在前面章节中我们谈到的体系大都是单一组分的体系，而在化工生产中我们要解决的体系并非都是单一组分，大部分是气体或液体的多组分混合物，混合物的组成也不是一成不变的，如：精馏、吸收过程要发生质量传递，化学反应使反应物在其质和量上都发生了变化。

均相混合物一般称为溶液，也就是说溶液是指均相混合物，包括气体混合物和液体混合物。溶液热力学由于涉及到组成对热力学性质的影响，因而使得溶液热力学性质变得复杂化。

对于单相的纯物质或定组成体系，热力学性质间的关系式为：

对1mol纯物质：

$$H = U + PV$$

$$A = U - TS$$

$$G = H - TS$$

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

$$dA = -SdT - PdV$$

$$dG = -SdT + VdP$$

对n mol纯物质：

$$nH = nU + P(nV)$$

$$nA = nU - T(nS)$$

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

$$d(nU) = Td(nS) - Pd(nV)$$

$$d(nH) = Td(nS) + (nV)dP$$

$$d(nA) = -(nS)dT - Pd(nV)$$

$$d(nG) = -(nS)dT + (nV)dP$$

对于可变组成的单相体系：

$$nU=f(nS, nV, n_1, n_2, \ldots\ldots n_i \ldots\ldots)$$

式中n_i是i组分的摩尔数。内能的全微分式为：

$$d(nU)=\left[\frac{\partial(nU)}{\partial(nS)}\right]_{nV,n} d(nS)+\left[\frac{\partial(nU)}{\partial(nV)}\right]_{nS,n} d(nV)+$$

$$\left[\frac{\partial(nU)}{\partial n_1}\right]_{nS,nV,n_{j\neq 1}} dn_1+\left[\frac{\partial(nU)}{\partial n_2}\right]_{nS,nV,n_{j\neq 2}} dn_2+\ldots\ldots$$

$$\left[\frac{\partial(nU)}{\partial n_i}\right]_{nS,nV,n_{j\neq i}} dn_i+\ldots\ldots$$

内能的全微分式为：

$$d(nU)=\left[\frac{\partial(nU)}{\partial(nS)}\right]_{nV,n}d(nS)+\left[\frac{\partial(nU)}{\partial(nV)}\right]_{nS,n}d(nV)$$

$$+\sum\left[\frac{\partial(nU)}{\partial n_i}\right]_{nS,nV,n_{j\neq i}}dn_i$$

$nH=f(nS, np, n_1, n_2, \ldots\ldots n_i\ldots\ldots)$,同理焓的全微分式为：

$$d(nH)=\left[\frac{\partial(nH)}{\partial(nS)}\right]_{p,n}d(nS)+\left[\frac{\partial(nH)}{\partial p}\right]_{nS,n}dp$$

$$+\sum\left[\frac{\partial(nH)}{\partial n_i}\right]_{nS,p,n_{j\neq i}}dn_i$$

$nA=f(T, nV, n_1, n_2, \ldots\ldots n_i \ldots\ldots)$,则：

$$d(nA)=\left[\frac{\partial(nA)}{\partial T}\right]_{nV,n}dT+\left[\frac{\partial(nA)}{\partial(nV)}\right]_{T,n}d(nV)+\sum\left[\frac{\partial(nA)}{\partial n_i}\right]_{nV,T,n_{j\neq i}}dn_i$$

$nG=f(T,p, n_1, n_2, \ldots\ldots n_i \ldots\ldots)$,则：

$$d(nG)=\left[\frac{\partial(nG)}{\partial T}\right]_{p,n}dT+\left[\frac{\partial(nG)}{\partial p}\right]_{T,n}dp+\sum\left[\frac{\partial(nG)}{\partial n_i}\right]_{T,p,n_{j\neq i}}dn_i$$

由Maxwell关系式知：

$$\left[\frac{\partial(nU)}{\partial(nS)}\right]_{nV,n}=\left[\frac{\partial(nH)}{\partial(nS)}\right]_{p,n}=T$$

$$\left[\frac{\partial(nU)}{\partial(nV)}\right]_{nS,n}=\left[\frac{\partial(nA)}{\partial(nV)}\right]_{T,n}=-p$$

$$\left[\frac{\partial(nH)}{\partial p}\right]_{nS,n}=\left[\frac{\partial(nG)}{\partial p}\right]_{T,n}=nV$$

$$\left[\frac{\partial(nA)}{\partial T}\right]_{nV,n}=\left[\frac{\partial(nG)}{\partial T}\right]_{p,n}=-nS$$

代入上述式子中得：

$$d(nU) = Td(nS) - pd(nV) + \sum\left[\frac{\partial(nU)}{\partial n_i}\right]_{nS,nV,n_{j\neq i}} dn_i$$

$$d(nH) = Td(nS) + (nV)dp + \sum\left[\frac{\partial(nH)}{\partial n_i}\right]_{nS,p,n_{j\neq i}} dn_i$$

$$d(nA) = -SdT - pd(nV) + \sum\left[\frac{\partial(nA)}{\partial n_i}\right]_{nV,T,n_{j\neq i}} dn_i$$

$$d(nG) = -SdT + (nV)dp + \sum\left[\frac{\partial(nG)}{\partial n_i}\right]_{T,p,n_{j\neq i}} dn_i$$

令： $\mu_i = \left[\frac{\partial(nU)}{\partial n_i}\right]_{nS,nV,n_{j\neq i}} = \left[\frac{\partial(nH)}{\partial n_i}\right]_{nS,p,n_{j\neq i}}$

$$= \left[\frac{\partial(nA)}{\partial n_i}\right]_{nV,T,n_{j\neq i}} = \left[\frac{\partial(nG)}{\partial n_i}\right]_{T,p,n_{j\neq i}}$$

$$d(nU)=Td(nS)-Pd(nV)+\sum_i \mu_i dn_i$$

$$d(nH)=Td(nS)+nVdP+\sum_i \mu_i dn_i$$

$$d(nA)=-nSdT-Pd(nV)+\sum_i \mu_i dn_i$$

$$d(nG)=-nSdT+nVdP+\sum_i \mu_i dn_i$$

对于上面推导出的热力学关系式，使用时要注意以下几点：

(1)适用于敞开体系、封闭体系；

(2)体系是均相和平衡态间的变化；

(3)当$dn_i=0$时，简化成适用于定组成、定质量体系；

(4)*Maxwell*关系式用于可变组成体系时，要考虑组成不变的因素。

4.2.1 化学位

$$\mu_i = \left[\frac{\partial(nU)}{\partial n_i}\right]_{nS,nV,n_{j\neq i}} = \left[\frac{\partial(nH)}{\partial n_i}\right]_{nS,p,n_{j\neq i}}$$

$$= \left[\frac{\partial(nA)}{\partial n_i}\right]_{nV,T,n_{j\neq i}} = \left[\frac{\partial(nG)}{\partial n_i}\right]_{T,p,n_{j\neq i}}$$

