

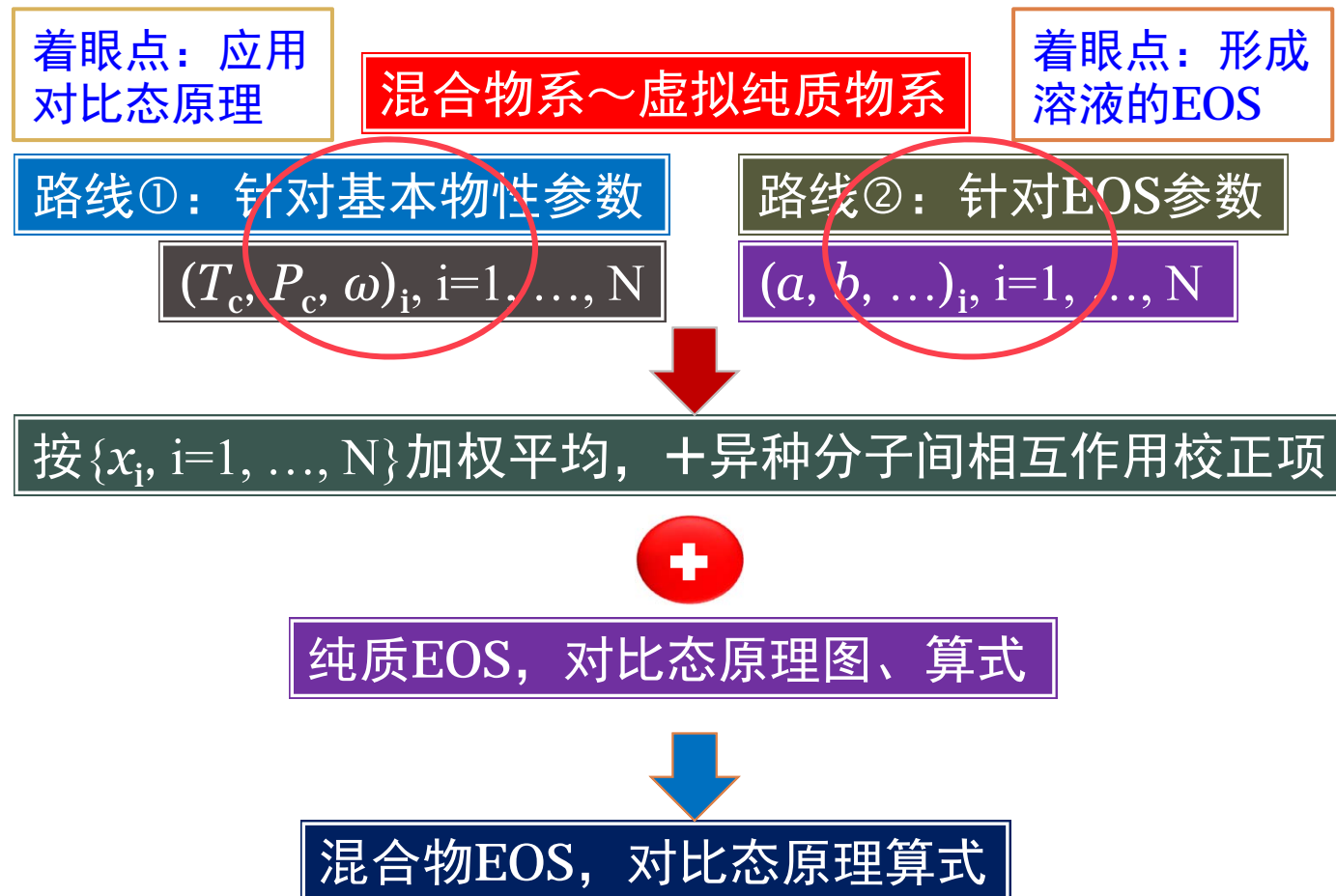
第4章 混合物的热力学性质

本章内容

□4.1 混合规则

□4.2 混合物的PVT关系

混合物的热力学性质如何计算？



4.1 混合规则

虚拟临界参数

Kay's linear combination

$$T_{c,mix} = \sum_i y_i T_{ci}, \quad P_{c,mix} = \sum_i y_i P_{ci}$$

需要说明的是虚拟临界温度和压力并不是混合物真实的临界参数。

适用范围

$$0.5 < T_{ci}/T_{c,max} < 2, \quad 0.5 < P_{ci}/P_{c,max} < 2$$

Prausnitz-Gunn Revised

$$T_{c,mix} = \sum_i y_i T_{ci}$$

$$P_{c,mix} = \frac{RT}{\sum_i (y_i V_{ci})} \sum_i (y_i z_{ci})$$

$$\omega_{mix} = \sum_i y_i \omega_i$$

