

IDEAL GAS

For an ideal (Boltzmann) gas consisting of N -distinguishable molecules of mass m , the single particle partition function has the following form:

$$z = \int_0^{\infty} g(\varepsilon) e^{-\beta \varepsilon} d\varepsilon,$$

where $g(\varepsilon) = \frac{4\pi V \sqrt{2}}{h^3} m^{3/2} \varepsilon^{1/2} d\varepsilon$, is the density of states. Using the standard integral

$$\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}, \text{ one can find}$$

$$z = \int_0^{\infty} g(\varepsilon) e^{-\beta \varepsilon} d\varepsilon = V \left(\frac{2\pi m k T}{h^2} \right)^{3/2} = V \left(\frac{2\pi m}{\beta h^2} \right)^{3/2}.$$

This is the partition function for a gas under the assumption that the energy levels are so closely spaced that they form a continuum. For N distinguishable particles, we have $Z = z^N$.

Quantity	Formula
Partition function	$Z = z^N = V^N \left(\frac{2\pi m k T}{h^2} \right)^{3N/2}$
Helmholtz free energy	$F = -kT \ln Z = -NkT \left[\ln V + \frac{3}{2} \ln \left(\frac{2\pi m}{\beta h^2} \right) \right]$
Entropy	$S = - \left(\frac{\partial F}{\partial T} \right)_{V,N} = Nk \left[\ln V + \frac{3}{2} \ln T + S_0 \right]$
Equation of state	$P = \frac{1}{\beta} \left(\frac{\partial \ln Z}{\partial V} \right)_{T,N} = \frac{1}{\beta} \frac{N}{V} \Rightarrow PV = NRT$
Internal energy	$U = - \left(\frac{\partial \ln Z}{\partial \beta} \right)_{V,N} = \frac{3}{2} \frac{N}{\beta} = N\bar{\varepsilon} \Rightarrow \bar{\varepsilon} = \frac{3}{2} kT$
Heat capacity	$C_V = \left(\frac{\partial U}{\partial T} \right)_{V,N} = \frac{3}{2} Nk$

$$S_0 = \frac{3}{2} \left[\ln \left(\frac{2\pi m k}{h^2} \right) + 1 \right] \text{ is a constant independent of } T, V, \text{ or } N.$$

The equation,

$$S = Nk \left[\ln V + \frac{3}{2} \ln T + S_0 \right], \quad (**)$$

is known as the Sackur-Tetrode equation for the entropy of a monatomic gas. Recalling that $s = S/n$, $Nk/n=R$, we have

$$s = c_v \ln T + R \ln v + s_o, \quad (***)$$

which we obtained earlier in thermodynamics.

Comments on Sackur-Tetrode equation: It is not correct and turns into the following difficulties:

- 1- S is not additive because the volume V (and not V/N) occurs in the argument of the logarithm. This prevents us from dividing the system in two parts and writing $S=S_1+S_2$. This difficulty is not so easily to handle classically. In fact, it leads to the famous Gibbs paradox.
- 2- It is not valid down to absolute zero since S does not approach zero as $T \rightarrow 0$. Such contradiction would not have occurred if we had used the original summation of Z. The replacement of sum by integral in Z is not justified near the absolute zero. At $T = 0$ the lowest state ($\epsilon = 0$) becomes important, while its contribution has been excluded altogether in the integration. In classical statistical, since p is a continuous variable and the size of the cell in the phase space is not fixed, we cannot estimate the third law. For this we have to go to quantum mechanics.

Gibbs' Paradox

Gibbs paradox appears when we mix two similar ideal gases.

(A) *Mixing of two different ideal gases at constant temperature:* The mixing of two different gases is an irreversible process. If we consider mixing of two different gases (N_1, V_1, T) and (N_2, V_2, T) with $V = V_1 + V_2$ and $N = N_1 + N_2$ then the change in entropy of (***) is

$$\Delta S = S - (S_1 + S_2) = N_1 k \ln \left(\frac{V}{V_1} \right) + N_2 k \ln \left(\frac{V}{V_2} \right) > 0,$$

This gives the entropy of mixing for two different ideal gases and is in agreement with experiments. For $N_1 = N_2 = N$, $V_1 = V_2 = V/2$, we get $\Delta S = 2Nk \ln 2$.

