

# Chapter 5:: The 2nd law of thermodynamics

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# Entropy

## Abstract

Entropy is a measure of the degree of disorder/randomness in an arbitrary system. We can use this concept to discuss matters such as spontaneous and non spontaneous processes.

## Spontaneous & non spontaneous processes

A spontaneous change is one that occurs without a continuous input of energy from an outside system. A good example would be gravitational potential. We can increase the rate of a spontaneous process by introducing a catalyst to the system. **A spontaneous process is not always fast.**

Non spontaneous processes aren't impossible, but they require input of external energy or a **more spontaneous** reaction to proceed.

## Example

A good example of an impossible spontaneous process is a ball starting to bounce on a surface spontaneously. This would require all particles under it (approx  $6.02E23$  particles) to start vibrating in the same direction at the same time. The chance of this being possible is basically 0.

## Estimating spontaneity

The first law of thermodynamics accounts for energy in a system, but it does not predict the spontaneity of the energy transfer involved. We will use entropy to do this. A process is spontaneous if and only if  $\Delta S > 0$ .

## Entropy as a state function

Entropy is a measure of how dispersed the energy of a system is (in units of  $\frac{J}{K}$ ). We can start with this property::

$$\Delta S_{\Omega} = \Delta S_{\sigma} + \Delta S_{\bar{\sigma}}$$

Where  $\Omega$  is the universe,  $\sigma$  is an arbitrary system, and  $\bar{\sigma}$  is the surroundings.

To calculate the absolute entropy of a system, the following formula is used::

$$S = k_b \ln(W) \implies \Delta S = k_b (\ln(W_0) - \ln(W_1))$$

Where  $k_b = 1.38E - 23 \frac{J}{K}$  is the boltzman constant, and  $W = 2^n$  is the number of possible arrangements of position and energy of all molecules in the system (microstates) for  $n \in \mathbb{N}$  particles. The macrostate with the **highest entropy** also has the **greatest dispersal of energy**.

## Multiplicity of energy

Assume we have a hypothetical solid system with four atoms and a total energy of  $E$ . How many ways can we distribute that energy among the 4 atoms? Clearly there are 4 ways to distribute 1 unit of energy among 4 atoms because the system is small. However, if there are  $N$  atoms, and total energy is  $qE$ , then the number of microstates is modelled by the following formula::

$$W(N, q) = \frac{(q + N - 1)!}{q!(N - 1)!}$$

## Bringing it all together

A hot and a cold bar, each made up of 4 atoms, are pushed together. What will happen? If the cold bar has 1 quantum of energy and the hot bar has 5 quanta of energy in the initial state, show that heat transfer is spontaneous by calculating  $\Delta S_{\Omega}$  for the process.

We can start by calculating the combinations of microstates for each process.

## Entropy at the molecular level

In any system, when  $T$  increases,  $S$  will also increase proportionally with it. This makes sense because the faster the particles move, the more disorder there is in the system overall.

## Statistical definition of entropy

We can model the change in entropy of a system between two states with the following formula::

$$\Delta S = S_2 - S_1 = k_b \ln\left(\frac{W_2}{W_1}\right)$$

This is possible since entropy is a state function.

## Entropy change due to mixing of ideal gases

Assume that mixing two ideal gases will sum up their entropies::

$$\Delta S_{mix} = \Delta S_A + \Delta S_B = n_A R \ln\left(\frac{V_A + V_B}{V_A}\right) + n_B R \ln\left(\frac{V_A + V_B}{V_B}\right)$$

By Avogadro's law,  $T \equiv \text{const} \wedge P \equiv \text{const} \implies V \propto n$ , so,

$$\Delta S_{mix} = n_A R \ln\left(\frac{n_A + n_B}{n_A}\right) + n_B R \ln\left(\frac{n_A + n_B}{n_B}\right)$$

Using the laws of logarithms, we have that::

$$\Delta S_{mix} = -n_A R \ln\left(\frac{n_A}{n_A + n_B}\right) - n_B R \ln\left(\frac{n_B}{n_A + n_B}\right)$$

