{T_2}{T_1} = \left(\frac{P_1}{P_2}\right)^{\frac{1-\gamma}{\gamma}}$$

By the first law of thermodynamics,

$$\Delta H + \cancel{\frac{g}{g_c}\Delta z} + \cancel{\frac{1}{2g_c}\Delta v^2} = \cancel{Q} + W$$

$$W = \Delta H = C_p(T_2 - T_1) = C_p T_2 \left[1 - \left(\frac{P_2}{P_1}\right)^{\frac{1-\gamma}{\gamma}}\right] = \underline{\underline{C_p T_2 \left[1 - \left(\frac{P_1}{P_2}\right)^{\frac{\gamma-1}{\gamma}}\right]}}$$

※雖以法(2)來說整體討論較為簡單，然而法(1)的討論在於介紹此類 polytropic 程序)isentropic process 為此種程序特例)可以怎麼做積分並得到最後的解。



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### **Problem 5**

#### **【Solution】**

By Gibbs-Duhem equation at constant T and P

$$x_1 d\overline{H}_1(x) + x_2 d\overline{H}_2(x) = 0$$

$$x_1 \left( \frac{d\overline{H}_1}{dx_1} \right) dx_1 = -x_2 d\overline{H}_2 = -(1-x_1) d\overline{H}_2$$

$$\frac{x_1}{x_1-1} \left( \frac{d\overline{H}_1}{dx_1} \right) = d\overline{H}_2, \quad \int_0^{x_1} \frac{x_1}{x_1-1} \left( \frac{d\overline{H}_1}{dx_1} \right) dx_1 = \int_{H_2}^{\overline{H}_2} d\overline{H}_2$$

$$\overline{H}_2 = H_2 + \int_0^{x_1} \frac{x_1}{x_1-1} \left( \frac{d\overline{H}_1}{dx_1} \right) dx_1,$$

where  $H_2$  is the molar enthalpy at pure state

$\therefore$  mixture enthalpy

$$H = n\overline{H} = \underline{\underline{(n_1 + n_2)(x_1 \overline{H}_1 + x_2 \overline{H}_2)}}$$

### **Problem 6**

#### **【Solution】**

$$\begin{aligned} \Delta \overline{G}_{mix} &= RT \sum x_i \ln a_i = RT \sum x_i (\ln r_i + \ln x_i) \\ &= RT(x_1 \ln r_1 + x_2 \ln r_2) + RT(x_1 \ln x_1 + x_2 \ln x_2) \\ &= Cx_1(1-x_1)^2 + Cx_2(1-x_2)^2 + RTx_1 \ln x_1 + RTx_2 \ln x_2 \end{aligned}$$

For stable system,

$$\begin{aligned} \frac{d^2 \Delta \overline{G}_{mix}}{dx_1^2} &= C(6x_1 - 4) + \frac{d^2}{dx_1^2} [C(1-x_1)(x_1^2)] + RT \left( \frac{1}{x_1} \right) + RT \frac{d^2}{dx_1^2} [(1-x_1) \ln(1-x_1)] \\ &= C(6x_1 - 4 - 6x_1 + 2) + RT \left( \frac{1}{x_1} + \frac{1}{1-x_1} \right) > 0 \\ &\quad \underline{\underline{\frac{1}{x_1(1-x_1)} > 2 \frac{C}{RT}}} \end{aligned}$$

(本題可參考：Smith, J.; Van Ness, H.; Abbott, M. *Introduction to Chemical Engineering*, 7th ed.;

p 578-579/p 589.)

# 110 年成大化熱

## Problem 1

### **【Solution】**

Assume the gas to be air,

$$M_{air} = 28.8 \text{ (kg / mol)}$$

By energy balance (open system, steady state),

$$\Delta H + \frac{1}{2g_c} \Delta v^2 + \frac{g}{g_c} \Delta z = Q + W$$

$$\Delta \dot{H} = \dot{n} C_p \Delta T = \frac{40}{3600} \times \frac{7}{2} \times 8.314 \times (500 - 300) = 64.66 \text{ (kJ / s)}$$

$$\frac{1}{2g_c} \Delta v^2 \cdot \dot{m} = \frac{1}{2 \times 1} \times (4.0^2 - 10^2) \times \frac{40 \times 28.8}{3600} \times 1 \times 10^{-3} = -0.01344 \text{ (kJ / s)}$$

$$\dot{Q} = \Delta \dot{H} + \frac{1}{2g_c} \Delta v^2 \cdot \dot{m} - \dot{W} = 64.66 - 0.01344 - 100.0 = \underline{\underline{-35.35 \text{ (kW)}}}$$

(本題改編自：Smith, J.; Van Ness, H.; Abbott, M.; Hwalek, J. *Introduction to Chemical Engineering Thermodynamics*, 7th ed.; p 54, Example 2.16.)

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## **Problem 2**

### **【Solution】**

※本題按字面題意為若將此 cycle 的每一步都變為不可逆的步驟，其 Q 與 W 將作何種改變，因每一個步驟的起終點明確，只是將步驟改為不可逆，因此以固定起終點的方式做計算。

#### **(a) Adiabatic process**

By energy balance (reversible case),

$$\Delta U = \cancel{Q} + W = W, \quad W = \Delta U = C_v \Delta T$$

For an adiabatic process with ideal gas,

$$\frac{T_f}{T_i} = \left(\frac{P_f}{P_i}\right)^{\frac{1}{\gamma}}, \quad T_f = 300 \left(\frac{5}{1}\right)^{\frac{1}{7/5}} = 475.14 \text{ (K)}$$

$$W_{ideal} = C_v(T_f - T_i) = \frac{5}{2} \times 8.314 \times (475.14 - 300) = 3640.28 \text{ (J / mol)}$$

$$W_{real} = \frac{3640.28}{0.8} = 4550.35 \text{ (J / mol)}$$

$$Q_{real} = \Delta U - W = 3640.28 - 4550.35 = -910 \text{ (J / mol)}$$

$$\begin{cases} Q_{real} = -910 \text{ (J / mol)} \\ W_{real} = 4550.35 \text{ (J / mol)} \end{cases}$$

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### **(b) Constant-Pressure Cooling**

By energy balance (reversible process),

$$\Delta U = Q + W$$

For ideal process,

$$Q_{ideal} = C_p \Delta T = \frac{7}{2} \times 8.314 \times (300 - 475.14) = -5096.39 \text{ (J / mol)}$$

$$\Delta U = C_v \Delta T = \frac{5}{2} \times 8.314 \times (300 - 475.14) = -3640.28 \text{ (J / mol)}$$

$$W_{ideal} = \Delta U - Q = -3640.28 + 5096.39 = 1456.11 \text{ (J / mol)}$$

=>

$$W_{real} = \frac{1456.11}{0.8} = 1820.13 \text{ (J / mol)}$$

$$Q_{real} = \Delta U - W_{real} = -3640.28 - 1820.13 = -5460.41 \text{ (J / mol)}$$

$$\begin{cases} Q_{real} = -5460.41 \text{ (J / mol)} \\ W_{real} = 1820.13 \text{ (J / mol)} \end{cases}$$

### **(c) Isothermal Expansion**

By energy balance (reversible process),

$$\Delta U = Q + W, \quad Q = -W$$

$$\begin{aligned} W_{ideal} &= -Q_{ideal} = -RT \ln \frac{V_2}{V_1} = -RT \ln \frac{P_1}{P_2} \\ &= -8.314 \times 300 \ln \frac{5}{1} = -4014.26 \text{ (J / mol)} \end{aligned}$$

$$W_{real} = -4014.26 \times 0.8 = -3211.40 \text{ (J / mol)}$$

$$\begin{cases} Q_{real} = 3211.40 \text{ (J / mol)} \\ W_{real} = -3211.40 \text{ (J / mol)} \end{cases}$$

(本題改編自：Smith, J.; Van Ness, H.; Abbott, M.; Hwalek, J. *Introduction to Chemical Engineering Thermodynamics*, 7th ed.; p 122, Problem 3.65.)

**Problem 3****【Solution】**

(1)

$$(dU^{IG})_T = 0$$

$$(dU)_T = \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$[d(U - U^{IG})_T] = (dU^R)_T = \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$\therefore \left(\frac{\partial U}{\partial V}\right)_T = -P + T\left(\frac{\partial S}{\partial V}\right)_T = -P + T\left(\frac{\partial P}{\partial T}\right)_V \text{ 代回}$$

$$(dU^R)_T = [T\left(\frac{\partial P}{\partial T}\right)_V - P]dV$$

For  $T\left(\frac{\partial P}{\partial T}\right)_V$ 

$$T\left[\frac{\partial}{\partial T}\left(\frac{RT}{V-b}\right)\right]_V - T\left[\frac{\partial}{\partial T}\left(\frac{\alpha}{V(V+b)}\right)\right]_V = \frac{RT}{V-b} - T\frac{\frac{\partial \alpha}{\partial T}}{V(V+b)}$$

$$(dU^R)_T = \left[\frac{RT}{V-b} - T\frac{\frac{\partial \alpha}{\partial T}}{V(V+b)} - P\right]dV = \left[\frac{\alpha}{V(V+b)} - \frac{T\frac{\partial \alpha}{\partial T}}{V(V+b)}\right]dV$$

$$\underline{\underline{U^R = \int_{\infty}^V \left[\frac{\alpha}{V(V+b)} - \frac{T\frac{\partial \alpha}{\partial T}}{V(V+b)}\right]dV}}$$

