General Physics II at EPFL

(2018-2019 SS, Wed 17:15-19:00 and Thu 8:15-10:00, Exercise Thu 10:15-12:00)

Thermodynamic (6th week)

Entropy and the second and third Laws of Thermodynamics

Reversible and irreversible process

Consider an isothermal expansion of an n-mol ideal gas at $T = T_0$ changing its state from $A(V_\mathrm{a}, P_\mathrm{a}, T_0)$ to $B(V_\mathrm{b}, P_\mathrm{b}, T_0)$ through a quasi-static path (see Lecture Note Thermodynamics 5th week). This process follows the line given by $PV = nRT_0$ on the V-P plane. Since there is no temperature change, $\Delta E_\mathrm{int} = 0$ and from the first law of thermodynamics, $Q = W$ where work W is given by

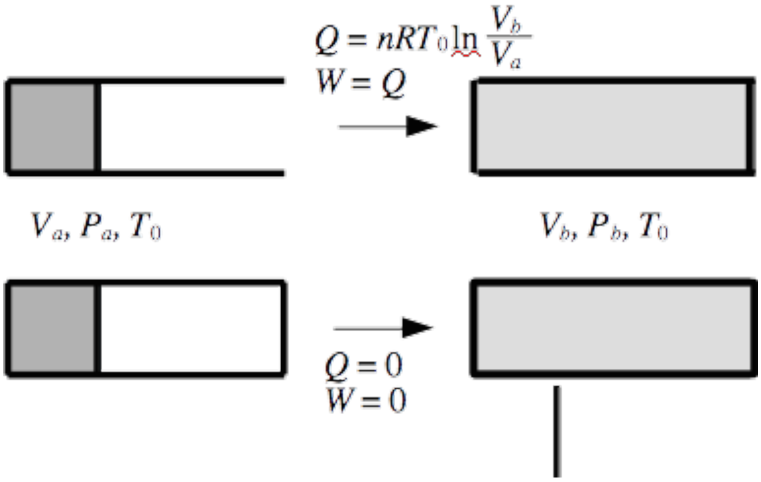
$$W_{\mathrm{A}\to\mathrm{B}} = \int_A^B P dV = nRT_0 \int_{V_\mathrm{a}}^{V_\mathrm{a}} \frac{dV}{V} = nRT_0 \ln \frac{V_\mathrm{b}}{V_\mathrm{a}}$$

thus

$$Q_{\mathrm{A}\to\mathrm{B}} = nRT_0 \ln \frac{V_\mathrm{b}}{V_\mathrm{a}}.$$

Once the system is at the state B, we can make the system to follow the same path back to A by applying $-Q_{\mathrm{A}\to\mathrm{B}}$ and $-W_{\mathrm{A}\to\mathrm{B}}$, just reversing the sign. Any process that can be reversed by changing the sign of Q and W is called reversible.

Now consider a process where a thermally isolated container with a volume V_b is divided into two by a tight thermally isolating wall. One section is filled with an n-mol ideal gas at $A(V_\mathrm{a}, P_\mathrm{a}, T_0)$ and the other vacuum. Now we remove the wall and let the gas to expand into the whole volume. Since the container is thermally isolated, $Q = 0$, since gas expands without moving anything, $W = 0$. The first law of thermodynamics leads to $\Delta E_\mathrm{int} = 0$. The final state is $B(V_\mathrm{b}, P_\mathrm{b}, T_0)$. Since the internal energy depends only on temperature, no change of temperature in this process. The process cannot be shown as a quasi-static path on the V-P plane. Clearly, this process cannot be reversed by simply changing the sign of Q and W. Any process that cannot be reversed by changing the sign of Q and W is called irreversible.



Entropy

For **a reversible process**, entropy changes of a system, ΔS, for a change of its state from A to B with heat Q and at a constant temperature T, is given by

$$\Delta S = \frac{Q}{T}$$

where the temperature is in Kelvin. If the temperature of the system is not constant, ΔS is given by

$$\Delta S = \int_A^B \mathrm{d}S = \int_A^B \frac{\tilde{\mathrm{d}}Q}{T}$$

where the integral follows a quasi-static path from A to B. Note that Q/T of infinitesimally small step on the path is given by $\tilde{\mathrm{d}}Q/T$. It can be shown that ΔS is independent of the path, unlike the heat. Thus the entropy, S, is a state variable such as volume and temperature and $\Delta S = S(\mathrm{B}) - S(\mathrm{A})$.