Further simplifying the expression, we get::

$$\Delta S_{mix} = -R(n_A \ln(\chi_A) + n_B \ln(\chi_B))$$

Recall that  $\chi_\xi < 1 \forall \xi \in U$

## Isothermal expansion of an ideal gas

To calculate change in entropy for a process like this, we use::

$$\Delta S = nR \ln\left(\frac{V_2}{V_1}\right)$$

Heat absorbed by the expansion is given by::

$$q_{rev} = nRT \ln \left( \frac{V_2}{V_1} \right)$$

So we have that::

$$\frac{q_{rev}}{T} = nR \ln \left( \frac{V_2}{V_1} \right) \implies \Delta S = \frac{q_{rev}}{T}$$

### Example

One mole of  $N_2$  at  $20.5^\circ C$  and  $6.00bar$  undergoes a transformation to the state described by  $145^\circ C$  and  $2.75bar$ . Calculate  $\Delta S$  if

$$C_{P,m}(T) = 30.81 - (11.87E - 3)T + (2.3968E - 5)T^2 - (1.0176E - 8)T^3$$

We can invoke the formula::

$$\Delta S = -nR \ln \left( \frac{P_2}{P_1} \right) + n \int_{T_1}^{T_2} \frac{C_{P,m}(T)}{T} dT$$

$$= \int_{293.65}^{418.15} \frac{30.81}{T} - (11.87E - 3) + (2.3968E - 5)T - (1.0176E - 8)T^2$$

After integrating each term and some calculations, we have that::

$$6.48 + \left[ 30.81 \ln(T) - (11.87E - 3)T + \frac{2.3969E - 5}{2}T^2 - \frac{1.0176E - 8}{3}T^3 \right]_{293.65}^{418.15} \approx 16.8 JK^{-1}$$

### The 2nd law of thermodynamics

Any system  $\sigma$  is significantly smaller than the surroundings. We can consider the surroundings  $\sigma^{-1}$  is an infinitely large reservoir. Thus, we can say::

$$dq_{surr,rev} = dq_{surr,irrev} = dq_{surr}$$

Since entropy is a state function, we can express change in entropy in the surroundings as the ratio::

$$\Delta S_{surr} = \frac{q_{surr}}{T_{surr}}$$

Consider the isothermal expansion of an ideal gas. Heat absorbed by the system is just  $q_{sys} = nRT \ln \left( \frac{V_2}{V_1} \right) \implies q_{surr} = -nRT \ln \left( \frac{V_2}{V_1} \right)$ . So for a **reversible** process,

$$\Delta S_{\Omega} = nR \ln \left( \frac{V_2}{V_1} \right) + \left[ -nR \ln \left( \frac{V_2}{V_1} \right) \right] = 0$$

For an irreversible process (i.e. a gas expanding into a vacuum),

$$\Delta S_{sys} = nR \ln \left( \frac{V_2}{V_1} \right)$$

### Cases (IMPORTANT)

- For a reversible process,  $\Delta S_{\Omega} = 0$
- For an irreversible process,  $\Delta S_{\Omega} > 0$
- Overall,  $\Delta S_{\Omega} \geq 0$

### Example

One mole of an ideal gas at  $25^{\circ}C$  is allowed to expand adiabatically and irreversibly from  $1L$  to  $10L$  with no work done. What is the final temperature of the gas? Calculate the values of  $\Delta S_{sys}$ ,  $\Delta S_{surr}$  and  $\Delta S_{univ}$ .

We know that  $q = 0 \wedge w = 0 \implies \Delta U = 0$  in this system. So we can use the formula to calculate.

$$\Delta S_{sys} = nR \ln \left( \frac{V_2}{V_1} \right)$$

$$\Delta S_{sys} = (8.3145) \ln \left( \frac{10}{1} \right) = 19.1 JK^{-1} mol^{-1}$$

$$q = 0 \implies \Delta S_{surr} = 0 \implies \Delta S_{\Omega} = 19.1 JK^{-1} mol^{-1} \implies R \equiv spont.$$

## Entropy change due to phase transitions

- In general,  $\Delta_{vap}S^\circ > \Delta_{fus}S^\circ$  for the same substance.
- Solid to liquid transitions result in relatively small increase in entropy.
- Arrangements of molecules in gaseous state is completely random, implying larger increase in entropy from liquid to gas.

