Solutions to Pathria's Statistical Mechanics
Chapter 4

SM-at-THU

March 25, 2016

Problem 4.1

Problem 4.4

The probability of a state with energy E_r and particle number N is

$$p_{r,N} = \frac{e^{-\beta E_{r,N}+\beta\mu N}}{\mathcal{Q}(\mu,V,\beta)} \tag{1}$$

in which $\mathcal{Q} = \sum_{r,N} e^{-\beta E_{r,N}+\beta\mu N}$ is the grand canonical partition function. Since we have define that $z = e^{\beta\mu}$, the probability can be written as:

$$p_{r,N} = \frac{z^N e^{-\beta E_{r,N}}}{\mathcal{Q}(z,V,\beta)} \tag{2}$$

So the probability that has exactly N particles will be:

$$p_N = \sum_r p_{r,N} = \frac{z^N \sum_r e^{-\beta E_{r,N}}}{\mathcal{Q}(z,V,\beta)} \tag{3}$$

easily we can find the summation in the numerator is the canonical partition function of system with V, N and β:

$$Q_N(V,\beta) = \sum_r e^{-\beta E_{r,N}} \tag{4}$$

Thus Eq.(**??**) will become:

$$p_N = \frac{z^N Q_N(V,\beta)}{\mathcal{Q}(z,V,\beta)} \tag{5}$$

For ideal classical gas, the canonical partition function is:

$$Q_N(V,T) = \frac{V^N}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{3N/2} \tag{6}$$

and the grand partition function is

$$\mathcal{Q}(z,V,\beta) = \sum_{N=0}^{\infty} z^N Q_N(V,T) = \exp\left[zV\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right] \tag{7}$$

Clearly the probability distribution of particle number is

$$p_N = \frac{1}{N!}\frac{(zV\lambda_T^{-3})^N}{e^{zV\lambda_T^{-3}}} \tag{8}$$

It is obvious that this distribution is a Poison distribution. From the knowledge of Poison distribution, we know the root-mean-square value of (ΔN) is

$$\Delta N = \sqrt{zV\lambda_T^{-3}} = \sqrt{e^{\beta\mu}V\left(\frac{2\pi mkT}{h^2}\right)^{3/2}} \tag{9}$$

We can also get this result from the formula of grand canonical ensemble:

$$\begin{aligned}\Delta N &= kT\sqrt{\left(\frac{\partial^2 \ln \mathcal{Q}}{\partial\mu^2}\right)_{T,V}} \\ &= \sqrt{e^{\beta\mu}V\left(\frac{2\pi mkT}{h^2}\right)^{3/2}} \end{aligned} \tag{10}$$

And this result is consistent with the one we get by Poison distribution.

Problem 4.5

We could know from 4.3.20:

$$S = kT(\frac{\partial q}{\partial T})_{z,V} - Nkln(z) + kq$$

We can know partial differential:

$$(\frac{\partial q}{\partial T})_{z,V} - (\frac{\partial q}{\partial T})_{\mu,V} = (\frac{\partial q}{\partial z})_{T,V}(\frac{\partial z}{\partial T})_{\mu,V}$$

$$(\frac{\partial q}{\partial z})_{T,V} = \frac{N}{z}$$

So we can infer that:

$$S = k[\frac{\partial(Tq)}{\partial T}]_{V,\mu}$$

Problem 4.14

The ClausiusClapeyron equation is

$$\frac{dP_\sigma}{dT} = \frac{L}{T\Delta v}$$

Since the volume of liquid is negligible compared to that of gas, we can alternate Δv by $v_g = kT/P_\sigma$. Put all of these into the ClausiusClapeyron equation, we can get a differential equation:

$$\frac{dP_\sigma}{P_\sigma} = \frac{L}{R}\frac{dT}{T^2} \tag{11}$$

so the solution to the differential equation will be:

$$P_\sigma(T) = P_0 \exp\left[\frac{L}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right] \tag{12}$$

From the problem we know that $L = 2260\text{kJ/kg} = 40680\text{J/mol}$, $T_0 = 373\text{K}$ and $P_0 = 101\text{kPa}$. Then we put all these numbers into Eq.(**??**) and we get the equilibrium vapor pressure is

$$P_\sigma(473\text{K}) = 1619\text{kPa}$$

Experiment result is $P_\sigma \sim 1500\text{kPa}$, and our calculation is approximately correct.

Problem 4.15

According to Clausius-Clapeyron equation.And ignore the volume of solid phase.

$$\frac{dP_\sigma}{dT} = \frac{L}{TV}$$

Use the gas equation.

$$ln(p) = -\frac{L}{kT} + A$$

Use the triple point parameter.

$$ln(p) = -\frac{L}{kT} + 6.6 \times 10^{26}$$