

溶剂化的热力学集团展开理论

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摘 要: 把二元溶液的过剩内能(excess energy)分成溶剂-溶剂、溶剂-溶质及溶质-溶质相互作用部分。利用集团展开方法给出了二元溶液在正则系综的配分函数的表达式,利用该表达式得到了溶质的偏摩尔内能(partial molar energy)和偏摩尔熵(partial molar entropy)的表达式。在无限稀溶液情形,过剩偏摩尔内能的溶剂-溶剂部分又称重组织内能(reorganization energy),它反映了溶质存在时对其周围溶剂分子之间的相互作用能的影响。研究表明,在溶质的粒子数密度相对较大时,溶质分子之间的相互作用将影响过剩偏摩尔内能的溶剂-溶剂部分,对于稀溶液,过剩偏摩尔内能的溶剂-溶剂部分与溶质的摩尔分数成线性关系。对低密度二元溶液,溶质的过剩偏摩尔内能和过剩偏摩尔熵也与溶质的摩尔分数成线性关系。

关键词: 集团展开; 过剩偏摩尔内能; 过剩偏摩尔熵; 重组织内能

中图分类号: O414.2

文献标识码: A

1 引 言

近年来,熵的多粒子相关函数理论^[1]已经成为研究溶解热力学的主要理论工具,并广泛应用于研究硬球混合物^[2]、水溶液^[3,4]等体系的热力学性质。应用熵的多粒子相关函数理论可以把溶液的熵及内能分成溶剂-溶剂、溶剂-溶质及溶质-溶质三部分。由于求解三粒子相关函数十分困难,通常用 Kirkwood 的叠加近似方法求出二粒子相关函数,从而进一步计算溶液的过剩能量、过剩熵、重组织能及重组织熵等热力学量。叠加近似方法对于压缩率很小的流体是一个很好的近似^[5],但是对于低密度的压缩率较大的流体,叠加近似方法存在着较大的误差^[6]。

溶剂的重组织能反映了溶质粒子存在时对溶剂分子之间相互作用能的影响,它提供了溶质分子周围的溶剂分子之间的相互作用信息,利用相关函数理论计算重组织能时,其计算结果只是反映了溶质粒子存在时对溶剂粒子之间相互作用能量影响的平均值,不能恰当地提供溶质粒子周围的溶剂粒子的信息。Lazaridis 的非均匀溶解热力学理论把溶质粒子当作产生外场的源粒子^[7,8],从而能较好地反映溶质粒子周围的溶剂粒子的信息。然而,非均匀溶解热力学只在溶质浓度无限稀时成立。

综上所述,对于低密度且溶质浓度相对较高时的二元溶液还没有一个较好的溶解热力学理论,最近的研究表明,利用正则系综的集团展开方法可以较正确地计算低密度且溶质浓度较高的二元溶液的热力学性质^[9,10]。本文给出了正则系综配分函数的集团展开方程,并把内能分成了溶质-溶质、溶质-溶剂、溶剂-溶剂三部分,给出了溶质浓度相对较高时溶液的过剩

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收稿日期: 2000-02-28; 修回日期: 2000-06-06。

能量及过剩熵的表达式, 并进一步研究了过剩偏摩尔内能的溶剂-溶剂部分与溶质浓度的关系。

2 二元溶液的过剩内能及过剩熵

设二元溶液中只存在二体力, 则系统的相互作用势能可以表示成:

$$U(\vec{r}_1^s, \vec{r}_2^s, \dots, \vec{r}_{N_s}^s, \vec{r}_1^w, \vec{r}_2^w, \dots, \vec{r}_{N_w}^w) \\ = \frac{1}{2} \sum_{ij}^{N_s(N_s-1)} V_{ss}(\vec{r}_i^s - \vec{r}_j^s) + \sum_{lk}^{N_s N_w} V_{sw}(\vec{r}_l^s - \vec{r}_k^w) + \frac{1}{2} \sum_{mn}^{N_w(N_w-1)} V_{ww}(\vec{r}_m^w - \vec{r}_n^w) \quad (1)$$

