

ELEMENTS OF ENSEMBLE THEORY

- Classically, a molecule of an ideal gas can be represented as a distinguishable and structureless particle. Its phase space (μ -space, where μ stands for molecule) has six dimensions whose coordinates are $(q_1, q_2, q_3, p_1, p_2, p_3)$ where q and p are the canonical coordinates of the spatial and momentum, respectively. A trajectory of a particle in which $(q_1, q_2, q_3, p_1, p_2, p_3)$ are given as a function of time can be described as the motion of a point in phase space.

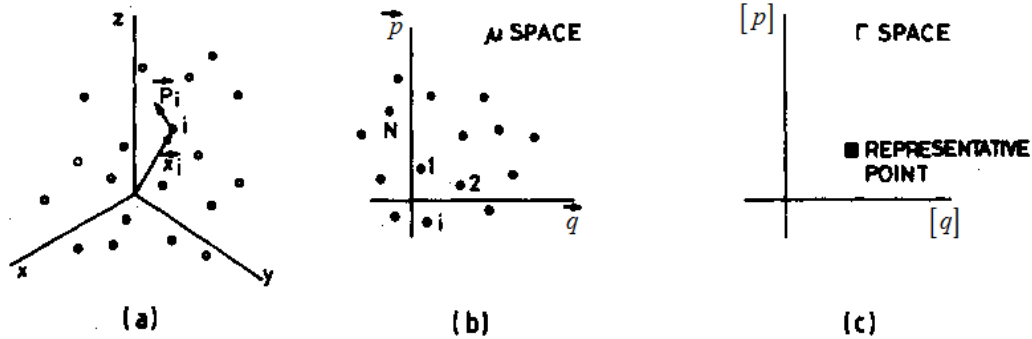


Fig. 1 (a) A gas containing N molecules (system). (b) μ space for the system. (c) Γ space and the representative point for the entire system.

- Γ -space (where Γ stands for gas): For a system of N molecules (gas) the instantaneous state spanned by $3N$ coordinate axes ($[q] \ll q_1, \dots, q_{3N}$) and $3N$ momentum axes ($[p] \ll p_1, \dots, p_{3N}$), which are the generalized coordinates of the Hamiltonian H . In general, if f independent position coordinates and f momentum coordinates are required to fully specify the state of a system, then the system is said to possess f degrees of freedom. The Γ -space is then a conceptual Euclidean space having $2f$ rectangular axis $[q]$, $[p]$. The notation $[q]$, $[p]$ stands for the $3N$ coordinate axis and $3N$ momentum axis.
- The system will follow the classical Hamiltonian equations of motion

$$\dot{q}_i = \frac{\partial H(q,p)}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H(q,p)}{\partial q_i}$$

where $H(p,q) = E$ is a hypersurface called **Ergodic** surface.

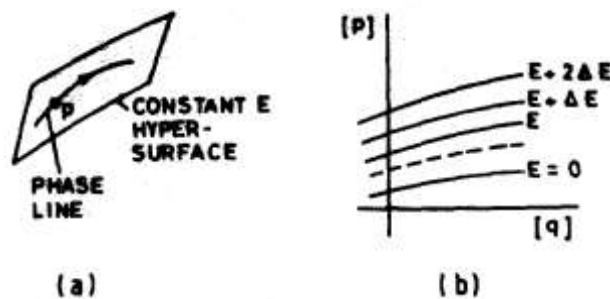


Fig. 2 (a) Ergodic surface. (b) Ergodic surfaces in the $2f$ -dimensional phase space.

Example: Consider a classical harmonic oscillator in one dimension. The Hamiltonian is

$$H(p, q) = \frac{p^2}{2m} + \frac{1}{2}kq^2$$

Where k is the spring constant and m is the mass of the oscillating particle.

- Solve the equations of motion to obtain $p(t)$ and $q(t)$.
- Show that the phase orbit of the harmonic oscillator in the two-dimensional phase space is an ellipse. Illustrate the orbit by a diagram and indicate on this the semi-major and semi-minor axes of the ellipse.
- Find the volume $\Gamma_o(E)$ in the phase space with energy below E .
- Find the number of quantum states $\Omega_o(E)$ with energy below E for this oscillator, and show that when with energy below E . Is large we have $\Omega_o(E) \approx \frac{\Gamma_o(E)}{h}$.