(2)

$$\therefore \alpha = kT^{-0.5}$$

$$\frac{\partial \alpha}{\partial T} = -\frac{1}{2}kT^{-1.5}$$

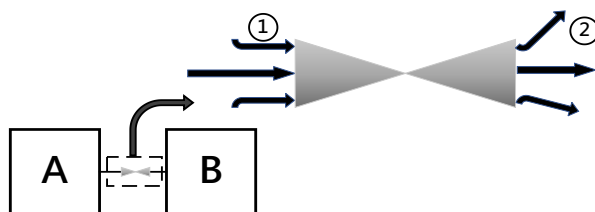
$$U^R = \int_{\infty}^V \left[\frac{\alpha}{V(V+b)} - \frac{T(-\frac{1}{2}kT^{-1.5})}{V(V+b)}\right]dV = \int_{\infty}^V \left[\frac{\alpha}{V(V+b)} + \frac{\frac{1}{2}\alpha}{V(V+b)}\right]dV$$

$$= \int_{\infty}^V \left[\frac{\frac{3}{2}\alpha}{V(V+b)}\right]dV = \frac{3\alpha}{2b} \int_{\infty}^V \left[\frac{1}{V} - \frac{1}{V+b}\right]dV = \underline{\underline{\frac{3\alpha}{2b} \ln \frac{V}{V+b}}}$$

### Problem 4

#### 【Solution】

【法(1)－開放系統（系統有很多種取法，假設以 compressor 為系統）】



By energy balance for the (compressor + gas across the compressor) system,

$$\cancel{\Delta H}_{T=\text{constant}} + \cancel{\frac{1}{2g_c}\Delta v^2} + \cancel{\frac{g}{g_c}\Delta z} = Q + W$$
$$Q = -W$$

By entropy balance,

$$\cancel{\frac{dS}{dt}}_{s.s} = \sum \dot{n}_i S_i + \sum \frac{\dot{Q}}{T} + \cancel{\dot{S}_{gen}}_{\text{reversible}}$$
$$\sum \frac{dQ}{dt} = \frac{dQ}{dt} = T \dot{n}(t) \left[ \cancel{C_p \ln \frac{T_2}{T_1}} - R \ln \frac{P_2}{P_1} \right]$$
$$= -RT \ln \frac{P_2}{P_1} \cdot \frac{dn}{dt} = \frac{-RT}{RT} V \ln \frac{P_2}{P_1} \cdot \frac{dP_2}{dt}$$

For  $P_1$  and  $P_2$ , by mole balance,

$$\frac{P_{1i}V}{RT} + \frac{P_{2i}V}{RT} = \frac{P_1V}{RT} + \frac{P_2V}{RT}, \quad \frac{V}{RT} \text{ 皆相同}$$
$$P_{1i} + P_{2i} = 2 + 2 = P_1 + P_2 = 4, \quad P_1 = 4 - P_2 \text{ 代回}$$

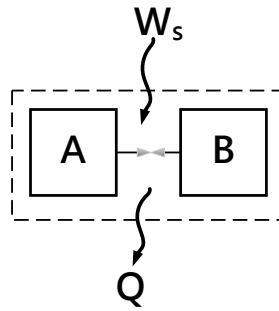
$$\frac{dQ}{dt} = -V \ln \frac{P_2}{4 - P_2} \frac{dP_2}{dt}$$

$$\int_0^Q dQ = 100 \times 10^{-3} \int_2^3 \ln \frac{P_2}{4 - P_2} dP_2 \times 1 \times 10^5$$

$$Q = -5232.48 \text{ (J)}$$

$$\underline{\underline{W = -Q = 5232.48 \text{ (J)}}}$$

【法(2)－ 封閉系統 (包含 A + compressor + B)】



By energy balance for the entire closed system,

$$\overbrace{\Delta U}^{\text{ideal gas, isothermal}} = Q + W$$

$$W = -Q$$

其中，功的貢獻有二：邊界移動功( $-PdV$ )以及軸功(shaft work,  $W_s$ )，此題因整體系統邊界並未移動做功，因此無邊界移動功；但因有 compressor 壓縮氣體，所以有外界所作之軸功，因此：

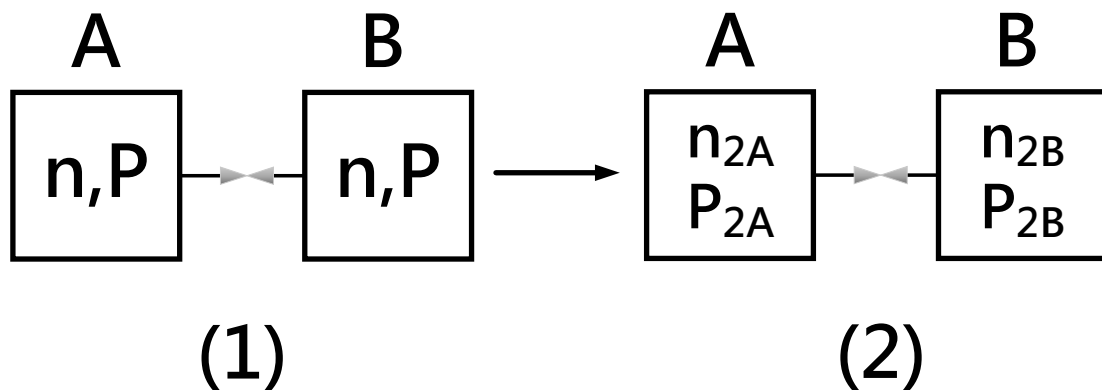
$$W = \cancel{W_{PV}} + W_s, \quad W_s = -Q$$

For  $Q$ , by entropy balance,

$$\Delta S = \frac{Q}{T} + \underbrace{S_{gen}}_{\text{reversible}} = S_2 - S_1$$

$$Q = T(S_2 - S_1)$$

定義：



$$\begin{aligned}
 S_2 - S_1 &= -n_{2A} R \ln\left(\frac{P_{2A}}{P_{ref}}\right) - n_{2B} R \ln\left(\frac{P_{2B}}{P_{ref}}\right) - \left[-n \ln\left(\frac{P}{P_{ref}}\right) - n \ln\left(\frac{P}{P_{ref}}\right)\right] \\
 &= 2n \ln\left(\frac{P}{P_{ref}}\right) - n_{2A} R \ln\left(\frac{P_{2A}}{P_{ref}}\right) - n_{2B} R \ln\left(\frac{P_{2B}}{P_{ref}}\right)
 \end{aligned}$$

※其中，因 ideal gas 的熵變化會跟溫壓有關，這裡取  $T_{ref} = 280K$ ，就可以忽略溫度影響，而壓

力則取  $P_{ref} = 1 \text{ bar}$ ，之所以可以這樣取即因為假設定量 ideal gas 經歷變溫壓縮，通常我們可直

接藉由公式算出：

$$\Delta S = -nR \ln\left(\frac{P_f}{P_i}\right) + nC_p \ln\left(\frac{T_f}{T_i}\right)$$

然而若當作初始條件皆各別由標準態經過某程序達成，亦即：

$$\Delta S = S_f - S_i = (S_f - S_{ref}) - (S_i - S_{ref})$$

$$S_f - S_{ref} = -nR \ln\left(\frac{P_f}{P_{ref}}\right) + nC_p \ln\left(\frac{T_f}{T_{ref}}\right)$$

$$S_i - S_{ref} = -nR \ln\left(\frac{P_i}{P_{ref}}\right) + nC_p \ln\left(\frac{T_i}{T_{ref}}\right)$$

$$\begin{aligned}
 \Delta S &= (S_f - S_{ref}) - (S_i - S_{ref}) = \left[-nR \ln\left(\frac{P_f}{P_{ref}}\right) + nC_p \ln\left(\frac{T_f}{T_{ref}}\right)\right] - \left[-nR \ln\left(\frac{P_i}{P_{ref}}\right) + nC_p \ln\left(\frac{T_i}{T_{ref}}\right)\right] \\
 &= \underline{\underline{-nR \ln\left(\frac{P_f}{P_i}\right) + nC_p \ln\left(\frac{T_f}{T_i}\right)}}
 \end{aligned}$$

因此題氣體皆為同種理想氣體，因此此方式在運用上相對簡單

以下接續：

$$S_2 - S_1 = \frac{2PV}{RT} \ln\left(\frac{P}{P_{ref}}\right) - \frac{P_{2A}V}{RT} R \ln\left(\frac{P_{2A}}{P_{ref}}\right) - \frac{P_{2B}V}{RT} R \ln\left(\frac{P_{2B}}{P_{ref}}\right)$$

又根據 mole balance,

$$\frac{P_{2A}V}{RT} + \frac{P_{2B}V}{RT} = \frac{PV}{RT} + \frac{PV}{RT}, \quad P_{2A} + P_{2B} = P + P$$

$$P_{2A} = P + P - P_{2B} = 2 + 2 - 3 = 1 \text{ (bar)}$$



代回數據：

$$S_2 - S_1 = \frac{V}{T} [2P \ln(\frac{P}{1}) - P_{2A} \ln(\frac{P_{2A}}{1}) - P_{2B} \ln(\frac{P_{2B}}{1})]$$

$$S_2 - S_1 = \frac{100 \times 10^{-3}}{280} [2 \times 2 \ln(\frac{2}{1}) - 1 \times \ln(\frac{1}{1}) - 3 \times \ln(\frac{3}{1})] \times 1.013 \times 10^5 = -18.687 \text{ (J / K)}$$

代回：

$$Q = T(S_2 - S_1) = 280 \times (-18.687) = \underline{\underline{-5232.48 \text{ (J)}}}$$

$$W_s = -Q = \underline{\underline{5232.48 \text{ (J)}}}$$



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### **Problem 5**

#### **【Solution】**

(1) False

@ Constant T, P,

$$\sum_i x_i d\bar{G}_i = \sum_i x_i d(RT \ln \hat{f}_i) = 0$$

$$\sum_i x_i d\bar{G}_i^{IG} = \sum_i x_i d(RT \ln P_i) = 0$$

相減

$$\sum_i x_i d(RT \ln \frac{\hat{f}_i}{P_i}) = \sum_i x_i d(RT \ln \hat{\phi}_i) = 0$$

$$\underline{\underline{\sum_i x_i d(\ln \hat{\phi}_i) = 0}}$$

(2) True

※題目應解讀為(原始題目似乎不清楚)：

$$V_i^{ig}(T, P) = \bar{V}_i^{ig}(T, P)$$

∴ For ideal gas mixture,

$$V^{ig}(T, P) = \sum_i y_i \bar{V}_i^{ig} = \sum_i y_i V_i^{ig}$$

For an ideal gas, the molar volume remains constant regardless of the type of gas molecules,

$$V_1^{ig} = V_2^{ig} = \dots = V_i^{ig}$$

$$V^{ig}(T, P) = \sum_i y_i V_i^{ig} = V_i^{ig} \sum_i y_i = V_i^{ig}$$

(3) True

$$\overline{H_i^{ig}}(T, P) \xleftarrow[\text{mixture}]{\text{ideal}} H_i^{ig}(T, P) \xleftarrow{\neq f(P)} H_i^{ig}(T, p_i)$$

