

Review of classical thermodynamics

Fundamental Laws, Properties and Processes (2)

Entropy and the Second Law

Concepts of equilibrium

Reversible and irreversible processes

The direction of spontaneous change

Entropy and spontaneous/irreversible processes

Calculation of entropy in isochoric and isobaric processes

Calculation of entropy in reversible and irreversible processes

Reading: Chapters 3.1 – 3.5, 3.14 – 3.17 of Gaskell
or the same material in any other textbook on thermodynamics

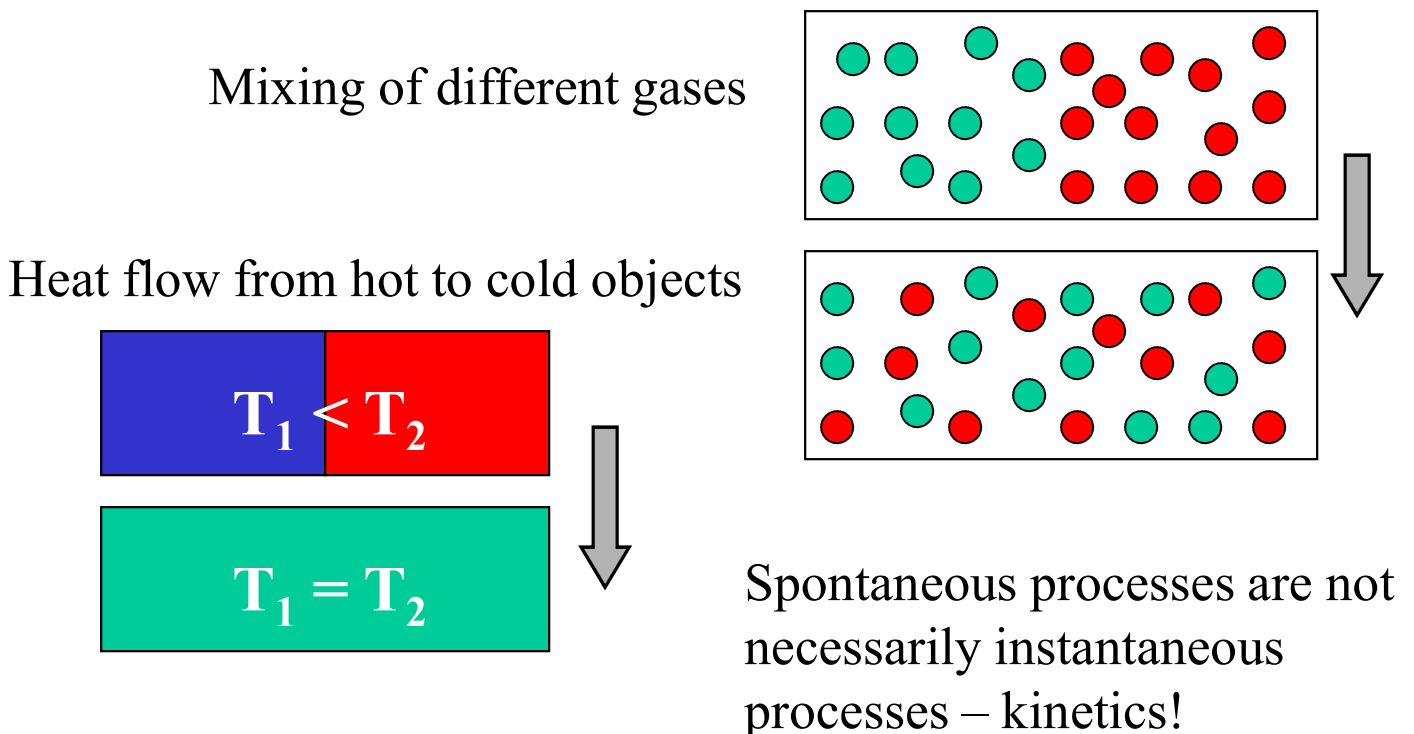
Spontaneous transitions

A system left to itself will either

1. Remains in the same state indefinitely (system is in **equilibrium**). The system will move from the equilibrium state only if acted on by some external impact.
2. Will move, of its own accord, to some other state. The system in this case is in a **non-equilibrium** state and will move towards equilibrium state in a natural or **spontaneous** process.