常用的混合规则

二次型混合规则

$$Q_{mix} = \sum_i \sum_j y_i y_j Q_{ij}, \quad Q_{ii} = Q_i, \quad Q_{jj} = Q_j,$$

若交叉项为线性，则

$$Q_{ij} = (Q_i + Q_j) / 2, \quad Q_m = \sum_i y_i Q_i$$

若交叉项为几何平均，则

$$Q_{ij} = (Q_i Q_j)^{1/2}, \quad Q_m = \left(\sum_i y_i Q_i^{1/2} \right)^2$$

若交叉项为体积平均，则

$$Q_{ij} = \left(\frac{Q_i^{1/3} + Q_j^{1/3}}{2} \right)^3, \quad Q_{mix} = \frac{1}{8} \sum_i \sum_j (Q_i^{1/3} + Q_j^{1/3})^3$$

4.2 混合物的P-V-T关系

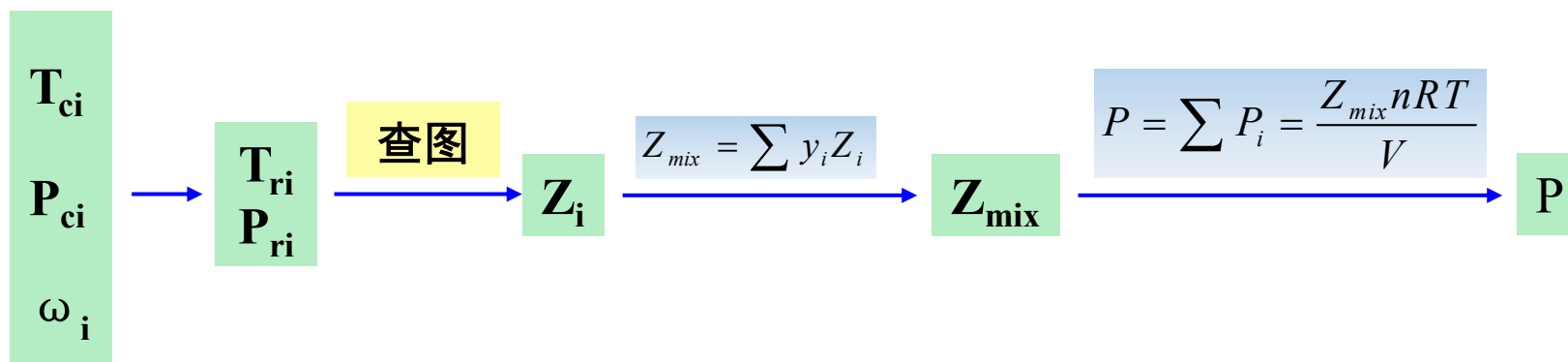
Dalton's Law (分压定律)

