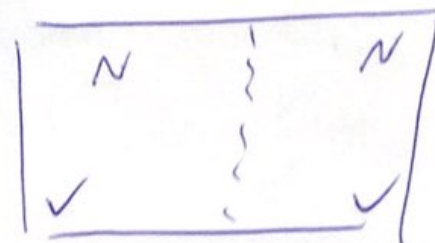


Example Similar experiment, calculate the change in entropy if

(i) the partition initially separates two different gases and (ii) it initially separates the same gas.

(i) $\Delta S = S^f - S^i$ ($f \equiv \text{final}$, $i \equiv \text{initial}$)



$$= \left(N_1 k_B \ln \frac{V_1^f}{N_1} + N_2 k_B \ln \frac{V_2^f}{N_2} \right) - \left(N_1 k_B \ln \frac{V_1^i}{N_1} + N_2 k_B \ln \frac{V_2^i}{N_2} \right)$$

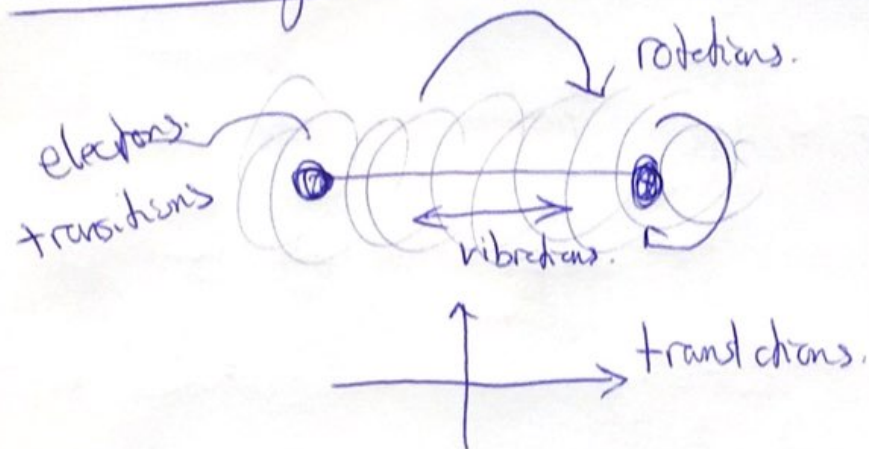
$$= N k_B \ln \frac{2V}{N} + N k_B \ln \frac{2V}{N} - N k_B \ln \frac{V}{N} - N k_B \ln \frac{V}{N}$$

$$= 2 N k_B \ln 2 > 0 \quad (\text{entropy of mixing})$$

(ii) $\Delta S = 0$ No entropy of mixing for 2 identical gases.

The $\frac{N!}{\gamma}$ term agrees with our intuition of mixing.

Diatomic gases.



The energy can be separated into

translational : E_{cm}

rotational : E_{rot}

vibrational : E_{vib}

electronic : E_{elec}

Adiabatic approximation / Born Oppenheimer - energies separable.

The partition function of a single diatomic molecule is

$$Z_1 = \sum_{\text{all states of molecule}} \exp \left[-\beta (E_{elec} + E_{cm} + E_{vib} + E_{rot}) \right]$$

$$= \sum_{\substack{\text{elec.} \\ \text{states}}} e^{-\beta E_{\text{elec}}} \sum_{\substack{\text{cm} \\ \text{states}}} e^{-\beta E_{\text{cm}}} \sum_{\substack{\text{vib} \\ \text{states}}} e^{-\beta E_{\text{vib}}} \sum_{\substack{\text{rot} \\ \text{states}}} e^{-\beta E_{\text{rot}}}. \quad (3)$$

$$Z = Z_{\text{elec.}} \cdot Z_{\text{cm.}} \cdot Z_{\text{vibr.}} \cdot Z_{\text{rot.}}$$

as one ~~red~~ would expect from independent contributions to the system.