式中, N_s 及 N_w 分别为溶质及溶剂的粒子数, V_{ss} 、 V_{sw} 及 V_{ww} 分别为一对溶质-溶质、溶质-溶剂、溶剂-溶剂粒子之间的相互作用势能, \vec{r}_i^s 及 \vec{r}_m^w 分别为第 i 个溶质粒子及第 m 个溶剂粒子的位置矢量。为了能够把过剩能量分成溶质-溶质、溶质-溶剂及溶剂-溶剂三部分, 我们引入带参数 ($\lambda_1, \lambda_2, \lambda_3$) 的相互作用势能:

$$U(\vec{r}_1^s, \vec{r}_2^s, \dots, \vec{r}_{N_s}^s, \vec{r}_1^w, \vec{r}_2^w, \dots, \vec{r}_{N_w}^w; \lambda_1, \lambda_2, \lambda_3) \\ = \sum_{ij}^{\frac{1}{2} N_s(N_s-1)} \lambda_1 V_{ss}(\vec{r}_i^s - \vec{r}_j^s) + \sum_{lk}^{N_s N_w} \lambda_2 V_{sw}(\vec{r}_l^s - \vec{r}_k^w) + \sum_{mn}^{\frac{1}{2} N_w(N_w-1)} \lambda_3 V_{ww}(\vec{r}_m^w - \vec{r}_n^w) \quad (2)$$

在正则系综中, 系统的配分函数可以写成:

$$Z(\lambda_1, \lambda_2, \lambda_3, N_s, N_w, T, V) = \frac{(\lambda_w^3 V)^{N_w} (\lambda_s^3 V)^{N_s}}{N_w! N_s!} Z_{\text{位}}(\lambda_1, \lambda_2, \lambda_3, N_s, N_w, T, V) \\ Z_{\text{位}}(\lambda_1, \lambda_2, \lambda_3, N_s, N_w, T, V) = \frac{1}{V^N} \int \exp(-\beta U) \prod_i d\vec{r}_i^s \prod_j d\vec{r}_j^w \quad (3)$$

式中, N 为系统的总粒子数; V 为系统的体积; $\beta = \frac{1}{k_B T}$, k_B 为玻尔兹曼常数; λ_w 和 λ_s 为溶剂和溶质的热波长。现在我们把 $Z_{\text{位}}$ 作集团展开, 令:

$$\exp[-\beta \lambda_1 V_{ss}(\vec{r}_i^s - \vec{r}_j^s)] = 1 + f_{ij}^{ss}(\lambda_1) \\ \exp[-\beta \lambda_2 V_{sw}(\vec{r}_l^s - \vec{r}_k^w)] = 1 + f_{lk}^{sw}(\lambda_2) \\ \exp[-\beta \lambda_3 V_{ww}(\vec{r}_m^w - \vec{r}_n^w)] = 1 + f_{mn}^{ww}(\lambda_3) \quad (4)$$

则配分函数 $Z_{\text{位}}$ 可以表示成:

$$Z_{\text{位}} = \sum_{m=0}^{N_s} \sum_{n=0}^{N_w} \frac{\rho^{m+n} x_s^m x_w^n}{m! n!} b_{mn} \quad (5)$$

式中, ρ 为溶液的粒子数密度; x_s 及 x_w 分别为溶质及溶剂的摩尔分数; b_{mn} 为 m 个溶质粒子和 n 个溶剂粒子的集团函数。其前几项的表达式为:

$$b_{00} = 1 \quad (6a)$$

$$b_{10} = b_{01} = 0 \quad (6b)$$

$$b_{20} = \int f_{12}^{ss}(\lambda_1) d\vec{r}_1^s d\vec{r}_2^s \quad (6c)$$

$$b_{02} = \int f_{12}^{ww}(\lambda_3) d\vec{r}_1^w d\vec{r}_2^w \quad (6d)$$

$$b_{11} = \int f_{12}^{sw}(\lambda_2) d\vec{r}_1^s d\vec{r}_2^w \quad (6e)$$

$$b_{30} = \int [3f_{12}^{ss}(\lambda_1)f_{23}^{ss}(\lambda_1) + f_{12}^{ss}(\lambda_1)f_{13}^{ss}(\lambda_1)f_{23}^{ss}(\lambda_1)] d\vec{r}_1^s d\vec{r}_2^s d\vec{r}_3^s \quad (6f)$$