(4) False

$$ndG = nVdP - nSdT + \sum_i \overline{G_i} dn_i$$

$$ndG^{IG} = nV^{IG}dP - nS^{IG}dT + \sum_i \overline{G_i^{IG}} dn_i$$

相減

$$d[n(G - G^{IG})] = d(nG^R) = nV^RdP - nS^RdT + \sum_i \overline{G_i^R} dn_i$$

又根據連鎖律：

$$d\left(\frac{nG^R}{RT}\right) = \frac{1}{RT}d(nG^R) - \frac{nG^R}{RT^2}dT$$

將

$$d(nG^R) = nV^RdP - nS^RdT + \sum_i \overline{G_i^R} dn_i$$

與

$$nG^R = nH^R - T(nS^R)$$

代入得

$$d\left(\frac{nG^R}{RT}\right) = \frac{1}{RT}d(nG^R) - \frac{nG^R}{RT^2}dT = \frac{nV^RdP - nS^RdT + \sum_i \overline{G_i^R} dn_i}{RT} - \frac{nH^R - T(nS^R)}{RT^2}dT$$

$$d\left(\frac{nG^R}{RT}\right) = \frac{nV^RdP}{RT} - \cancel{\frac{nS^RdT}{RT}} + \frac{\sum_i \overline{G_i^R} dn_i}{RT} - \frac{nH^R}{RT^2}dT + \cancel{\frac{T(nS^R)}{RT^2}dT}$$

$$\underline{\underline{d\left(\frac{nG^R}{RT}\right) = \frac{nV^R}{RT}dP - \frac{nH^R}{RT^2}dT + \sum_i \frac{\overline{G_i^R}}{RT}dn_i}}$$

或

$$\begin{aligned}d\left(\frac{nG^R}{RT}\right) &= \frac{nV^R}{RT}dP - \frac{nH^R}{RT^2}dT + \sum_i \frac{\overline{G}_i^R}{RT}dn_i = \frac{nV^R}{RT}dP - \frac{n(G^R + TS^R)}{RT^2}dT + \sum_i \frac{\overline{G}_i^R}{RT}dn_i \\&= \underline{\underline{\frac{nV^R}{RT}dP - \frac{nG^R}{RT^2}dT - \frac{nS^R}{RT} + \sum_i \frac{\overline{G}_i^R}{RT}dn_i}}\end{aligned}$$



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### **Problem 6**

#### **【Solution】**

By Summability equation,

$$M = x_1 \overline{M}_1 + x_2 \overline{M}_2 \cdots (1)$$

By Gibbs-Duhem equation at T, P,

$$\sum_i x_i d\overline{M}_i = x_1 d\overline{M}_1 + x_2 d\overline{M}_2 = 0 \cdots (2)$$

From (1)

$$dM = x_1 d\overline{M}_1 + \overline{M}_1 dx_1 + x_2 d\overline{M}_2 + \overline{M}_2 dx_2 \cdots (3)$$

(2)代入(3)

$$\overline{M}_1 dx_1 + \overline{M}_2 dx_2 = dM$$

$\because dx_1 = -dx_2$  , 且同除  $dx_1$

$$\frac{dM}{dx_1} = \overline{M}_1 - \overline{M}_2 \cdots (4)$$

又  $x_1 = 1 - x_2$  代入(1)

$$M = \overline{M}_1 - x_2 (\overline{M}_1 - \overline{M}_2) \cdots (5)$$

$x_2 = 1 - x_1$  代入(1)

$$M = x_1 (\overline{M}_1 - \overline{M}_2) + \overline{M}_2 \cdots (6)$$

(4)代入(5)

$$\underline{\underline{\overline{M}_1 = M + x_2 \frac{dM}{dx_1}}}$$

(4)代入(6)

$$\underline{\underline{\overline{M}_2 = M - x_1 \frac{dM}{dx_1}}}$$

(本題可參考：Smith, J.; Van Ness, H.; Abbott, M.; Hwalek, J. *Introduction to Chemical Engineering Thermodynamics*, 7th ed.; p 385~386.)

# 111 年成大化熱

## Problem 1

### 【Solution】

※題目應改為 isothermal "compression"

(1)

For process (I), the work needed is, (二步驟反應)

$$\begin{aligned} W &= \cancel{W_{\text{constant } V}} + W_{\text{isobaric}} = -\int P dV = -P(V_2 - V_1) \\ &= -P\left(\frac{nRT_2}{P} - \frac{nRT_1}{P}\right) = nR(T_1 - T_2) = 1 \times 8.314 \times (840 - 560) = 2327.92 \text{ (J)} \end{aligned}$$

For process (II), the work needed is, (一步驟反應)

$$W = -\int P dV = -\int_{V_1}^{V_2} \frac{nRT}{V} dV = nRT \ln \frac{V_1}{V_2} = nRT \ln \frac{P_2}{P_1}$$

$$W = 1 \times 8.314 \times 560 \times \ln \frac{P}{4} = 2327.92$$

$$\underline{\underline{P = 6.59 \text{ (bar)}}}$$

(2)

As above, the work for both process is 2327.92 (J)

Also, for both process,

$$\Delta U = nC_v \cancel{\Delta T} = \underline{\underline{0}}$$

$$\Delta H = nC_p \cancel{\Delta T} = \underline{\underline{0}}$$

$$Q = \Delta U - W = \underline{\underline{-2327.92 \text{ (J)}}}$$

(本題改編自：Smith, J.; Van Ness, H.; Abbott, M. *Introduction to Chemical Engineering*, 7th ed.;

p 115, Problem 3.24。原題的二步驟過程為從高溫冷卻至目標壓力 P，題目最後用詞為 expansion；

而此題之二步驟反應為升溫至高溫，所以應相反為 compression。)

## **Problem 2**

### **【Solution】**

For  $W$ ,  $\Delta U$ , and  $\Delta H$ ,

$$\Delta U = \int_{T_1}^{T_2} nC_V dT = \int_{300}^{750} 1 \times [8.314(3.8 + 0.5 \times 10^{-3}T) - 8.314] dT = \underline{\underline{11457.7 \text{ (J)}}}$$

$$\Delta H = \int_{T_1}^{T_2} nC_P dT = \int_{300}^{750} 1 \times [8.314(3.8 + 0.5 \times 10^{-3}T)] dT = \underline{\underline{15199.0 \text{ (J)}}}$$

$$W = \Delta U - \oint_{adiabatic} = \Delta U = \underline{\underline{11457.7 \text{ (J)}}}$$

For  $P_2$ , because the process is adiabatic, by 1<sup>st</sup> law of thermodynamics,

$$dU = dQ + dW = 0 - PdV = nC_V dT$$

$$\frac{-nRT}{V} dV = nC_V dT$$

$$-\frac{nR}{V} dV = \frac{C_V}{T} dT$$

兩邊積分：

$$nR \ln \frac{V_1}{V_2} = \int_{T_1}^{T_2} \frac{C_V}{V} dT, \quad nR \ln \frac{T_1 P_2}{P_1 T_2} = \int_{T_1}^{T_2} \frac{C_V}{T} dT$$

$$1 \times 8.314 \times \ln \frac{300 P_2}{0.5 \times 750} = \int_{300}^{750} \frac{[8.314(3.8 + 0.5 \times 10^{-3}T) - 8.314]}{T} dT$$

$$\underline{\underline{P_2 = 20.36 \text{ (bar)}}}$$

(本題改編自：Smith, J.; Van Ness, H.; Abbott, M. *Introduction to Chemical Engineering*, 7th ed.;

p 153, Problem 4.17.)

**Problem 3****【Solution】**

(a)

$$dA = -PdV - SdT$$

(b)

At constant T,

$$\frac{dA}{dT} = \frac{-PdV}{dT} - \cancel{\frac{SdT}{dT}}$$

$$\left[ \frac{\partial(A/T)}{\partial V} \right]_T = \frac{-P}{T}$$

(b)

$$\therefore d\left(\frac{A}{T}\right) = \frac{1}{T} dA - \frac{A}{T^2} dT$$

Also,  $A = U - TS$ ,  $dA = dU - SdT - TdS$ 

$$d\left(\frac{A}{T}\right) = \frac{1}{T} (-PdV - SdT) - \frac{U - TS}{T^2} dT = \frac{-P}{T} dV - \cancel{\frac{S}{T} dT} - \frac{U}{T^2} dT + \cancel{\frac{S}{T} dT}$$

$$\left[ \frac{\partial(\frac{A}{T})}{\partial T} \right]_V = -\frac{U}{T^2} = -\frac{1}{T} \cdot \frac{U}{T}$$

**Problem 4****【Solution】**

(a)

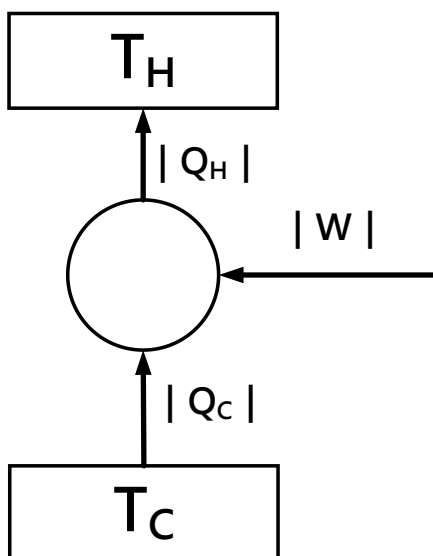
$$COP_{pump} = \frac{|Q_c|}{W}$$

(此題答案可參考社團補充檔案)



(b)

For a heat pump,



For an ideal heat pump, the COP can be calculated as,

$$COP_{pump} = \frac{|Q_c|}{W} = \frac{|Q_c|}{|Q_H| - |Q_c|} = \frac{T_c}{T_H - T_c} = \frac{273.15 + 30}{260 - 30} = \underline{\underline{1.318}}$$

$$\therefore 0.5 < 1.318$$

**The claim is believable**

(本題可參考：Smith, J.; Van Ness, H.; Abbott, M. *Introduction to Chemical Engineering*, 7th ed.;

p 318. For the coefficient of performance calculated from a refrigerator operating on a Carnot cycle, it gives the maximum possible value of COP for any refrigerator operating between given

values of  $T_H$  and  $T_C$ .)