Answer

$$(a) \quad H(p, q) = \frac{p^2}{2m} + \frac{1}{2}kq^2$$

The equations of motion are

$$\dot{q} = \frac{\partial H(q, p)}{\partial p} = \frac{p}{m}, \quad \dot{p} = -\frac{\partial H(q, p)}{\partial q} = -kq$$

Then

$$\frac{d^2 q}{dt^2} = \frac{1}{m} \dot{p} = -\frac{k}{m} q, \Rightarrow \frac{d^2 q}{dt^2} + \omega^2 q = 0, \quad \omega = \sqrt{\frac{k}{m}}$$

The general solution of the differential equation is

$$q(t) = A \cos(\omega t + \varphi)$$

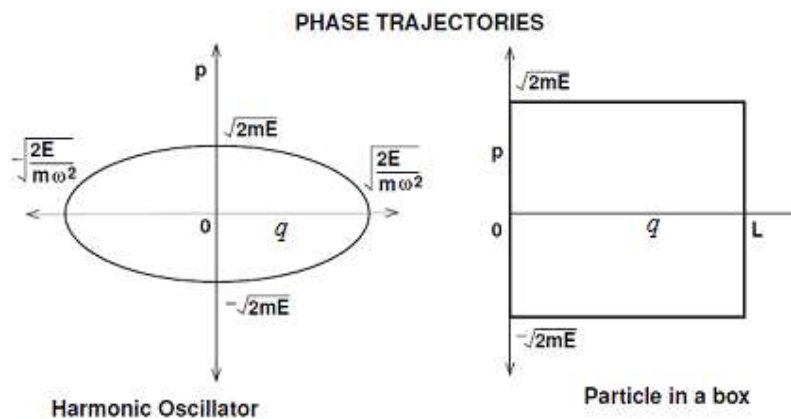
where A is the amplitude, the other equation gives

$$p(t) = m\dot{q} = -mA\omega \sin(\omega t + \varphi)$$

(b)

$$H(q(t), p(t)) = \frac{1}{2}m\omega^2 A^2 = E = \text{constant} \quad \Rightarrow \quad \frac{p^2}{2mE} + \frac{q^2}{(2E/k)} = 1$$

which is equation of an ellipse. The two-dimension phase space is:



(c) The volume (in this case, the area) $\Gamma_o(E)$ in the phase space with energy below E is given by:

$$\Gamma_o(E) = \pi ab = \pi \sqrt{2mE} \sqrt{2E/m\omega^2} = \frac{2\pi E}{\omega}.$$

According to the quantum mechanics, the energy Eigenvalues of the harmonic oscillator are given by:

$$E_n = (n + \frac{1}{2})\hbar\omega, \quad n = 0, 1, 2, \dots$$

The difference of energy between two successive trajectories is: $\Delta E = \hbar\omega$.

The area of the phase space enclosed between two successive trajectories of which $E = \hbar\omega$ is $\omega_o = \frac{2\pi\hbar\omega}{\omega} = h$. So, h is the area of the phase space per eigenstate. The number of quantum

states $\Omega_o(E)$ with energy below E for this oscillator is:

$$\Omega_o(E) \approx \frac{\Gamma_o(E)}{\omega_o} \approx \frac{\Gamma_o(E)}{h}$$

4. **Ensemble:** It is a hypothetical collection of a very large number (M) of similar, non-interacting, independent systems each of which is a replica on a macroscopic scale of the actual thermodynamic system of interest. All members of an ensemble, which are identical in feature like N , V , and E are referred to as elements.