$$P = \sum P_i = \frac{Z_{mix} nRT}{V}$$

$$P_i = \frac{Z_i n_i RT}{V}$$

$$Z_{mix} = \sum y_i Z_i$$

查找出纯组分临界值



在压力小于5MPa的低压下才适用！

4.2 混合物的P-V-T关系

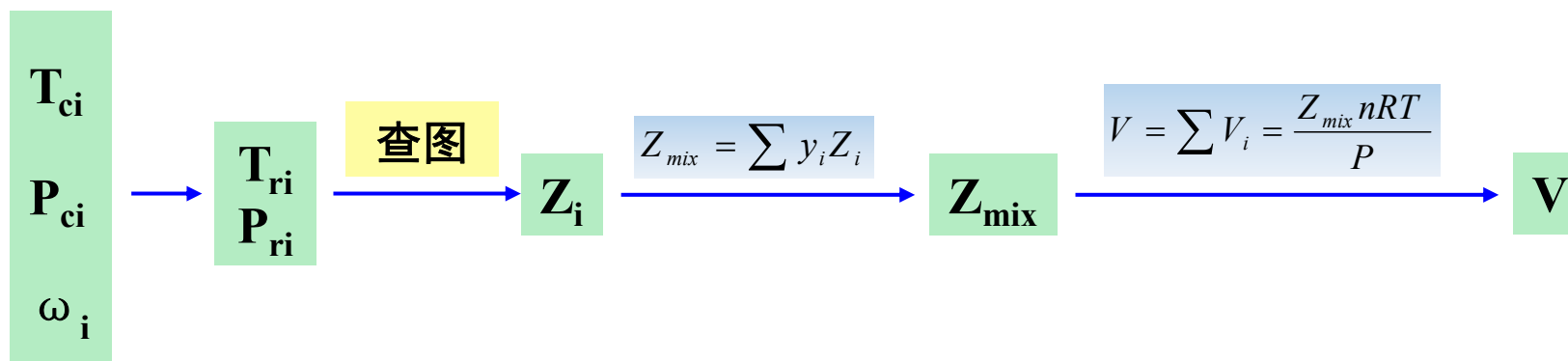
Amagat's Law (分体积定律)

$$V = \sum V_i = \frac{Z_{mix} nRT}{P}$$

$$V_i = \frac{Z_i n_i RT}{P}$$

$$Z_{mix} = \sum y_i Z_i$$

查找出纯组分临界值



在压力大于30MPa的高压下才适用！但对极性气体的计算偏差较大.

例. N₂:H₂=1/3(摩尔比) $p=40.532\text{MPa}$, $T=573\text{K}$, $V_m=?$

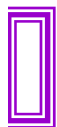
解 : a) 采用理想气体定律

$$V_m = RT / P = \frac{(8.314)(300 + 273.2)}{40.5 \times 10^6} = 1.176 \times 10^{-4} \text{ m}^3/\text{mol}$$

b) 采用Amagat定律

$$\text{H}_2: p_c=1.31 \text{ MPa}, T_c=33.20 \text{ K}, \omega=0.216$$

$$\text{N}_2: p_c=3.40 \text{ MPa}, T_c=126.2 \text{ K}, \omega=0.038$$



$$\text{H}_2: \quad T_r = \frac{573.2}{33.2 + 8} = 13.91 \quad P_r = \frac{40.5}{1.31 + 0.8106} = 19.10$$

$$\text{N}_2: \quad T_r = \frac{573.2}{126.2} = 4.54 \quad P_r = \frac{40.5}{3.40} = 11.91$$

经查普遍化压缩因子图可得：

$$Z_{H_2} = 1.15$$

$$Z_{N_2} = 1.20$$


$$Z_{mix} = \sum y_i Z_i = 0.75 \times 1.15 + 0.25 \times 1.20 = 1.163$$

$$V_m = \frac{1.163 \times 8.314 \times 10^3 \times 573.2}{40.5 \times 10^6} = 1.367 \times 10^{-4} m^3 / mol$$

维里方程

$$Z = \frac{PV_m}{RT} \approx 1 + \frac{BP}{RT}$$

$$B_{mix} = \sum_i \sum_j (y_i y_j B_{ij})$$

For binary system, $i=1,2$ and $j=1,2$:

$$B_{mix} = y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22}$$

Pitzer

$$BP_c / RT_c = B^0 + \omega B^1$$

Prausnitz

$$B_{ij} = \frac{RT_{cij}}{P_{cij}} (B^0 + \omega_{ij} B^1)$$

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}}$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}}$$