### **Problem 5**

#### **【Solution】**

The boundary between one phase and two-phase separation is,

$$\frac{d^2(\Delta G / RT)}{dx_1^2} = 0$$

又

$$\Delta G = \Delta G_{mix} + G^E$$

$$\frac{\Delta G}{RT} = x_1 \ln x_1 + x_2 \ln x_2 + \frac{G^E}{RT} \text{ 代入}$$

可推得

$$\frac{d^2(G^E / RT)}{dx_1^2} = \frac{-1}{x_1 x_2}$$

$G^E / RT = Ax_1 x_2$  代入，

$$\frac{d^2(G^E / RT)}{dx_1^2} = -2A = \frac{-1}{x_1 x_2}, \quad A = \frac{1}{2x_1 x_2}$$

$\because 0.3 \leq x_1 \leq 0.7$  系統將呈現不穩定狀態

$$A = \frac{1}{2 \times 0.3 \times 0.7} = \underline{\underline{2.38}} \text{ 時，系統將在 } 0.3 \leq x_1 \leq 0.7 \text{ 產生相分離}$$

**Problem 6****【Solution】****(a)**

By the equilibrium relation of the species 2 (solvent) between the compartments,

$$\hat{f}_2(T, P + \Pi, x_2) = f_2(T, P)$$

Beacuse both compartments are in the same temperature,

$$\hat{f}_2(P + \Pi, x_2) = f_2(P)$$

Furthermore,

$$\hat{f}_2(T, P + \Pi, x_2) = f_2(P) \cdot \frac{\hat{f}_2(P, x_2)}{f_2(P)} \cdot \frac{\hat{f}_2(P + \Pi, x_2)}{\hat{f}_2(P, x_2)}$$

Also,

$$\frac{\hat{f}_2(P, x_2)}{f_2(P)} = x_2 r_2$$

( $r_2 = \text{activity coefficient of } 2$ )

To find the expression of  $\frac{\hat{f}_2(P + \Pi, x_2)}{\hat{f}_2(P, x_2)}$ ,

$$\mu_i = RT \ln \hat{f}_i, \quad \left(\frac{\partial \mu_i}{\partial P}\right)_T = RT \left[\frac{\partial(\ln \hat{f}_i)}{\partial P}\right]_T$$

Also,

$$\left(\frac{\partial \mu_i}{\partial P}\right)_T = \bar{V}_i$$

$$\left(\frac{\partial \mu_2}{\partial P}\right)_T = RT \left[\frac{\partial(\ln \hat{f}_2)}{\partial P}\right]_T, \quad \left[\frac{\partial(\ln \hat{f}_2)}{\partial P}\right]_T = \frac{\bar{V}_2}{RT}$$

$$\frac{\hat{f}_2(P + \Pi, x_2)}{\hat{f}_2(P, x_2)} = \exp\left[\int_P^{P+\Pi} \frac{\bar{V}_2}{RT} dP\right]$$

代回：

$$\hat{f}_2(T, P + \Pi, x_2) = f_2(P) x_2 r_2 \exp\left[\int_P^{P+\Pi} \frac{\bar{V}_2}{RT} dP\right] = f_2(P)$$

$$x_2 r_2 \exp\left[\int_P^{P+\Pi} \frac{\bar{V}_2}{RT} dP\right] = 1, \quad \int_P^{P+\Pi} \frac{\bar{V}_2}{RT} dP = -\ln(x_2 r_2)$$

Because for a liquid system, the change of volume according to pressure is negligible,

$$\int_P^{P+\Pi} \frac{\bar{V}_2}{RT} dP \approx \bar{V}_2 \int_P^{P+\Pi} \frac{1}{RT} dP = -\ln(x_2 r_2)$$

$$\Pi = -\frac{RT[\ln(x_2 r_2)]}{\bar{V}_2} \approx -\frac{RT[\ln(x_2 r_2)]}{V_2}$$

$\therefore$  The solution system is very dilute

$$r_2 \rightarrow 1, \quad x_1 \rightarrow 0$$

$$\ln(x_2 r_2) \approx \ln(x_2) = \ln(1 - mx_1) \approx -mx_1$$

$$(\text{Recall the Taylor expansion, } \ln(1-x) = -x - \frac{x^2}{2} + \dots \approx -x)$$

$$\Pi = -\frac{RT[\ln(x_2 r_2)]}{V_2} \approx \frac{RTmx_1}{V_2}$$

$$\therefore mx_1 = \frac{m \cdot n_{\text{solute}}}{m \cdot n_{\text{solute}} + n_{\text{solvent}}} \approx \frac{m \cdot n_{\text{solute}}}{n_{\text{solvent}}} = \frac{m \cdot C_{\text{solute}} / W_{\text{solute}}}{C_{\text{solvent}} / W_{\text{solvent}}} \quad (C = \text{mass} / \text{volume})$$

$$C_{\text{solvent}} / W_{\text{solvent}} = V_{\text{solvent}} = V_2, \quad C_{\text{solute}} / W_{\text{solute}} = c$$

$$\Pi \approx \frac{RTmx_1}{V_2} = mcRT$$

(本題可參考：Smith, J.; Van Ness, H.; Abbott, M. *Introduction to Chemical Engineering*,

7th ed.; p 622~623.)

(b)

$$\Pi = mcRT = 2 \times \frac{3.5}{58.443} \times 0.082 \times (25 + 273.15) = \underline{\underline{2.93 \text{ (atm)}}}$$

假設室溫

# 112 年成大化熱

## Problem 1

### **【Solution】**

※題目所給 isothermal compressibility 有誤，應為：

$$\kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

To calculate the compression work, by definition,

$$W = -n \int_{V_i}^{V_f} P dV$$

Under isothermal condition,

$$\kappa = \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = \frac{a}{V(P+b)}, \quad \left( \frac{\partial V}{\partial P} \right)_T = -\frac{a}{(P+b)}$$

$$dV = -\frac{a}{(P+b)} dP, \quad \text{代回：}$$

$$W = -n \int_{V_i}^{V_f} P dV = n \int_{P_i}^{P_f} \frac{aP}{(P+b)} dP$$

$$W = n \int_{P_i}^{P_f} \frac{0.24P}{(P+210)} dP$$

For  $n$ ,

$$n = \frac{100}{146} = 0.685 \text{ (mol)}$$

$$W = 0.685 \times \int_1^{250} \frac{0.24P}{(P+210)} dP = 14.027 \text{ (cm}^3 \cdot \text{bar)} = 14.027 \times 10^{-6} \times 1 \times 10^5 = \underline{\underline{1.4 \text{ (J)}}}$$

(本題改編自：Smith, J.; Van Ness, H.; Abbott, M.; Hwalek, J. *Introduction to Chemical Engineering*

*Thermodynamics*, 7th ed.; p 111, Problem 3.4.)

### **Problem 2**

#### **【Solution】**

For ideal gas,

$$\Delta U = C_V \Delta T = a \Delta(PV) = a \Delta(RT)$$

$$a = \frac{C_V}{R} = \frac{C_P - R}{R} = \underline{\underline{\frac{3}{2}}}$$

$$\Delta H = C_P \Delta T = b \Delta(PV) = b \Delta(RT)$$

$$b = \frac{C_P}{R} = \underline{\underline{\frac{5}{2}}}$$

### **Problem 3**

#### **【Solution】**

(1)

$$PV^{1.33} = \text{constant}$$

$$P_1 \left( \frac{nRT_1}{P_1} \right)^{1.33} = P_2 \left( \frac{nRT_2}{P_2} \right)^{1.33}$$

$$P_1^{-0.33} T_1^{1.33} = P_2^{-0.33} T_2^{1.33}$$

$$\left( \frac{1}{8.5} \right)^{-0.33} = \left( \frac{T_2}{300} \right)^{1.33}, \quad \underline{\underline{T_2 = 510.2 \text{ (K)}}}$$

(2)

By the 1<sup>st</sup> law of thermodynamics (assume 1 mol of ideal gas),

$$dQ = dU - dW = C_V dT + PdV$$

$\therefore$  ideal gas,

$$PV = RT, \quad PdV + VdP = RdT$$

$\therefore PV^k = \text{constant}$

$$V^k dP + kV^{k-1} PdV = 0$$

$$VdP = -kPdV \text{ 代回 :}$$

$$PdV - kPdV = RdT, \quad PdV = \frac{R}{(1-k)} dT$$

代回：

$$dQ = dU - dW = C_v dT + \frac{R}{(1-k)} dT = (C_p - R) dT + \frac{R}{(1-k)} dT$$

$$dQ = (C_p - R) dT + \frac{R}{(1-k)} dT = \underline{\underline{[C_p + \frac{kR}{(1-k)}] dT}}$$

If  $C_p = \text{constant}$

$$\underline{\underline{Q = \int_{T_1}^{T_2} [C_p + \frac{kR}{(1-k)}] dT = [C_p + \frac{kR}{(1-k)}] (T_2 - T_1)}}$$

(3)

$\because C_p \neq \text{constant}$

$$dQ = [C_p + \frac{kR}{(1-k)}] dT = R [\frac{C_p}{R} + \frac{k}{(1-k)}] dT$$

$$dQ = R [3.5 + 0.6 \times 10^{-3} T + \frac{1.33}{(1-1.33)}] dT = R [-0.53 + 0.6 \times 10^{-3} T] dT$$

$$Q = \int_{300}^{510.2} 8.314 \times [-0.53 + 0.6 \times 10^{-3} T] dT = \underline{\underline{-501.96 \text{ (J / mol)}}}$$

(本題改編自：Smith, J.; Van Ness, H.; Abbott, M.; Hwalek, J. *Introduction to Chemical Engineering*

*Thermodynamics*, 7th ed.; p 153, Problem 4.17.)