Spontaneous transition from non-equilibrium state to the equilibrium state cannot be reversed without application of an external force – it is an **irreversible** process.

Examples of spontaneous/irreversible processes:



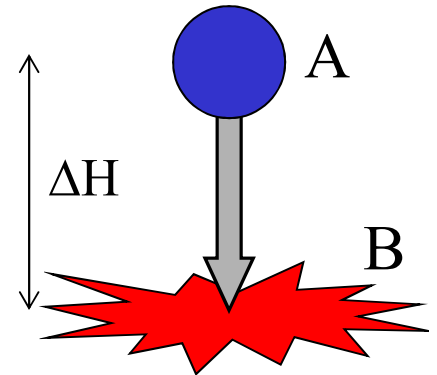
How to predict which process will proceed spontaneously?

1st law: U and H are state functions - if the system is going from A to B, $\Delta U(A \rightarrow B) = -\Delta U(B \rightarrow A)$ or $\Delta H(A \rightarrow B) = -\Delta H(B \rightarrow A)$

But first law does not tell us which reaction, forward or reverse is natural or spontaneous one.

Intuition:

The energetic driving force- the tendency to fall to a lower potential energy, e.g. release heat in a reaction.



Indeed, often spontaneous changes are exothermic (reaction produces heat),

e.g. $\text{H}_2 (\text{gas}) + \frac{1}{2} \text{O}_2 (\text{gas}) \rightarrow \text{H}_2\text{O} (\text{liquid}) \quad \Delta H = -286 \text{ kJmol}^{-1}$

But, reactions can also occur spontaneously which are endothermic,

e.g. $\text{H}_2\text{O} (\text{liquid}, 105^\circ\text{C}) \rightarrow \text{H}_2\text{O} (\text{gas}, 105^\circ\text{C}) \quad \Delta H = +44 \text{ kJmol}^{-1}$

A negative sign of ΔH favors but does not guarantee spontaneity.

Quantification of irreversibility

It is desirable to find some common measure of the tendency of a system to change spontaneously. This measure should be

- A thermodynamic property (state function).
- It should change in a characteristic manner (e.g. always increase) when a process proceeds spontaneously.

Such function, entropy (from τροπή - *transformation* in Greek), has been introduced by Clausius in 1850.

Second Law of Thermodynamics can be formulated in different ways. One possible formulation is:

There exist a state function, the entropy S , which for all reversible processes is defined by $dS = \delta q_{\text{rev}}/T$

and for all irreversible processes is such that $dS > \delta q/T$

or in general, $dS \geq \delta q/T$

Entropy is a state function whose change is defined for a reversible process at T where q is the heat absorbed:

$$\Delta S = q/T$$

For an isolated system $\delta q = 0 \Rightarrow dS \geq 0$. **Entropy is maximized in any spontaneous process.** This will be the basis for definition of the equilibrium conditions.

