HW #1 Solutions

#2 Pathria 1.2

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

$$\frac{dS}{d\Omega_1} = \Omega_2 f'(\Omega_1 \Omega_2) = f'(\Omega_1) + \cancelto{0}{\frac{df(\Omega_2)}{d\Omega_1}}$$

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

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

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

Left and right sides are functions of different variables. The only way this can be satisfied is if both sides are a constant.

$$\Omega_1 f'(\Omega_1) = k$$

$$f'(\Omega_1) = \frac{k}{\Omega_1}$$

$$f(\Omega_1) = k \ln \Omega_1$$

Pathria 1.11

Entropy of ideal gas

$$S = Nk \ln \frac{V}{N\lambda^3} + \frac{5}{2} Nk \qquad \lambda = \frac{h}{\sqrt{2\pi m k T}}$$

$$\frac{V}{N} = \frac{kT}{P}$$

initial entropy

$$S_i = N_N k \ln \frac{V_N}{N_N \lambda_N^3} + \frac{5}{2} N_N k + N_O k \ln \frac{V_O}{N_O \lambda_O^3}$$

final entropy

$$S_f = N_N k \ln \frac{V_T}{N_N \lambda_N^3} + \frac{5}{2} N_N k + N_O k \ln \frac{V_T}{N_O \lambda_O^3}$$

$$\Delta S = S_f - S_i \qquad V_T = V_O + V_N$$

$$= N_N k \ln \frac{V_T}{V_N} + N_O k \ln \frac{V_T}{V_O}$$

$$\frac{\Delta S}{N_T} = \frac{N_N}{N_T} k \ln \frac{V_T}{V_N} + \frac{N_O}{N_T} k \ln \frac{V_T}{V_O}$$

N_A = Avogadro constant $\quad R = k N_A$ = gas constant

$$\frac{\Delta S}{(N_T / N_A)} = R\left(\frac{4}{5} \ln \frac{5}{4} + \frac{1}{5} \ln \frac{5}{1}\right)$$

$$\simeq 0.5 R \simeq 4.2 \frac{J}{\text{mol K}}$$

5) Pathria 1.16

$$d\Omega = -S\,dT - P\,dV - N\,d\mu \qquad \Omega = -PV$$
$$d\Omega = -P\,dV - V\,dP$$

set these equal

$$-S\,dT - \cancel{P\,dV} - N\,d\mu = -\cancel{P\,dV} - V\,dP$$

at constant μ | at constant T

$$-S\,dT = -V\,dP \qquad -N\,d\mu = -V\,dP$$
$$\boxed{S = V\left(\frac{\partial P}{\partial T}\right)_\mu} \qquad \boxed{N = V\left(\frac{\partial P}{\partial \mu}\right)_T}$$

now we have

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

for ideal gas $= kT\ln\left(\frac{P}{kT}\lambda^3\right)$ ← from lecture notes

$$P = \frac{kT}{\lambda^3}e^{\mu/kT}$$

$$V\left(\frac{\partial P}{\partial \mu}\right)_T = \frac{VkT}{\lambda^3}\,\frac{1}{kT}\,e^{\mu/kT}$$
$$= \frac{V}{kT}P$$
$$= N \checkmark$$

1.16 cont $\left(\frac{\partial P}{\partial T}\right)_\mu = \frac{k}{\lambda^3} e^{\mu/kT} + \frac{kT}{\lambda^3}\left(\frac{-\mu}{kT^2}\right) e^{\mu/kT} - 3\frac{kT}{\lambda^4} e^{\mu/kT} \frac{\partial \lambda}{\partial T}$

$$= \frac{e^{\mu/kT}}{\lambda^3}\left[k - \frac{\mu}{T} + \frac{3}{2}k\right]$$

$\lambda = \sqrt{\frac{h^2}{2m\pi kT}}$

$\frac{d\lambda}{\partial T} = \frac{-1}{2T}\lambda$

$$= \frac{P}{kT}\left[\frac{5}{2}k - \frac{\mu}{T}\right]$$

$$V\left(\frac{\partial P}{\partial T}\right)_\mu = \underbrace{\frac{VP}{kT}}_{N}\left[\frac{5}{2}k - \frac{\mu}{T}\right]$$

$$= \frac{5}{2}Nk - \frac{N\mu}{T}$$

$$= \frac{5}{2}Nk + Nk\ln\frac{kT}{P\lambda^3}$$

$$= \frac{5}{2}Nk + Nk\ln\frac{V}{N\lambda^3}$$

$$= S$$

5). The total energy E is the sum of the individual energies

$$E = \hbar\omega \sum_{i=1}^{N} (n_i + \tfrac{1}{2}) = \frac{N\hbar\omega}{2} + \hbar\omega \sum n_i$$

this means there are $R = \frac{(E - \frac{N\hbar\omega}{2})}{\hbar\omega}$ "packets" of energy to be distributed among N oscillators.

