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？

着眼点：应用对比态原理

混合物系～虚拟纯质物系

着眼点：形成溶液的EOS

路线①：针对基本物性参数

$(T_c, P_c, \omega)_i$, i=1, …, N

路线②：针对EOS参数

$(a, b, \ldots)_i$, i=1, …, N

按$\{x_i$, i=1, …, N$\}$加权平均，＋异种分子间相互作用校正项

＋

纯质EOS，对比态原理图、算式

混合物EOS，对比态原理算式

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

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

Prausnitz-Gunn Revised

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

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

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

常用的混合规则

二次型混合规则

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

若交叉项为线性，则

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

若交叉项为几何平均，则

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

若交叉项为体积平均，则

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

4.2 混合物的P-V-T关系

Dalton's Law（分压定律）

$$P = \sum P_i = \frac{Z_{mix} nRT}{V} \qquad P_i = \frac{Z_i n_i RT}{V} \qquad Z_{mix} = \sum y_i Z_i$$

查找出纯组分临界值

$$\begin{matrix} T_{ci} \\ P_{ci} \\ \omega_i \end{matrix} \longrightarrow \begin{matrix} T_{ri} \\ P_{ri} \end{matrix} \xrightarrow{\text{查图}} Z_i \xrightarrow{Z_{mix} = \sum y_i Z_i} Z_{mix} \xrightarrow{P = \sum P_i = \frac{Z_{mix} nRT}{V}} P$$

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）

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

$$V_i=\frac{Z_in_iRT}{P}$$

$$Z_{mix}=\sum y_iZ_i$$

查找出纯组分临界值

$$\begin{matrix} T_{ci} \\ P_{ci} \\ \omega_i \end{matrix} \rightarrow \begin{matrix} T_{ri} \\ P_{ri} \end{matrix} \xrightarrow{\text{查图}} Z_i \xrightarrow{Z_{mix}=\sum y_iZ_i} Z_{mix} \xrightarrow{V=\sum V_i=\frac{Z_{mix}nRT}{P}} V$$

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=40.532MPa, T=573K, V_m=?

解：a) 采用理想气体定律

$$V_m = RT / P = \frac{(8.314)(300+273.2)}{40.5\times10^6} = 1.176\times10^{-4}\,\mathrm{m^3/mol}$$

b) 采用Amagat定律

H_2: p_c=1.31 MPa，T_c=33.20 K，ω=0.216

N_2: p_c=3.40 MPa，T_c=126.2 K，ω=0.038

H_2: $$T_r = \frac{573.2}{33.2+8} = 13.91 \qquad P_r = \frac{40.5}{1.31+0.8106} = 19.10$$

N_2: $$T_r = \frac{573.2}{126.2} = 4.54 \qquad P_r = \frac{40.5}{3.40} = 11.91$$

经查普遍化压缩因子图可得：

$$Z_{H_2} = 1.15 \qquad Z_{N_2} = 1.20$$

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

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

维里方程

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

$$B_{mix}=\sum_i\sum_i(y_iy_jB_{ij})$$

For binary system, i＝1,2 and j＝1,2 :

$$B_{mix}=y_1^2B_{11}+2y_1y_2B_{12}+y_2^2B_{22}$$

Pitzer

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

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

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

Prausnitz

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

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：

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

查找出纯组分临界值

T_{ci}

P_{ci}

V_{ci}

Z_{ci}

ω_i

$$P_{cij}=\frac{Z_{cij}RT_{cij}}{V_{cij}} \qquad \omega_{ij}=\frac{\omega_i+\omega_j}{2}$$

T_{cij}

P_{cij}

ω_{ij}

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

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

B^0_{ij}

B^1_{ij}

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

B_{ij}

$$B_{mix}=y_1^2B_{11}+2y_1y_2B_{12}+y_2^2B_{22}$$

B_m

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

V

RK方程

For a mixture:

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

$$a_{mix}=\sum_i\sum_j(y_iy_ja_{ij})\qquad b_{mix}=\sum_i y_ib_i\qquad a_{ij}=a_{ji}$$