$$b_{12} = \int [f_{12}^{su}(\lambda_2)f_{13}^{su}(\lambda_2) + f_{12}^{su}(\lambda_2)f_{13}^{su}(\lambda_2)f_{23}^{uw}(\lambda_3)] d\vec{r}_1^s d\vec{r}_2^w d\vec{r}_3^w \quad (6g)$$

$$b_{21} = \int [f_{13}^{su}(\lambda_2)f_{23}^{su}(\lambda_2) + f_{12}^{ss}(\lambda_1)f_{13}^{su}(\lambda_2)f_{23}^{su}(\lambda_2)] d\vec{r}_1^s d\vec{r}_2^s d\vec{r}_3^w \quad (6h)$$

$$b_{03} = \int [3f_{12}^{uw}(\lambda_3)f_{23}^{uw}(\lambda_3) + f_{12}^{uw}(\lambda_3)f_{13}^{uw}(\lambda_3)f_{23}^{uw}(\lambda_3)] d\vec{r}_1^w d\vec{r}_2^w d\vec{r}_3^w \quad (6i)$$

对于高阶项 b_{mn} 可以按下列方式求出 :

(1) 令相互作用线 $\overset{i}{\bullet} - \overset{j}{\bullet}$ 、 $\overset{l}{\bullet} \dots \overset{k}{\bullet}$ 、 $\overset{m}{\blacklozenge} \dots \overset{n}{\blacklozenge}$ 分别代表 $f_{ij}^{ss}(\lambda_1)$ 、 $f_{lk}^{su}(\lambda_2)$ 、 $f_{mn}^{uw}(\lambda_3)$ 。

(2) 画出每个粒子至少有一根相互作用线与其他粒子相联的 m 个溶质粒子和 n 个溶剂粒子的所有拓扑不等价图, 例如 : 对于 $m=2, n=2$ 情形, 相应的图为 :

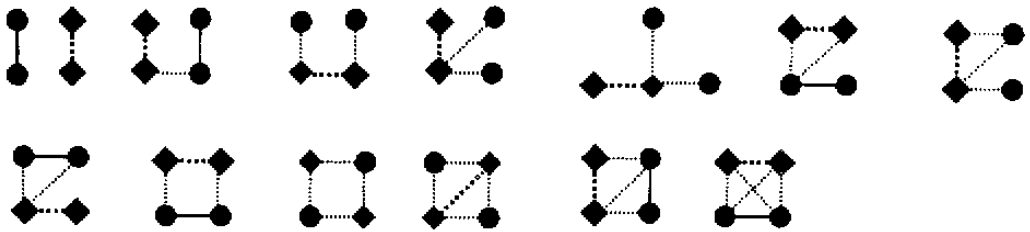


图 1 两个溶质粒子和两个溶剂粒子集团的图形表示

Fig. 1 Schematic representation of the cluster of two solute and two solvent particles

(3) 给每个粒子一个编号, 同时每个图乘以值 σ_{mn} , σ_{mn} 为给该图的粒子编号后交换同种粒子所产生的拓扑不同的图形数。

(4) 每个图形等于积分 $\sigma_{mn} \int \dots \int \prod_{i=1}^m d\vec{r}_i^s \prod_{j=1}^n d\vec{r}_j^w \times [\text{所有相互作用线的乘积}]$, 例如 :

$$\frac{1}{1} \frac{2}{2} = 2 \int d\vec{r}_1^s d\vec{r}_2^s d\vec{r}_1^w d\vec{r}_2^w f_{12}^{ss}(\lambda_1) f_{11}^{su}(\lambda_2) f_{12}^{uw}(\lambda_3) f_{12}^{su}(\lambda_2)$$