(1)偏摩尔性质的定义

在恒温、恒压下，物系的广度性质随某种组分摩尔数的变化率叫做该组分的偏摩尔性质。

偏摩尔性质有三个重要的要素：①恒温、恒压；②广度性质（容量性质）；③随某组分摩尔数的变化率。这三个要素缺一不可，由此我们可以写出偏摩尔性质的通式：

$$\bar{M}_i = \left[\frac{\partial(nM)}{\partial n_i}\right]_{T,P,n_j}$$

(2)偏摩尔性质的物理意义：

在恒温、恒压下，物系中某组分摩尔数的变化所引起物系的一系列热力学性质的变化。偏摩尔性质的物理意义可通过实验来理解。

如：在一个无限大的、颈部有刻度的容量瓶中，盛入大量的乙醇水溶液，在乙醇水溶液的温度、压力、浓度都保持不变的情况下，加入*1mol*乙醇，充分混合后，量取瓶上的溶液体积的变化，这个变化值即为乙醇在这个温度、压力和浓度下的偏摩尔体积。

(3)偏摩尔性质与溶液摩尔性质间的关系

在溶液热力学中有三种性质，这三种性质要用不同的符号加以区别。

溶液的摩尔性质M：H、S、A、U、G、V等；

纯i组分的摩尔性质M_i：H_i、S_i、A_i、U_i、G_i、V_i等；

组分i在溶液中的偏摩尔性质$\overline{M}_i$：$\overline{S}_i$、$\overline{H}_i$、$\overline{A}_i$、$\overline{G}_i$、$\overline{U}_i$、$\overline{V}_i$等。

对于溶液的热力学性质，它不但是温度和压力的函数，还是组成的函数，用数学式表示就是：

$$nM=f(T,p,n_1,n_2,\ldots\ldots)$$

写成全微分的形式：

$$d(nM)=\left[\frac{\partial(nM)}{\partial T}\right]_{p,x}dT+\left[\frac{\partial(nM)}{\partial P}\right]_{T,x}dP+\sum\left[\frac{\partial(nM)}{\partial n_i}\right]_{T,P,n_{j\neq i}}dn_i$$

$$d(nM)=\left[\frac{\partial(nM)}{\partial T}\right]_{p,x}dT+\left[\frac{\partial(nM)}{\partial P}\right]_{T,x}dP+\sum\overline{M}_i dn_i$$

恒温、恒压下，上式变为：

$$d(nM)=\sum\overline{M}_i dn_i$$

积分上式得：

$$nM=\sum n_i\overline{M}_i$$

两边同除以n，得到另一种形式：

$$M=\sum x_i\overline{M_i}$$

上述式是由偏摩尔性质计算混合物性质的重要关系式。只要知道了组成该溶液各组分的偏摩尔性质及摩尔分率，就可以解决该溶液的热力学性质的计算。由此得出下述结论：

a、对于纯组分：$M_i=\overline{M_i}$

b、对于溶液中的组分：$M_i\neq\overline{M_i}$

(4)偏摩尔性质间的关系

与关联纯物质各摩尔热力学性质间的方程式相似，溶液中某组分的偏摩尔性质间的关系式为：

$$\overline{H}_i = \overline{U}_i + P\overline{V}_i \qquad d\overline{U}_i = Td\overline{S}_i - Pd\overline{V}_i$$

$$\overline{A}_i = \overline{U}_i - T\overline{S}_i \qquad d\overline{H}_i = Td\overline{S}_i + \overline{V}_i dP$$

$$\overline{G}_i = \overline{H}_i - T\overline{S}_i \qquad d\overline{A}_i = -\overline{S}_i dT - Pd\overline{V}_i$$

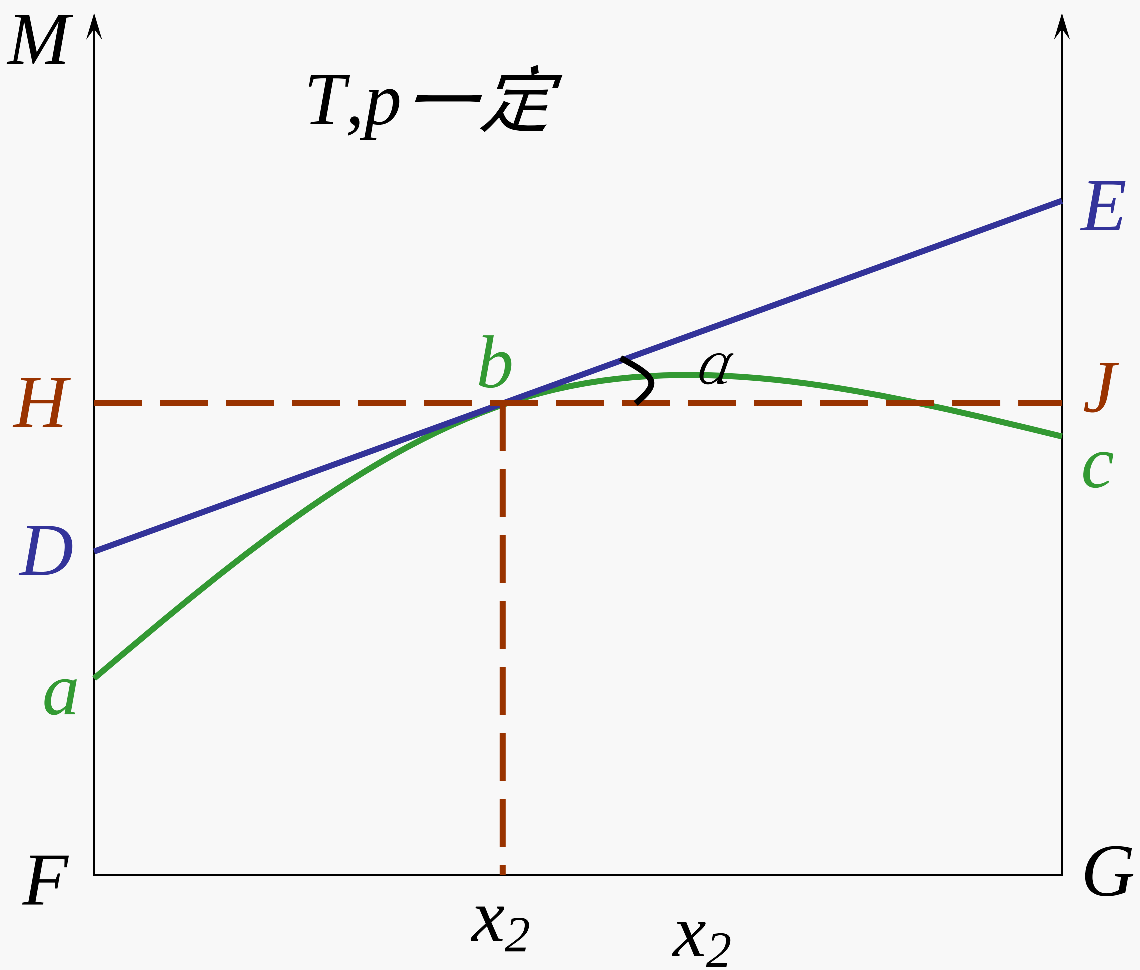
$$d\overline{G}_i = -\overline{S}_i dT + \overline{V}_i dP$$

