

Entropy

In Physics and Mathematics

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Entropy :

- Physically Entropy of a system is a measure of disorder of its molecular motion.
- Greater is disorder of molecular motion greater is the entropy.
- The connection between statistical mechanics is provided by entropy.
- **Natural processes tend to move toward a state of greater disorder.**

Entropy in Statistical Mechanics

From the principles of thermodynamics the thermodynamic entropy S has the following important properties:

- dS is an exact differential and is equal to dQ/T for a reversible process, where dQ is the heat quantity added to the system.
- Entropy is additive: $S=S_1+S_2$.
- $\Delta S \geq 0$. If the state of a closed system is given macroscopically at any instant, the most probable state at any other instant is one of equal or greater entropy.

State Function

This statement means that entropy is a **state function** in that the value of entropy does not depend on the past history of the system but only on the actual state of the system...

The **entropy** σ of a system (in classical statistical physics) in statistical equilibrium can be defined as

$$\sigma = \ln \Delta\Gamma$$

where $\Delta\Gamma$ is the volume of phase space accessible to the system, i.e., the volume corresponding to the energies between E and $E+\Delta$.

Change in entropy

Let us show first, that **changes in the entropy are independent** of the system of units used to measure $\Delta\Gamma$.

As $\Delta\Gamma$ is a volume in the phase space of N point particles it has dimensions

$$(\text{Momentum} \times \text{Length})^{3N} = (\text{Action})^{3N}$$

Let \hbar denote the unit of action; then $\Delta\Gamma/\hbar^{3N}$ is dimensionless. If we were to define

$$\sigma = \ln \frac{\Delta\Gamma}{\hbar^{3N}} = \ln \Delta\Gamma - 3N \ln \hbar$$

we see that for changes

$$\delta\sigma = \delta \ln \Delta\Gamma$$

independent of the system units. \hbar =Plank's constant is a natural unit of action in phase space.

It is obvious that the entropy σ , has a definite value for an ensemble in statistical equilibrium; thus *the change in entropy is an exact differential.*

We see that, if $\Delta\Gamma$ is interpreted as a measure of the imprecision of our knowledge of a system or ***as a measure of the "randomness"*** of a system then the entropy is also to be interpreted ***as a measure of the imprecision or randomness.***

Entropy is an additive

It can be easily shown that σ is an additive. Let us consider a system made up of two parts, one with N_1 particles and the other with N_2 particles. Then

$$N = N_1 + N_2$$

and the phase space of the combined system is the product space of the phase spaces of the individual parts:

$$\Delta\Gamma = \Delta\Gamma_1 \Delta\Gamma_2$$

The additive property of the entropy follows directly:

$$\sigma = \ln \Delta\Gamma = \ln \Delta\Gamma_1 \Delta\Gamma_2 = \ln \Delta\Gamma_1 + \ln \Delta\Gamma_2 = \sigma_1 + \sigma_2$$

Principle Of Entropy Increase

The entropy of a system remains constant in reversible process but increase inevitably in all irreversible process. Since a reversible process represents a limiting ideal case, all actual processes are inherently irreversible.

That means after each cycle of operation the entropy of system increases and tends to a maximum.

"The entropy of an isolated system either increases or remains constant or remains constant according as processes is undergoes are irreversible or reversible."

Equilibrium conditions

We have supposed that the *condition of statistical equilibrium* is given by the most probable condition of a closed system, and therefore we may also say that the entropy σ is a *maximum* when a closed system is in equilibrium condition.

The value of σ for a system in equilibrium will depend on the energy $E (\equiv \langle E \rangle)$ of the system; on the number N_i of each molecular species i in the system; and on external variables, such as volume, strain, magnetization, etc.