化工製造所

**Problem 4****【Solution】**

(1)

$$\left[\frac{\partial}{\partial P}\left(\frac{nG^R}{RT}\right)\right]_{T,n} = \frac{nV^R}{RT}$$

$$\left[\frac{\partial}{\partial T}\left(\frac{nG^R}{RT}\right)\right]_{P,n} = -\frac{nH^R}{RT^2}$$

$$\left[\frac{\partial}{\partial n_i}\left(\frac{nG^R}{RT}\right)\right]_{T,P,n_j} = \frac{\bar{G}_i^R}{RT}$$

From the exact relations,

**【Maxwell relation 1】**

$$\frac{\partial}{\partial T} \left\{ \left[ \frac{\partial}{\partial P} \left( \frac{nG^R}{RT} \right) \right]_{T,n} \right\}_{n,P} = \frac{\partial}{\partial P} \left\{ \left[ \frac{\partial}{\partial T} \left( \frac{nG^R}{RT} \right) \right]_{P,n} \right\}_{n,T}$$

$$\frac{\partial}{\partial T} \left[ \frac{nV^R}{RT} \right]_{P,n} = - \frac{\partial}{\partial P} \left[ \frac{nH^R}{RT^2} \right]_{T,n}$$

$$\frac{T \left[ \frac{\partial V^R}{\partial T} \right]_P - V^R}{T^2} = - \left[ \frac{1}{T^2} \frac{\partial (G^R + TS^R)}{\partial P} \right]_T = - \left[ \frac{V^R}{T^2} + \frac{1}{T} \frac{\partial S^R}{\partial P} \right]_T$$

$$\boxed{\left( \frac{\partial V^R}{\partial T} \right)_P = - \left( \frac{\partial S^R}{\partial P} \right)_T}$$

**【Maxwell relation 2】**

$$\frac{\partial}{\partial n_i} \left\{ \left[ \frac{\partial}{\partial P} \left( \frac{nG^R}{RT} \right) \right]_{T,n} \right\}_{T,P,n_j} = \frac{\partial}{\partial P} \left\{ \left[ \frac{\partial}{\partial n_i} \left( \frac{nG^R}{RT} \right) \right]_{T,P,n_j} \right\}_{n,T}$$

$$\frac{\partial}{\partial n_i} \left( \frac{nV^R}{RT} \right)_{T,P,n_j} = \frac{\partial}{\partial P} \left[ \frac{\bar{G}_i^R}{RT} \right]_T$$

$$\boxed{\frac{\partial}{\partial P} \left[ \frac{\bar{G}_i^R}{RT} \right]_T = \bar{V}^R}$$



【Maxwell relation 3】

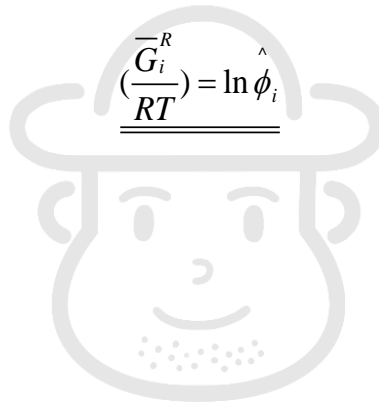
$$\frac{\partial}{\partial n_i} \left\{ \left[ \frac{\partial}{\partial T} \left( \frac{nG^R}{RT} \right) \right]_{P,n} \right\}_{T,P,n_j} = \frac{\partial}{\partial T} \left\{ \left[ \frac{\partial}{\partial n_i} \left( \frac{nG^R}{RT} \right) \right]_{T,P,n_j} \right\}_{n,P}$$

$$\frac{\partial}{\partial n_i} \left( -\frac{nH^R}{RT^2} \right)_{T,P,n_j} = \frac{\partial}{\partial T} \left[ \frac{\bar{G}_i^R}{RT} \right]_P$$

$$\boxed{\frac{\partial}{\partial n_i} \left( -\frac{nH^R}{RT^2} \right)_{T,P,n_j} = \frac{\partial}{\partial T} \left[ \frac{\bar{G}_i^R}{RT} \right]_P}$$

(2)

$$d\left(\frac{\bar{G}_i^R}{RT}\right) = d(\bar{G}_i - \bar{G}_i^{IG}) = [d \ln \hat{f}_i - d \ln P_i] = d \ln \hat{\phi}_i$$



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### Problem 5

#### 【Solution】

(1)

$$\begin{cases} (4) = \bar{G}_1^{id} \\ (5) = \bar{G}_2^{id} \end{cases}$$

(2)

$$\because G^E = x_1 \bar{G}_1^E + x_2 \bar{G}_2^E$$

$$dG^E = \bar{G}_1^E dx_1 + x_1 d\bar{G}_1^E + \bar{G}_2^E dx_2 + x_2 d\bar{G}_2^E$$

$$\because x_1 d\bar{G}_1^E + x_2 d\bar{G}_2^E = 0 \quad (\text{Gibbs-Duhem equation})$$

$$dG^E = \bar{G}_1^E dx_1 + \bar{G}_2^E dx_2 = -\bar{G}_1^E dx_2 + \bar{G}_2^E dx_2 = (\bar{G}_2^E - \bar{G}_1^E) dx_2$$

$$(dx_1 = -dx_2)$$

$$\frac{dG^E}{dx_2} = (\bar{G}_2^E - \bar{G}_1^E)$$

又：

$$G^E = x_1 \bar{G}_1^E + x_2 \bar{G}_2^E = (1-x_2) \bar{G}_1^E + x_2 \bar{G}_2^E = \bar{G}_1^E - x_2 (\bar{G}_1^E - \bar{G}_2^E)$$

$$G^E = \bar{G}_1^E + x_2 \frac{dG^E}{dx_2}, \quad \underline{\underline{\bar{G}_1^E = G^E - x_2 \frac{dG^E}{dx_2}}}$$

同理：

$$\underline{\underline{\bar{G}_2^E = G^E + (1-x_2) \frac{dG^E}{dx_2}}}$$

### **Problem 6**

#### **【Solution】**

For the magnitude, assume  $S = S(T, V)$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

For  $\left(\frac{\partial S}{\partial T}\right)_V$ , by  $dU = TdS - PdV$

$$\left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V = C_V, \quad \left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$$

For  $\left(\frac{\partial S}{\partial V}\right)_T$ , by Maxwell relation,

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$dS = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV$$

$$\Delta S_{sys} = \int_{T_1}^{T_2} \frac{C_V}{T} dT + \int_{V_1}^{V_2} \left(\frac{\partial P}{\partial T}\right)_V dV$$

For the sign of the total entropy change, by entropy balance of the closed system,

$$\Delta S_{sys} = \frac{Q}{T} + S_{gen} > 0$$

By entropy balance on the surrounding,

$$\Delta S_{sur} = \frac{Q}{T} = 0$$

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{sur} = S_{gen} > 0$$

**Problem 7****【Solution】**

(1)

For ideal gas, the internal energy changes is only depending on temperature,

$$\underline{\underline{\Delta U^{IG} = 0}}$$

(2)

For the general form of the internal change of a substance,

$$dU = TdS - PdV$$

From the result of the **Problem 6**

$$dS = \frac{C_v}{T} dT + \left(\frac{\partial P}{\partial T}\right)_v dV$$

(這裡容許偷懶一下，借用上題有用到的結果)

$$dU = \cancel{C_v dT}_{\text{isothermal}} + [T\left(\frac{\partial P}{\partial T}\right)_v - P]dV$$

For  $T\left(\frac{\partial P}{\partial T}\right)_v$ ,

$$T\left(\frac{\partial P}{\partial T}\right)_v = T\left(\frac{R}{V-b} + \frac{a}{2T^{3/2}V(V+b)}\right) = \frac{RT}{V-b} + \frac{a}{2\sqrt{TV}(V+b)}$$

$$T\left(\frac{\partial P}{\partial T}\right)_v - P = \frac{RT}{V-b} + \frac{a}{2\sqrt{TV}(V+b)} - \left[\frac{RT}{(V-b)} - \frac{a}{\sqrt{TV}(V+b)}\right] = \frac{3a}{2\sqrt{TV}(V+b)}$$

$\therefore P = P \rightarrow 0, V = V \rightarrow \infty$

$$\Delta U = \int_v^\infty \left[\frac{3a}{2\sqrt{TV}(V+b)}\right]dV = \frac{3a}{2\sqrt{Tb}} \ln\left(\frac{V}{V+b}\right) \Bigg|_v^\infty = \underline{\underline{\frac{3a}{2\sqrt{Tb}} \ln(V+b)}}$$

If we only have data of pressure, we can input the values into the equation of state and calculate the values of corresponding volumes to prevent trivial calculations.