*Maxwell*关系是同样也是用于偏摩尔性质。

(5)偏摩尔性质的计算

①截距法

由试验获得溶液某容量性质的摩尔值与溶液浓度(摩尔分率)的关系，以溶液某容量性质的摩尔值为纵坐标，溶液中溶质的摩尔分率为横坐标，得到一条曲线，过曲线指定浓度处作切线，则此切线截两纵轴的截距分别代表两组分的偏摩尔性质。这种方法的要点有三：**a.**由试验数据作恒温、恒压下的**M-x**曲线；**b.**作所求浓度下的切线；**c.**切线两端的截距为偏摩尔性质。


M
T,p 一定
E
b
α
H
J
c
D
a
F
G
x_2
x_2

证明：由图知：

$$\overline{GE} = \overline{GJ} + \overline{JE}$$

$$\overline{GJ} = M$$

$$\overline{JE} = \overline{bJ} \times tg\alpha = (1 - x_2)\frac{dM}{dx_2} = -x_1\frac{dM}{dx_1} = -x_1\left(\frac{\partial M}{\partial x_1}\right)_{T,p}$$

$$\therefore \overline{GE} = M - x_1\left(\frac{\partial M}{\partial x_1}\right)_{T,p}$$

设M为溶液的摩尔性质，则体系的溶液性质为：

$$nM=(n_1+n_2)M$$

将M在T、p不变的条件下对n_2求导得：

$$\overline{M_2}=\left[\frac{\partial(nM)}{\partial n_2}\right]_{T,P,n_1}=\left[\frac{\partial(n_1+n_2)M}{\partial n_2}\right]_{T,P,n_1}$$

$$\overline{M_2}=M+(n_1+n_2)\left[\frac{\partial M}{\partial n_2}\right]_{T,P,n_1}$$

$$\because x_1=\frac{n_1}{n_1+n_2}\qquad \therefore dx_1=-\frac{n_1dn_2}{(n_1+n_2)^2}=-x_1\frac{dn_2}{n_1+n_2}$$

$$dx_1 = -\frac{n_1 dn_2}{(n_1+n_2)^2} = -x_1 \frac{dn_2}{n_1+n_2}$$

即：$\dfrac{n_1+n_2}{dn_2} = -\dfrac{x_1}{dx_1}$

$$\therefore (n_1+n_2)\left(\frac{\partial M}{\partial n_2}\right)_{T,p,n_1} = -x_1\left(\frac{\partial M}{\partial x_1}\right)_{T,p,n_1}$$

$\overline{M_2} = M - x_1\left(\dfrac{\partial M}{\partial x_1}\right)_{T,p,n_1}$ 或 $\overline{M_2} = M - x_1\dfrac{dM}{dx_1}$

$\therefore \overline{GE} = \overline{M_2}$ 同理：$\overline{FD} = \overline{M_1}$

②解析法：自学

结论：对于二元溶液，摩尔性质和偏摩尔性质间有如下关系：

$$\bar{M}_1 = M - x_2 \frac{dM}{dx_2} \quad 或 \quad \bar{M}_1 = M + x_2 \frac{dM}{dx_1}$$

$$\bar{M}_2 = M - x_1 \frac{dM}{dx_1} \quad 或 \quad \bar{M}_2 = M + x_1 \frac{dM}{dx_2}$$

对多元：$\bar{M}_i = M - \sum_{k \neq i} \left[x_k \left(\frac{\partial M}{\partial x_k} \right)_{T,P,x_{j \neq i,k}} \right]$

例4-1：实验室需配制含有20%(质量分数)的甲醇的水溶液$3\times10^{-3}m^3$作为防冻剂。需要多少体积的20 ℃的甲醇与水混合。已知：20 ℃时20%(质量分数)甲醇溶液的偏摩尔体积：

$$\bar{V}_1 = 37.8cm^3/mol, \bar{V}_2 = 18.0cm^3/mol;$$

20 ℃时纯甲醇的体积$V_1=40.46cm^3/mol$；纯水的体积$V_2=18.04cm^3/mol$。

解：将组分的质量分数换算成摩尔分数：

$$x_1 = \frac{20/32}{20/32+80/18} = 0.1233 \qquad x_2 = 0.8767$$

溶液的摩尔体积为：

$$V = x_1\overline{V}_1 + x_2\overline{V}_2 = 0.1233\times 37.8 + 0.8767\times 18$$
$$= 20.44 cm^3/mol$$

配制防冻剂所需要物质的摩尔数

$$n = \frac{3000}{20.44} = 146.77 mol$$

所需甲醇和水的体积分别为

$$V_{1t}=x_1nV_1=0.1233\times146.77\times40.46=732cm^3$$

$$V_{2t}=x_2nV_2=0.8767\times146.77\times18.04=2321cm^3$$

例4-2：某二元液体混合物在293K和0.10133MPa下的焓可用下式表示：

$$H = 100x_1 + 150x_2 + x_1x_2(10x_1 + 5x_2) \quad J/mol \qquad (A)$$

确定在该温度和压力下：

(a) 用x_1表示的$\overline{H}_1$和$\overline{H}_2$；

(b) 纯组分的焓H_1的H_2值；

(c)无限稀释溶液的偏摩尔焓$\overline{H_1^\infty}$和$\overline{H_2^\infty}$

解：用$x_2 = 1 - x_1$代入A式得：

$$H = 100x_1 + 150(1 - x_1) + x_1(1 - x_1)[10x_1 + 5(1 - x_1)]$$

$$H = 150 - 45x_1 - 5x_1^3 \; J/mol \qquad (B)$$

$$\frac{dH}{dx_1} = -45 - 15x_1^2$$

$$\overline{H}_1 = H + x_2 \frac{dH}{dx_1} = H + (1 - x_1)\frac{dH}{dx_1}$$

$$\overline{H}_1 = 150 - 45x_1 - 5x_1^3 + (1 - x_1)(-45 - 15x_1^2)$$

$$\overline{H}_1 = 105 - 15x_1^2 + 10x_1^3 \, J/mol \qquad (C)$$

$$\overline{H}_2 = H - x_1 \frac{dH}{dx_1}$$

$$\overline{H}_2 = 150 - 45x_1 - 5x_1^3 - x_1(-45 - 15x_1^2)$$

$$\overline{H}_2 = 150 + 10x_1^3 \, J/mol \qquad (D)$$

$$H = 150 - 45x_1 - 5x_1^3 \ J/mol \qquad (B)$$

$$H_1 = 150 - 45\times1 - 5\times1^3 = 100 J/mol$$

$$H_2 = 150 - 45\times0 - 5\times0^3 = 150 J/mol$$

$$\overline{H}_1^\infty = \lim_{x_1\to0} \overline{H}_1 = 105 J/mol$$

$$\overline{H}_2^\infty = \lim_{x_2\to0} \overline{H}_2 = \lim_{x_1\to1} \overline{H}_2 = 150 + 10 = 160 J/mol$$

