Solutions to Pathria's Statistical Mechanics Chapter 1

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Problem 1.1

Problem 1.2

Utilizing the additive characteristic of $S = f(\Omega)$ and get

$$S = S_1 + S_2 = f(\Omega_1) + f(\Omega_2) \tag{1}$$

$$(\frac{dS}{d\Omega_1})_{\Omega_2} = f'(\Omega_1) \tag{2}$$

$$(\frac{dS}{d\Omega_2})_{\Omega_1} = f'(\Omega_2) \tag{3}$$

Inspect a small pertubation near the equilibrium state using the fact that $S = f(\Omega) = f(\Omega_1\Omega_2)$

$$(\frac{dS}{d\Omega_1})_{\Omega_2} = \lim_{\Delta\to 0} \frac{f((\Omega_1 + \Delta)\Omega_2) - f(\Omega_1\Omega_2)}{\Delta} \tag{4}$$

Assume that $\delta = \Delta\Omega_2$

$$(\frac{dS}{d\Omega_1})_{\Omega_2} = \lim_{\Delta\to 0} \Omega_2 \frac{f(\Omega_1\Omega_2 + \Delta\Omega_2) - f(\Omega_1\Omega_2)}{\Delta\Omega_2} = \lim_{\delta\to 0} \Omega_2 \frac{f(\Omega+\delta) - f(\Omega)}{\delta} = \Omega_2 f'(\Omega) \tag{5}$$

Apply to $(\frac{dS}{d\Omega_2})_{\Omega_1}$, we can get similar result.

$$(\frac{dS}{d\Omega_2})_{\Omega_1} = \Omega_1 f'(\Omega) \tag{6}$$

Finally,

$$f'(\Omega_1) = \Omega_2 f'(\Omega) = \frac{\Omega_2}{\Omega_1} f'(\Omega_2) \tag{7}$$

$$\Omega_1 f'(\Omega_1) = \Omega_2 f'(\Omega_2) \tag{8}$$

$$\tag{9}$$

It is obvious that this equation holds for all Ω. Set the value of the equation constant k.

$$\Omega \frac{df(\Omega)}{d\Omega} = k \tag{10}$$

$$f(\Omega) = kln\Omega + C \tag{11}$$

$$\tag{12}$$

Using a special value $\Omega = 1$

$$f(\Omega * 1) = f(\Omega) + f(1) \tag{13}$$
$$C = f(1) = 0 \tag{14}$$
$$\tag{15}$$

And get the result

$$S = f(\Omega) = kln\Omega \tag{16}$$

Problem 1.3

Problem 1.4

Suppose N is the number of particles, v_0 is the volume occupied by one particle and therefore the total number of microstates Ω is

$$\Omega = \frac{1}{N!}(\frac{V}{v_0})\dots(\frac{V}{v_0} - N + 1) \tag{17}$$

Following (1.4.2), we have

$$\frac{P}{T} = k\left(\frac{\partial \ln \Omega}{\partial V}\right)_{N,E} \tag{18}$$
$$= k\frac{\partial \Omega}{\Omega \partial V} \tag{19}$$
$$= k\frac{N}{V}\left(1 + \frac{(N-1)v_0}{2V} + \dots\right) \tag{20}$$

Considering only the first two terms, it corresponds to $P(V - b) = NkT$ with $b = Nv_0/2$.
Notes: I don't know why the problem says $b = 4Nv_0$ since this gas is hard sphere gas. Anyone has an idea?

Problem 1.5

Using equation $(A.11)$, and setting $K = \pi\sqrt{\varepsilon}/L$, it is straight forward to achieve

$$\Sigma_1(\varepsilon) = \frac{\pi}{6}\varepsilon^{3/2} \pm \frac{3\pi}{8}\varepsilon \tag{21}$$

where the first term is the volume term ($V = L^3$) and the next one is the surface correction ($S = 6L^2$).

Problem 1.6

Use the formula for ideal gas $PV = NkT$.

$$Nk \times 300 = 10^5 \times \frac{\pi}{10} \tag{22}$$

Thus $\Delta T = 10^4/Nk \sim 955K$.

Problem 1.10

Just use equation (1.4.21) and (1.4.23), we have:

$$S(N, V, E) = Nk \ln \left[V \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right] + \frac{3}{2} Nk \tag{23}$$

Since He and Ar have the same N,V. We can get the T that He and Ar have the same entropy:

$$T = 0K(?)$$

Problem 1.11

As N_2 and O_2 are mixed together at the same pressure and temperature, we can know that the volume of mixed gas is: $V = V_1 + V_2$. And we can get the entropy of mixing by utilizing equation (1.5.3):

$$\Delta S = k \left[N_1 \ln \frac{V}{V_1} + N_2 \ln \frac{V}{V_2} \right] \tag{24}$$

for per mole of the air formed:

$$\begin{aligned} \Delta S_n &= k \left[N_1 \ln \frac{V}{V_1} + N_2 \ln \frac{V}{V_2} \right] / (n_1 + n_2) \\ &= R \left[n_1 \ln \frac{V}{V_1} + n_2 \ln \frac{V}{V_2} \right] / (n_1 + n_2) \\ &= 4.16 \ J \cdot mol^{-1} \cdot K^{-1} \end{aligned} \tag{25}$$

Problem 1.12

Problem 1.16

Theorem:
If $f(x, y, z) = 0$,then we have

$$\left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial x} \right)_z = 1$$

$$\left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x \left(\frac{\partial z}{\partial z} \right)_y = -1$$

(a)

$$\frac{S}{N} = -\left(\frac{\partial \mu}{\partial T} \right)_P$$

$$\frac{V}{N} = \left(\frac{\partial \mu}{\partial P} \right)_T$$

$$\frac{S}{V} = -\frac{\left(\frac{\partial \mu}{\partial T} \right)_P}{\left(\frac{\partial \mu}{\partial P} \right)_T} = -\frac{1}{\left(\frac{\partial T}{\partial \mu} \right)_P \left(\frac{\partial \mu}{\partial P} \right)_T} = \left(\frac{\partial P}{\partial T} \right)_\mu$$

(b)

$$\frac{V}{N} = \left(\frac{\partial \mu}{\partial P}\right)_T$$

$$V\left(\frac{\partial P}{\partial \mu}\right)_T = N$$