# Thermodynamic definition of entropy

It is (was) convenient to introduce
another state variable   entropy   $S$
(joining other state variables   $P, V, T, E_{int}, n$)

## Entropy

$$dS = \frac{dQ}{T}$$

$$\Delta S = \int_{state\ 1}^{state\ 2} \frac{dQ}{T}$$

Adiabatic :   $dQ = 0$   $dS = 0$   $S = const$

Isothermal :   $T = const$   $\Delta S = \frac{1}{T}\int_{state\ 1}^{state\ 2} dQ = \frac{Q}{T} = nR \ln \frac{V_2}{V_1}$

The expression   $\Delta S = \Delta Q / T$   also valid for
phase transitions ( melting, evaporation, etc.)
   $Q = m \cdot L$      $\Delta S = Q/T = m \cdot L / \underline{T}$
                                      in Kelvin !
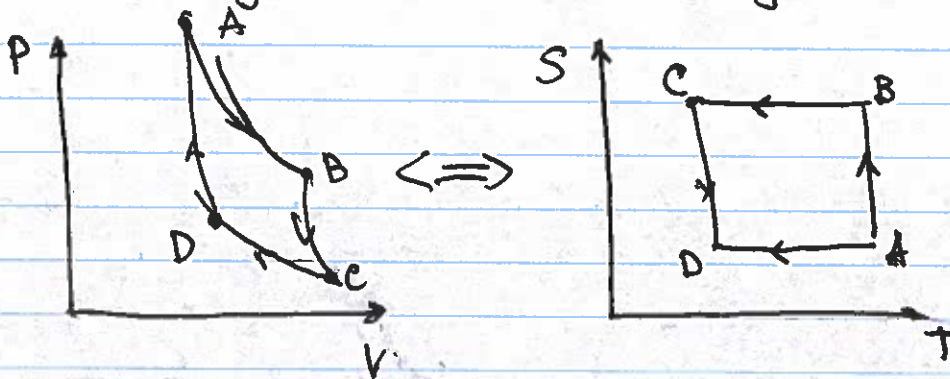
Isochoric process :   $dQ = nC_v \, dT$

$$\Delta S = \int_{T_1}^{T_2} \frac{nC_v \, dT}{T} = nC_v \ln \frac{T_2}{T_1}$$

For solid / liquids   $dQ = mC \, dT$   $\Rightarrow$   $\Delta S = mC \ln \frac{T_2}{T_1}$

Isobaric process:   $dQ = nC_p \, dT$

$$\Delta S = \int_{T_1}^{T_2} \frac{nC_p \, dT}{T} = nC_p \ln \frac{T_2}{T_1}$$

Carno cycle on a S-T diagram



area of the cycle
represent total wore

$$W = \int P dV$$

area of the cycle
represents total heat

$$Q = \int T dS$$

Since entropy is a state variable, any ideal closed cycle is _reversible_ and can be done in the opposite direction, with no other changes in the universe.

Moreover, in an ideal reversible process a _system_ must always stay in equilibrium (i.e., the whole system is in the same state, and any of its part is described by the same state variables.

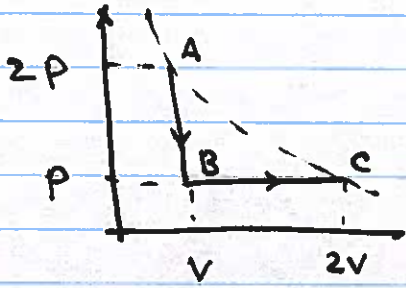So to approach such ideal process, we have to do everything slowly!
  - isothermal compression / expansion
  - slow adiabatic           "

Imperfections arise from any channels in which the energy can escape
  - friction of parts
  - interaction with unisolated environment
  - irreversible processes (mixing of different substances, quick expansion)

Entropy calculations

What is a change in entropy along the path ABC?