$$nM = \sum n_i \bar{M}_i$$

$$d(nM) = \sum \left(n_i d\bar{M}_i\right) + \sum \left(\bar{M}_i dn_i\right)$$

$$nM = f\left(T, P, n_1, n_2, \cdots, n_i, \cdots\right)$$

$$d(nM) = \left[\frac{\partial (nM)}{\partial T}\right]_{P,n} dT + \left[\frac{\partial (nM)}{\partial P}\right]_{T,n} dP + \sum \left(\bar{M}_i dn_i\right)$$

$$d(nM) = n\left(\frac{\partial M}{\partial T}\right)_{P,x} dT + n\left(\frac{\partial M}{\partial P}\right)_{T,x} dP + \sum \left(\bar{M}_i dn_i\right)$$

比较式可得

$$n\left(\frac{\partial M}{\partial T}\right)_{P,x} dT + n\left(\frac{\partial M}{\partial P}\right)_{T,x} dP = \sum n_i d\bar{M}_i$$

Gibbs-Duhem 方程的一般形式

$$\left(\frac{\partial M}{\partial T}\right)_{P,x} dT + \left(\frac{\partial M}{\partial P}\right)_{T,x} dP - \sum x_i d\bar{M}_i = 0$$

当T、P恒定时

$$\sum \left(x_i d\bar{M}_i\right)_{T,P} = 0$$

当 M=G时

$$\sum\left(x_i d\bar{G}_i\right)_{T,P}=0$$

Gibbs-Duhem 方程的应用

(1)检验实验测得的混合物热力学性质数据的正确性;

(2)从一个组元的偏摩尔量推算另一组元的偏摩尔量。

二元系等温、等压条件下

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

$$\left(1-x_2\right)\frac{d\bar{M}_1}{dx_2}=-x_2\frac{d\bar{M}_2}{dx_2}$$

$$d\overline{M}_1 = -\frac{x_2}{1-x_2}\frac{d\overline{M}_2}{dx_2}dx_2$$

$$x_2 = 0时 \qquad \overline{M}_1 = M_1$$

$$\overline{M}_1 = M_1 - \int_0^{x_2}\frac{x_2}{1-x_2}\frac{d\overline{M}_2}{dx_2}dx_2$$

只要已知从 $x_2=0$ 到 $x_2=x_2$ 范围内的 $\overline{M}_2$ 值，就可以根据上式求另一组元在x_2时的偏摩尔量 $\overline{M}_1$ 。当然还需知道纯物质的摩尔性质M_1。

由不同物质混合形成混合物时，不仅应关注混合后的热力学性质，有时更关注混合过程的热力学性质变化。

一般地，混合性质或称混合过程性质变化是指在指定T、p下由纯物质混合形成一摩尔混合物过程中，系统某容量性质的变化。用符号ΔM表示混合过程性质变化，其定义为:

$$\Delta M = M - \sum x_i M_i$$

$$\Delta M = M - \sum x_i M_i$$

Mi是与混合物同温、同压下纯组分i的摩尔性质。

混合物的摩尔性质与偏摩尔性质的关系

$$M = \sum x_i \overline{M}_i$$

$$\Delta M = \sum x_i \overline{M}_i - \sum x_i M_i = \sum x_i \left(\overline{M}_i - M_i \right)$$

4.3 逸度与逸度系数

在相平衡的计算中，离不逸度及其系数的计算。由于引入了逸度及其系数，使相平衡的计算成为可能。

逸度可理解为有效的压力，它的单位与压力相同。它表示了物质的逸散程度。

逸度包括三种，即：纯组分的逸度及纯组分的逸度系数；溶液中组分的分逸度及溶液中组分的分逸度系数；混合物的逸度及混合物的逸度系数 。

由热力学微分方程得：

$$dG = VdP - SdT$$

在恒温下．将此关系式应用于1摩尔纯流体i时，得

$$dG_i = V_i dp \qquad (等温)$$

对于理想气体, $V=RT/P$, 则

$$dG_i = RT\frac{dP}{P} \qquad (等温)$$

$$dG_i = RTd\ln P \qquad (等温)$$

对于真实气体，定义逸度f_i

$$dG_i = RTd\ln f_i \qquad (\text{等温})$$

$$\lim_{P\to 0}\frac{f_i}{P} = 1$$

逸度系数的定义

$$\phi_i = \frac{f_i}{P}$$

逸度与压力具有相同的单位，逸度系数是无因次的。

理想气体的逸度系数等于1，真实气体的逸度系数可以大于1，也可以小于1，它是温度、压力的函数。由变组成系统热力学关系式可知，将纯物质性质关系式推广到混合物，只需增加对组成变量的考虑，而定组成混合物偏摩尔性质关系式与纯物质性质关系式是一一对应的，即：

$$d\overline{G}_i = \overline{V}_i dP - \overline{S}_i dT$$

与纯组分的逸度定义一样，考虑温度恒定的情况下，可得到溶液中组分的分逸度的定义：

$$d\bar{G}_i = RTd\ln\hat{f}_i \qquad (等温)$$

$$\lim_{P\to 0}\frac{\hat{f}_i}{y_iP} = 1$$

溶液中组分i 的分逸度系数的定义为

$$\hat{\phi}_i = \frac{\hat{f}_i}{y_iP}$$

混合物的逸度的定义为

$$dG = RTd\ln f \qquad (等温)$$

$$\lim_{P\to 0}\frac{f}{P}=1$$

混合物的逸度系数的定义为

$$\phi = \frac{f}{P}$$

有三种逸度及逸度系数，它们分别是：

纯组分的逸度：f_i

混合物的逸度：f

溶液中组分的分逸度：$\hat{f}_i$

纯组分的逸度系数：ϕ_i

混合物的逸度系数：ϕ

溶液中组分的分逸度系数：$\hat{\phi}_i$

$$\ln\frac{\hat{f}_i}{x_i}=\left[\frac{\partial(n\ln f)}{\partial n_i}\right]_{T,P,n_j} \qquad \ln\hat{\phi}_i=\left[\frac{\partial(n\ln\phi)}{\partial n_i}\right]_{T,P,n_j}$$