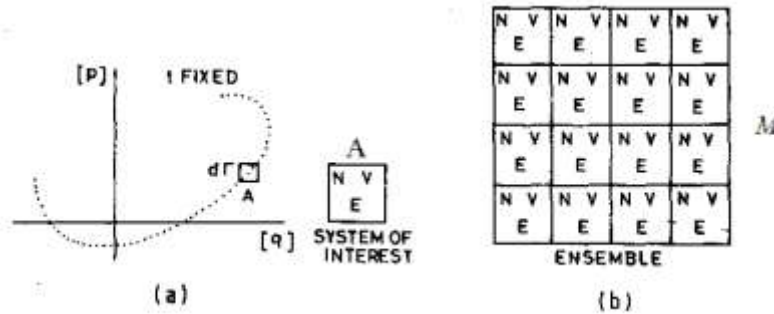


Fig. 3 (a) The ensemble (a small portion) at one time. Any region like A will appear to contain a swarm of phase points. (b) Schematic 'lattice' representation of an ensemble of M ($M \rightarrow \infty$) imaginary systems, at one time, each with same N , V , E .

Q1: What is the difference between our system (A) and the element of the ensemble?

- (i) The system of interest is a macroscopic system consisting of a large number of molecules ($N \rightarrow \infty$) which we can make direct measurements for all the macroscopic variables.
- (ii) The number of imagined elements that form the ensemble at one time is large ($M \rightarrow \infty$) so that they can truly represent the range of states available to the actual system over really long period of time ($t \rightarrow \infty$).

5. The ensemble is represented by a distribution of points (systems) continuous in phase space and described by the density function $\rho(q, p, t)$.

6. Define

$\rho(q,p,t) d^{3N}q d^{3N}p =$ number of representative points contained in the volume element $d^{3N}q d^{3N}p$ located at $[q,p]$ in Γ -space at the instant t .

which follows Liouville's theorem:

$$\frac{D\rho}{Dt} = \frac{\partial\rho}{\partial t} + \sum_{i=1}^{3N} \left(\frac{\partial p_i}{\partial t} \frac{\partial\rho}{\partial p_i} + \frac{\partial q_i}{\partial t} \frac{\partial\rho}{\partial q_i} \right) = 0$$

i.e. the distribution of points in Γ -space moves like an incompressible fluid, which implies that $\rho(q,p)$ is the same for all times. An ensemble is said to be stationary if ρ does not depend explicitly on time, i.e. at all times

$$\frac{\partial\rho}{\partial t} = 0$$

In such case the ensemble qualifies to represent a system in *equilibrium*.

7. **Microcanonical Ensemble (M.E.):** It is a statistical ensemble which is isolated from its surroundings, so it has $N, V,$ and E are constants. It represented by the stationary density $\rho(q,p),$

$$\rho(q,p) = \begin{cases} \text{constant} & E_o - \frac{\Delta}{2} \leq E \leq E_o + \frac{\Delta}{2}, (\text{or at } E = E_o) \\ 0 & \text{otherwise} \end{cases}$$

Also, $\rho(q,p)$ can be expressed as:

$$\rho(q,p) = \text{constant} \times \delta(E - E_o),$$

where δ is the Dirac's delta function with the property

$$f(x') = \int_{-\infty}^{\infty} \delta(x - x') f(x) dx,$$

and $f(x)$ is an arbitrary well-behaved function.

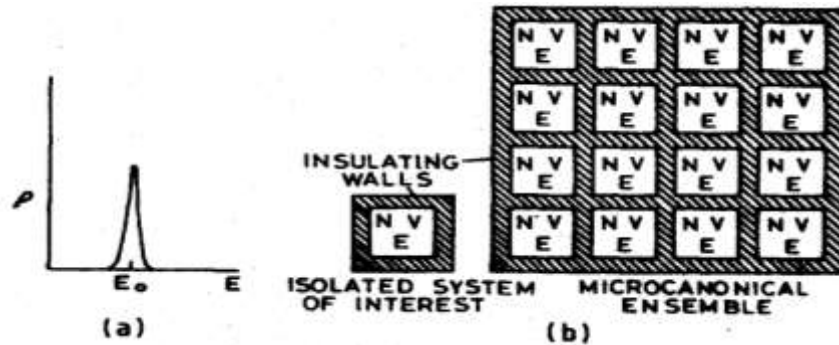


Fig. 4 (a) Density distribution for the microcanonical ensemble. (b) Schematic lattice representation of the microcanonical ensemble. The shaded walls are nonconducting for heat and impermeable to all molecules.

