

Solutions to Pathria's Statistical Mechanics

Chapter 4

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Problem 4.1

Problem 4.4

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

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

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:

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

So the probability that has exactly N particles will be:

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

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

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

Thus Eq.(??) will become:

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

For ideal classical gas, the canonical partition function is:

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

and the grand partition function is

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

Clearly the probability distribution of particle number is

$$p_N = \frac{1}{N!} \frac{(z V \lambda_T^{-3})^N}{e^{z V \lambda_T^{-3}}} \quad (8)$$

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

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

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

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

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

Problem 4.5

We could know from 4.3.20:

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

We can know partial differential:

$$\begin{aligned} \left(\frac{\partial q}{\partial T}\right)_{z,V} - \left(\frac{\partial q}{\partial T}\right)_{\mu,V} &= \left(\frac{\partial q}{\partial z}\right)_{T,V} \left(\frac{\partial z}{\partial T}\right)_{\mu,V} \\ \left(\frac{\partial q}{\partial z}\right)_{T,V} &= \frac{N}{z} \end{aligned}$$

So we can infer that:

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

Problem 4.12

$$\overline{NE} = \frac{\sum NE e^{-\alpha N - \beta E}}{\sum e^{-\alpha N - \beta E}} = \frac{\frac{\partial}{\partial \alpha} \left(\frac{\partial}{\partial \beta} \Xi\right)}{\Xi} = \frac{\frac{\partial}{\partial \alpha} \left(\Xi \frac{\partial}{\partial \beta} \ln \Xi\right)}{\Xi} = \frac{1}{\Xi} \frac{\partial \Xi}{\partial \alpha} \frac{\partial}{\partial \beta} \ln \Xi + \frac{\partial}{\partial \alpha} \left(\frac{\partial}{\partial \beta} \ln \Xi\right) \quad (11)$$

While the first part can be written as

$$\frac{1}{\Xi} \frac{\partial \Xi}{\partial \alpha} \frac{\partial}{\partial \beta} \ln \Xi = \frac{\partial \ln \Xi}{\partial \alpha} \frac{\partial}{\partial \beta} \ln \Xi = \overline{N} * \overline{E} \quad (12)$$

So the equation equals

$$\overline{NE} - \overline{N} * \overline{E} = \frac{\partial}{\partial \alpha} \left(\frac{\partial}{\partial \beta} \ln \Xi\right) = -\frac{\partial}{\partial \alpha} U = -\frac{\partial U}{\partial N} \frac{\partial N}{\partial \alpha} = \left(\frac{\partial U}{\partial N}\right)(\Delta N)^2 \quad (13)$$

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:

$$\frac{dP_\sigma}{P_\sigma} = \frac{L}{R} \frac{dT}{T^2} \quad (14)$$

so the solution to the differential equation will be:

$$P_{\sigma}(T) = P_0 \exp \left[\frac{L}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \right] \quad (15)$$

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.

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