(5) b_{mn} 为每个粒子至少有一根相互作用线与其他粒子相联的 m 个溶质粒子和 n 个溶剂粒子的所有拓扑不等价图形的和。

利用正则系综的配分函数, 我们可以把过剩内能写成 :

$$E^{ex} = E_{ss}^{ex} + E_{sw}^{ex} + E_{uw}^{ex} \quad (7)$$

式中, E_{ss}^{ex} 、 E_{sw}^{ex} 、 E_{uw}^{ex} 分别为溶质 - 溶质、溶质 - 溶剂、溶剂 - 溶剂粒子之间的相互作用势能,

$$E_{ss}^{ex} = -k_B T \lim_{\lambda_3 \rightarrow 1} \lim_{\lambda_2 \rightarrow 1} \lim_{\lambda_1 \rightarrow 1} \frac{\partial}{\partial \lambda_1} \ln Z_{\text{位}}(\lambda_1, \lambda_2, \lambda_3) \quad (7a)$$

$$E_{sw}^{ex} = -k_B T \lim_{\lambda_3 \rightarrow 1} \lim_{\lambda_2 \rightarrow 1} \lim_{\lambda_1 \rightarrow 1} \frac{\partial}{\partial \lambda_2} \ln Z_{\text{位}}(\lambda_1, \lambda_2, \lambda_3) \quad (7b)$$

$$E_{uw}^{ex} = -k_B T \lim_{\lambda_3 \rightarrow 1} \lim_{\lambda_2 \rightarrow 1} \lim_{\lambda_1 \rightarrow 1} \frac{\partial}{\partial \lambda_1} \ln Z_{\text{位}}(\lambda_1, \lambda_2, \lambda_3) \quad (7c)$$

溶液的过剩熵为 :

$$S^{ex} = k_B \ln Z_{\text{位}}(1, 1, 1) + E^{ex}/T \quad (8)$$

在这里我们不能把过剩熵分成溶质-溶质、溶质-溶剂及溶剂-溶剂三部分,不过这对我们研究偏摩尔熵没有影响。

1.3 溶质偏摩尔内能及偏摩尔熵的表达式

当溶质及溶剂的粒子数很大时,溶质的化学势 μ_s 可以用下式求出

$$\mu_s = \left(\frac{\partial A}{\partial N_s} \right)_{T,V} = \left(\frac{\partial E}{\partial N_s} \right)_{T,V} + T \left(\frac{\partial S}{\partial N_s} \right)_{T,V} \quad (9)$$

式中, A 为系统的自由能,因此,溶质的偏摩尔内能为:

$$\bar{\mu}_s = \left(\frac{\partial E}{\partial N_s} \right)_{T,V} = \frac{3}{2} k_B T + \left(\frac{\partial E^{ex}}{\partial N_s} \right)_{T,V} \quad (10)$$

而系统的偏摩尔熵为:

$$\bar{s}_s = \left(\frac{\partial S}{\partial N_s} \right)_{T,V} = \left[\frac{5}{2} k_B - k \ln(\rho_s \lambda_s^3) \right] + \left(\frac{\partial S^{ex}}{\partial N_s} \right)_{T,V} \quad (11)$$

式中, ρ_s 为溶质的粒子数密度; λ_s 为溶质的热波长。从(10)式和(11)式中减去理想气体的贡献就可以得到过剩偏摩尔能量及过剩偏摩尔熵,

$$\bar{\mu}_s^{ex} = \left(\frac{\partial E^{ex}}{\partial N_s} \right)_{T,V} \quad (12)$$

$$\bar{s}_s^{ex} = \left(\frac{\partial S^{ex}}{\partial N_s} \right)_{T,V} \quad (13)$$

把(7)式代入(12)式得:

$$\bar{\mu}_s^{ex} = \left(\frac{\partial E_{ss}^{ex}}{\partial N_s} \right)_{T,V} + \left(\frac{\partial E_{sw}^{ex}}{\partial N_s} \right)_{T,V} + \left(\frac{\partial E_w^{ex}}{\partial N_s} \right)_{T,V} \quad (14)$$

(14)式右端第一项为过剩偏摩尔内能的溶质-溶质项,它代表增加一个溶质粒子对溶质-溶质粒子之间相互作用能的影响。特别是在无限稀溶液极限下:

$$\lim_{x_s \rightarrow 0} \left(\frac{\partial E_{ss}^{ex}}{\partial N_s} \right)_{T,V} = 0 \quad (15)$$