8. **Ergodic Hypothesis:** *The time average of some property of a system in equilibrium is same as the instantaneous ensemble average.* In other words: As the number of the systems (M) in the ensemble becomes very large, the ensemble average of mechanical variable $\langle f \rangle$ approaches the long-time average of that variable in the real system. The average is defined by

$$\langle f \rangle = \frac{\int f(q,p) \rho(q,p;t) d^{3N}q d^{3N}p}{\int \rho(q,p,t) d^{3N}q d^{3N}p} = \frac{1}{w} \int_{\omega} f(q,p) \rho(q,p;t) d\omega$$

where w denotes the total "volume" of the accessible region of the phase space. The integration, in the above equation, extends over the whole of the phase space; however, it is only the populated regions of the phase space ($\rho \neq 0$) that actually contribute to the integrals. Since we considered our ensemble is stationary, the $\langle f \rangle$ must be independent of time; accordingly, taking a time average thereof will not produce any new result. Thus

$$\begin{aligned} \langle f \rangle &= \text{the ensemble average of } f \\ &= \text{time average of (the ensemble average of } f) \\ &= \text{the ensemble average of (the time average of } f) \\ &= \text{the long-time average of } f. \\ &= f_{\text{exp}} \end{aligned}$$

i.e. *the ensemble average of any physical quantity f is identical with the value one expects to obtain, or making, an appropriate measurement on the given system.*

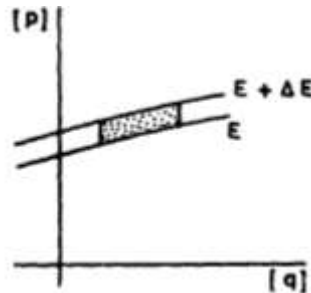


Fig. 1.10 The microcanonical ensemble representing an isolated system (gas contained in a finite volume) with energy between E and $E + \Delta E$. The shaded region represents the accessible portion of the phase space. It corresponds to a uniform distribution of representative points bounded by the ergodic surfaces of constant energy E and $E + \Delta E$ and the surfaces corresponding to the physical boundary of the container.

9. *Volume in Γ Space occupied by the microcanonical ensemble:* (the dependence on N, V, E and Δ is understood)

$$w(N, V, E) \equiv \frac{1}{h^{3N}} \int_{E < H(q,p) < E + \Delta} \rho(q,p) d^{3N}q d^{3N}p \quad \Delta \ll E$$

$$\Sigma(N, V, E) \equiv \frac{1}{h^{3N}} \int_{H(q,p) < E+\Delta} d^{3N}q d^{3N}p \quad \Delta \ll E$$

Note that: h is a constant of the dimension of action (momentum \times distance = action) and introduced to make Γ and Σ dimensionless. The factor h^{3N} comes from quantal model of matter in which is the volume of phase space in which one energy state is possible and then Σ will be the number of quantum state in the energy interval. Then

$$\begin{aligned} w(E) &= \Sigma(E + \Delta) - \Sigma(E) = (\Sigma(E) + \frac{\partial \Sigma(E)}{\partial E} \Delta + \dots) - \Sigma(E) \\ &= a(E)\Delta \end{aligned}$$

where $a(E) = \frac{\partial \Sigma(E)}{\partial E}$ is the density of the states of the system (the dependence on N , and V is understood).

10. *Equivalent definitions for the entropy:* The following definitions are equivalent, up to additive constant terms of order $\log N$ or smaller.

$$\begin{aligned} S &= k_B \log [a(E)] \\ &= k_B \log [w(E)] \\ &= k_B \log [\Sigma(E)] \end{aligned}$$

The above three equations possesses all the properties of the entropy function in thermodynamics.