# 113 年成大化熱

## Problem 1

### 【Solution】

(a)

By the definition of internal energy, we have,

$$dU = TdS - PdV$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

For ideal gas,

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P = T\left(\frac{R}{V}\right) - \frac{RT}{V} = 0$$

For van der Waals equation,

$$(P + \frac{a}{V^2})(V - b) = RT, \quad P = \frac{RT}{(V - b)} - \frac{a}{V^2}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P = T\left[\frac{R}{(V - b)}\right] - \left[\frac{RT}{(V - b)} - \frac{a}{V^2}\right] = \underline{\underline{\frac{a}{V^2}}}$$

(b)

By energy balance,

$$\Delta U = Q + W$$

For  $\Delta U$ ,

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \cancel{\left(\frac{\partial U}{\partial T}\right)_V dT} = \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$\Delta U = \int_{V_1}^{V_2} \left(\frac{\partial U}{\partial V}\right)_T dV = \int_{V_1}^{V_2} \frac{a}{V^2} dV = a\left(\frac{1}{V_1} - \frac{1}{V_2}\right)$$

$$\Delta U = a\left(\frac{1}{V_1} - \frac{1}{V_2}\right) = 1.4\left[\frac{1}{\left(\frac{2.5}{5}\right)} - \frac{1}{\left(\frac{10}{5}\right)}\right] = 2.1 \text{ (atm} \cdot \text{dm}^3 / \text{mol}) = 2.1 \times 1.013 \times 10^2 \times 5 = \underline{\underline{1063.7 \text{ (J)}}}$$

$$W = -\int_{V_1}^{V_2} PdV = -\int_{V_1}^{V_2} \left(\frac{RT}{V - b} - \frac{a}{V^2}\right) dV = RT \ln\left(\frac{V_1 - b}{V_2 - b}\right) + a\left(\frac{1}{V_1} - \frac{1}{V_2}\right)$$

$$W = RT \ln\left(\frac{V_1 - b}{V_2 - b}\right) + a\left(\frac{1}{V_1} - \frac{1}{V_2}\right) = 5 \times 8.314 \times 300 \ln\left(\frac{\frac{2.5}{5} - 0.04}{\frac{10}{5} - 0.04}\right) + 1063.7 = \underline{\underline{-17012.7 \text{ (J)}}}$$

$$Q = W - \Delta U = -17012.7 - 1063.7 = \underline{\underline{-18076 \text{ (J)}}}$$

For the change in enthalpy,

$$dH = dU + d(PV) = \left(\frac{\partial U}{\partial V}\right)_T dV + d(PV)$$

$$\Delta H = a\left(\frac{1}{V_1} - \frac{1}{V_2}\right) + (PV)_2 - (PV)_1 = a\left(\frac{1}{V_1} - \frac{1}{V_2}\right) + \frac{RTV_2}{(V_2 - b)} - \frac{a}{V_2} - \frac{RTV_1}{(V_1 - b)} + \frac{a}{V_1}$$

$$\begin{aligned} \Delta H &= a\left(\frac{2}{V_1} - \frac{2}{V_2}\right) + \frac{RTV_2}{(V_2 - b)} - \frac{RTV_1}{(V_1 - b)} \\ &= 2 \times 1063.7 + 8.314 \times 300 \left( \frac{10}{10 - 5 \times 0.04} - \frac{2.5}{2.5 - 5 \times 0.04} \right) = \underline{\underline{1961.4 \text{ (J)}}} \end{aligned}$$

## **Problem 2**

### **【Solution】**

Assume the process takes place in an environment of 465K, and the vapor behaves as an ideal gas,

$$\Delta S_{\text{sys}} = \Delta S_{450\text{K}(l) \rightarrow (g)} + \Delta S_{450\text{K}(g) \rightarrow 465\text{K}(g)}$$

$$\Delta S_{\text{sys}} = \frac{\Delta H_{\text{vap}}}{T_{\text{vap}}} + C_{P,g} \ln\left(\frac{T_2}{T_1}\right) = \frac{45.6 \times 10^3}{450} + 35 \ln\left(\frac{465}{450}\right) = 102.48 \text{ (J / mol} \cdot \text{K)}$$

$$\Delta S_{\text{sur}} = \frac{-\Delta H_{\text{vap}} + \Delta H_{450\text{K}(g) \rightarrow 465\text{K}(g)}}{T_{\text{sur}}} = \frac{-45.6 \times 10^3 - 35 \times (465 - 450)}{465} = -99.19 \text{ (J / mol} \cdot \text{K)}$$

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}} = 102.47 - 99.19 = \underline{\underline{3.27 \text{ (J / mol} \cdot \text{K)} > 0}}$$

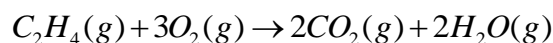
**The process is spontaneous.**

### Problem 3

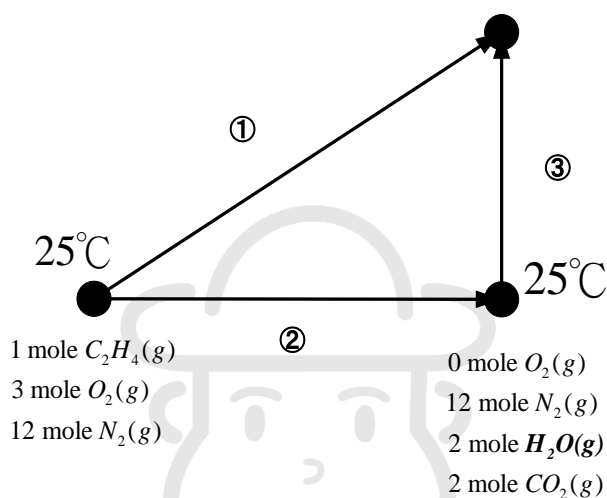
#### 【Solution】

(a)

Reaction :



$$\begin{aligned}\Delta H_{combustion}^{\circ} &= 2\Delta H_f^{\circ}(H_2O_{(g)}) + 2\Delta H_f^{\circ}(CO_{2(g)}) - \Delta H_f^{\circ}(C_2H_{4(g)}) \\ &= 2(-241.8) - 2 \times 393.5 - 52.5 = \underline{\underline{-1269.1 \text{ (kJ / mol)}}}\end{aligned}$$



By the path diagram,

$$\Delta H_1 = \Delta H_2 + \Delta H_3$$

By the first law of thermodynamics,

$$\cancel{\Delta H} + \cancel{\frac{g}{g_c} \Delta z} + \cancel{\frac{1}{2g_c} \Delta v^2} = Q + W$$

For the temperature to be maximum, the process should be adiabatic (no heat is released toward the surroundings),

$$\Delta H = 0, \quad \Delta H_1 = \Delta H_2 + \Delta H_3 = 0$$

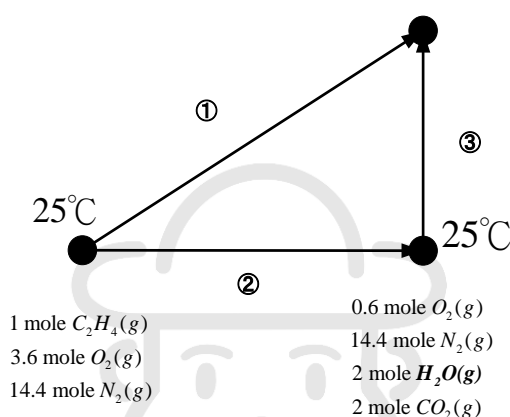
$$\Delta H_2 = \Delta H_{combustion}^{\circ} = -1269.1 \text{ (kJ / mol)}$$

$$\begin{aligned}\Delta H_3 &= \int_{298}^T \sum_i n_i (A_i + B_i T) dT \\ &= \int_{298}^T \sum_i [12(28.6 + 3.8 \times 10^{-3} T) + 2(30.5 + 10.3 \times 10^{-3} T) + 2(44.2 + 8.8 \times 10^{-3} T)] dT \\ &= 0.0419 T^2 + 492.6 T - 150515.69\end{aligned}$$

$$\Delta H_2 + \Delta H_3 = -1269.1 \times 10^3 + 0.0419 T^2 + 492.6 T - 150515.69 = 0$$

$$\underline{\underline{T = 2394.3 \text{ (K)}}}$$

(b)



$$\Delta H = 0, \quad \Delta H_1 = \Delta H_2 + \Delta H_3 = 0$$

$$\Delta H_2 = \Delta H_{\text{combustion}}^{\circ} = -1269.1 \text{ (kJ / mol)}$$

$$\begin{aligned}\Delta H_3 &= \int_{298}^T \sum_i n_i (A_i + B_i T) dT \\ &= \int_{298}^T \sum_i [0.6(30.0 + 4.2 \times 10^{-3} T) + 14.4(28.6 + 3.8 \times 10^{-3} T) + 2(30.5 + 10.3 \times 10^{-3} T) + 2(44.2 + 8.8 \times 10^{-3} T)] dT \\ &= 0.04772 T^2 + 579.2 T - 176851.25\end{aligned}$$

$$\Delta H_2 + \Delta H_3 = -1269.1 \times 10^3 + 0.04772 T^2 + 579.2 T - 176851.25 = 0$$

$$\underline{\underline{T = 2124.5 \text{ (K)}}}$$

※注意在計算  $\Delta H_2$  時，因題目強調 complete combustion，且水蒸氣在末溫應為水蒸氣，因此計算燃燒熱時，採用  $H_2O(g)$  做計算。然而實際使用  $H_2O(g)$  之原因可參考原文書對於反應熱的段落說明，與大部分標準反應熱使用  $H_2O(l)$  的想法不太相同，詳情請參考：

Smith, J.; Van Ness, H.; Abbott, M. *Introduction to Chemical Engineering*, 7th ed.; p 136~144)



**Problem 4****【Solution】**

(1)

$$dU^R = C_v dT + [T(\frac{\partial P}{\partial T})_v - P]dV - C_v^{IG} dT = C_v^R dT + \underline{\underline{[T(\frac{\partial P}{\partial T})_v - P]dV}}$$

Or

$$H^R = RT(Z-1) + \int_{\infty}^V [T(\frac{\partial P}{\partial T})_v - P]dV$$

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \text{ 代入 :}$$

$$H^R = RT(Z-1) + \int_{\infty}^V [\frac{RT}{V-b} - P]dV = RT(Z-1) + \int_{\infty}^V \frac{a}{V^2}dV$$

$$H^R = RT(Z-1) + \int_{\infty}^V \frac{a}{V^2}dV = RT(Z-1) - \frac{a}{V}$$

$$U^R = H^R - PV^R = RT(Z-1) - \frac{a}{V} - P \times \frac{RT}{P}(Z-1) = \underline{\underline{-\frac{a}{V}}}$$

(2)

$$dH^R = C_p dT + [V - T(\frac{\partial V}{\partial T})_p]dP - C_p^{IG} dT = C_p^R dT + \underline{\underline{[V - T(\frac{\partial V}{\partial T})_p]dP}}$$