For binary system:

$$a_{mix}=y_1^2a_{11}+2y_1y_2a_{12}+y_2^2a_{22}\qquad b_{mix}=y_1b_1+y_2b_2$$

$$a_{ij}=\frac{0.42748R^2T_{cij}^{2.5}}{P_{cij}}\qquad b_i=\frac{0.08664RT_{ci}}{P_{ci}}$$

其中,

$$\mathrm{T_{cij}}=(\mathrm{T_{ci}T_{cj}})^{1/2}(1-\mathrm{k_{ij}})\qquad V_{cij}=\left(\frac{V_{ci}^{1/3}+V_{cj}^{1/3}}{2}\right)^3\qquad Z_{cij}=\frac{Z_{ci}+Z_{cj}}{2}\qquad P_{cij}=\frac{Z_{cij}RT_{cij}}{V_{cij}}\qquad \omega_{ij}=\frac{\omega_i+\omega_j}{2}$$

RK方程一般解题步骤

查找出纯组分临界值

T_{ci}

P_{ci}

V_{ci}

Z_{ci}

ω_i

$$b_i = \frac{0.08664 R Tc_i}{Pc_i}$$

$\longrightarrow b_i$

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

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

$\longrightarrow T_{cij}$, P_{cij}

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

$\longrightarrow a_{ij}$

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

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

$\longrightarrow$ a， b

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

$\longrightarrow$ V

例. CO_2 40%, C_3H_8 60%, T=151+273.15=424.15K, p=13.78MPa. V_m=?

解: $T_{c12}=(T_{c1}T_{c2})^{1/2}(1\text{-}k_{12})\approx(304.2\times369.8)^{1/2}=335.4K$

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

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

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

$$p_{ci12}=\frac{Z_{c12}RT_{c12}}{V_{c12}}=\frac{0.2775\times8.314\times335.4}{0.1416\times10^{-3}}=5.465\times10^6\ \text{Pa}=5.465\ \text{MPa}$$

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

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

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

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

$$a_{mix} = \sum_i \sum_j (y_i y_j a_{ij}) = y_1^2 a_{11} + 2 y_1 y_2 a_{12} + y_2^2 a_{22}$$

$$= (0.4)^2 \times (6.467) + 2 \times 0.4 \times 0.6 \times 11.12 + 0.6^2 \times 18.28$$

$$= 12.95 \quad \mathrm{m^6.MPa.kmol^{-1}.K^{1/2}}$$

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

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

采用迭代计算，最终可得：

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

$$\mathrm{V_m} = \frac{Z_{mix} R T}{P} = \frac{0.5971 \times 0.008314 \times 424}{13.78} = 0.1527 \ m^3.kmol^{-1}$$

(b) 采用普遍化压缩因子图:

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

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

$$\omega_{\text{mix}} = \text{y}_1 \omega_{11} + \text{y}_2 \omega_{22} = 0.4 \times 0.225 + 0.6 \times 0.152 = 0.1812$$

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

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

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

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

(c) 采用普遍化第二维里系数关系式

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

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

$$B_{11}P_{c11}/(RT_{c11})=B_{11}{}^{0}+\omega_{11}B_{11}{}^{1}=-0.1649+0.225\times0.09642=-0.1432$$

$$B_{11}=-4.9109\times10^{-5}\,\mathrm{m}^{3}/\mathrm{mol}$$

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

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

$$B_{12}P_{c12}/(RT_{c12})=B_{12}{}^{0}+\omega_{12}B_{12}{}^{1}=-0.2069+0.189\times0.0748=-0.1928$$

$$B_{12}=-9.818\times10^{-5}m^{3}/mol$$

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

$$B_{mix} = y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22}$$
$$= 0.4^2 \times (-0.04915) + 2 \times 0.4 \times 0.6 \times (-0.09824) + 0.6^2 \times (-0.1804)$$
$$= -0.11996\ \mathrm{m^3.kmol^{-1}}$$

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

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

计算方法	V m^3/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

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