We demonstrate the fact that ΔS does not depend on the path, by calculating ΔS explicitly for a change of state $A(V_\mathrm{a}, P_\mathrm{a}, T_0)$ to $B(V_\mathrm{b}, P_\mathrm{b}, T_0)$ for an n-mol ideal gas in two different reversible paths. As demonstrated above, the state from A to B can be achieved through isothermal expansion, where heat is given by

$$Q = nRT_0 \ln \frac{V_\mathrm{b}}{V_\mathrm{a}}.$$

Since the temperature does not change in the process, the entropy change is then given by

$$\Delta S_\mathrm{ab} = \frac{Q}{T_0} = nR \ln \frac{V_\mathrm{b}}{V_\mathrm{a}}.$$

We then consider reaching B in two steps, first decreasing the pressure under constant volume to reach $D(V_\mathrm{a}, P_\mathrm{b}, T_\mathrm{d})$, followed by increasing the volume under constant pressure (see again Lecture Note Thermodynamics 5th week). For the heat, we have:

$$\mathrm{A}\rightarrow\mathrm{D}\ \ Q_\mathrm{ad} = nC_\mathrm{V}dT \ \text{ and } \ \mathrm{D}\rightarrow\mathrm{B}\ \ Q_\mathrm{db} = nC_\mathrm{P}dT$$

which lead to

$$\Delta S_\mathrm{ad} = nC_\mathrm{V}\int_{T_0}^{T_\mathrm{d}} \frac{dT}{T} = nC_\mathrm{V} \ln \frac{T_\mathrm{d}}{T_0} \text{ for } \mathrm{A} \rightarrow \mathrm{D} \text{ and } \Delta S_\mathrm{db} = nC_\mathrm{P}\int_{T_\mathrm{d}}^{T_0} \frac{dT}{T} = n(C_\mathrm{V} + R)\ln \frac{T_0}{T_\mathrm{d}} \text{ for } \mathrm{D} \rightarrow \mathrm{B}.$$

The total entropy change is given by

$$\Delta S'_\mathrm{ab} = \Delta S_\mathrm{ad} + \Delta S_\mathrm{db} = nC_\mathrm{V} \ln \frac{T_\mathrm{d}}{T_0} + n(C_\mathrm{V} + R)\ln \frac{T_0}{T_\mathrm{d}} = nR \ln \frac{T_0}{T_\mathrm{d}}$$

Using the gas low, $PV=nRT$, we obtain,

$$\frac{T_0}{T_\mathrm{d}} = \frac{V_\mathrm{b}P_\mathrm{b}}{V_\mathrm{a}P_\mathrm{b}}$$

which follows that

$$\frac{T_0}{T_\mathrm{d}} = \frac{V_\mathrm{b}}{V_\mathrm{a}}$$

showing that the two different paths give same ΔS. Since $V_\mathrm{a} < V_\mathrm{b}$, we have $\Delta S > 0$.

Considered paths can be indeed reversed, i.e. C→A, by changing the sign of Q and W, with negative entropy $-\Delta S$. Therefore, entropy change for a loop such as A→B→C→A,

$$\Delta S_\mathrm{ab} + \Delta S_\mathrm{bc} + \Delta S_\mathrm{ca} = \oint \frac{\tilde{\mathrm{d}}Q}{T} = 0$$

i.e. it is always 0. We conclude that ΔS does not depends on the path, **thus *S* is a state variable**.

For irreversible process, it turns out

$$\Delta S = \int_A^B \frac{\tilde{\mathrm{d}}Q_{\text{reversible}}}{T} > \int_A^B \frac{\tilde{\mathrm{d}}Q_{\text{irreversible}}}{T}$$

For the state change of $A(V_{\mathrm{a}},\ P_{\mathrm{a}},\ T_0)$ to $B(V_{\mathrm{b}},\ P_{\mathrm{b}},\ T_0)$ discussed above, indeed we have

$$\int_A^B \frac{\tilde{\mathrm{d}}Q_{\text{reversible}}}{T} = nRT_0 \ln\frac{V_{\mathrm{b}}}{V_{\mathrm{a}}} > 0 \text{ and } \int_A^B \frac{\tilde{\mathrm{d}}Q_{\text{ireversible}}}{T} = 0\ .$$

Therefore, we can write,

$$\Delta S \geq \int_A^B \frac{\tilde{\mathrm{d}}Q}{T}$$

where the equal sign holds only for reversible processes, i.e. entropy change is given by

$$\Delta S = \int_A^B \frac{\tilde{\mathrm{d}}Q}{T}$$

only for the reversible process. If we consider a thermally isolated system, no heat for any process, i.e. $\Delta S \geq 0$.