Or

$$H^R = RT(Z-1) + \int_{\infty}^V [T(\frac{\partial P}{\partial T})_v - P]dV = RT(Z-1) - \frac{a}{V}$$

(計算過程如(1))

(3)

$$\left(\frac{\partial C_v}{\partial V}\right)_T = \frac{\partial}{\partial V} \left[ \left(\frac{\partial U}{\partial T}\right)_V \right]_T = \frac{\partial}{\partial T} \left[ \left(\frac{\partial U}{\partial V}\right)_T \right]_V$$

$$\because U = C_v dT + [T \left(\frac{\partial P}{\partial T}\right)_V - P] dV$$

$$\left(\frac{\partial C_v}{\partial V}\right)_T = \frac{\partial}{\partial T} \left[ \left(\frac{\partial}{\partial V} (C_v dT + [T \left(\frac{\partial P}{\partial T}\right)_V - P] dV) \right)_T \right]_V$$

$$\left(\frac{\partial C_v}{\partial V}\right)_T = \frac{\partial}{\partial T} [T \left(\frac{\partial P}{\partial T}\right)_V - P]_V = \frac{\partial}{\partial T} [T \left(\frac{\partial P}{\partial T}\right)_V]_V - \left(\frac{\partial P}{\partial T}\right)_V$$

$$\left(\frac{\partial C_v}{\partial V}\right)_T = \frac{\partial}{\partial T} [T \left(\frac{\partial P}{\partial T}\right)_V]_V - \left(\frac{\partial P}{\partial T}\right)_V = \cancel{\left(\frac{\partial P}{\partial T}\right)_V} + T \left(\frac{\partial^2 P}{\partial T^2}\right)_V - \cancel{\left(\frac{\partial P}{\partial T}\right)_V} = T \left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \text{ 代入:}$$

$$\left(\frac{\partial C_v}{\partial V}\right)_T = T \left(\frac{\partial^2 P}{\partial T^2}\right)_V = 0$$

### Problem 5

#### 【Solution】

For reversible process,

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{r-1}{r}}, \quad \frac{T_2}{300} = \left(\frac{8}{2}\right)^{\frac{1.4-1}{1.4}}$$

$$T_2 = 445.8 \text{ (K)}$$

$$W = \Delta U = C_v \Delta T = 2.5 \times 8.314 \times (445.8 - 300) = 3030.4 \text{ (J)}$$

For irreversible process, it requires 40% more work than the reversible one,

$$\Delta U = W_{\text{irrev}} = 1.4 W_{\text{rev}} = 3030.4 \times 1.4 = 4242.6 \text{ (J)}$$

$$\Delta U = 2.5 \times 8.314 \times (T_{2,\text{real}} - 300) = 4242.6, \quad \underline{\underline{T_{2,\text{real}} = 504.12 \text{ (K)}}}$$

$$\Delta S = C_p \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{P_2}{P_1}\right) = 3.5 \times 8.314 \ln\left(\frac{504.12}{300}\right) - 8.314 \ln\left(\frac{8}{2}\right) = \underline{\underline{3.57 \text{ (J / K)}}}$$

(本題改編自: Smith, J.; Van Ness, H.; Abbott, M.; Hwalek, J. *Introduction to Chemical*

*Engineering Thermodynamics*, 7th ed.; p 194, Problem 5.21.)

**Problem 6****【Solution】**

By the definition of  $G^E / RT$ ,

$$G^E / RT = x_1 \ln r_1 + x_2 \ln r_2$$

$\therefore G^E / RT = \ln r_1 = \ln r_2$  at a point, let

$$x_1 \ln r_1 + x_2 \ln r_2 = \ln r_1 = (x_1 + x_2) \ln r_1$$

移項整理：

$$x_2 \ln r_2 = x_2 \ln r_1, \quad r_1 = r_2$$

That is, when  $r_1 = r_2$ , at that point the three will intersect together.

**Problem 7****【Solution】**

(1) True

(2) False

By Gibbs-Duhem equation,

$$x_1 d \ln r_1 + x_2 d \ln r_2 = 0$$

$$x_1 \frac{d \ln r_1}{dx_1} + x_2 \frac{d \ln r_2}{dx_1} = 0, \quad \frac{d \ln r_1}{dx_1} = -\frac{x_2}{x_1} \frac{d \ln r_2}{dx_1}$$

When “ $x_2 \rightarrow 0$ ”

$$\frac{d \ln r_1}{dx_1} = 0$$

When “ $x_1 \rightarrow 0$ ”

$$\frac{d \ln r_2}{dx_1} = 0$$

### Problem 8

#### 【Solution】

因(a)壓力小於Raoult's law所計算出之壓力值，推測為負偏差(negative deviation)，

又負偏差代表  $r_i < 1$ ，因此選(c)

### Problem 9

#### 【Solution】

(a) 因為共沸物所產生之壓力小於分別兩個純成分(比 Raoult's law 預測低)，應為負偏差，應選(c)(d)。

(b) 因共沸點以左，相比液相分率(x)，(c)線的氣相分率(y)較低；同樣在共沸點以右，相比液相分率(x)，(d)線的氣相分率(y)較高，因此選(c)(d)。

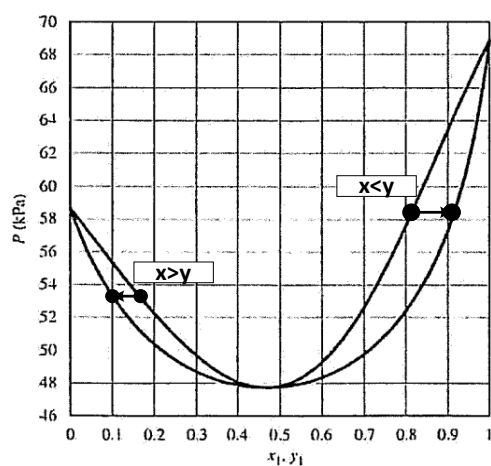


Fig. 1 Pxy diagram for vapor/liquid equilibrium of a mixed-solvent system at 50°C.

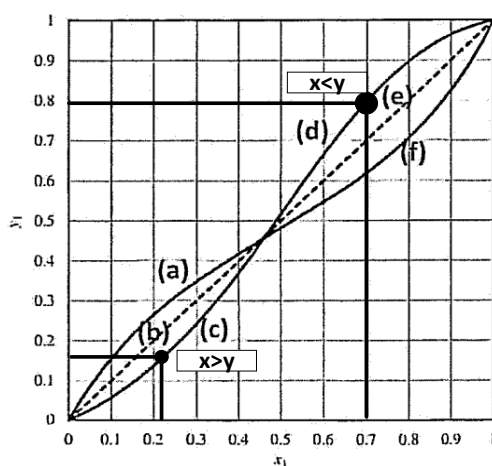


Fig. 2 xy diagram for different mixed-solvent system at 1 bar.

# 114 年成大化熱

## Problem 1

### 【Solution】

(1)

By the definition of internal energy, we have,

$$a = \frac{27}{64} \frac{R^2 T_c^2}{P_c} = \frac{27 \times 8.314^2 \times 507.6^2}{64 \times 30.25 \times 1 \times 10^5} = \underline{\underline{2.48 \text{ (Pa} \cdot \text{m}^6 / \text{mol}^2)}} \\ b = \frac{RT_c}{8P_c} = \frac{8.314 \times 507.6}{8 \times 30.25 \times 1 \times 10^5} = \underline{\underline{1.74 \times 10^{-4} (\text{m}^3 / \text{mol})}}$$

(2)

By the 1st law,

$$dU = dQ + dW = dQ - PdV$$

$$dQ = dU + PdV$$

對於凡德瓦氣體：

$$dQ = C_v dT + [T(\frac{\partial P}{\partial T})_v - P]dV + PdV$$

$$dQ = [T(\frac{\partial P}{\partial T})_v]dV = T(\frac{R}{V-b})dV = \frac{RT}{V-b}dV$$

$$Q = \int_{V_1}^{1000V_1} \frac{RT}{V-b} dV = RT \ln(\frac{1000V_1 - b}{V_1 - b})$$

For  $V_1$ ,

$$1.013 \times 10^5 = \frac{8.314 \times 300}{V_1 - 1.74 \times 10^{-4}} - \frac{2.48}{V_1^2}, \quad V_1 = 0.0002247 \text{ m}^3$$

$$Q = 8.314 \times 300 \ln(\frac{1000 \times 0.0002247 - 1.74 \times 10^{-4}}{0.0002247 - 1.74 \times 10^{-4}}) = \underline{\underline{20940.9 \text{ (J)}}}$$

(3)

$$\frac{PV}{RT} = \frac{V}{V-b} - \frac{a}{RTV} = \frac{1}{1-\frac{b}{V}} - \frac{a}{RTV} = 1 - \frac{a}{RTV} + \left(\frac{b}{V}\right) + \left(\frac{b}{V}\right)^2 + \left(\frac{b}{V}\right)^3 \dots = 1 + \frac{(b - \frac{a}{RT})}{V} + \left(\frac{b}{V}\right)^2 \dots$$

$$\begin{cases} B = b - \frac{a}{RT} \\ C = b^2 \end{cases}$$

### Problem 2

#### **【Solution】**

(1) False (例如可逆絕熱膨脹，即非循環過程)

(2) False

$$dH = TdS + VdP$$

在 H-S 相圖中的高低，可以用固定 S 下的高低關係去看

$$dH = \cancel{TdS} + VdP = VdP$$

$$\because V > 0, \quad dH \uparrow, dP \uparrow$$

### Problem 3

#### **【Solution】 (1)(4)(5)**

To derive the equations, we need,

$$\frac{dV}{V} - \frac{du}{u} - \frac{dA}{A} = 0 \quad (1)$$

By

$$\frac{dV}{V} = \frac{\beta T}{C_p} dS - \frac{V}{c^2} dP \quad (4)$$

$$-udu = TdS + VdP \quad (5)$$

$$\frac{\beta T}{C_p} dS - \frac{V}{c^2} dP + \frac{TdS + VdP}{u^2} - \frac{dA}{A} = 0$$

同乘  $u^2$  可得：

$$\left(1 - \frac{u^2}{c^2}\right)VdP + \left(1 + \frac{\beta u^2}{C_p}\right)TdS - \frac{u^2}{A}dA = 0 \quad (\text{題目左式})$$

與(5)做對照，可得：

$$VdP = \frac{-(1 + \frac{\beta u^2}{C_p})TdS + \frac{u^2}{A}dA}{(1 - \frac{u^2}{c^2})}$$
$$-udu = TdS + \frac{-(1 + \frac{\beta u^2}{C_p})TdS + \frac{u^2}{A}dA}{(1 - \frac{u^2}{c^2})}$$

$$udu + \frac{(\frac{\beta u^2}{C_p} + \frac{u^2}{c^2})TdS}{(1 - \frac{u^2}{c^2})} + \frac{1}{(1 - \frac{u^2}{c^2})} \frac{u^2}{A}dA = 0$$

 (題目右式)

(本題可參考：Smith, J.; Van Ness, H.; Abbott, M. *Introduction to Chemical Engineering*, 7th ed.;  
p 255~258.)



