热力学统计物理第十三次作业

董建宇

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1

由归一化条件可知:

$$\sum_s \rho_s = 1.$$

则熵为:

$$S = k \ln \Omega = -k \sum_s \rho_s \ln \frac{1}{\Omega} = -k \sum_s \rho_s \ln \rho_s.$$

2

对于组元 A，配分函数为:

$$\begin{aligned}
Z_1 =& \frac{1}{N_1! h^{3N_1}} \int e^{-\beta E} \, d\Omega \\
=& \frac{1}{N_1! h^{3N_1}} \int e^{-\beta \sum_{i=1}^{3N} \frac{p_i^2}{2m_A}} \, dx_1 \cdots dx_{3N} dp_1 \cdots dp_{3N} \\
=& \frac{V^{N_1}}{N_1! h^{3N_1}} \left(\frac{2\pi m_A}{\beta} \right)^{\frac{3N_1}{2}}
\end{aligned}$$

同理可知，组元 B 对应的配分函数为:

$$Z_2 = \frac{1}{N_2! h^{3N_2}} \int e^{-\beta E} \, d\Omega = \frac{V^{N_2}}{N_2! h^{3N_2}} \left(\frac{2\pi m_B}{\beta} \right)^{\frac{3N_2}{2}}.$$

则系统的配分函数为:

$$Z = Z_1 \times Z_2 = \frac{V^{N_1+N_2}}{N_1! N_2! h^{3N_1+3N_2}} \left(\frac{2\pi}{\beta} \right)^{\frac{3}{2}(N_1+N_2)} m_A^{\frac{3N_1}{2}} m_B^{\frac{3N_2}{2}}.$$

压强 p 为:

$$p = \frac{1}{\beta}\frac{\partial}{\partial V}\ln Z = kT\frac{N_1+N_2}{V} = \frac{(n_A+n_B)RT}{V}.$$

则混合理想气体物态方程为:

$$pV = (n_A+n_B)RT.$$

混合理想气体的内能为:

$$U = -\frac{\partial}{\partial\beta}\ln Z = \frac{3(N_1+N_2)}{2}\frac{1}{\beta} = \frac{3(N_1+N_2)kT}{2}.$$

混合理想气体的熵为:

$$\begin{aligned}S =& k\left(\ln Z - \beta\frac{\partial}{\partial\beta}\ln Z\right)\\ =& k\left(N_1\ln\frac{V}{N_1} + N_2\ln\frac{V}{N_2} + (N_1+N_2)\left(\frac{5}{2}+\frac{3}{2}\ln\frac{2\pi kT}{h^2} + \frac{3N_1}{2}\ln m_A + \frac{3N_2}{2}\ln m_B\right)\right).\end{aligned}$$

其中 $N_1 = n_A N_A$，$N_2 = n_B N_A$。N_A 为阿伏伽德罗常数。

3

等压摩尔热熔为:

$$C_V = \left(\frac{dU}{dT}\right)_V = \frac{f}{2}R.$$

等压摩尔热熔为:

$$\begin{aligned}C_p =& \left(\frac{dU+pdV}{dT}\right)_p\\ =& \frac{f}{2}R + \frac{a}{V^2}\left(\frac{\partial V}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p\\ =& C_V + \left(p+\frac{a}{V^2}\right)\left(\frac{\partial V}{\partial T}\right)_p\end{aligned}$$

一摩尔范德瓦尔斯气体状态方程为:

$$\left(p+\frac{a}{V^2}\right)(V-b) = RT.$$

两侧在等压条件下对温度 T 微分:

$$\left(\frac{RTV^3-2aV^2+4abV-2ab^2}{V^3(V-b)}\right)\left(\frac{\partial V}{\partial T}\right)_p=R.$$

则有:

$$C_p-C_V=\frac{RT}{V-b}\left(\frac{\partial V}{\partial T}\right)_p=\frac{R}{1-\frac{2a}{RTV}+\frac{4ab}{RTV^2}-\frac{2ab^2}{RTV^3}}\approx R\left(1+\frac{2a}{RTV}\right)=R+\frac{2a}{TV}.$$

即:

$$C_V=\frac{f}{2}R,\ \ C_p-C_V\approx R+\frac{2a}{TV}.$$

4

希望 b 数量级约为 $10^{-5}m^3/mol$ 数量级, b 为考虑分子大小带来的影响。约等于 1mol 气体分子体积总和的 4 被, 即有:

$$b=4N_A\times\frac{4\pi}{3}\left(\frac{d}{2}\right)^3\approx 10^{-5}m^3/mol.$$

假设该气体内能为: $U=U(T,V)$, 要证明内能只依赖温度, 只需证明 $\left(\frac{\partial U}{\partial V}\right)_T=0$。由 $dU=T\,dS-p\,dV$ 可知:

$$\left(\frac{\partial U}{\partial V}\right)_T=-p+T\left(\frac{\partial S}{\partial V}\right)_T=-p+T\left(\frac{\partial p}{\partial T}\right)_V=-p+\frac{TR}{V-b}=0.$$

即内能只是温度的函数。