

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

$$S = S_1 + S_2 = f(\Omega_1) + f(\Omega_2) \quad (1)$$

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

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

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

$$\left(\frac{dS}{d\Omega_1}\right)_{\Omega_2} = \lim_{\Delta \rightarrow 0} \frac{f((\Omega_1 + \Delta)\Omega_2) - f(\Omega_1\Omega_2)}{\Delta} \quad (4)$$

Assume that $\delta = \Delta\Omega_2$

$$\left(\frac{dS}{d\Omega_1}\right)_{\Omega_2} = \lim_{\Delta \rightarrow 0} \Omega_2 \frac{f(\Omega_1\Omega_2 + \Delta\Omega_2) - f(\Omega_1\Omega_2)}{\Delta\Omega_2} = \lim_{\delta \rightarrow 0} \Omega_2 \frac{f(\Omega + \delta) - f(\Omega)}{\delta} = \Omega_2 f'(\Omega) \quad (5)$$

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

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

Finally,

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

$$\Omega_1 f'(\Omega_1) = \Omega_2 f'(\Omega_2) \quad (8)$$

$$(9)$$

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

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

$$f(\Omega) = k \ln \Omega + C \quad (11)$$

$$(12)$$

Using a special value $\Omega = 1$

$$f(\Omega * 1) = f(\Omega) + f(1) \quad (13)$$

$$C = f(1) = 0 \quad (14)$$

$$(15)$$

And get the result

$$S = f(\Omega) = k \ln \Omega \quad (16)$$

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

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

Following (1.4.2), we have

$$\frac{P}{T} = k \left(\frac{\partial \ln \Omega}{\partial V} \right)_{N,E} \quad (18)$$

$$= k \frac{\partial \Omega}{\Omega \partial V} \quad (19)$$

$$= k \frac{N}{V} \left(1 + \frac{(N-1)v_0}{2V} + \dots \right) \quad (20)$$

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

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

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 $PV = NkT$.

$$Nk \times 300 = 10^5 \times \frac{\pi}{10} \quad (22)$$

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

Problem 1.10

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

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

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):

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

for per mole of the air formed:

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

Problem 1.12

(a) 1

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

$$\begin{aligned} (\Delta S)^* &= k \left[N_1 \ln \frac{N}{N_1} + N_2 \ln \frac{N}{N_2} \right] \\ &= k [N \ln N - N_1 \ln N_1 - N_2 \ln N_2] \end{aligned} \quad (26)$$

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

$$\begin{aligned} \frac{d(\Delta S)^*}{dN_1} &= -\ln N_1 - \frac{\partial N_2}{\partial N_1} \ln N_2 \\ &= -(\ln N_1 - \ln N_2) \end{aligned} \quad (27)$$

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

$$\frac{d(\Delta S)^*}{dN_1} \begin{cases} < 0 & N_1 > N_2 \\ = 0 & N_1 = N_2 \\ > 0 & N_1 < N_2 \end{cases} \quad (28)$$

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

$$\max (\Delta S)^* = (N_1 + N_2 \ln 2) \quad (29)$$

Then we get:

$$\max (\Delta S)^* \leq (N_1 + N_2 \ln 2) \quad (30)$$

The equality holding when and only when $N_1 = N_2$

Problem 1.16

Theorem:

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

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

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

(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)

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

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