对照偏摩尔性质的定义

$$\overline{M}_i=\left[\frac{\partial(nM)}{\partial n_i}\right]_{T,P,n_j}$$

$\ln\frac{\hat{f}_i}{x_i}$是$\ln f$的偏摩尔性质

$\ln\hat{\phi}_i$是$\ln\phi$的偏摩尔性质

溶液性质	偏摩尔性质	二者关系式
M	$\overline{M}_i$	$M=\sum x_i\overline{M}_i$
$\ln f$	$\ln\dfrac{\hat{f}_i}{x_i}$	$\ln f=\sum x_i \ln\dfrac{\hat{f}_i}{x_i}$
$\ln\phi$	$\ln\hat{\phi}_i$	$\ln\phi=\sum x_i \ln\hat{\phi}_i$

4.4.3.1 温度对逸度的影响

温度对纯组分逸度的影响

$$\left(\frac{\partial \ln f_i}{\partial T}\right)_P = -\frac{H^R}{RT^2} = \frac{H_i^{ig} - H_i}{RT^2}$$

温度对混合物中组分逸度的影响

$$\left(\frac{\partial \ln \hat{\phi}_i}{\partial T}\right)_{P,y} = \left(\frac{\partial \ln \hat{f}_i}{\partial T}\right)_{P,y} = \frac{H_i^{ig} - \bar{H}_i}{RT^2}$$

4.4.3.2 压力对逸度的影响

压力对纯组分逸度的影响

$$\left(\frac{\partial \ln f_i}{\partial P}\right)_T = \frac{V_i}{RT}$$

压力对混合物中组分逸度的影响

$$\left(\frac{\partial \ln \hat{f}_i}{\partial P}\right)_{T,y} = \frac{\bar{V}_i}{RT}$$

4.4.4.1 纯物质逸度系数的计算

$$RTd\ln f_i = V_i dP$$

对 ϕ_i 的定义表达式取对数并微分得：

$$d\ln\phi_i = d\ln f_i - d\ln P = d\ln f_i - \frac{dP}{P}$$

$$d\ln\phi_i = \frac{V_i dP}{RT} - \frac{dP}{P} = (Z_i - 1)\frac{dp}{p}$$

将上式从压力为零的状态积分到压力为P的状态，并考虑到当$P\to 0$时，$\phi_i = 1$，得

$$\ln\phi_i = \frac{1}{RT}\int_0^p \left(V_i - \frac{RT}{p}\right)dp = \int_0^p (Z_i - 1)\frac{dp}{p}$$

a.用状态方程计算逸度系数

对立方型状态方程，应有以T、V为自变量的求解逸度系数计算方法，推导如下：

$$\because \ln\phi_i = \frac{1}{RT}\int_{p_0}^{p}\left(V_i - \frac{RT}{p}\right)dp = \int_{p_0}^{p}(Z_i - 1)\frac{dp}{p}$$

$$\therefore \ln\phi_i = \frac{1}{RT}\int_{p_0}^{p}\left(V_i - \frac{RT}{p}\right)dp = \frac{1}{RT}\int_{p_0}^{p}V_i dp - \int_{p_0}^{p}\frac{dp}{p}$$

$$又 \because Vdp = d(pV) - pdV$$

$$\therefore \ln\phi_i = \frac{1}{RT}\int_{p_0}^{p}d(pV) - \frac{1}{RT}\int_{V_0}^{V}pdV - \int_{0}^{p}\frac{dp}{p}$$

将RK方程代入上式得：

$$\ln\phi_i = \frac{pV - p_0V_0}{RT} - \ln\frac{V-b}{V_0-b} + \frac{a}{bRT^{1.5}}\ln\left[\frac{V}{V_0}\left(\frac{V_0+b}{V+b}\right)\right] - \ln\frac{p}{p_0}$$

$$\because\ pV = ZRT \quad p_0V_0 = RT$$

$$\therefore \ln\phi_i = Z - 1 - \ln\frac{pV-pb}{RT-p_0b} + \frac{a}{bRT^{1.5}}\ln\left[\frac{V}{V_0}\left(\frac{V_0+b}{V+b}\right)\right]$$

当$p_0 \to 0$、$\mathrm{d}V_0 \to \infty$时，$(RT - p_0b) \to RT, \dfrac{V_0+b}{V_0} \to 1$

$$\therefore \ln\phi_i = Z - 1 - \ln\left(Z - \frac{pb}{RT}\right) - \frac{a}{bRT^{1.5}}\ln\left(1 + \frac{b}{V}\right)$$

用*RK*方程迭代形式：

$$\frac{\mathrm{pb}}{RT}=Bp,\frac{b}{V}=\frac{Bp}{Z},\frac{a}{bRT^{1.5}}=\frac{A}{B},h=\frac{b}{V}$$

$$\therefore \ln\phi_i=Z-1-\ln\left(Z-Bp\right)-\frac{A}{B}\ln\left(1+h\right)$$

$$SRK\text{方程}:\ln\phi_i=Z-1-\ln\frac{P\left(V-b\right)}{RT}-\frac{a}{bRT}\ln\left(1+\frac{b}{V}\right)$$

$$PR\text{方程}:\ln\phi_i=Z-1-\ln\frac{P\left(V-b\right)}{RT}-\frac{1}{2\sqrt{2}bRT}\ln\frac{V+\left(\sqrt{2}+1\right)b}{V-\left(\sqrt{2}-1\right)b}$$

对维里方程：

$$\because Z = \frac{pV}{RT} = 1 + \frac{B\,p}{RT}$$

$$\therefore \frac{V}{RT} - \frac{1}{p} = \frac{B}{RT} \text{代入} \ln\phi_i = \int_0^p \left(\frac{V}{RT} - \frac{1}{p}\right) dp$$

$$\ln\phi_i = \int_0^p \frac{B}{RT} dp = \frac{B\,p}{RT}$$

b. 用对比态原理计算逸度系数

$$\because \ln\phi_i = \int_0^p (Z_i - 1)\frac{dp}{p} = \int_0^p (Z_i - 1)\frac{d(p_r p_C)}{p_r p_C}$$

$$\therefore \ln\phi_i = \int_0^p \frac{Z_i - 1}{p_r} dp_r$$

当$V_r \geq 2$或在图上时

$$Z_i = 1 + \frac{Bp_c}{RT_c}\left(\frac{p_r}{T_r}\right)$$

$$\frac{Bp_c}{RT_c} = B^0 + \omega B^1$$

当$V_r \geq 2$或在图上时

$$Z_i = 1 + \frac{Bp_c}{RT_c}\left(\frac{p_r}{T_r}\right) \quad \frac{Bp_c}{RT_c} = B^0 + \omega B^1$$