Entropy Second and third laws of thermodynamics

The second law of thermodynamic is: In any process in which a **thermally isolated system** goes from one state to another state, the entropy cannot be decreased; i.e. $\Delta S \geq 0$.

The third law of thermodynamic is: The entropy of a system converges to a constant value $S_0 = 0$ for $T \to 0$ independent of all the other properties for the particular system.

Entropy and the first law of thermodynamic

For reversible processes with a fixed temperature, T, heat, Q, can be obtained from the change of the entropy, ΔS as $Q = \Delta S T$ or **for an infinitesimally small path**, $\tilde{d}Q = TdS$. Then, The first law of thermodynamics can be written as

$$\mathrm{d}E_{\mathrm{int}} = Q - W = T\mathrm{d}S - P\mathrm{d}V$$

where all the terms consist of state variables, not depending on the path. Therefore, it is valid even for irreversible process. One may summarise as:

$\tilde{d}Q = TdS$	only for reversible case
$\tilde{d}W = PdV$	only for reversible case
$\mathrm{d}E_{\mathrm{int}} = \tilde{d}Q - \tilde{d}W$	always valid
$\mathrm{d}E_{\mathrm{int}} = T\mathrm{d}S - P\mathrm{d}V$	always valid

For irreversible process, we have $T\mathrm{d}S \geq \tilde{\mathrm{d}}Q$, thus $P\mathrm{d}V \leq \tilde{d}W$.

Statistical interpretation of Entropy

Once we obtain, $\mathrm{d}E_{\mathrm{int}} = T\mathrm{d}S - P\mathrm{d}V$, temperature, T, can be given by

$$\frac{1}{T} = \frac{1}{\left(\partial E_{\mathrm{int}}/\partial \mathrm{S}\right)_V} = \left(\frac{\partial S}{\partial E_{\mathrm{int}}}\right)_V$$

While deriving the Boltzmann constant during the Thermodynamics 3 lecture, we encounter an expression:

$$\frac{\mathrm{d}\ln\Omega(E)}{\mathrm{d}E} = \frac{1}{kT}$$

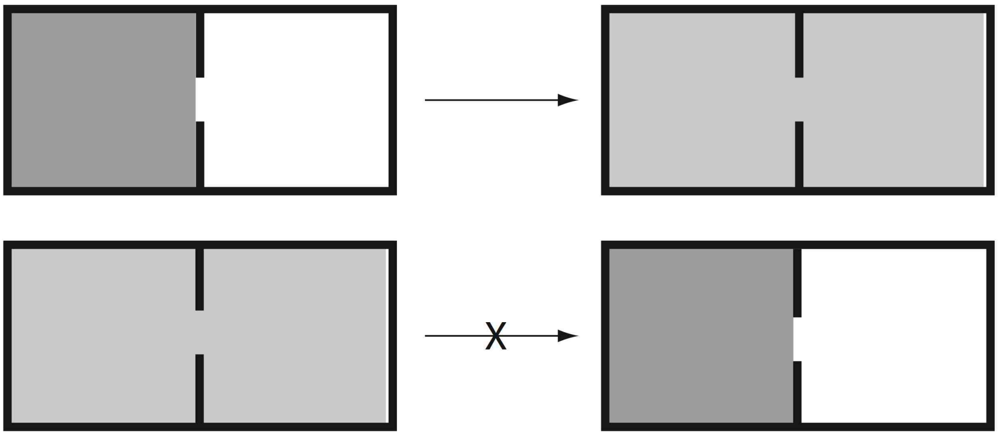
where, k is the Boltzmann constant, and $\Omega(E)$ is the number of states with energy E. as an thermal equilibrium condition. This leads to

$$k\frac{\mathrm{d}\ln\Omega\left(E_{\mathrm{int}}\right)}{\mathrm{d}E_{\mathrm{int}}}=\left(\frac{\partial S}{\partial E_{\mathrm{int}}}\right)_V$$

By integrating the both sides, we identify

$$S=k\ln\Omega$$

which is the definition of entropy in statistical physics: the entropy of a particular macrostate, S, is given by the formula, $S=k\ln\Omega$, where Ω is the number of microstates associated to the particular macrostate. At $T=0$, there is only one state. Evolution of a thermal system is in the direction from an "ordered" state to a more "chaotic" state: e.g. vacuum expansion.



