

Thermodynamics of materials

16. Chemical potential of ideal gas

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October 3, 2024

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 - Standard State, Activity



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- In quantum world, the governing equation is Schrödinger equation. The time-independent Schrödinger equation with a particle of mass m and energy E is

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x)$$

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Particle in a box

- When the potential is given by

$$V(x) = \begin{cases} 0 & 0 < x < L \\ \infty & \text{otherwise} \end{cases}$$

- At $0 < x < L$,

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} = E\psi(x)$$

the general solution is

$$\psi(x) = A \sin(kx) + B \cos(kx) \quad k = \sqrt{\frac{2mE}{\hbar^2}}$$

With a boundary condition $\psi(0) = 0$, $B = 0$.

- From another boundary condition $\psi(L) = 0$,

$$\sqrt{\frac{2mE}{\hbar^2}}L = n\pi \quad (n = 0, 1, 2, \dots)$$

Then the energy of the system is

$$E = \frac{n^2\pi^2\hbar^2}{2mL^2} = \frac{n^2h^2}{8mL^2} \quad (n = 0, 1, 2, \dots)$$

The energy of the bounded state is usually assumed by the particle-in-a-box system.

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Gaussian Integral

- To evaluate $I(\alpha)$,

$$I(\alpha) = \int_{-\infty}^{\infty} e^{-\alpha x^2} dx \quad (1)$$

Since there is no problem in replacing x with y in Eq. 1,

$$\begin{aligned} [I(\alpha)]^2 &= \int_{-\infty}^{\infty} e^{-\alpha x^2} dx \int_{-\infty}^{\infty} e^{-\alpha y^2} dy = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\alpha(x^2+y^2)} dx dy \\ &= \int_0^{\infty} \int_0^{2\pi} r e^{-\alpha r^2} dr d\phi = 2\pi \times \frac{1}{2\alpha} = \frac{\pi}{\alpha} \end{aligned}$$

- Then we can estimate the Gaussian integration.

$$I(\alpha) = \int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}} \quad (2)$$

and

$$\int_0^{\infty} e^{-\alpha x^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{\alpha}}$$



Translation energy of a molecule

- Assume only one-dimensional translation, the partition function for the translation mode is

$$\begin{aligned} Z_{\text{tr}} &= \sum_{s=1}^{\infty} \exp\left(-\frac{E_s}{k_{\text{B}}T}\right) = \sum_{n=1}^{\infty} \exp\left(-\frac{h^2 n^2}{8mL^2 k_{\text{B}}T}\right) \\ &= \int_0^{\infty} \exp\left(-\frac{h^2 n^2}{8mL^2 k_{\text{B}}T}\right) dn \end{aligned}$$

- Let

$$x^2 = \frac{h^2 n^2}{8mL^2 k_{\text{B}}T} \rightarrow dx = \sqrt{\frac{h^2 n^2}{8mL^2 k_{\text{B}}T}} dn$$

then

$$Z_{\text{tr}} = \sqrt{\frac{8mL^2 k_{\text{B}}T}{h^2}} \int_0^{\infty} \exp(-x^2) dx = \frac{1}{2} \sqrt{\frac{8\pi m L^2 k_{\text{B}}T}{h^2}} = \frac{L}{l_q}$$



Translation energy of a molecule

- The quantum length is given by

$$l_q = \frac{h}{\sqrt{2\pi m k_B T}}$$

- In a three-dimensional system,

$$Z_{\text{tr}} = \frac{L_x}{l_q} \frac{L_y}{l_q} \frac{L_z}{l_q} = \frac{V}{v^g}$$

where

$$v^g = \left(\frac{h^2}{2\pi m k_B T} \right)^{3/2} = \frac{1}{N^g}$$

which means the volume per atom for the gas and N^g , density of states for an ideal gas, and its inverse as the volume for each state.



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Chemical Potential of Ideal Gas

- The chemical potential μ [J per atom] for a single component ideal gas is given by

$$\mu(T, p) = -k_{\text{B}}T \left\{ \ln \left[\frac{v}{v^g} \right] \right\} = -k_{\text{B}}T \left\{ \ln \left[\frac{k_{\text{B}}T}{p} \left(\frac{2\pi m k_{\text{B}}T}{h^2} \right)^{3/2} \right] \right\}$$

In the unit of [J mol⁻¹],

$$\mu(T, p) = -RT \left\{ \ln \left[\frac{k_{\text{B}}T}{p} \left(\frac{2\pi m k_{\text{B}}T}{h^2} \right)^{3/2} \right] \right\}$$

Standard State, Activity

- at $p = p^\circ = 1 \text{ atm}$, the chemical potential is

$$\mu^\circ(T, p^\circ) = -RT \left\{ \ln \left[\frac{k_B T}{p^\circ} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right] \right\}$$

Then, we have

$$\mu(T, p) = \mu^\circ(T, p^\circ) + RT \ln \left(\frac{p}{p^\circ} \right)$$

and we introduce the unit-less quantity, activity as

$$a = \frac{p}{p^\circ}$$

therefore, we have

$$\mu(T, p) = \mu^\circ(T, p^\circ) + RT \ln a$$