The molar entropy for oxygen gas ( $O_2$ ) is shown on **slide 52**. We can see that phase changes have a large vertical jump on the entropy axis.

We can model the entropy change of the system during a phase change as the following equation::

$$\Delta S_{sys} = \frac{\Delta H_{trans}}{T_{trans}} \implies \Delta S_{surr} = -\frac{\Delta H_{trans}}{T_{trans}}$$

So at a phase transition,  $\Delta S_\Omega = 0$

For temperature dependence, we can model entropy change as::

$$\Delta S = n\bar{C}_P \ln\left(\frac{T_2}{T_1}\right)$$

To find total entropy change of water over an interval of temperature with 1 phase change (liquid to gas), we can say::

$$\Delta S_\Omega = \sum_{S \in \Omega} \Delta S_i = C_P(H_2O(l)) \ln\left(\frac{T_2}{T_1}\right) + \frac{\Delta H_{trans}}{T_2} + C_P(H_2O(g)) \ln\left(\frac{T_3}{T_2}\right)$$

## The 3rd law of thermodynamics

In essence, the entropy of a perfect crystal at  $0K$  is 0. This law gives us the basis in calculating absolute entropies.

### Proof

$\exists$  **exactly one** microstate at  $T = 0K$ , so  $W = 1^{6.02E23} = 1$ . So  $S = k_b \ln(W) = k_b \ln(1) = 0$  ■

We can also express heat capacities and entropy of a perfect crystal as the following limits::



$$\lim_{T \rightarrow 0} S = 0, \lim_{T \rightarrow 0} C_P = 0, \lim_{T \rightarrow 0} C_V = 0$$

We have never reached  $0K$ . The world record for lowest temperature is  $100pK$ .

## Absolute entropy

Assume that the following holds::

$$q_{rev,P} = C_P dT$$

Therefore at  $298K$ ,

$$S_{gas}(T) = S(0K) + \int_0^{T_{fus}} \frac{C_{P,sol}}{T} dT + \frac{\Delta H_{fus}}{T_{fus}} + \int_{T_{fus}}^{T_{boil}} \frac{C_{P,liq}}{T} dT + \frac{\Delta H_{vap}}{T_{boil}} + \int_{T_{boil}}^{T_f} \frac{C_{P,gas}}{T} dT$$

If not at  $298K$ ,

$$\Delta S^T = \Delta S_{298.15K} + \int_{298.15}^T \frac{n\Delta C_p}{T} dT = \Delta S_{298.15K} + nC_P \ln \left( \frac{T}{298.15} \right)$$

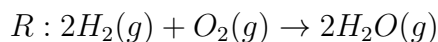
## Entropy changes for chemical reactions

Simply invoke Hess' law for entropy.

$$\Delta S_r = \sum v_p S_p - \sum v_r S_r$$

## Example

If a spark is applied to a mixture of  $H_2(g)$  and  $O_2(g)$ , an explosion occurs and water is formed. The gaseous water is cooled to  $100^\circ C$ . Calculate the entropy change when  $2mol$  of gaseous  $H_2O$  is formed at  $100^\circ C$  and  $1atm$  from  $H_2(g)$  and  $O_2(g)$  at the same temperature and each at a particular pressure of  $1atm$ .



$$\Delta S(25^\circ C) = 2\bar{S}_{H_2O(g)} - \bar{S}_{O_2(g)} - 2\bar{S}_{H_2(g)}$$

$$= 2(188.72) - 205.04 - 2(130.57) = -88.74 \frac{J}{K}$$

In order to find  $\Delta S$  at  $100^\circ C, 1 atm$ , we need to know the heat capacities of the reactants and products from the table.

$$\Delta C_P(25^\circ C) = 2\bar{C}_P(H_2O(g))\bar{C}_P(O_2(g)) - 2\bar{C}_P(H_2(g))$$

$$= 2(33.6) - 29.4 - 2(28.8) = -19.8 \frac{J}{K}$$

$$\Delta S(100^\circ C) = \Delta S(25^\circ C) + \int_{298}^{373} \frac{\Delta C_P}{T} dT$$

$$-88.74 \frac{J}{K} - 19.8 \ln \left( \frac{373}{298} \right) = -93.18 \frac{J}{K}$$