Solution 1. $\Delta S_{ABC} = \Delta S_{AB} + \Delta S_{BC}$

AB - isochoric process $\qquad$ $dQ = nC_v\,dT$

$$\Delta S_{AB} = \int_{T_A}^{T_B} \frac{dQ}{T} = nC_v \int_{T_A}^{T_B} \frac{dT}{T} = nC_v \ln \frac{T_B}{T_A} < 0$$

BC - isobaric process $\qquad$ $dQ = nC_p\,dT$

$$\Delta S_{BC} = \int_{T_B}^{T_C} \frac{dQ}{T} = nC_p \int_{T_B}^{T_C} \frac{dT}{T} = nC_p \ln \frac{T_C}{T_B}$$

$$T_A = T_C = \frac{2PV}{nR} \qquad\qquad T_B = \frac{PV}{nR}$$

$$\Delta S_{ABC} = \Delta S_{AB} + \Delta S_{BC} = -nC_v \ln 2 + nC_p \ln 2 = n(C_p - C_v)\ln 2 = nR\ln 2$$
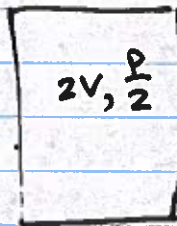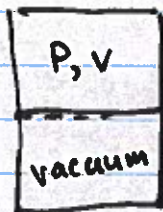
Solution 2 $\qquad$ Since $T_A = T_C$ one can change the state of gas following an isothermal expansion, and the change in entropy is the same, since it is a state variable.
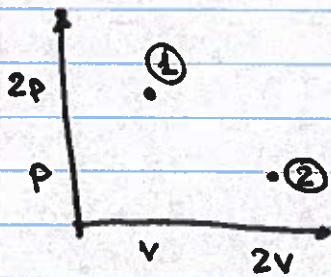
$$\Delta S_{A\to C} = \frac{Q_{AC}}{T_A} = \frac{W_{AC}}{T_A} = \frac{nRT_A \ln V_C/V_A}{T_a} = nR \ln \frac{V_C}{V_A} = nR \ln 2$$

This is a powerful observation, since it will allow us to find the entropy change even for irreversible processes

Example:   free gas expands   $V \to 2V$

P, V

vacuum

$\Rightarrow$

$2V, \frac{P}{2}$

$T = $ const , $\Delta E_{int} = 0$
$Q = 0$ , yet
entropy increases
Sign that the process is
irreversible

Physically , ~~so~~ the gas "jumped" from ① to ②
However, since we can find a ~~process~~ reversible process with the same initial and final conditions, the change in entropy will be the same

$$\Delta S = nR \ln \frac{V_2}{V_1} = nR \ln 2 \quad \text{for } V_2 = 2V_1$$

In ideal reversible cycle the change in entropy is zero.

However, for any natural process $\Delta S > 0$

Second law of thermodynamics ! ~~the entropy~~ of an isolated system can never be negative

or

The entropy of the Universe always increases.

Van-der-Waals gas: accounts for finite
molecule size and inter-molecular interactions

Van-der-Waals equation of state:

$$\left(P + a\left(\frac{n}{V}\right)^2\right)(V - nb) = nRT$$

<span style="color:red">interactions</span>     <span style="color:red">finite size</span>

The values of $a$ and $b$ are determined
experimentally

Can use to calculate the entropy change
at constant temperature $T$ as gas expands $V \to 3V$?

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

$$W = \int_V^{3V} P\,dV = \int_V^{3V}\left[\frac{nRT}{V-nb} - a\left(\frac{n}{V}\right)^2\right] dV =$$

$$= \int_V^{3V} \frac{nRT}{V-nb}\,dV - an^2 \int_V^{3V} \frac{dV}{V^2} = nRT\ln(V-nb)\Big|_V^{3V} +$$

$$+ \frac{2an^2}{V}\Big|_V^{3V} = nRT\ln\left(\frac{3V-nb}{V-nb}\right) - \frac{2an^2}{3V}$$

$$\Delta S = \frac{W}{T} = nR\ln\left(\frac{3V-nb}{V-nb}\right) - \frac{2an^2}{3V\cdot T}$$