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} \quad B^1 = 0.039 - \frac{0.172}{T_r^{4.2}}$$

$$\therefore \ln \phi_i = \int_0^p \frac{Z_i - 1}{p_r} dp_r = \int_0^p \left[(B^0 + \omega B^1)\left(\frac{p_r}{T_r}\right) \right] \frac{dp_r}{p_r}$$

$$\therefore \ln \phi_i = (B^0 + \omega B^1)\frac{p_r}{T_r}$$

当$V_r < 2$或在图下时

$$\ln \phi_i = \ln \phi_i^0 + \omega \ln \phi_i^1$$

式中ϕ_i^0、ϕ_i^1可由图查得

例4—7用RK方程和普遍化法计算正丁烷在460K,1.520MPa下的逸度和逸度系数

解:(1).RK方程

$$T_r=\frac{460}{425.12}=1.082\quad p_r=\frac{1.520}{3.796}=0.4004$$

用RK方程迭代形式:

$$\frac{\text{pb}}{RT}=Bp,\frac{b}{V}=\frac{Bp}{Z},\frac{a}{bRT^{1.5}}=\frac{A}{B},h=\frac{b}{V}$$

$$\therefore \ln\phi_i=Z-1-\ln\left(Z-Bp\right)-\frac{A}{B}\ln\left(1+h\right)$$

$$Z = 0.8851 \quad h = 0.0362$$

$$\frac{A}{B} = 4.3818 \quad Bp = 0.0320$$

$$\ln \phi_i = Z - 1 - \ln(Z - Bp) - \frac{A}{B}\ln(1 + h)$$

$$\ln \phi_i = 0.8851 - 1 - \ln(0.8851 - 0.0320) - 4.3818 \times 1.0362$$

$$\ln \phi_i = 0.8942$$

$$f_i = \phi_i p = 0.8942 \times 1.520 = 1.359 MPa$$

解:(2).普遍化关系式

$$T_r = 1.082 \quad p_r = 0.4004$$

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} = 0.083 - \frac{0.422}{1.082^{1.6}} = -0.289$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} = 0.139 - \frac{0.172}{1.082^{4.2}} = 0.0155$$

$$\ln\phi_i = (B^0 + \omega B^1)\frac{p_r}{T_r}$$

$$\ln\phi_i = (-0.289 - 0.199 \times 0.0155) \times \frac{0.4004}{1.082}$$

$$\ln\phi_i = 0.8975 \quad \therefore\ f_i = \phi_i p = 0.8975 \times 1.52 = 1.364MPa$$

参照纯组分逸度计算公式

$$\ln\phi_i = \frac{1}{RT}\int_0^p\left(V_i - \frac{RT}{p}\right)dp = \int_0^p (Z_i - 1)\frac{dp}{p}$$

可得混合物中组分的分逸度系数的计算式

$$\ln\hat{\phi}_i = \frac{1}{RT}\int_0^p\left(\overline{V}_i - \frac{RT}{p}\right)dp = \int_0^p \left(\overline{Z}_i - 1\right)\frac{dp}{p} \quad (T、y恒定)$$

对理想气体:$\overline{Z}_i=Z_i=1 \quad \hat{\phi}_i^{ig} = \phi_i = 1$

$$\bar{V}_i = \left[\frac{\partial(nV)}{\partial n_i}\right]_{T,p,n_{j\neq i}} = \left(\frac{\partial V_t}{\partial n_i}\right)_{T,p,n_{j\neq i}}$$

代入上式得:

$$\ln\hat{\phi}_i = \frac{1}{RT}\int_0^p \left(\left(\frac{\partial V_t}{\partial n_i}\right)_{T,p,n_{j\neq i}} - \frac{RT}{p}\right)dp$$

$$\ln\hat{\phi}_i = \frac{1}{RT}\int_{\mathrm{V_t}}^{\infty} \left[\left(\frac{\partial p}{\partial n_i}\right)_{T,V,n_{j\neq i}} - \frac{RT}{V_t}\right]dV_t - \ln Z$$

a.用维里方程计算分逸度系数

$$Z = 1 + \frac{BP}{RT} \Rightarrow nZ - n = \frac{nBP}{RT}$$

对二元混合物，当T, p, n_2不变时，对n_1微分得

$$\therefore \overline{Z_1} = \left[\frac{\partial(nZ)}{\partial n_i}\right]_{T,p,n_2} = \frac{p}{RT}\left[\frac{\partial(nB)}{\partial n_i}\right]_{T,p,n_2} + 1$$

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

令δ_{12}＝$2B_{12}$－B_{11}－B_{22}　则

$$B = y_1 B_{11} + y_2 B_{22} + y_1 y_2 \delta_{12}$$　两边乘n得

$$B = y_1 B_{11} + y_2 B_{22} + y_1 y_2 \delta_{12}$$ 两边乘n得

$$nB = n_1 B_{11} + n_2 B_{22} + \frac{n_1 n_2}{n}\delta_{12}$$ 对n_1微分得

$$\left[\frac{\partial(nB)}{\partial n_1}\right]_{T,p,n_2} = B_{11} + \left(\frac{1}{n} - \frac{n_1}{n^2}\right)n_2\delta_{12} = B_{11} + (1 - y_1)\,y_2\delta_{12}$$

$$\left[\frac{\partial(nB)}{\partial n_1}\right]_{T,p,n_2} = B_{11} + y_2^2\delta_{12}$$

$$\therefore \overline{Z_1} = \frac{p}{RT}\left[\frac{\partial(nB)}{\partial n_i}\right]_{T,p,n_2} + 1$$

$$\therefore \overline{Z_1} = \frac{p}{RT}\left(B_{11} + y_2^2\delta_{12}\right) + 1$$ 代入前式得

$$\therefore \ln\hat{\phi}_i = \int_0^p (\overline{Z_1} - 1)\frac{dp}{p} = \int_0^p \left[\frac{p}{RT}\left(B_{11} + y_2^2\delta_{12}\right)\right]\frac{dp}{p}$$

$$\ln\hat{\phi}_1 = \frac{P}{RT}\left[B_{11} + y_2^2\delta_{12}\right]$$

$$\ln\hat{\phi}_2 = \frac{P}{RT}\left[B_{22} + y_1^2\delta_{12}\right]$$

$$\ln\hat{\phi}_i = \frac{P}{RT}\left[B_{ii} + \frac{1}{2}\sum_{j=1}^{n}\sum_{k=1}^{n} y_j y_k (2\delta_{ji} - \delta_{jk})\right]$$

