Nikhil Patten
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Dr. Tang
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1.2 Assuming that the entropy S and the statistical number Ω of a physical system are related through an arbitrary functional form

$$S = f(\Omega) \tag{1}$$

show that the additive character of S and the multiplicative character of Ω necessarily require that the function $f(\Omega)$ be of the form (1.2.6).

$$S = f(\Omega) \tag{2}$$
$$S_1 + S_2 = S_{tot} \tag{3}$$
$$\Omega_1 \Omega_2 = \Omega_{tot} \tag{4}$$
$$f(\Omega_1) + f(\Omega_2) = f(\Omega_{tot}) \tag{5}$$
$$f(\Omega_1) + f(\Omega_2) = f(\Omega_1 \Omega_2) \tag{6}$$
$$\tag{7}$$

Differentiate both sides with respect to Ω_1.

$$\frac{\partial}{\partial \Omega_1}\Big(f(\Omega_1) + f(\Omega_2)\Big) = \frac{\partial}{\partial \Omega_1}\Big(f(\Omega_1 \Omega_2)\Big) \tag{8}$$
$$f'(\Omega_1) = \Omega_2 f'(\Omega_1 \Omega_2) \tag{9}$$
$$f'(\Omega_1 \Omega_2) = \frac{f'(\Omega_1)}{\Omega_2} \tag{10}$$

Now differentiate original expression with respect to Ω_2.

$$\frac{\partial}{\partial \Omega_2}\Big(f(\Omega_1) + f(\Omega_2)\Big) = \frac{\partial}{\partial \Omega_2}\Big(f(\Omega_1 \Omega_2)\Big) \tag{11}$$
$$f'(\Omega_2) = \Omega_1 f'(\Omega_1 \Omega_2) \tag{12}$$
$$f'(\Omega_1 \Omega_2) = \frac{f'(\Omega_2)}{\Omega_1} \tag{13}$$

Since $f(\Omega_1 \Omega_2)$ was found to be equal to two different expressions, these expressions must equal each other.

$$\frac{f'(\Omega_1)}{\Omega_2} = \frac{f'(\Omega_2)}{\Omega_1} \tag{14}$$
$$\Omega_1 f'(\Omega_1) = \Omega_2 f'(\Omega_2) \tag{15}$$

Because these are functions of two different variables, the only way the above relation can be true is if it equals a constant, k.

$$\Omega_1 f'(\Omega_1) = k \tag{16}$$

From (10):

$$f'(\Omega_1 \Omega_2) = \frac{f'(\Omega_1)}{\Omega_2} \tag{17}$$

Plug (16) into (17).

$$f'(\Omega_1\Omega_2) = \left(\frac{k}{\Omega_1}\right)\frac{1}{\Omega_2} \tag{18}$$

$$f'(\Omega_1\Omega_2) = \frac{k}{\Omega_1\Omega_2} \tag{19}$$

$$f'(\Omega_{tot}) = \frac{k}{\Omega_{tot}} \tag{20}$$

$$\int f'(\Omega_{tot})\, d\Omega_{tot} = \int \frac{k}{\Omega_{tot}} d\Omega_{tot} \tag{21}$$

$$f(\Omega_{tot}) = k \log \Omega_{tot} \tag{22}$$

$$\boxed{f(\Omega_{tot}) = k \log \Omega_{tot}}$$

1.10 A mole of argon and a mole of helium are contained in vessels of equal volume. If argon is at 300 **K, what should the temperature of helium be so that the two have the same entropy?**
Begin with equation for the entropy of an Ideal Gas.

$$S = Nk\left(\log\left[\frac{V}{Nh^3}\left(\frac{4\pi mE}{3N}\right)^{3/2}\right] + \frac{5}{2}\right) \tag{23}$$

Plug in the parameters for He and Ar, and solve for T_{He}.

$$S_{He} = S_{Ar} \tag{24}$$

$$N_{He}k\left(\log\left[\frac{V_{He}}{N_{He}h^3}\left(\frac{4\pi m_{He}E_{He}}{3N_{He}}\right)^{3/2}\right]+\frac{5}{2}\right) = N_{Ar}k\left(\log\left[\frac{V_{Ar}}{N_{Ar}h^3}\left(\frac{4\pi m_{Ar}E_{Ar}}{3N_{Ar}}\right)^{3/2}\right]+\frac{5}{2}\right) \tag{25}$$

$$N_{He} = N_{Ar} \tag{26}$$

$$\log\left[\frac{V_{He}}{N_{He}h^3}\left(\frac{4\pi m_{He}E_{He}}{3N_{He}}\right)^{3/2}\right]+\frac{5}{2} = \log\left[\frac{V_{Ar}}{N_{Ar}h^3}\left(\frac{4\pi m_{Ar}E_{Ar}}{3N_{Ar}}\right)^{3/2}\right]+\frac{5}{2} \tag{27}$$

$$\log\left[\frac{V_{He}}{N_{He}h^3}\left(\frac{4\pi m_{He}E_{He}}{3N_{He}}\right)^{3/2}\right] = \log\left[\frac{V_{Ar}}{N_{Ar}h^3}\left(\frac{4\pi m_{Ar}E_{Ar}}{3N_{Ar}}\right)^{3/2}\right] \tag{28}$$

$$\frac{V_{He}}{N_{He}h^3}\left(\frac{4\pi m_{He}E_{He}}{3N_{He}}\right)^{3/2} = \frac{V_{Ar}}{N_{Ar}h^3}\left(\frac{4\pi m_{Ar}E_{Ar}}{3N_{Ar}}\right)^{3/2} \tag{29}$$

$$V_{He}\left(\frac{4\pi m_{He}E_{He}}{3N_{He}}\right)^{3/2} = V_{Ar}\left(\frac{4\pi m_{Ar}E_{Ar}}{3N_{Ar}}\right)^{3/2} \tag{30}$$

