溶液热力学1：化学势的引入

2022年3月21日　　16:28

I. 化学势的引入

△ 多组份体系的内能，在孤立时，是 $(S,V,\{n_i\})$ 的函数 $U=U(S,V,\{n_i\})$

$$dU=\left.\frac{\partial U}{\partial S}\right|_{V,\{n_i\}}dS+\left.\frac{\partial U}{\partial V}\right|_{S,\{n_i\}}dV+\sum_i\left.\frac{\partial U}{\partial n_i}\right|_{S,V,\{n_{j\neq i}\}}dn_i$$

与第一、二定律比较得（准静态过程）　$dU=TdS-pdV+\mu_i dn_i$

$$T=\left.\frac{\partial U}{\partial S}\right|_{V,\{n_i\}},\quad -p=\left.\frac{\partial U}{\partial V}\right|_{S,\{n_i\}},\quad \mu_i\equiv\left.\frac{\partial U}{\partial n_i}\right|_{S,V,\{n_{j\neq i}\}}$$

μ_i 是由于组份 i 分子数变化 dn_i 造成内能的变化，引入为化学势。

△ 常见体系平衡态由 $(T,p,\{n_i\})$ 决定的情况，此时热力学势是吉布斯自由能。

$(T,p,\{n_i\})$ 约束体系（开放）

$$G\overset{\text{def}}{=}U-TS+pV,\quad dG=dU-TdS-SdT+pdV+Vdp$$

$$=TdS-pdV+\mu_i dn_i-TdS-SdT+pdV+Vdp$$

$$=-SdT+Vdp+\mu_i dn_i$$

$$=\left.\frac{\partial G}{\partial T}\right|_{p,\{n_i\}}dT+\left.\frac{\partial G}{\partial p}\right|_{T,\{n_i\}}dp+\left.\frac{\partial G}{\partial n_i}\right|_{T,p,\{n_{j\neq i}\}}dn_i$$

$$\Rightarrow\quad -S=\left.\frac{\partial G}{\partial T}\right|_{p,\{n_i\}},\quad V=\left.\frac{\partial G}{\partial p}\right|_{T,\{n_i\}},\quad \mu_i=\left.\frac{\partial G}{\partial n_i}\right|_{T,p,\{n_{j\neq i}\}}$$

Maxwell 关系：

$$\left.\frac{\partial S}{\partial p}\right|_{T,\{n_i\}}=-\frac{\partial}{\partial p}\left(\left.\frac{\partial G}{\partial T}\right|_{p,\{n_i\}}\right)\Bigg|_{T,\{n_i\}}=-\frac{\partial}{\partial T}\left(\left.\frac{\partial G}{\partial p}\right|_{T,\{n_i\}}\right)\Bigg|_{p,\{n_i\}}=-\left.\frac{\partial V}{\partial T}\right|_{p,\{n_i\}}$$

$$\left.\frac{\partial S}{\partial n_i}\right|_{T,p,\{n_{j\neq i}\}}=-\frac{\partial}{\partial n_i}\left(\left.\frac{\partial G}{\partial T}\right|_{p,\{n_i\}}\right)\Bigg|_{T,p,\{n_{j\neq i}\}}=-\frac{\partial}{\partial T}\left(\left.\frac{\partial G}{\partial n_i}\right|_{T,p,\{n_{j\neq i}\}}\right)\Bigg|_{p,\{n_i\}}=-\left.\frac{\partial \mu_i}{\partial T}\right|_{p,\{n_i\}}$$

$$\left.\frac{\partial V}{\partial n_i}\right|_{T,p,\{n_{j\neq i}\}}=\frac{\partial}{\partial n_i}\left(\left.\frac{\partial G}{\partial p}\right|_{T,\{n_i\}}\right)\Bigg|_{T,p,\{n_{j\neq i}\}}=\frac{\partial}{\partial p}\left(\left.\frac{\partial G}{\partial n_i}\right|_{T,p,\{n_{j\neq i}\}}\right)\Bigg|_{T,\{n_i\}}=\left.\frac{\partial \mu_i}{\partial p}\right|_{T,\{n_i\}}$$

$$\left.\frac{\partial \mu_i}{\partial n_j}\right|_{T,p,\{n_{k\neq j}\}}=\frac{\partial}{\partial n_j}\left(\left.\frac{\partial G}{\partial n_i}\right|_{T,p,\{n_{l\neq i}\}}\right)\Bigg|_{T,p,\{n_{k\neq j}\}}=\frac{\partial}{\partial n_i}\left(\left.\frac{\partial G}{\partial n_j}\right|_{T,p,\{n_{k\neq j}\}}\right)\Bigg|_{T,p,\{n_{l\neq i}\}}=\left.\frac{\partial \mu_j}{\partial n_i}\right|_{T,p,\{n_{k\neq i}\}}$$

II. 偏摩尔量

上述 Maxwell 关系中的

$$\left.\frac{\partial V}{\partial n_i}\right|_{T,p,\{n_{j\neq i}\}}\overset{\text{def}}{=}v_i\quad\text{偏摩尔体积}$$

$$\left.\frac{\partial S}{\partial n_i}\right|_{T,p,\{n_{j\neq i}\}}\overset{\text{def}}{=}s_i\quad\text{偏摩尔熵}$$

△ 更多偏摩尔量可被类似地定义，例如

$$g_i\overset{\text{def}}{=}\left.\frac{\partial G}{\partial n_i}\right|_{p,T,n_{j\neq i}},\quad\text{偏摩尔 Gibbs 自由能}$$

一般地，某广延状态量 $Y=Y(T,p,\{n_i\})$ 的全微分是

$$dY=\left.\frac{\partial Y}{\partial T}\right|_{p,\{n_i\}}dT+\left.\frac{\partial Y}{\partial p}\right|_{T,\{n_i\}}dp+\sum_i\underline{\left.\frac{\partial Y}{\partial n_i}\right|_{T,p,\{n_{j\neq i}\}}}dn_i$$

$$= \frac{\partial Y}{\partial T}\Big|_{p,\{n_i\}} dT + \frac{\partial Y}{\partial p}\Big|_{T,\{n_i\}} dp + \sum_i y_i dn_i$$

其中 Y 的偏摩尔量 $y_i \overset{def}{=} \frac{\partial Y}{\partial n_i}\Big|_{T,p,\{n_{j\neq i}\}}$.