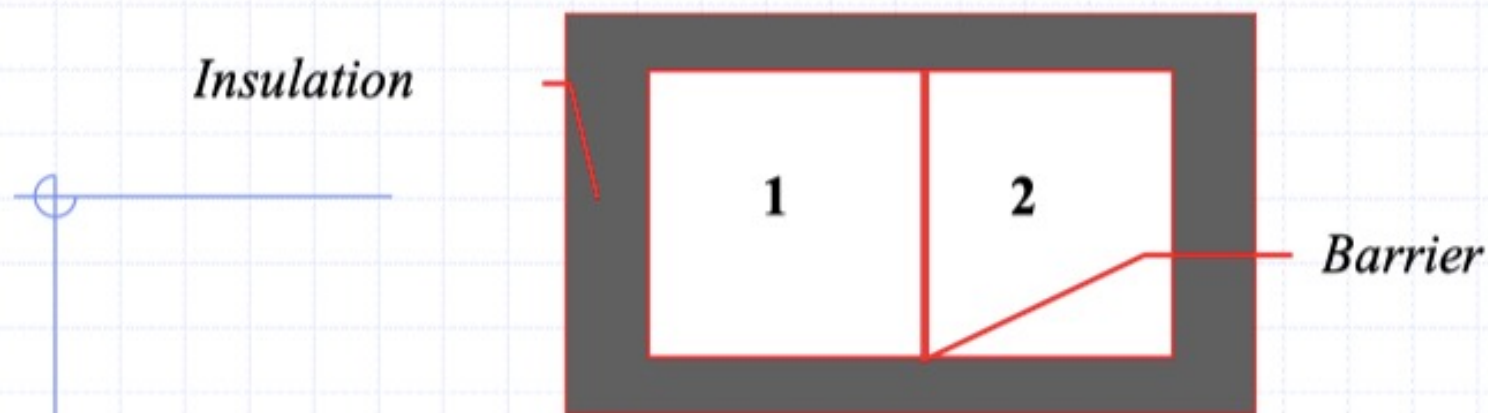


Fig. 3.1.

Let us consider the condition for equilibrium in a system made up of two interconnected subsystems, as in Fig. 3.1. Initially a *rigid, insulating, non-permeable barrier* separates the subsystems from each other.

Thermal equilibrium

Thermal contact - *the systems can exchange the energy. In equilibrium, there is no any flow of energy between the systems.* Let us suppose that the barrier is allowed to transmit energy, the other inhibitions remaining in effect. If the conditions of the two subsystems 1 and 2 do not change we say they are in ***thermal equilibrium***.

In the thermal equilibrium the entropy σ of the total system must be a maximum with respect to small transfers of energy from one subsystem to the other. Writing, by the additive property of the entropy

$$\sigma = \sigma_1 + \sigma_2$$

we have in equilibrium

$$\delta\sigma = \delta\sigma_1 + \delta\sigma_2 = 0$$

$$\delta\sigma = \left(\frac{\partial\sigma_1}{\partial E_1} \right) \delta E_1 + \left(\frac{\partial\sigma_2}{\partial E_2} \right) \delta E_2 = 0$$

We know, however, that

$$\delta E = \delta E_1 + \delta E_2 = 0$$

as the total system is thermally closed, the energy in a microcanonical ensemble being constant. Thus

$$\delta\sigma = \left[\left(\frac{\partial\sigma_1}{\partial E_1} \right) - \left(\frac{\partial\sigma_2}{\partial E_2} \right) \right] \delta E_1 = 0$$

As δE_1 was an arbitrary variation we must have

$$\left(\frac{\partial \sigma_1}{\partial E_1} \right) = \left(\frac{\partial \sigma_2}{\partial E_2} \right)$$

in thermal equilibrium. If we define a quantity θ by

$$\frac{1}{\theta} = \frac{\partial \sigma}{\partial E}$$

then in thermal equilibrium

$$\theta_1 = \theta_2$$

Here θ is known as the **temperature** and will shown later to be related to the absolute temperature T by $\theta = kT$, where k is the **Boltzmann constant**, 1.380×10^{-23} j/deg K.

Mechanical equilibrium

Mechanical contact the systems are separated by the mobile barrier; The equilibrium is reached in this case by adequation of pressure from both sides of the barrier.

We now imagine that the wall is allowed to move and also passes energy but do not passes particles. The volumes V_1 , V_2 of the two systems can readjust to maximize the entropy. In mechanical equilibrium

$$\delta\sigma = \left(\frac{\partial\sigma_1}{\partial V_1}\right)\delta V_1 + \left(\frac{\partial\sigma_2}{\partial V_2}\right)\delta V_2 + \left(\frac{\partial\sigma_1}{\partial E_1}\right)\delta E_1 + \left(\frac{\partial\sigma_2}{\partial E_2}\right)\delta E_2 = 0$$

After thermal equilibrium has been established the last two terms on the right add up to zero, so we must have

$$\left(\frac{\partial \sigma_1}{\partial V_1}\right) \delta V_1 + \left(\frac{\partial \sigma_2}{\partial V_2}\right) \delta V_2 = 0$$

Now the total volume $V=V_1+V_2$ is constant, so that

$$\delta V = \delta V_1 + \delta V_2$$

We have then

$$\delta \sigma = \left[\left(\frac{\partial \sigma_1}{\partial V_1}\right) - \left(\frac{\partial \sigma_2}{\partial V_2}\right) \right] \delta V_1 = 0$$

As δV_1 was an arbitrary variation we must have

$$\left(\frac{\partial \sigma_1}{\partial V_1} \right) = \left(\frac{\partial \sigma_2}{\partial V_2} \right)$$

in mechanical equilibrium. If we define a quantity Π by

$$\frac{\Pi}{\theta} = \left(\frac{\partial \sigma}{\partial V} \right)_{E, N}$$

we see that for a system in thermal equilibrium the condition for mechanical equilibrium is

$$\Pi_1 = \Pi_2$$

We show now that Π has the essential characteristics of the usual pressure p .