其中， k_{ij} 为交互系数，至今尚未得到交互系数的理论值或是经验值，一般拟合得到。

$$T_{cij} = (T_{ci} T_{cj})^{1/2} (1 - k_{ij})$$

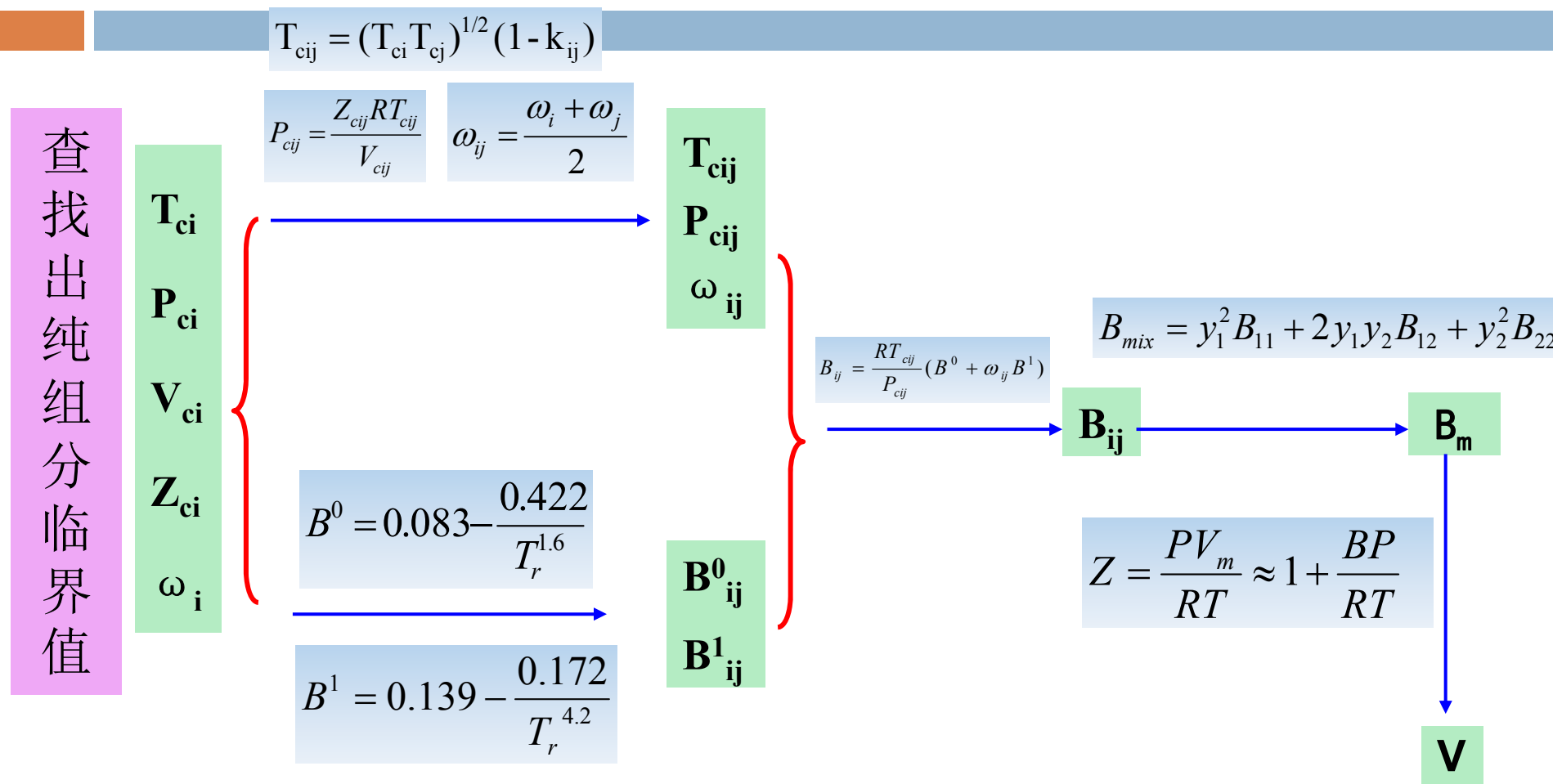
$$V_{cij} = \left(\frac{V_{ci}^{1/3} + V_{cj}^{1/3}}{2} \right)^3$$

$$Z_{cij} = \frac{Z_{ci} + Z_{cj}}{2}$$

$$P_{cij} = \frac{Z_{cij} RT_{cij}}{V_{cij}}$$

$$\omega_{ij} = \frac{\omega_i + \omega_j}{2}$$

维里方程一般计算步骤:



RK方程

For a mixture:

$$P = \frac{RT}{V_m - b_{mix}} - \frac{a_{mix}}{T^{1/2}V_m(V_m + b_{mix})}$$

$$a_{mix} = \sum_i \sum_j (y_i y_j a_{ij})$$

$$b_{mix} = \sum_i y_i b_i$$

$$a_{ij} = a_{ji}$$

For binary system:

$$a_{mix} = y_1^2 a_{11} + 2y_1 y_2 a_{12} + y_2^2 a_{22}$$

$$b_{mix} = y_1 b_1 + y_2 b_2$$

$$a_{ij} = \frac{0.42748 R^2 T_{cij}^{2.5}}{P_{cij}}$$

$$b_i = \frac{0.08664 R T_{ci}}{P_{ci}}$$

其中，

$$T_{cij} = (T_{ci} T_{cj})^{1/2} (1 - k_{ij})$$

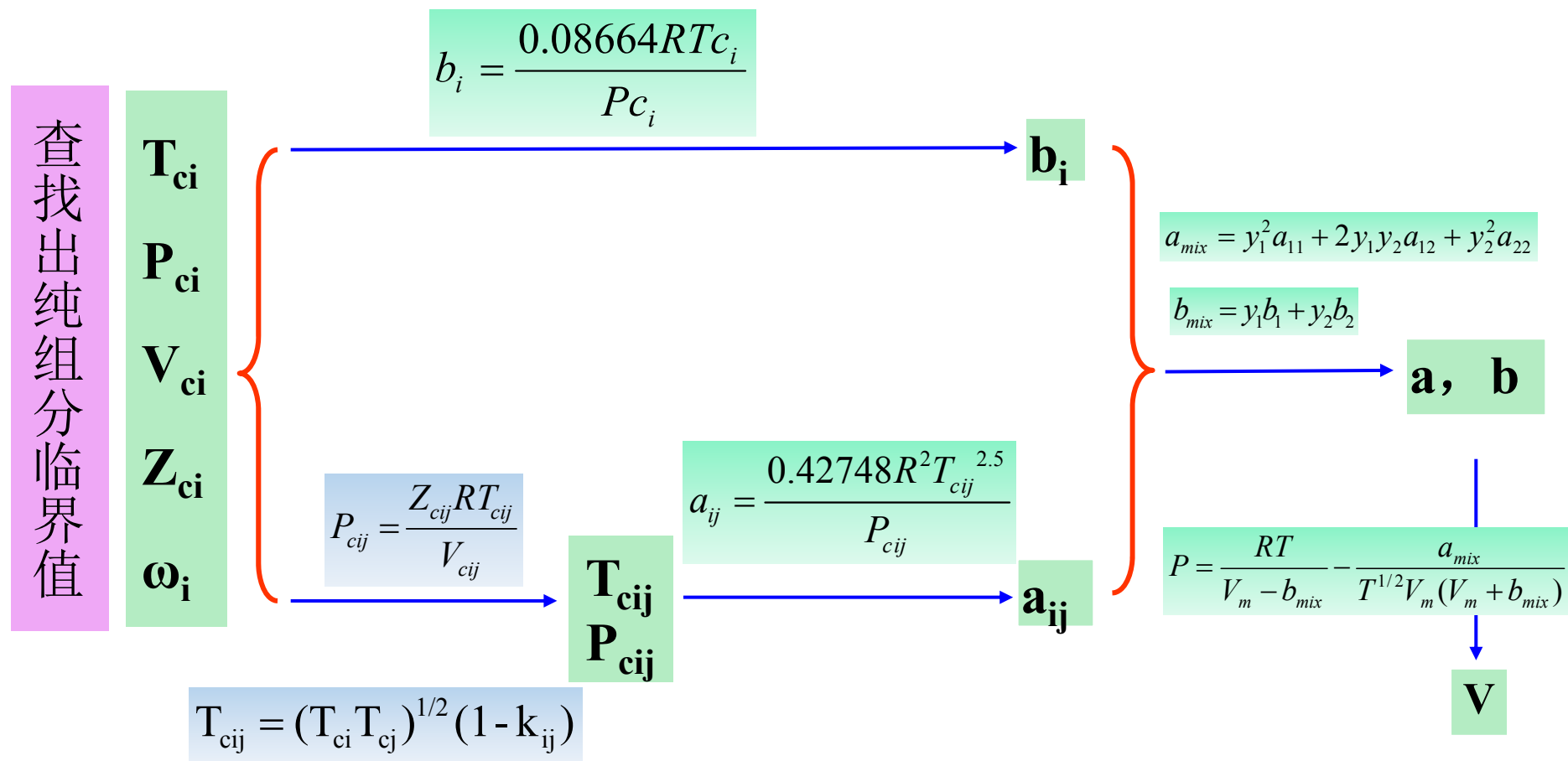
$$V_{cij} = \left(\frac{V_{ci}^{1/3} + V_{cj}^{1/3}}{2} \right)^3$$