$$V_{He} = V_{Ar} \tag{31}$$

$$\left(\frac{4\pi m_{He}E_{He}}{3N_{He}}\right)^{3/2} = \left(\frac{4\pi m_{Ar}E_{Ar}}{3N_{Ar}}\right)^{3/2} \tag{32}$$

$$\frac{4\pi m_{He}E_{He}}{3N_{He}} = \frac{4\pi m_{Ar}E_{Ar}}{3N_{Ar}} \tag{33}$$

$$m_{He}E_{He} = m_{Ar}E_{Ar} \tag{34}$$

$$E = \frac{3}{2}NkT \tag{35}$$

$$m_{He}\left(\frac{3}{2}N_{He}kT_{He}\right) = m_{Ar}\left(\frac{3}{2}N_{Ar}kT_{Ar}\right) \tag{36}$$

$$m_{He}T_{He} = m_{Ar}T_{Ar} \tag{37}$$

$$T_{He} = \frac{m_{Ar}}{m_{He}}T_{Ar} \tag{38}$$

$$m_{He} = 4.0026 \text{ amu} \tag{39}$$

$$m_{Ar} = 39.948 \text{ amu} \tag{40}$$

$$T_{Ar} = 300 \text{ K} \tag{41}$$

$$\tag{42}$$

$$\boxed{T_{He} = 2994 \text{ K}}$$

1.11 Four moles of nitrogen and one mole of oxygen at $P = 1$ atm and $T = 300$ K are mixed together to form air at the same pressure and temperature. Calculate the entropy of mixing per mole of the air formed.

$$\Delta S = k\left[N_1 \ln\frac{N_1+N_2}{N_1} + N_2 \ln\frac{N_1+N_2}{N_2}\right] \tag{43}$$

$$N_1 = 4 \text{ mol} \times \frac{6.02\times10^{23} \text{ particles}}{1 \text{ mol}} = 2.41\times10^{24} \text{ particles} \tag{44}$$

$$N_2 = 1 \text{ mol} \times \frac{6.02\times10^{23} \text{ particles}}{1 \text{ mol}} = 6.02\times10^{23} \text{ particles} \tag{45}$$

$$\Delta S = 20.79 \text{ J/k} \tag{46}$$

$$N_f = 5 \text{ mol} \tag{47}$$

$$\boxed{\Delta S = 4.16 \text{ J/K mol}}$$

1. For a solid that contains N oscillators and has a total energy unit q ($q >> N$), show:

$$S = Nk\left[\ln\left(\frac{q}{N}\right) + 1\right]$$

Determine $E = E(T)$. Use:

$$\ln(q+N) \approx \ln q + \frac{N}{q} \text{ for } q >> N$$

$$S = k\ln\Omega \tag{48}$$
$$\Omega = \frac{(N+q-1)!}{(N+q-1)!q!} \tag{49}$$
$$S = k\ln\frac{(N+q-1)!}{(N-1)!q!} \tag{50}$$
$$S = k\left[\ln(N+q-1)! - \ln(N-1)! - \ln q!\right] \tag{51}$$
$$S = k\left[\ln(N+q)! - \ln(N)! - \ln q!\right] \tag{52}$$
$$S = k\left[(N+q)\ln(N+q) - (N+q) - N\ln N + N - q\ln q + q\right] \tag{53}$$
$$S = k\left[(N+q)\ln(N+q) - N\ln N - q\ln q\right] \tag{54}$$
$$S = k\left[(N+q)\left(\ln q + \frac{N}{q}\right) - N\ln N - q\ln q\right] \tag{55}$$
$$S = k\left[N\ln q + \frac{N^2}{q} + q\ln q + N - N\ln N - q\ln q\right] \tag{56}$$
$$S = k\left[N\ln q + \frac{N^2}{q} + N - N\ln N\right] \tag{57}$$
$$S = Nk\left[\ln q - \ln N + \frac{N}{q} + 1\right] \tag{58}$$
$$S = Nk\left[\ln\frac{q}{N} + 1 + \frac{N}{q}\right] \tag{59}$$
$$\frac{N}{q} \approx 0 \tag{60}$$
$$S = NK\left[\ln\frac{q}{N} + 1\right] \tag{61}$$

$$\boxed{S = Nk\left[\ln\frac{q}{N} + 1\right]}$$

Find $E\left(T\right)$.

$$\begin{aligned}
E &= \left(q+\frac{N}{2}\right)\hbar\omega && (62)\\
q &>> N && (63)\\
E &\approx \left(q\right)\hbar\omega && (64)\\
q &= \frac{E}{\hbar\omega} && (65)\\
S &= Nk\left(\ln\frac{q}{N}+1\right) && (66)\\
S &= Nk\left(\ln\left[\left(\frac{E}{\hbar\omega}\right)\frac{1}{N}\right]+1\right) && (67)\\
S &= Nk\ln\frac{E}{\hbar N\omega}+Nk && (68)\\
\left(\frac{\partial S}{\partial E}\right)_{N,V} &\equiv \frac{1}{T} && (69)\\
\frac{\partial}{\partial E}\left(Nk\ln\frac{E}{N\hbar\omega}+Nk\right) &= \frac{1}{T} && (70)\\
Nk\frac{\partial}{\partial E}\left(\ln\frac{E}{N\hbar\omega}\right) &= \frac{1}{T} && (71)\\
Nk\frac{N\hbar\omega}{E}\frac{1}{N\hbar\omega} &= \frac{1}{T} && (72)\\
\frac{Nk}{E} &= \frac{1}{T} && (73)\\
E &= NkT && (74)
\end{aligned}$$

$$\boxed{E=NkT}$$