Comments:

- i- Definitions of the entropy have to be taken to be equivalent although $w(E)$ is the volume of a shell of thickness ΔE at E , while $\Sigma(E)$ is the volume of the whole sphere from 0 to E in the phase space. It works because in the microcanonical ensemble $\log[w(E)]$ is not sensitive to the value of ΔE . This is a great advantage because we do not know how to choose ΔE in each case of interest.
- ii- Let $\Sigma(P)$ denote the number of microstates available to a free particle confined to volume V of the physical space, its momentum p being less than or equal to a specified value P . We then have

$$\Sigma(E) \square \frac{1}{h^3} \int \int_{p \leq P} d^3p d^3q \square \frac{V}{h^3} \frac{4\pi}{3} P^3$$

whence we obtain for the number of microstates with momentum lying between p and $p+dp$

$$g(p)dp = \frac{d\Sigma(p)}{dp} dp \simeq \frac{V}{h^3} 4\pi p^2 dp.$$

Expressed in terms of the particle energy $E = P^2/2m$, these expressions assume the form

$$\Sigma(E) \square \frac{V}{h^3} \frac{4\pi}{3} (2mE)^{3/2}$$

The density of the states between the energy E and $E + dE$ is given by:

$$a(E)dE = \frac{\partial \Sigma(E)}{\partial E} dE \square \frac{V}{h^3} 2\pi (2m)^{3/2} E^{1/2} dE$$

H.W. prove the following expression for N -dimension

$$\Gamma(E) = V^N \Omega_{\Gamma}(E) = V^N \frac{\pi^f}{(\frac{f}{2} - 1)!} (2mE)^{\frac{f}{2}}, \quad f = 3N$$

Then

$$\Sigma(E) = \left(\frac{V}{h^3}\right)^N \Omega_f(E) = C_f \left[\frac{V}{h^3} (2mE)^{\frac{3}{2}}\right]^N,$$

$$C_f = \frac{2\pi^f}{\Gamma(\frac{f}{2} + 1)} \quad f = 3N$$

Then the entropy of the ideal gas will be:

$$S(N, E, V) = k \log \Gamma(E) = k[\ln C_{3N} + N \ln \frac{V}{h^3} + \frac{3}{2} N \ln(2mE)]$$

and check the following results:

$$S(N, E, V) = Nk \ln V + \frac{3}{2} Nk \left\{ 1 + \ln \left(\frac{2\pi m k T}{h^2} \right) \right\}$$

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

The above results are only asymptotic in character; they hold only if the physical dimensions of the enclosure are "infinitely" large. To be applicable to systems of finite extent, they must be suitably corrected. We have used the Stirling approximation $(n!) \square (n/e)^n$ or $\ln(n!) \square n \ln n - n$ with $e = 2.71828$ as the base of the natural logarithm.

Hence it follows that

$$E(N, S, V) = \frac{3h^2 N}{4\pi m V^{2/3}} \exp \left[\frac{2S}{3Nk} - 1 \right].$$

The temperature of the gas then given by:

$$T = \left(\frac{\partial E}{\partial S} \right)_{N,V} = \frac{2}{3} \frac{E}{Nk}$$

then

$$E = N \left(\frac{3}{2} kT \right) = n \left(\frac{3}{2} RT \right).$$

where n is the number of moles of the gas R is the gas constant. The following parameters and equation of state could be also calculated:

$$C_V = \left(\frac{\partial E}{\partial T} \right)_{N,V} = \frac{3}{2} Nk = \frac{3}{2} nR$$

$$P = - \left(\frac{\partial E}{\partial V} \right)_{N,S} = \frac{2}{3} \frac{E}{V}$$

$$C_P = - \left(\frac{\partial(E + PV)}{\partial T} \right)_{N,P} = \frac{5}{2} nR$$

The above equation for the entropy is not correct. It turns into two main difficulties:

- i- The expression that we used, $\Sigma(E) = \int \int_{p \leq P} d^3 p d^3 q = V \frac{4\pi}{3} P^3$, or $\Gamma(E)$, has the dimension of (momentum \times distance = action). this difficulty is removed by measuring the phase space volume in terms of h , So

$$S(E, V) = k_B \ln \frac{\Gamma(E)}{h^f} = Nk_B \ln \left[V \left(\frac{E}{N} \right)^{3/2} \right] + NS_o$$

$$\text{where } S_o = \frac{3}{2} \left[\ln \left(\frac{2\pi m k_B}{h^2} \right) + 1 \right]$$

- i- S is not additive because the volume V (and not N/V) occurs in the argument of the logarithm. This prevents us from dividing the system in two parts and writing $S = S_1 + S_2$.