For N (non-interacting) molecules we get

$$Z_N = (Z_{\text{elec}})^N \frac{(Z_{\text{cm}})^N}{N!} (Z_{\text{vibr}})^N (Z_{\text{rot}})^N \quad (\text{Gibbs Paradox}).$$

Hence $\ln Z_N = N \ln(Z_{\text{elec}}) + N \left[\ln \left(\frac{Z_{\text{cm}}}{N} \right) + 1 \right] + N \ln(Z_{\text{vib}}) + N \ln(Z_{\text{rot}})$

$$[\text{Note: } \ln(Z_{N!}^N) = \ln Z^N - \ln N! = N \ln Z - N \ln N + N = N(\ln(Z_{\text{cm}}) + 1)]$$

(4)

So free energy is

$$F = -Nk_B T \ln(Z_{\text{dec}}) = \overbrace{Nk_B T \ln \left[\ln \left(\frac{Z_{\text{cm}}}{N} \right) + 1 \right]} - Nk_B T \ln(Z_{\text{vib}}) - Nk_B T \ln(Z_{\text{rot}}).$$

Note that the cm (translational) contribution to free energy is the same as the mono-atomic case.

$$\text{i.e. } Z_{\text{cm}} = V/\lambda_D^3 \Rightarrow U_{\text{cm}} = \frac{3}{2} Nk_B T, C_V = \frac{3}{2} Nk_B.$$

Contribution from electrons. The electronic energy scale is much larger than the rest. Electrons get excited on the $\sim 10 \text{ eV}$ but the energy scales of motion is of the order $\sim 10 \text{ meV}$.

⑤

$$Z_{\text{elec}} = e^{-\beta \epsilon_0} + e^{-\beta \epsilon_1} + e^{-\beta \epsilon_2} = e^{-\beta \epsilon_0} \left[1 + \underbrace{e^{-\beta(\epsilon_1 - \epsilon_0)}}_{\sim e^{-\frac{10 \text{ eV}}{k_B T}}} + \dots \right]$$

But we know $\epsilon_1 - \epsilon_0 \sim 10 \text{ eV} \Rightarrow e^{-\beta(\epsilon_1 - \epsilon_0)} \sim e^{-\frac{10 \text{ eV}}{k_B T}}$

When is this term relevant $k_B T \sim 10 \text{ eV} \Rightarrow T_{\text{elec}} \sim 10^5 \text{ K}.$

we can say that electrons are in their ground state is $T \ll 10^5 \text{ K}.$

The partition function for electron becomes $Z_{\text{elec}} \approx e^{-\beta \epsilon_0}$

hence $\ln Z_{\text{elec}} = -\beta \epsilon_0$ the electronic contribution to internal energy and heat capacity is :

$$\frac{U}{N} = - \frac{\partial}{\partial \beta} \ln Z_{\text{elec}} = \epsilon_0 ; \quad C_v^{\text{elec}} = \frac{\partial U}{\partial T} \Big|_v \Rightarrow \frac{\partial}{\partial T} \epsilon_0 = \underline{\underline{0.}}$$

⑧

Vibrations. The diatomic molecule is a SHO, therefore

$$\epsilon_n = (n + 1/2) h \omega$$

Previously we obtained the partition function $Z_{\text{vib}} = \frac{e^{-\beta h \omega / 2}}{1 - e^{-\beta h \omega}}$

$$\text{Hence } U_{\text{vib}} = -N \frac{\partial \ln Z_{\text{vib}}}{\partial \beta} = \frac{N h \omega}{2} + \frac{N h \omega}{e^{\beta h \omega} - 1}$$

$$\Rightarrow C_v^{\text{vibr}} = \left. \frac{\partial U}{\partial T} \right|_V = \frac{N k_B (h \omega \beta)^2 e^{\beta h \omega}}{(e^{\beta h \omega} - 1)^2}$$



The O_2 molecule vibrates at around 62 THz . Energy to temperature conversion of 62 THz gives around $5000 \text{ K} \equiv T_{\text{vib}}$.

For $T \ll T_{\text{vib}}$ the result is similar to the electronic contribution,

$$U_{\text{vib}} = N \frac{k\omega}{2} + Nk_B T \Rightarrow C_v = Nk_B.$$