这一结果与文献^[7]是一致的。然而,当溶质的粒子数密度较小但仍为有限时,过剩偏摩尔内能不为零,对于稀溶液, x_s 远小于1,把(5)式代入(7)式,再将 E_{ss}^{ex} 展开成 x_s 的泰勒级数,得:

$$E_{ss}^{ex} = -k_B T \sum_{n=0}^{N_w} \frac{\rho^{n+2} x_w^n}{n!} \left(\frac{\partial b_{2n}}{\partial \lambda_1} \right)_0 \frac{x_s^2}{Z_w} + \dots \quad (16)$$

式中的 Z_w 为纯溶剂的位置配分函数:

$$Z_w = \lim_{\lambda_1 \rightarrow 0} \lim_{\lambda_2 \rightarrow 0} \lim_{\lambda_3 \rightarrow 1} Z_w(\lambda_1, \lambda_2, \lambda_3) \quad (16a)$$

$$\left(\frac{\partial b_{2n}}{\partial \lambda_1} \right)_0 = \lim_{\lambda_1 \rightarrow 1} \lim_{\lambda_2 \rightarrow 1} \lim_{\lambda_3 \rightarrow 1} \left(\frac{\partial b_{2n}}{\partial \lambda_1} \right) \quad (16b)$$

把(16)式代入(14)式得过剩偏摩尔能量的溶质-溶质部分:

$$\left(\frac{\partial E_{ss}^{ex}}{\partial N_s} \right)_{T,V} = -\frac{2}{N} k_B T \sum_{n=0}^{N_w} \frac{\rho^{n+2} x_w^n}{n!} \left(\frac{\partial b_{2n}}{\partial \lambda_1} \right)_0 \frac{x_s}{Z_w} + \dots \quad (17)$$

(17)式表明,在稀溶液情形下过剩偏摩尔能量的溶质-溶质部分与溶质的摩尔分数 x_s 成正比,这一点是不难理解的,因为在保持体积和温度不变的条件下,改变溶质的粒子数将改变溶

质粒子之间的平均距离,从而改变溶质粒子之间的相互作用能。(14)式右端第二项为偏摩尔内能的溶质-溶剂项,当 $x_s \ll 1$ 时,把(5)式代入(7b)式再对溶质的摩尔分数 x_s 作泰勒展开得:

$$E_{sw}^{ex} = -k_B T \sum_{n=0}^{N_w} \frac{\rho^{n+1} x_w^n}{n!} \left(\frac{\partial b_{1n}}{\partial \lambda_2} \right)_0 \frac{x_s}{Z_w} - \frac{k_B T x_s^2}{2 Z_w} \sum_{n=0}^{N_w} \frac{\rho^{n+2} x_w^n}{n!} \left(\frac{\partial b_{2n}}{\partial \lambda_2} \right)_0 + \frac{k_B T x_s^2}{Z_w^2} \left[\sum_{n=0}^{N_w} \frac{\rho^{n+1} x_w^n}{n!} \left(\frac{\partial b_{1n}}{\partial \lambda_2} \right)_0 \right] \left[\sum_{n=0}^{N_w} \frac{\rho^{n+1} x_w^n (b_{1n} \lambda)}{n!} \right] \quad (18)$$

(18)式中

$$\left(\frac{\partial b_{2n}}{\partial \lambda_2} \right)_0 = \lim_{\lambda_1 \rightarrow 1} \lim_{\lambda_2 \rightarrow 1} \lim_{\lambda_3 \rightarrow 1} \left(\frac{\partial b_{2n}}{\partial \lambda_2} \right) \quad (18a)$$

$$\left(\frac{\partial b_{1n}}{\partial \lambda_2} \right)_0 = \lim_{\lambda_1 \rightarrow 1} \lim_{\lambda_2 \rightarrow 1} \lim_{\lambda_3 \rightarrow 1} \left(\frac{\partial b_{1n}}{\partial \lambda_2} \right) \quad (18b)$$

$$(b_{1n} \lambda) = \lim_{\lambda_1 \rightarrow 1} \lim_{\lambda_2 \rightarrow 1} \lim_{\lambda_3 \rightarrow 1} b_{1n} \quad (18c)$$

