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 $\Omega = 1$

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

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

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

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

(a) Equation (1.5.3a) can be written as:

$$\begin{aligned}(\Delta S)_{1\equiv 2} &= N_1\ln\frac{(V_1+V_2)N_1}{V_1(N_1+N_2)} + N_2\ln\frac{(V_1+V_2)N_2}{V_2(N_1+N_2)} \\ &= (N_1+N_2)\left[y\ln\frac{y}{x} + (1-y)\ln\frac{1-y}{1-x}\right]\end{aligned} \tag{26}$$

Here $x = V_1/(V_1+V_2), y = N_1/(N_1+N_2)$.

Consider the function $f(x,y) = y\ln\frac{y}{x}$, we can get the second derivatives:

$$D^2 f(x,y) = \begin{bmatrix} y/x^2 & -1/x \\ -1/x & 1/y \end{bmatrix} \tag{27}$$

Since $D^2 f(x,y)$ is a positive-semidefinite, $f(x,y)$ is a convex function. Then we can know that:

$$\frac{1}{2}f(x,y) + \frac{1}{2}f(1-x,1-y) \geq f(1/2,1/2) = 0 \tag{28}$$

This means $(\Delta S)_{1\equiv 2} \geq 0$ and the equality holding only when $N_1/V_1 = N_2/V_2$

(b) Suppose that $N = N_1 + N_2$. And we have $(\Delta S)^*$ by utilizing equation (1.5.4) :

$$\begin{aligned}(\Delta S)^* &= k\left[N_1 \ln \frac{N}{N_1} + N_2 \ln \frac{N}{N_2}\right] \\ &= k\left[N \ln N - N_1 \ln N_1 - N_2 \ln N_2\right]\end{aligned} \tag{29}$$

Then we have the derivative of $(\Delta S)^*$ with respect to N_1:

$$\begin{aligned}\frac{d(\Delta S)^*}{dN_1} &= -\ln N_1 - \frac{\partial N_2}{\partial N_1} \ln N_2 \\ &= -(\ln N_1 - \ln N_2)\end{aligned} \tag{30}$$

It shows that $\frac{d(\Delta S)^*}{dN_1}$ satisfies:

$$\frac{d(\Delta S)^*}{dN_1}\begin{cases} < 0 & N_1 > N_2 \\ = 0 & N_1 = N_2 \\ > 0 & N_1 < N_2 \end{cases} \tag{31}$$

So we can know that $(\Delta S)^*$ have the only maximum value at $N_1 = N_2$:

$$\max(\Delta S)^* = (N_1 + N_2 \ln 2) \tag{32}$$

Then we get:

$$\max(\Delta S)^* \leq (N_1 + N_2 \ln 2) \tag{33}$$

The equality holding when and only when $N_2 = N_2$

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)

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

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