$$Z_{cij} = \frac{Z_{ci} + Z_{cj}}{2}$$

$$P_{cij} = \frac{Z_{cij} R T_{cij}}{V_{cij}}$$

$$\omega_{ij} = \frac{\omega_i + \omega_j}{2}$$

RK方程一般解题步骤



例. CO₂ 40%, C₃H₈ 60%, T=151+273.15=424.15K,
p=13.78MPa. V_m=?

解: $T_{c12} = (T_{c1}T_{c2})^{1/2}(1-k_{12}) \approx (304.2 \times 369.8)^{1/2} = 335.4 K$

$$V_{c12} = \left(\frac{V_{c1}^{1/3} + V_{c2}^{1/3}}{2} \right)^3 = \left(\frac{0.094^{1/3} + 0.203^{1/3}}{2} \right)^3 = 0.1416 m^3 \cdot kmol^{-1}$$

$$Z_{c12} = \frac{Z_{c1} + Z_{c2}}{2} = \frac{0.274 + 0.281}{2} = 0.2775$$

$$\omega_{12} = \frac{\omega_1 + \omega_2}{2} = \frac{0.225 + 0.152}{2} = 0.1885$$

$$p_{ci12} = \frac{Z_{c12}RT_{c12}}{V_{c12}} = \frac{0.2775 \times 8.314 \times 335.4}{0.1416 \times 10^{-3}} = 5.465 \times 10^6 Pa = 5.465 MPa$$

ij	T_{cij}	$p_{cij}(Mpa)$	$V_{cij}(m^3.kmol^{-1})$	Z_{cij}	ω_{ij}
11	304.2	7.375	0.0940	0.274	0.225
22	369.8	4.250	0.2030	0.281	0.152
12	335.4	5.475	0.1416	0.278	0.189

(a) R-K方程

ij	$b_i(\text{m}^3.\text{kmol}^{-1})$	$a_{ij}(\text{m}^6.\text{Mpa}.\text{kmol}^{-2}.\text{K}^{1/2})$
11	0.02971	6.467
22	0.06268	18.28
12	11.12



$$a_{11} = \frac{0.42748 R^2 T_{c11}^{2.5}}{P_{c11}} = \frac{0.42748 R^2 \times 304.2^{2.5}}{7.375 \times 10^6} = 6.467 \text{ m}^6.\text{Pa}.\text{mol}^{-2}.\text{K}^{1/2}$$

$$b_1 = \frac{0.08664 RT_{c1}}{P_{c1}} = \frac{0.08664 R \times 304.2}{7.375 \times 10^6} = 2.971 \times 10^{-5} \text{ m}^3.\text{mol}^{-1}$$

$$a_{12} = \frac{0.42748 R^2 T_{c12}^{2.5}}{P_{c12}} = \frac{0.42748 R^2 \times 335.4^{2.5}}{5.475 \times 10^6} = 11.12 \text{ m}^6.\text{Pa}.\text{mol}^{-2}.\text{K}^{1/2}$$

$$\begin{aligned}
 a_{mix} &= \sum_i \sum_j (y_i y_j a_{ij}) = y_1^2 a_{11} + 2 y_1 y_2 a_{12} + y_2^2 a_{22} \\
 &= (0.4)^2 \times (6.467) + 2 \times 0.4 \times 0.6 \times 11.12 + 0.6^2 \times 18.28 \\
 &= 12.95 \text{ m}^6 \cdot \text{MPa} \cdot \text{kmol}^{-1} \cdot \text{K}^{1/2}
 \end{aligned}$$

$$b_{mix} = y_1 b_1 + y_2 b_2 = 0.4 \times 0.02971 + 0.6 \times 0.06268 = 0.04949 \text{ m}^3 \cdot \text{kmol}^{-1}$$



$$Z_{mix} = \frac{1}{1 - h_{mix}} - \frac{a_{mix}}{b_{mix} RT^{1.5}} \left(\frac{h_{mix}}{1 + h_{mix}} \right) \quad h_{mix} = \frac{b_{mix} P}{Z_{mix} RT}$$