把(18)式代入(14)式右端第二项,得稀溶液情形偏摩尔内能的溶质-溶剂项:

$$\left(\frac{\partial E_{sw}^{ex}}{\partial N_s} \right)_{T,V} = -\frac{k_B T}{N} \sum_{n=0}^{N_w} \frac{\rho^{n+1} x_w^n}{n!} \left(\frac{\partial b_{1n}}{\partial \lambda_2} \right)_0 \frac{1}{Z_w} - \frac{k_B T x_s}{Z_w N} \sum_{n=0}^{N_w} \frac{\rho^{n+2} x_w^n}{n!} \left(\frac{\partial b_{2n}}{\partial \lambda_2} \right)_0 + \frac{2 k_B T x_s}{Z_w^2 N} \left[\sum_{n=0}^{N_w} \frac{\rho^{n+1} x_w^n}{n!} \left(\frac{\partial b_{1n}}{\partial \lambda_2} \right)_0 \right] \left[\sum_{n=0}^{N_w} \frac{\rho^{n+1} x_w^n (b_{1n} \lambda)}{n!} \right] \quad (19)$$

式右端第一项及第三项代表插入一个溶质粒子时所引起的溶质-溶剂相互作用能的增加,第二项代表插入两个存在相互作用的溶质粒子时所引起的溶质-溶剂相互作用能的增加。

(14)式右端第三项为过剩偏摩尔内能的溶剂-溶剂项,在无限稀溶液极限条件下该项也称重组织能,把(5)式代入(7c)式再对溶质的摩尔分数 x_s 作泰勒展开得:

$$E_{ww}^{ex} = -k_B T \left[\sum_{n=0}^{N_w} \frac{\rho^{n+1} x_w^n}{n!} \left(\frac{\partial b_{1n}}{\partial \lambda_3} \right)_0 \right] \frac{x_s}{Z_w} - \frac{k_B T x_s^2}{2 Z_w} \left[\sum_{n=0}^{N_w} \frac{\rho^{n+2} x_w^n}{n!} \left(\frac{\partial b_{2n}}{\partial \lambda_3} \right)_0 \right] + \frac{k_B T x_s^2}{Z_w^2} \left[\sum_{n=0}^{N_w} \frac{\rho^{n+1} x_w^n}{n!} \left(\frac{\partial b_{1n}}{\partial \lambda_3} \right)_0 \right] \left[\sum_{n=0}^{N_w} \frac{\rho^{n+1} x_w^n b_{1n}}{n!} \right] - \frac{k_B T x_s^2}{2 Z_w^3} \left[\sum_{n=0}^{N_w} \frac{\rho^n x_w^n}{n!} \left(\frac{\partial b_{0n}}{\partial \lambda_3} \right)_0 \right] \left\{ 2 \left[\sum_{n=0}^{N_w} \frac{\rho^{n+1} x_w^n (b_{1n} \lambda)}{n!} \right]^2 - \sum_{n=0}^{N_w} \frac{\rho^{n+2} x_w^n (b_{2n} \lambda)}{n!} \right\} - \frac{k_B T}{Z_w} \left[\sum_{n=0}^{N_w} \frac{\rho^n x_w^n}{n!} \left(\frac{\partial b_{0n}}{\partial \lambda_3} \right)_0 \right] \quad (20)$$