$$\delta_{ji} = 2B_{ji} - B_{jj} - B_{ii}$$

$$\delta_{jk} = 2B_{jk} - B_{jj} - B_{kk}$$

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

$$B = \sum_{i=1}^{n}\sum_{j=1}^{n} y_i y_j B_{ij}$$

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

$$\omega_{ij} = \frac{\omega_i + \omega_j}{2} \qquad T_{cij} = \sqrt{T_{ci}T_{cj}}(1 - k_{ij}) \qquad P_{cij} = \frac{Z_{cij}RT_{cij}}{V_{cij}}$$

$$Z_{cij} = \frac{Z_{ci} + Z_{cj}}{2} \qquad V_{cij} = \left[\frac{V_{ci}^{1/3} + V_{cj}^{1/3}}{2}\right]^3$$

b. 用RK方程计算组分逸度系数

$$P=\frac{RT}{V-b}-\frac{a}{T^{1/2}V\left(V+b\right)}$$

$$a=\sum_{i=1}^{N}\sum_{j=1}^{N}y_i y_j a_{ij} \qquad b_m=\sum_{i=1}^{N}y_i b_i$$

$$a_{ij}=\left(a_i a_j\right)^{0.5}\left(1-k_{ij}\right)$$

$$\ln\hat{\phi}_i=\ln\frac{V}{V-b}+\frac{b_i}{V-b}-\frac{2\sum_j y_j a_{ij}}{RT^{1.5}b}\ln\frac{V+b}{V}+\frac{ab_i}{RT^{1.5}b^2}\left(\ln\frac{V+b}{V}-\frac{b}{V+b}\right)-\ln Z$$

例4—8 试计算313K、1.5MPa下CO_2和丙烷的等摩尔混合物中各组分的分逸度系数。

ij	T_{Cij} K	p_{cij} MPa	V_{cij} cm^3/mol	Z_{cij}	w_{ij}
11	304.19	7.382	94.0	0.274	0.228
22	369.83	4.248	200.0	0.277	0.152
12	335.40	5.482	140.4	0.2766	0.190

解：$T_{c12} = (1-k_{12})\sqrt{T_{c1}T_{c2}} = \sqrt{307.19 \times 369.83} = 335.41$

$$V_{c12} = \left(\frac{V_{c1}^{1/3} + V_{c2}^{1/3}}{2}\right)^3 = \left(\frac{94.0^{1/3} + 200^{1/3}}{2}\right)^3 = 140.4$$

$$Z_{C12}=\frac{Z_{C1}+Z_{C2}}{2}=\frac{0.274+0.277}{2}=0.2755$$

$$p_{c12}=\frac{Z_{c12}RT_{c12}}{V_{c12}}=\frac{0.2755\times 8.314\times 335.4}{140.4}=5.472$$

$$\omega_{12}=\frac{\omega_1+\omega_2}{2}=\frac{0.228+0.152}{2}=0.190$$

ij	T_{rij}	$B^{(0)}$	$B^{(1)}$	$B_{ij}/cm_3/mol$
11	1.029	-0.320	-0.014	-110.7
22	0.846	-0.464	-0.201	-357.9
12	0.933	-0.389	-0.091	-206.7

$$T_{r12}=\frac{T}{T_{c12}}=\frac{313}{335.4}=0.933$$

$$B_{12}^{0}=0.083-\frac{0.422}{T_{r12}^{1.6}}=0.083-\frac{0.422}{0.933^{1.6}}=-0.3885$$

$$B_{12}^{1}=0.139-\frac{0.172}{T_{r12}^{4.2}}=0.139-\frac{0.172}{0.933^{4.2}}=-0.0912$$

$$B_{12}=\frac{RT_{c12}}{p_{c12}}(B_{12}^{0}+\omega_{12}B_{12}^{1})$$

$$=\frac{8.314\times335.40}{5.482}[-0.3885+0.190\times(-0.0912)]=-206.44$$

$$\delta_{12} = 2B_{12} - B_{11} - B_{22} = 2\times(-206.7)-(-110.7)-(-357.9)$$

$$= 55.2cm^3/mol$$

$$\ln\hat{\phi}_1 = \frac{p}{RT}(B_{11} + y_2^2\delta_{12})$$

$$= \frac{1.5}{8.314\times313}(-110.7+0.5^2\times55.2) = -0.05585$$

$$\ln\hat{\phi}_2 = \frac{p}{RT}(B_{22} + y_1^2\delta_{12})$$

$$= \frac{1.5}{8.314\times313}(-357.9+0.5^2\times55.2) = -0.1983$$

$$\hat{\phi}_1 = 1.0574 \quad \hat{\phi}_2 = 0.820$$

例4—9 已知二元体系H_2-C_3H_8,$y_1=0.208$,其体系压力和温度为3197.26kPa、344.75K，试用RK方程计算混合物中氢的分逸度系数。$k_{ij}=0.07$

组分	T_c K	p_c kPa	V_c cm^3/mol	W
H_2	33.18	1313.0	64.2	-0.220
C_3H_8	369.83	4248.0	200	0.152

$$a_{11}=\frac{0.42748R^2T_{c1}^{2.5}}{p_{c1}}=\frac{0.42748\times 8.314^2\times 33.18^{2.5}}{1313.0}$$

$$=1.4284\times 10^8\,cm^6\cdot K^{0.5}/kPa\cdot mol^2$$

$$a_{22}=\frac{0.42748R^2T_{c2}^{2.5}}{p_{c2}}=\frac{0.42748\times 8.314^2\times 369.83^{2.5}}{4248.0}$$

$$=1.8313\times 10^{10}\,cm^6\cdot K^{0.5}/kPa\cdot mol^2$$

$$b_1=\frac{0.08664RT_{c1}}{p_{c1}}=\frac{0.08664\times 8.314\times 33.18}{1313.0}=18.2171cm^3/mol$$

$$b_2=\frac{0.08664RT_{c2}}{p_{c2}}=\frac{0.08664\times 8.314\times 369.83}{4248.0}=62.3983cm^3/mol$$

$$T_{c12} = (1-k_{12})\sqrt{T_{c1}T_{c2}} = (1-0.07)\sqrt{369.83\times 33.18} = 103.02K$$

$$V_{c12} = \left(\frac{V_{c1}^{1/3}+V_{c2}^{1/3}}{2}\right)^3 = \left(\frac{64.2^{1/3}+200^{1/3}}{2}\right)^3 = 119.54cm^3/mol$$

$$Z_{C12} = \frac{Z_{C1}+Z_{C2}}{2} = \frac{0.305+0.277}{2} = 0.291$$

$$p_{c12} = \frac{Z_{c12}RT_{c12}}{V_{c12}} = \frac{0.291\times 8.314\times 103.02}{119.54} = 2042.2kPa$$

$$\omega_{12} = \frac{\omega_1+\omega_2}{2} = \frac{-0.220+0.152}{2} = -0.034$$

$$a_{11}=\frac{0.42748R^2T_{c1}^{2.5}}{p_{c1}}=\frac{0.42748\times 8.314^2\times 103.02^{2.5}}{2042.2}$$