注意到偏摩尔量 y_i 是强度量. 在恒定 (T,p) 下, y_i 是组份 $\{n_i\}$ 的函数 $y_i = y_i(\{n_i\})$

△ 下面进一步推导: "$Y = \sum_i y_i n_i$" 记 $x_i \equiv n_i / \sum_i n_i$ 为组份 i 的摩尔份数. $n \equiv \sum_i n_i$ 为总摩尔数. 则

在恒定 (T,p) 下 $(dT = dp = 0)$

$$dY = \left(\sum_i y_i x_i\right) dn$$ ，用到了 $dn_i = x_i dn$

积分 ⇒ $Y = \left(\sum_i y_i x_i\right) n + C$, C 是积分常数 , 再由当 $n=0$ 时 $Y=0$ 的规定, 得 $C=0$. 因此有

$$Y = \sum_i n_i y_i \quad (\text{恒定 } T, p)$$

即当已知 $\{n_i\}$ 时, $y_i = y_i(\{n_i\})$ 也都已知, Y 与 y_i 满足上式. 特别地, 恒定 (T,p) 下,

$$G = \sum_i n_i g_i = \sum_i n_i \mu_i \quad (\text{因此条件下恰有 } \mu_i = g_i)$$

由于对吉布斯自由能, 偏摩尔量在恒定 (T,p) 下恰好是化学势, 故进一步有

$$dG = \sum_i \mu_i dn_i \quad (\text{由 } G = G(T,p,\{n_i\}),\ dT = dp = 0)$$

$$= \sum_i n_i d\mu_i + \sum_i \mu_i dn_i \quad (\text{偏摩尔量})$$

$$\Rightarrow \sum_i n_i d\mu_i = 0 \underset{\text{同除}n}{\Rightarrow} \sum_i x_i d\mu_i = 0$$ 即吉布斯-杜亥姆方程的混合物版.

△ 实验上常只测得混合物体系的摩尔量随组份的变化, 如何由这个数据求得各组份的偏摩尔量?

摩尔量: 恒定 (T,p) 下, 体系的广度量 Y 的摩尔量 $Y_m \overset{def}{=} Y/n$, 其中 $n \equiv \sum_i n_i$

以双组份体系为例, 恒定 (T,p) 下 $(dT = dp = 0)$ $Y_m = Y_m(n_1, n_2)$

$$dY_m = dY/n = d(n_1 y_1 + n_2 y_2)/n = d(x_1 y_1 + x_2 y_2)$$

$$= \underbrace{x_1 dy_1 + x_2 dy_2}_{\equiv 0 \text{ 推广的 Gibbs-Duhem 方程}} + y_1 dx_1 + y_2 dx_2$$

$$\Leftrightarrow dY_m = y_1 dx_1 + y_2 dx_2, \quad \text{恒定}(p,T)$$

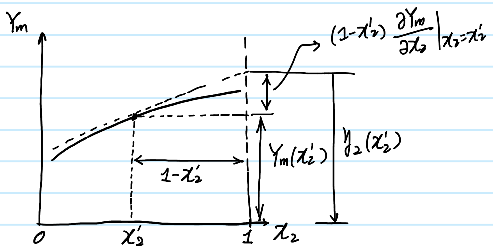
$$\Rightarrow \frac{\partial Y_m}{\partial x_2}\Big|_{T,p} = -y_1 + y_2 \quad (\text{用到了 } dx_1 \equiv -dx_2 \text{ , } \because x_1 + x_2 = 1)$$

$$\Rightarrow x_1 \frac{\partial Y_m}{\partial x_2}\Big|_{T,p} = -x_1 y_1 + x_1 y_2$$

又由 $Y = n_1 y_1 + n_2 y_2 \Rightarrow Y_m = x_1 y_1 + x_2 y_2$, 故上式 ⇔

$$x_1 \frac{\partial Y_m}{\partial x_2}\Big|_{T,p} = -Y_m + y_2 \quad \text{或} \quad y_2 = Y_m + x_1 \frac{\partial Y_m}{\partial x_2}\Big|_{p,T}$$

$$y_2 = Y_m + (1 - x_2) \frac{\partial Y_m}{\partial x_2}\Big|_{p,T}$$



多组份体系的推导, 见 Darken (1950) 和 Hilbert and co-workers (1998) 书 …

$$y_i = Y_m + (1 - x_i) \frac{\partial Y_m}{\partial x_i}\Big|_{T,p,\{x_j/x_k, \dots x_n/x_k\}} \quad (j \neq k \neq i,\ n \neq k \neq i)$$

$$y_i = Y_m + \frac{\partial Y_m}{\partial x_i}\Big|_{T,p,\{x_{j\neq i}\}} - \sum_{j=i}^{n} \frac{\partial Y_m}{\partial x_j}\Big|_{p,T,x_{j\neq i}}$$

JACS 72:2909 (1950).

Hillert (2008), Phase Equilibria, Phase Diagrams and Phase Transformations, 2nd ed., Cambridge University Press.