Concentration Equilibrium

The systems can be exchange by the particles. Let us suppose that the wall allows diffusion through it of molecules of the *i*th chemical species. We have

$$\delta N_{i1} = -\delta N_{i2}$$

For equilibrium

$$\delta\sigma = \left[\left(\frac{\partial\sigma_1}{\partial N_{i1}} \right) - \left(\frac{\partial\sigma_2}{\partial N_{i2}} \right) \right] \delta N_{i1} = 0$$

or

$$\frac{\partial\sigma_1}{\partial N_{i1}} = \frac{\partial\sigma_2}{\partial N_{i2}}$$

We define a quantity μ_i by the relation

$$-\frac{\mu_i}{\theta} = \left(\frac{\partial \sigma}{\partial N_i} \right)_{E,V}$$

The quantity μ_i is called the **chemical potential** of the *ith* species. For equilibrium at constant temperature

$$\mu_{i1} = \mu_{i2}$$

Gibbs Paradox

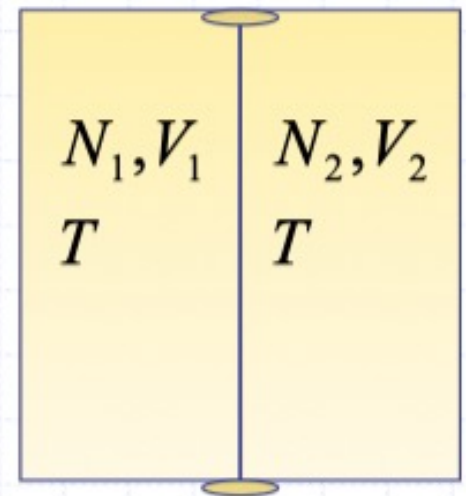
i) Mixing Of Two Different Ideal Gas

It can be regarded as the expansion of each of the gases to the volume

$$V = V_1 + V_2$$

The change in entropy,

$$\begin{aligned}\Delta\sigma &= \sigma_{12} - (\sigma_1 + \sigma_2) \\ &= (N_1 \ln V + N_2 \ln V) - (N_1 \ln V_1 + N_2 \ln V_2) \\ &= N_1 \ln \left(\frac{V}{V_1} \right) + N_2 \ln \left(\frac{V}{V_2} \right) > 0\end{aligned}$$



Mixing of two gases

For this case

$$V_1 = V_2 = \frac{1}{2}V \quad \& \quad N_1 = N_2 = N$$

We get,

$$\Delta\sigma = 2N \ln 2$$

This gives the entropy of mixing for two different ideal gases and is in agreement with experiments.

ii) Mixing Of one Ideal Gas with the same ideal gas

The removal of the partition should not affect the distribution of the system over the accessible states.

The change in entropy,

$$\Delta\sigma = \sigma_{12} - (\sigma_1 + \sigma_2) = 0$$

in particular, for the case

$$V_1 = V_2 = \frac{1}{2}V \quad \& \quad N_1 = N_2 = N$$

we get an un observed and therefore unaccountable increase of entropy **$2N\ln 2$** when a partition is removed from a box containing the same gas the entropy becomes zero. This is the *Gibbs paradox*.

Resolution Of Gibbs Paradox

- ✓ In the case (i) Removal of partition leads to diffusion of molecules which is an irreversible process therefore increase of entropy makes sense.
- ✓ We can imagine mixing of gases interchanges the position of molecules, creates a new state

Therefore, the no. of accessible states increases or equivalently the entropy increase.

Cont'd...

- ✓ In the case (ii) no new state is created when partition is removed.

If there are N molecules $N!$ permutations are possible, also the mixing is indistinguishable.

Therefore no. of accessible states is too large by a factor of $N!$,

$$\Delta\Gamma \rightarrow \Delta\Gamma/N!$$

$$\sigma = \ln\left(\frac{\Delta\Gamma}{N!h^{3N}}\right) = \ln\left(\frac{\Delta\Gamma}{h^{3N}}\right) - \ln N!$$

$$= \ln\left(\frac{\Delta\Gamma}{h^{3N}}\right) - (N \ln N - N)$$

This extra term resolves the gibbs paradox.it makes entropy properly additive.

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Thank You