#### **Problem 4**

#### **【Solution】**

For the open system of a single speices,

$$ndG = nVdP - nSdT + \sum_i \bar{G}_i dn_i$$

又根據連鎖律：

$$d\left(\frac{nG}{RT}\right) = \frac{1}{RT} d(nG) - \frac{nG}{RT^2} dT$$

將

$$d(nG) = nVdP - nSdT + \sum_i \bar{G}_i dn_i$$

與

$$nG = nH - T(nS)$$

代入得

$$d\left(\frac{nG}{RT}\right) = \frac{1}{RT} d(nG) - \frac{nG}{RT^2} dT = \frac{nVdP - nSdT + \sum_i \bar{G}_i dn_i}{RT} - \frac{nH - T(nS)}{RT^2} dT$$

$$d\left(\frac{nG}{RT}\right) = \frac{nVdP}{RT} - \cancel{\frac{nSdT}{RT}} + \frac{\sum_i \bar{G}_i dn_i}{RT} - \frac{nH}{RT^2} dT + \cancel{\frac{T(nS)}{RT^2} dT}$$

$$\boxed{d\left(\frac{nG}{RT}\right) = \frac{nV}{RT} dP - \frac{nH}{RT^2} dT + \sum_i \frac{\bar{G}_i}{RT} dn_i}$$

$$\boxed{\left[\frac{\partial}{\partial P}\left(\frac{nG}{RT}\right)\right]_{T,n} = \frac{nV}{RT}}, \quad \boxed{\left[\frac{\partial}{\partial T}\left(\frac{nG}{RT}\right)\right]_{P,n} = -\frac{nH}{RT^2}}, \quad \boxed{\left[\frac{\partial}{\partial n_i}\left(\frac{nG}{RT}\right)\right]_{T,P,n_j} = \frac{\bar{G}_i}{RT}}$$



From the exact relations,

**【Maxwell relation 1】**

$$\frac{\partial}{\partial T} \left\{ \left[ \frac{\partial}{\partial P} \left( \frac{nG}{RT} \right) \right]_{T,n} \right\}_{n,P} = \frac{\partial}{\partial P} \left\{ \left[ \frac{\partial}{\partial T} \left( \frac{nG}{RT} \right) \right]_{P,n} \right\}_{n,T}$$

$$\frac{\partial}{\partial T} \left[ \frac{nV}{RT} \right]_{P,n} = - \frac{\partial}{\partial P} \left[ \frac{nH}{RT^2} \right]_{T,n}$$

$$\frac{T \left[ \frac{\partial V}{\partial T} \right]_P - V}{T^2} = - \left[ \frac{1}{T^2} \frac{\partial(G+TS)}{\partial P} \right]_T = - \left[ \frac{V}{T^2} + \frac{1}{T} \frac{\partial S}{\partial P} \right]_T$$

$$\left( \frac{\partial V}{\partial T} \right)_P = - \left( \frac{\partial S}{\partial P} \right)_T$$

**【Maxwell relation 2】**

$$\frac{\partial}{\partial n_i} \left\{ \left[ \frac{\partial}{\partial P} \left( \frac{nG}{RT} \right) \right]_{T,n} \right\}_{T,P,n_j} = \frac{\partial}{\partial P} \left\{ \left[ \frac{\partial}{\partial n_i} \left( \frac{nG}{RT} \right) \right]_{T,P,n_j} \right\}_{n,T}$$

$$\frac{\partial}{\partial n_i} \left( \frac{nV}{RT} \right)_{T,P,n_j} = \frac{\partial}{\partial P} \left[ \frac{\bar{G}_i}{RT} \right]_T$$

$$\frac{\partial}{\partial P} \left[ \frac{\bar{G}_i}{RT} \right]_T = \bar{V}$$

**【Maxwell relation 3】**

$$\frac{\partial}{\partial n_i} \left\{ \left[ \frac{\partial}{\partial T} \left( \frac{nG}{RT} \right) \right]_{P,n} \right\}_{T,P,n_j} = \frac{\partial}{\partial T} \left\{ \left[ \frac{\partial}{\partial n_i} \left( \frac{nG}{RT} \right) \right]_{T,P,n_j} \right\}_{n,P}$$

$$\frac{\partial}{\partial n_i} \left( - \frac{nH}{RT^2} \right)_{T,P,n_j} = \frac{\partial}{\partial T} \left[ \frac{\bar{G}_i}{RT} \right]_P$$

$$\frac{\partial}{\partial n_i} \left( - \frac{nH}{RT^2} \right)_{T,P,n_j} = \frac{\partial}{\partial T} \left[ \frac{\bar{G}_i}{RT} \right]_P$$

(本題與 110 年成大化熱 Problem 5-(4)相關，與 112 年成大化熱 Problem 4 雷同)

**Problem 5****【Solution】**

(1)

By the definition of the K values,

$$y_1 = K_1 x_1, \quad y_2 = K_2 x_2, \quad K_1 x_1 + K_2 x_2 = 1$$

$$K_1 x_1 + K_2 (1 - x_1) = 1$$

$$x_1 = \frac{1 - K_2}{K_1 - K_2}$$

代入：

$$y_1 = K_1 x_1 = \frac{K_1 (1 - K_2)}{K_1 - K_2}$$

(2)

Assume the system behaves ideally, at equilibrium,

$$\mu_v^1 = \mu_l^1, \quad \mu_v^0 + RT \ln(y_1 P) = \mu_l^0 + RT \ln(x_1)$$

$$RT \ln\left(\frac{y_1 P}{x_1}\right) = RT \ln\left(\frac{y_1}{x_1}\right) = \mu_l^0 - \mu_v^0 = -\Delta G_m^{1,l \rightarrow v}$$

$$\frac{y_1}{x_1} = K_1 = \exp\left[-\frac{\Delta G_m^{1,l \rightarrow v}}{RT}\right] = \exp\left[-\frac{-7.5 \times 10^3}{8.314 \times (600 + 273.15)}\right] = 2.809$$

In the same way,

$$K_2 = \exp\left[-\frac{\Delta G_m^{2,l \rightarrow v}}{RT}\right] = \exp\left[-\frac{6.8 \times 10^3}{8.314 \times (600 + 273.15)}\right] = 0.392$$

By the relation,

$$x_1 = \frac{1 - 0.392}{2.809 - 0.392} = \underline{\underline{0.251}}$$

$$y_1 = \frac{K_1 (1 - K_2)}{K_1 - K_2} = \frac{2.809 \times (1 - 0.392)}{2.809 - 0.392} = \underline{\underline{0.707}}$$

(3)

By the lever-arm rule,

$$\frac{L}{V} = \frac{y_1 - z_1}{z_1 - x_1} = \frac{0.707 - 0.35}{0.35 - 0.251} = \underline{\underline{3.61}}$$

**Problem 6**

**【Solution】**

(1)

$$V = Ax_1 + Bx_2 + (Cx_1 + Dx_2)x_1x_2$$

$$V = Ax_1 + B(1-x_1) + Cx_1^2(1-x_1) + Dx_1(1-x_1)^2$$

For  $\bar{V}_1$  :

$$\bar{V}_1 = V + (1-x_1)\left(\frac{dV}{dx_1}\right) = (A+D) + (2C-4D)x_1 + (-4C+5D)x_1^2 + (2C-2D)x_1^3$$

For  $\bar{V}_2$  :

$$\bar{V}_2 = V - x_1\left(\frac{dV}{dx_1}\right) = B + (-C+2D)x_1^2 + (2C-2D)x_1^3$$

(2)

By Gibbs-Duhem equation, we have,

$$x_1 d\bar{V}_1 + x_2 d\bar{V}_2 = 0$$

To show the expressions satisfy this relation,

$$d\bar{V}_1 = [(2C-4D) + (-8C+10D)x_1 + (6C-6D)x_1^2]dx_1$$

$$d\bar{V}_2 = [(-2C+4D)x_1 + (6C-6D)x_1^2]dx_1$$

$$x_1 d\bar{V}_1 + x_2 d\bar{V}_2 = x_1 d\bar{V}_1 + (1-x_1)d\bar{V}_2$$

$$\begin{aligned} x_1 d\bar{V}_1 + (1-x_1)d\bar{V}_2 &= \{[(2C-4D)x_1 + (-8C+10D)x_1^2 + (6C-6D)x_1^3] \\ &+ [(-2C+4D)x_1 + (6C-6D)x_1^2] - [(-2C+4D)x_1^2 + (6C-6D)x_1^3]\}dx_1 = \underline{\underline{0}} \end{aligned}$$

(3)

$$\left(\frac{d\bar{V}_1}{dx_1}\right)_{x_1=1} = [(2C - 4D) + (-8C + 10D) + (6C - 6D)] = \underline{\underline{0}}$$

$$\left(\frac{d\bar{V}_2}{dx_1}\right)_{x_1=0} = [(-2C + 4D) \times 0 + (6C - 6D) \times 0^2] = \underline{\underline{0}}$$



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