(B) *Mixing of the same two ideal gases at constant temperature:* If the two gases are the same, the process is **reversal** one. The final entropy ought to be the same with, or without mixing, then the change in entropy is

$$\Delta S = S - (S_1 + S_2) = 0.$$

This result is in agreement with the thermodynamics of reversible processes and also with experiments, but contradict Eq. (**). The derivation of Eq. (**) does not depend on the identity of the molecules and would give the same increase in entropy as two different gases.

Comments:

- 1- In the case (A), mixing leads to diffusion of the molecules through the whole volume V (twice the initial volumes). There is a random mixing of the different

molecules and so an increase in the disorder. This irreversible process and the increase of entropy make sense. The mixing is a process in which the positions of molecules one gas are interchanged with those of the other gas. Each such exchange creates a new states, i.e. increasing the number of microstates or equivalently the entropy increases.

2- In case (B), any such interchange is always an interchange between two identical molecules. Therefore, no new state is created. In this case, the application of Eq. (**) overestimates the number of accessible states because classically we have taken all the molecules, even of the same gas, as distinguishable. To solve this paradox, we have to change Z by $z^N/N!$ The final results read

$$\ln Z = N \ln z - (N \ln N - N),$$

$$S = Nk \left[\ln \frac{V}{N} + \frac{3}{2} \ln T + \sigma_o^* \right] \quad , \quad (+)$$

where $\sigma_o^* = S_o + 1 = \frac{3}{2} \ln \left(\frac{2\pi mk}{h^2} \right) + \frac{5}{2}$.

Eq. (+) has the properties of the entropy, and gives the correct answer for both cases, but it is not accurate at very low temperature.

Example: Using the corrected entropy formula (Sackur-Tetrode equation)

$$S = kN \ln \frac{V}{N} + \frac{3}{2} kN \left[\ln \left(\frac{2\pi mkT}{h^2} \right) + \frac{5}{2} \right],$$

work out the entropy of mixing for the case of different gases and for identical gases, thus showing explicitly that there is no Gibbs paradox.

Answer:

(A) Mixing of two different ideal gases at the same temperature, the entropies of the gases before mixing are:

$$S_i = kN_i \ln \frac{V_i}{N_i} + \frac{3}{2} kN_i \left[\ln \left(\frac{2\pi m_i kT}{h^2} \right) + \frac{5}{2} \right], \quad i = 1, 2 ,$$

Mixing of the gases in the volume $V=V_1+V_2$ implies the total entropy after mixing is

$$S_{total} = \sum_{i=1}^2 \left\{ kN_i \ln \frac{V}{N_i} + \frac{3}{2} kN_i \left[\ln \left(\frac{2\pi m_i kT}{h^2} \right) + \frac{5}{2} \right] \right\}$$

The entropy of mixing for the case of two different gases is:

$$\Delta S = S_{total} - (S_1 + S_2) = kN_1 \ln \frac{V}{V_1} + kN_2 \ln \frac{V}{V_2}$$

i.e. $\Delta S > 0$ for the mixing of two different gases.

(B) Mixing of two identical gases: $m_1 = m_2 = m$. Assume the densities are the same, i.e. $\frac{N}{V} = \frac{N_1}{V_1} = \frac{N_2}{V_2}$, then

$$S_{total} = kN \ln \frac{V}{N} + \frac{3}{2} kN \left[\ln \left(\frac{2\pi mkT}{h^2} \right) + \frac{5}{2} \right]$$

The entropy of mixing is

$$\begin{aligned} \Delta S &= S_{total} - (S_1 + S_2) = Nk \ln \left(\frac{V}{N} \right) - N_1 k \ln \left(\frac{V_1}{N_1} \right) - N_2 k \ln \left(\frac{V_2}{N_2} \right) \\ &= k(N - N_1 - N_2) \ln \frac{V}{N} = 0 \end{aligned}$$

$\Delta S = 0$ for the mixing of two identical gases with the same particle density, i.e. no Gibbs paradox.