A02

(2009 2.1)

Mixing 2 gases, different initial temperatures T_1, T_2; N_1, N_2; V_1, V_2. Evaluate change in entropy upon mixing when (i) gases are identical. (ii) distinct gases. Show that (ii) case is larger and explain.

Solution (Huang 6.6 – Gibbs Paradox):

We have shown in class that entropy of ideal gas

$$S(E,V) = Nk \ln\left(V\left(\frac{4\pi m}{3h^2}\frac{E}{N}\right)^{3/2}\right] + \frac{3}{2}Nk$$

using $u = \frac{3}{2}kT$

$$S_0 = \frac{3k}{2}\left(1 + \ln\frac{4\pi m}{3h^2}\right)$$

we have

$$S = Nk\ln\left(Vu^{3/2}\right) + NS_0.$$

Therefore when we mix 2 different gases we have

$$S = S_1 + S_2 \quad \rightarrow \quad \Delta S = \Delta S_1 + \Delta S_2$$

$$\Delta S_i = S_i^{after} - S_i^{before} = N_i k\left(\ln\left(Vu^{3/2}\right) - \ln\left(V_i u_i^{3/2}\right)\right)$$

$$= N_i k \ln\left(\frac{V}{V_i}\left(\frac{T}{T_i}\right)^{3/2}\right)$$

$$\frac{\Delta S}{k} = N_1 \ln\left(\frac{V_1+V_2}{V_1}\left(\frac{T}{T_1}\right)^{3/2}\right) + N_2 \ln\left(\frac{V_1+V_2}{V_2}\left(\frac{T}{T_2}\right)^{3/2}\right) > 0$$

$\left(T = \frac{N_1T_1 + N_2T_2}{N_1+N_2}\right)$ according to $E_1 = \frac{3}{2}N_1kT_1$ $E_2 = \frac{3}{2}N_2kT_2$

$E = E_1 + E_2 = \frac{3}{2}(N_1+N_2)kT = \frac{3}{2}N_1kT_1 + \frac{3}{2}N_2kT_2$

What happens when $T_1 = T_2$, and gases are the same?
assume $V_1 = V_2 = \frac{V}{2}$, $T_1 = T_2 = T$, $N_1 = N_2 = \frac{N}{2}$

we get

$$\Delta S^{\text{identical}} = \frac{N}{2}\ln\left(\frac{V}{V/2}\right) + \frac{N}{2}\ln\left(\frac{V}{V/2}\right) = N\ln 2 > 0$$

Problem! This is the Gibbs paradox.
Since we can imagine any gas as a series of smaller gases mixing then we have $S \to \infty$

Gibbs' solution:

We assume particles are indistinguishable therefore we have over-counted the states $\Sigma(E)$ by a factor of $N!$ This means we must

$$S \to S - \ln(N!) \approx S - N\ln N + N$$

$$\frac{S_i}{k} = N_i \ln\left(\frac{V_i}{N_i} u_i^{3/2}\right) \quad \text{giving}$$

$$\frac{S_{before}}{k} = N_1 \ln\left(\frac{V_1}{N_1} u_1^{3/2}\right) + N_1 s_0 + N_2 \ln\left(\frac{V_2}{N_2} u_2^{3/2}\right) + N_2 s_0$$

$$\frac{S_{after}}{k} = (N_1 + N_2)\ln\left(\frac{V_1 + V_2}{N_1 + N_2} U^{3/2}\right) + (N_1 + N_2)s_0$$

$\frac{\Delta S}{k}$ = for different gases we have $N_1 \ln\left(\frac{V}{V_1}\frac{N_1}{N}\left(\frac{T}{T_1}\right)^{3/2}\right) + N_2 \ln\left(\frac{V}{V_2}\frac{N_2}{N}\left(\frac{T}{T_2}\right)^{3/2}\right)$

but now for $N_1 = N_2 = \frac{N}{2}$, $V_1 = V_2 = \frac{V}{2}$, $T_1 = T_2 = T$ we have

$$\frac{\Delta S}{k} = \frac{N}{2}\ln\left(2 \cdot \frac{1}{2}\right) + \frac{N}{2}\ln\left(2 \cdot \frac{1}{2}\right) = N\ln(1) \equiv 0$$