式中

$$\left(\frac{\partial b_{0n}}{\partial \lambda_3} \right)_0 = \lim_{\lambda_1 \rightarrow 1} \lim_{\lambda_2 \rightarrow 1} \lim_{\lambda_3 \rightarrow 1} \left(\frac{\partial b_{0n}}{\partial \lambda_3} \right) \quad (20a)$$

$$\left(\frac{\partial b_{1n}}{\partial \lambda_3} \right)_0 = \lim_{\lambda_1 \rightarrow 1} \lim_{\lambda_2 \rightarrow 1} \lim_{\lambda_3 \rightarrow 1} \left(\frac{\partial b_{1n}}{\partial \lambda_3} \right) \quad (20b)$$

$$\left(\frac{\partial b_{2n}}{\partial \lambda_3} \right)_0 = \lim_{\lambda_1 \rightarrow 1} \lim_{\lambda_2 \rightarrow 1} \lim_{\lambda_3 \rightarrow 1} \left(\frac{\partial b_{2n}}{\partial \lambda_3} \right) \quad (20c)$$

$$(b_{2n}) = \lim_{\lambda_1 \rightarrow 1} \lim_{\lambda_2 \rightarrow 1} \lim_{\lambda_3 \rightarrow 1} b_{2n} \quad (20d)$$

把(20)式代入(14)式右端第三项,得稀溶液情形偏摩尔内能的溶剂-溶剂项:

$$\begin{aligned} \left(\frac{\partial E_{ww}^{ex}}{\partial N_s} \right)_{T,V} = & -\frac{k_B T}{N} \left[\sum_{n=0}^{N_w} \frac{\rho^{n+1} x_w^n}{n!} \left(\frac{\partial b_{1n}}{\partial \lambda_3} \right)_0 \right] \frac{1}{Z_w} - \frac{k_B T x_s}{2 Z_w N} \left[\sum_{n=0}^{N_w} \frac{\rho^{n+2} x_w^n}{n!} \left(\frac{\partial b_{2n}}{\partial \lambda_3} \right)_0 \right] \\ & + \frac{k_B T x_s}{Z_w^2 N} \left[\sum_{n=0}^{N_w} \frac{\rho^{n+1} x_w^n}{n!} \left(\frac{\partial b_{1n}}{\partial \lambda_3} \right)_0 \right] \left[\sum_{n=0}^{N_w} \frac{\rho^{n+1} x_w^n (b_{1n})}{n!} \lambda \right] - \frac{k_B T x_s}{2 N Z_w^3} \left[\sum_{n=0}^{N_w} \frac{\rho^n x_w^n}{n!} \left(\frac{\partial b_{0n}}{\partial \lambda_3} \right)_0 \right] \\ & \times \left\{ 2 \left[\sum_{n=0}^{N_w} \frac{\rho^{n+1} x_w^n (b_{1n})}{n!} \lambda \right]^2 - \sum_{n=0}^{N_w} \frac{\rho^{n+2} x_w^n (b_{2n})}{n!} \lambda \right\} \end{aligned} \quad (21)$$

(21)式右端第一项代表插入一个溶质粒子时所引起的溶剂-溶剂相互作用能的增加,即重组内能。(21)式右端第二项代表插入两个存在相互作用的溶质粒子时所引起的溶剂-溶剂相互作用能的增加,由于溶质粒子影响其周围的溶剂粒子的空间分布,导致某一溶质粒子附近的溶剂粒子与另一溶质粒子周围的溶剂粒子的相互作用能量发生改变(21)式右端第三项及第四项代表了这种相互能量发生改变对过剩偏摩尔内能的溶剂-溶剂项的贡献。

类似地,把(5)式代入(8)式再对 x_s 作泰勒展开得到过剩熵的表达式:

$$\begin{aligned} S^{ex} = & k_B \ln Z_w + \frac{k_B x_s}{Z_w} \sum_{n=0}^{N_w} \frac{\rho^{n+1} x_w^n (b_{1n})}{n!} \lambda + \frac{k_B x_s^2}{2 Z_w^2} \left\{ \sum_{n=0}^{N_w} \frac{\rho^{n+2} x_w^n (b_{2n})}{n!} \lambda \right. \\ & \left. - \left[\sum_{n=0}^{N_w} \frac{\rho^{n+1} x_w^n (b_{1n})}{n!} \lambda \right]^2 \right\} + \frac{1}{T} (E_{ss}^{ex} + E_{sw}^{ex} + E_{ww}^{ex}) \end{aligned} \quad (22)$$