Entropy of free expansion a la statistical mechanics

We now try to obtain the entropy change for the free expansion. A total of N ideal gas molecules is placed in a container with volume V_a. In that volume, there are m possible states that the gas molecule can take. The number of possible configuration taken by the N molecules, Ω, is then given by

$$\Omega={}_mC_N=\frac{m!}{N!(m-N)!}$$

and entropy by

$$S=k\ln\Omega=k\ln\frac{m!}{N!(m-N)!}$$

Since we are considering a macroscopic system, both m and N are large, where $\ln n!\approx n\ln n-n$ (Starling's approximation) can be used. This leads to

$$S=k\ln\frac{m!}{N!(m-N)!}\approx k\left[m\ln m-N\ln N-(m-N)\ln(m-N)\right].$$

Since we are considering an ideal gas, the gas density must be very small, thus we have $m>>N$, and the following approximation holds:

$$\begin{aligned}m\ln m-N\ln N-(m-N)\ln(m-N)&=m\ln\frac{m}{m-N}-N\ln\frac{N}{m-N}\\&\approx m\ln\left(1+\frac{N}{m}\right)-N\ln\frac{N}{m}\left(1+\frac{N}{m}\right)\\&\approx N-N\ln\frac{N}{m}\end{aligned}$$

and

$$S \approx k\left(N - N\ln\frac{N}{m}\right).$$

When the volume of the container is increased to V_b, the number of possible states in the container also increases from m to xm, where $x = V_2/V_1$. Entropy is then given by

$$S' \approx k\left(N - N\ln\frac{N}{xm}\right)$$

and entropy change

$$\Delta S = S' - S \approx kN\ln x$$

Converting it to the mole number, n, and universal gas constant R, it follows that

$$\Delta S \approx nR\ln\frac{V_b}{V_a}$$

in agreement with the thermodynamics calculation.

Special demonstration: Entropy of mixing

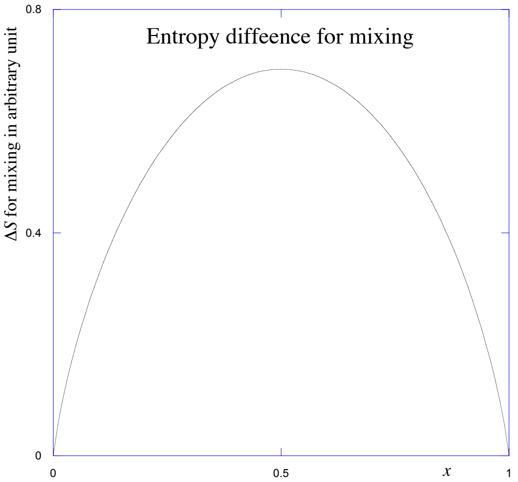
A thermally isolated container with a volume V is split into two, $V_1 = xV$ and $V_2 = (1-x)V$ where $0 \le x \le 1$, by a thermally isolated wall. They are filled with two different ideal gasses of $n_1 = xn$-mol and $n_2 = (1-x)n$-mole, respectively. Both gasses have a same pressure, $P_1 = P_2 \equiv P$, and a same temperature, $T_1 = T_2 \equiv T$. Now we remove the wall, and gas-1 expands to volume-2 and gas-2 to volume-1.

Since there is no temperature difference between the two regions, the temperature remains constant in this process. The two gasses do not provide any work either, since they have nothing to move when they expand. Therefore, this process can be dealt as two gasses making free expansion independently. Then the entropy changes of the two gasses are given by

$$\Delta S_1 = xnR\ln\frac{V}{xV} \text{ and } \Delta S_2 = (1-x)nR\ln\frac{V}{(1-x)V}$$

and the total entropy change

$$\Delta S = \Delta S_1 + \Delta S_2 = xnR\ln\frac{V}{xV} + (1-x)nR\ln\frac{V}{(1-x)V} = -nR\left[x\ln x + (1-x)\ln(1-x)\right]$$



As seen from the figure above, $\Delta S \ge 0$, where $\Delta S = 0$ at $x = 0$ and $= 1$, i.e. with one gas and no mixing, and maximum at $x = 0.5$, i.e. mixing of two equal amount of gasses. This makes sense for two different ideal gasses. Since mixing two different gasses is an irreversible process.

However, if the two gasses are completely identical, i.e. gas molecules are indistinguishable, no change occurs after removing the wall. The original state can be restored by simply putting back the wall, thus ΔS must be = 0, which is not in agreement with the result above. This depends on how to interpret "distinguishable" and "indistinguishable" and their statistical treatment showing a limitation of classical thermodynamics description.