The second difficulty is not so easily. In fact, it leads to the famous Gibbs paradox.

Final Comments on Microcanonical Ensemble (M.E.)

The M.E. provides a general basis for statistical mechanics. It has the following **important properties**:

1. It deals with the simplest system known, that is, an isolated system.
2. The postulate of equal priori probability is strictly applicable in this case.
3. Other ensembles can be deduced easily from the M.E.

But in the other side it has the following **drawbacks**:

1. It deals with unpractical system, isolated system with given E , which do not occur in the laboratory.
2. We don't know how to specify the width of the ergodic shell between E and $E + \Delta E$ in any given case.
3. Calculation of the number of microstates that have specific energy is not always simple.

Sackur-Tetrode equation

The equation,

$$S = Nk_B \left[\ln V + \frac{3}{2} \ln T + S_0 \right], \quad S_0 = \frac{3}{2} \left[\ln \left(\frac{2\pi mk_B}{h^2} \right) + 1 \right], \quad (**)$$

is known as the Sackur-Tetrode equation for the entropy of a monatomic gas. Here S_0 is a constant independent of T , V , or N . Recalling that $s = S/n$, $R = Nk/n$, we have

$$s = c_v \ln T + R \ln v + s_0, \quad (***)$$

which has 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 ($\varepsilon = 0$) 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.

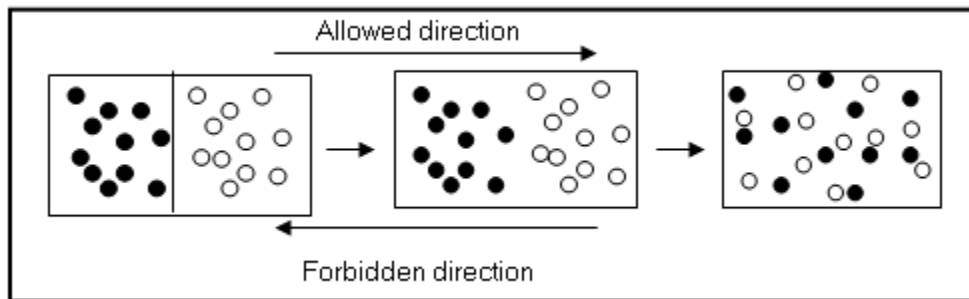


Figure: Mixing of two different ideal gases at constant temperature

(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 $\Delta S = 2Nk \ln 2$.

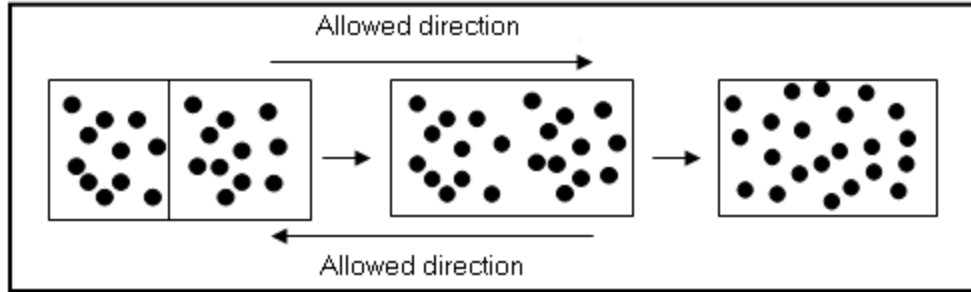


Figure: Mixing of the same two ideal gases ideal gases at constant temperature

(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 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

$$\begin{aligned} \ln Z &= N \ln z - (N \ln N - N), \\ S &= Nk \left[\ln \frac{V}{N} + \frac{3}{2} \ln T + \sigma_o^* \right], \end{aligned} \quad (+)$$

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)

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

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.

$$\frac{N}{V} = \frac{N_1}{V_1} = \frac{N_2}{V_2}, \text{ then}$$

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

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.