把(21)式代入(13)式得,溶质的过剩偏摩尔熵的表达式为:

$$\begin{aligned} \left(\frac{\partial S^{ex}}{\partial N_s} \right)_{T,V} = & \frac{k_B}{N Z_w} \sum_{n=0}^{N_w} \frac{\rho^{n+1} x_w^n (b_{1n})}{n!} \lambda + \frac{k_B x_s}{N Z_w^2} \left\{ \sum_{n=0}^{N_w} \frac{\rho^{n+2} x_w^n (b_{2n})}{n!} \lambda \right. \\ & \left. - \left[\sum_{n=0}^{N_w} \frac{\rho^{n+1} x_w^n (b_{1n})}{n!} \lambda \right]^2 \right\} + \frac{1}{T} \left[\left(\frac{\partial E_{ss}^{ex}}{\partial N_s} \right)_{T,V} + \left(\frac{\partial E_{sw}^{ex}}{\partial N_s} \right)_{T,V} + \left(\frac{\partial E_{ww}^{ex}}{\partial N_s} \right)_{T,V} \right] \end{aligned} \quad (23)$$

4 结 论

1. 集团展开方法是研究低密度二元稀溶液的溶解热力学的较好方法,溶液的过剩内能、过剩熵及溶质的过剩偏摩尔内能、过剩偏摩尔熵等物理量可以展开成溶质的摩尔分数的幂级数。在溶质的摩尔分数较小的情况下,溶质的过剩偏摩尔内能及过剩偏摩尔熵与溶质的摩尔分数成线性关系。

2. 无限稀溶液条件下,溶剂的重组能量与溶质的粒子数密度无关,它反映了一个溶质粒子对其周围溶剂粒子之间相互作用能的影响,在稀溶液情形,过剩偏摩尔内能的溶剂-溶剂部分不仅与溶质周围的溶剂粒子之间的相互作用能的改变有关,而且与某一溶质粒子附近的溶剂粒子与另一溶质粒子附近的溶剂粒子的相互作用能量的改变有关,前者为溶剂的重组能量,后者在稀溶液情形与溶质的摩尔分数成正比。

参 考 文 献

- [2] Laird B B , Haymet A D J. *J. Chem. Phys.* , 1992 , **97** : 2153
- [3] Matubayasi N , Reed L H , Levy R M. *J. Phys. Chem.* , 1994 , **98** : 10640
- [4] Lazaidis T J , Panlalis M E. *J. Phys. Chem.* , 1994 , **98** : 635
- [5] Wallace D C. *Phys. Rev. A* , 1989 , **39** : 4838
- [6] Alder B. *J. Phys. Rev. Lett.* , 1964 , **12** : 317
- [7] Lazaidis T. *J. Phys. Chem. B* , 1998 , **102** : 3531
- [8] Lazaidis T. *J. Phys. Chem. B* , 1998 , **102** : 3542
- [9] Guiwu Lu(卢贵武) Jun Chu(储 浚). *Journal of the University of Petroleum , China(石油大学学报)* , 1998 , **22** : 86
- [10] Guiwu Lu(卢贵武) , Kaixue Zhou(周开学). *Chin. J. Comput. Phys.(计算物理学报)* , 1999 , **16** : 351

Virial Expansion Theory for Thermodynamics for Solvation

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Abstract A theory for solvation thermodynamics of binary solution is developed by Virial expansion method. The excess energy of binary solution is divided into three interactive terms of solvent – solvent solvent – solute and solute – solute. Using the approach of Virial expansion the partial function of canonical ensemble for a binary solution is expressed. The expression of partial molar energy and entropy of solute are obtained by this expression. Under the condition of infinite dilution , the solvent – solvent term of the excess partial molar energy can also be called as reorganization energy. It shows that the presentation of solute affects interactive energy of solvent molecules around solute molecules. The study in this paper shows that when the molar fraction of solute particles is relatively higher , the interaction among solute molecules would affect the solvent – solvent term of excess partial molar energy. For diluted solution , the solvent – solvent term of excess partial molar energy is linear to the molar fraction of solute. For binary solution with low density , the excess partial molar energy and excess partial molar entropy of solute is also linear to the density of particles.

Key words Virial expansion , Excess partial molar energy , Excess partial molar entropy , Reorganization energy