$$=1.560\times 10^9 cm^6\cdot K^{0.5}/kPa\cdot mol^2$$

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

$$=0.208^2\times 1.4284\times 10^8+0.798^2\times 1.8313\times 10^{10}$$

$$+2\times 0.208\times 0.798\times 1.560\times 10^9$$

$$=1.200\times 10^{10} cm^6\cdot K^{0.5}/kPa\cdot mol^2$$

$$b=\sum_i y_i b_i=y_1 b_1+y_2 b_2$$

$$=0.208\times 18.2171+0.798\times 62.3983=53.5830 cm^3/mol$$

$$p=\frac{RT}{V-b}-\frac{a}{T^{1/2}V(V+b)}\Rightarrow\left[p+\frac{a}{T^{1/2}V(V+b)}\right](V-b)=RT$$

$$\left[3797.26+\frac{1.200\times10^{10}}{344.75^{1/2}V(V+53.5830)}\right](V-53.5830)=8314.73\times344.8$$

解得：$V=554cm^3/mol$

$$\ln\hat{\phi}_i=\ln\frac{V}{V-b}+\frac{b_i}{V-b}-\frac{2\sum_j y_j a_{ij}}{RT^{1.5}b}\ln\frac{V+b}{V}+\frac{ab_i}{RT^{1.5}b^2}\left(\ln\frac{V+b}{V}-\frac{b}{V+b}\right)-\ln Z$$

$$\ln\hat{\phi}_1=\ln\frac{V}{V-b}+\frac{b_1}{V-b}-\frac{2\sum_j y_j a_{1j}}{RT^{1.5}b}\ln\frac{V+b}{V}+\frac{ab_1}{RT^{1.5}b^2}\left(\ln\frac{V+b}{V}-\frac{b}{V+b}\right)-\ln Z$$

$$\ln\hat{\phi}_1 = \ln\frac{V}{V-b} + \frac{b_1}{V-b} - \frac{2\sum_j y_j a_{1j}}{RT^{1.5}b}\ln\frac{V+b}{V} + \frac{ab_1}{RT^{1.5}b^2}\left(\ln\frac{V+b}{V} - \frac{b}{V+b}\right) - \ln Z$$

$$= \ln\frac{554}{554-53.5830} + \frac{18.2171}{554-53.5830}$$

$$-\frac{2\left(0.208\times1.4284\times10^{8} + 0.792\times1.560\times10^{9}\right)}{8314.73\times344.8^{1.5}\times53.5830}\times\ln\frac{554+53.5830}{554}$$

$$+\frac{1.200\times10^{10}\times18.2171}{8314.73\times344.8^{1.5}\times53.5830^2}\times\left(\ln\frac{554+53.5830}{554} - \frac{554}{554+53.5830}\right)$$

$$-\ln\frac{3797.26\times554}{8314.73\times344.8}$$

$$= -0.8061$$

$$\hat{\phi}_1 = 0.4466$$

在相平衡时，饱和液体的逸度与饱和蒸汽的逸度相等：$f_i^{lv} = f_i^s = p_i^s \phi_i^s$

由纯物质逸度的定义式：$dG_i = RTd\ln f_i$

结合$dG_i = V_i dp \Rightarrow d\ln f_i = \frac{V_i}{RT}dp$

将上式从饱和液体（压力为p_i^s）积分到过冷液体（压力为p）得：

$$\ln\frac{f_i^l}{f_i^s} = \int_{p_i^s}^{p}\frac{V_i^l}{RT}dp \Rightarrow f_i^l = f_i^s\exp\int_{p_i^s}^{p}\frac{V_i^l}{RT}dp$$

$$\ln\frac{f_i^l}{f_i^s}=\int_{p_i^s}^{p}\frac{V_i^l}{RT}dp \Rightarrow f_i^l=f_i^s\exp\int_{p_i^s}^{p}\frac{V_i^l}{RT}dp$$

对于液体的体积V_i^l是温度和压力的弱函数，可视为常数.则：

$$f_i^l=f_i^s\exp\left[\frac{V_i^l\left(p-p_i^s\right)}{RT}\right]$$

压力比较低时,$\exp\left[\frac{V_i^l\left(p-p_i^s\right)}{RT}\right]\approx 1$，则：$f_i^l=f_i^s$

注意：纯液体的逸度计算应分两步，首先求出饱和液体（也即饱和蒸汽）的逸度，然后再按下式计算纯液体的逸度。

$$f_i^l = f_i^s \exp\left[\frac{V_i^l\left(p - p_i^s\right)}{RT}\right]$$

$$\ln\frac{f_i^l}{f_i^s} = \frac{V_i^l\left(p - p_i^s\right)}{RT}$$

当压力很低时：$f_i^l = f_i^s$

例4—10　试求液态异丁烷在360.98K、1.02×10^{7} Pa下的逸度。已知360.9K时，液体异丁烷的平均摩尔体积$V_{C_4H_{10}}=0.119\times10^{-3}m^3/mol$，饱和蒸气压$p_{C_4H_{10}}^{s}=1.574\times10^{6}Pa$。

解：由附录查得异丁烷的热力学数据：

$$T_c=408.1K, p_c=3.6\times10^{6}Pa,\omega=0.176$$

首先计算$f_{C_4H_{10}}^s$

$$T_r=\frac{T}{T_c}=\frac{360.96}{408.1}=0.88$$

$$p_r^s=\frac{p_{C_4H_{10}}^s}{p_c}=\frac{1.574\times10^6}{3.6\times10^6}=0.44$$

用普遍化第二维里系数法：

$$\mathrm{B}^0=0.083-\frac{0.422}{T_r^{1.6}}=0.083-\frac{0.422}{0.88^{1.6}}=-0.435$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} = 0.139 - \frac{0.172}{0.88^{4.2}} = -0.155$$

$$\ln \phi_{C_4H_{10}} = \frac{p_r^s}{T_r}\left[B^0 + \omega B^1 \right]$$

$$= \frac{0.44}{0.88}[-0.435 - 0.176 \times 0.155] = -0.229$$

$$\phi_{C_4H_{10}} = 0.795$$

$$f_{C_4H_{10}}^s = \phi_{C_4H_{10}} p_{C_4H_{10}}^s = 0.795 \times 1.574 = 1.251 MPa$$

$$f_{C_4H_{10}}^{l} = f_{C_4H_{10}}^{s} \exp\left[\frac{V_{C_4H_{10}}^{l}\left(p - p_{C_4H_{10}}^{s}\right)}{RT}\right]$$

$$= 1.251 \times \exp\left[\frac{0.119 \times 10^{-1}\left(1.02 - 0.1574\right) \times 10^{7}}{8.314 \times 360.96}\right]$$

$$= 1.764 MPa$$