采用迭代计算，最终可得：

$$h_{mix} = 0.3241, Z_{mix} = 0.5971,$$

$$V_m = \frac{Z_{mix} RT}{P} = \frac{0.5971 \times 0.008314 \times 424}{13.78} = 0.1527 \text{ m}^3 \cdot \text{kmol}^{-1}$$

(b) 采用普遍化压缩因子图:

$$T_{c,mix} = y_1 T_{c11} + y_2 T_{c22} = 0.4 \times 304.2 + 0.6 \times 369.8 = 343.6\text{K}$$

$$P_{c,mix} = y_1 P_{c11} + y_2 P_{c22} = 0.4 \times 7.375 + 0.6 \times 4.25 = 5.500\text{MPa}$$

$$\omega_{mix} = y_1 \omega_{11} + y_2 \omega_{22} = 0.4 \times 0.225 + 0.6 \times 0.152 = 0.1812$$

$$T_{r,mix} = \frac{424}{343.6} = 1.234 \quad P_{r,mix} = \frac{13.78}{5.500} = 2.505$$

With 3-parameter correlation : $Z^0 = 0.57$ $Z^1 = 0.16$

$$Z_{mix} = Z^0 + \omega Z^1 = 0.57 + 0.1812 \times 0.16 = 0.5990$$

$$V_m = \frac{Z_{mix} RT}{P} = \frac{0.5990 \times 0.008314 \times 424}{13.78} = 0.1532 \text{ m}^3.\text{kmol}^{-1}$$

(c) 采用普遍化第二维里系数关系式

$$B_{11}^0 = 0.083 - \frac{0.422}{T_{r11}^{1.6}} = 0.083 - \frac{0.422}{(424.15 / 304.2)^{1.6}} = -0.1649$$

$$B_{11}^1 = 0.139 - \frac{0.172}{T_{r11}^{4.2}} = 0.139 - \frac{0.172}{(424.15 / 304.2)^{4.2}} = 0.09642$$

$$B_{11}P_{c11}/(RT_{c11}) = B_{11}^0 + \omega_{11}B_{11}^1 = -0.1649 + 0.225 \times 0.09642 = -0.1432$$

$$B_{11} = -4.9109 \times 10^{-5} \text{ m}^3/\text{mol}$$

$$B_{12}^0 = 0.083 - \frac{0.422}{T_{r12}^{1.6}} = 0.083 - \frac{0.422}{(424.15 / 335.4)^{1.6}} = -0.2069$$

$$B_{12}^1 = 0.139 - \frac{0.172}{T_{r12}^{4.2}} = 0.139 - \frac{0.172}{(424.15 / 335.4)^{4.2}} = 0.0748$$

$$B_{12}P_{c12}/(RT_{c12}) = B_{12}^0 + \omega_{12}B_{12}^1 = -0.2069 + 0.189 \times 0.0748 = -0.1928$$

$$B_{12} = -9.818 \times 10^{-5} \text{ m}^3 / \text{mol}$$

ij	B ⁰	B ¹	B _{ij} (m ³ .kmol ⁻¹)
11	-0.1650	0.09638	-0.04915
22	-0.2558	0.04231	-0.18040
12	-0.2070	0.07470	-0.09824


$$B_{mix} = y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22}$$

$$= 0.4^2 \times (-0.04915) + 2 \times 0.4 \times 0.6 \times (-0.09824) + 0.6^2 \times (-0.1804)$$

$$= -0.11996 \text{ m}^3 \cdot \text{kmol}^{-1}$$

$$Z_{mix} = 1 + \frac{B_{mix} P}{RT} = 1 + \frac{(-0.11996) \times 13.78}{0.008314 \times 424} = 1 - 0.4689 = 0.5311$$

$$V_m = \frac{Z_{mix} RT}{P} = \frac{0.5311 \times 0.008314 \times 424}{13.78} = 0.1359 \text{ m}^3 \cdot \text{kmol}^{-1}$$



计算方法	$V \text{ m}^3/\text{mol} \times 10^4$
R-K 方程	1.527
普遍化 Z	1.532
普遍化 Virial	1.359

在高压下(13MPa)，普遍化维里系数关系的计算结果明显偏离其他两种方法，因此，为了保证计算精度，应注意其适用范围。

Home Work

2.26