One easy way to visualize the problem is to put the energy packets on a line, and place movable "walls" that describe the energy of each oscillator (see Pathria sec 3.8)

energy packets → ● ● | ● ● ● || ● ● | ● | ● ● | ● ● || ● ● ...

$n_1 = 0$ $n_2 = 3$ $n_3 = 0$ $n_4 = 2$ $n_5 = 1$ $n_6 = 2$ $n_7 = 2$ $n_8 = 0$ etc.

~~We see~~ in this linear geometry we have two types of "particles": We have: ~~balls & lines~~

R balls

$N-1$ lines

How many distinct ways are there to mix these two "particles" together?

$$\Omega = \frac{(R+N-1)!}{R!\,(N-1)!}$$

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$n_1 = 0$ $n_2 = 3$ $n_3 = 0$ $n_4 = 2$ $n_5 = 1$ $n_6 = 2$ $n_7 = 2$ $n_8 = 0$ etc.

~~By~~ use of this linear geometry we have two types of "particles".
We have:

R balls

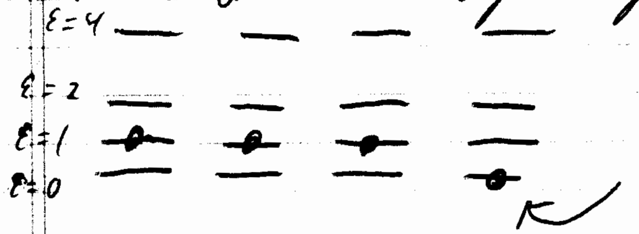
$N-1$ lines

How many distinct ways are there to mix these two "particles" together?

$$\Omega = \frac{(R + N - 1)!}{R!\,(N-1)!}$$

a) $\varepsilon = 3$

There are two ways to get $\varepsilon = 3$

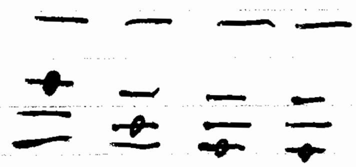


$3 \times 1\varepsilon + 0_\varepsilon \times 1 = 3_\varepsilon$

4 places to put 0ε particle

$\Omega = 4 = \frac{4!}{3!\,1!}$

or



$1 \times 2\varepsilon + 1 \times 1\varepsilon + 2 \times 0\varepsilon = 3_\varepsilon$

4 places to put 2ε particle
3 remaining places to put 1ε particle

$\Omega = \frac{4!}{2!\,1!\,1!} = 4 \times 3 = 12$

$S = k_B \ln(12 + 4)$

b) 4 ways ~~to~~ make 4ε

$1 \times 4\varepsilon + 3 \times 0\varepsilon$ $\qquad \frac{4!}{3!\,1!} = 4$

$2 \times 2\varepsilon + 2 \times 2\varepsilon$

4 places to put 1st 2ε particle, 3 remaining 2ε particle. Then divide by 2 to fix double counting.

$$\frac{4!}{2!\,2!} = 6$$

$1 \times 2\varepsilon + 2 \times 1\varepsilon + 1 \times 0\varepsilon$ $\qquad \frac{4!}{1!\,2!\,1!} = 12$

$4 \times 1\varepsilon$ $\qquad \frac{4!}{4!} = 1$

$$S = k_B \ln(4 + 6 + 12 + 1) = k_B \ln(23)$$

c) $\varepsilon = 8$

$2\times 4\varepsilon + 2\times 0\varepsilon \qquad \frac{4!}{2!2!} = 6$

$1\times 4\varepsilon + 2\times 2\varepsilon + 1\times 0\varepsilon \qquad \frac{4!}{1!2!1!} = 12$

$1\times 4\varepsilon + 1\times 2\varepsilon + 2\times 1\varepsilon \qquad \frac{4!}{1!1!2!} = 12$

$4\times 2\varepsilon \qquad \frac{4!}{4!} = 1$

$$S = k_B \ln(6+12+12+1) = k_B \ln(31)$$

d) $\varepsilon = 12$

$3\times 4\varepsilon + 1\times 0\varepsilon \qquad \frac{4!}{3!\,1!} = 4$

$2\times 4\varepsilon + 2\times 2\varepsilon \qquad \frac{4!}{2!2!} = 6$

$$S = k_B \ln(10)$$

e) $\varepsilon = 16$

$4\times 4\varepsilon \qquad S = k_B \ln(1) = 0$