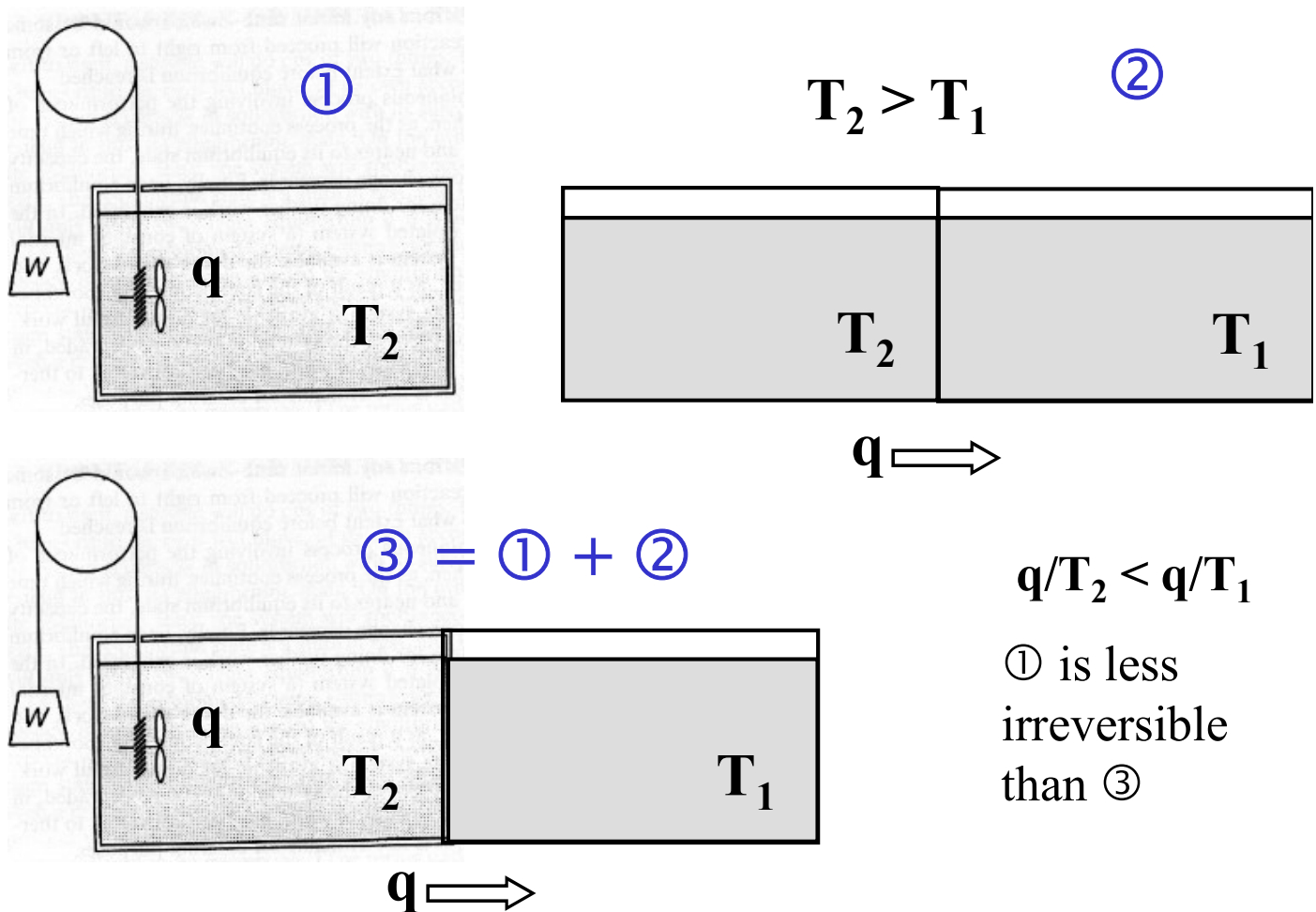
Why q/T ?

For qualitative understanding of why the quantity q/T is used as a measure of the degree of irreversibility let's consider an example from Gaskell, §3.3.

Let's consider two irreversible processes:

1. Conversion of work to heat
2. Flow of heat down a T gradient

Three processes with different degree of irreversibility:

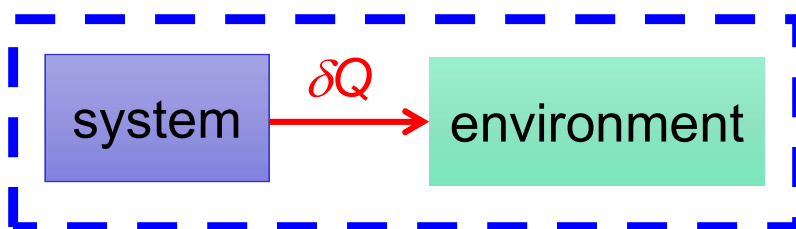


All three processes are irreversible. The ③ is just a sum of ① and ②: should be the most irreversible. Both heat production and temperatures are important in defining a scale of irreversibility.

Summary on Entropy

- Entropy is a state function.
- When the weight-heat reservoir system, discussed above, undergoes a spontaneous process which causes the adsorption of heat q at a constant temperature T , the entropy produced by the system $\Delta S = q/T$. The increase in entropy, caused by the process, is thus a measure of the degree of irreversibility. Thus, S is not conserved.
- The increase in entropy due to the occurrence of an irreversible process arises from the degradation of energy potentially available for useful work into heat.
- In a reversible process (the driving force is infinitesimal and the process proceeds at an infinitesimal rate) the system moves through a continuum of equilibrium states and the entropy is not created, it can only be transferred from one part of the system to another. For more on entropy in reversible processes see Gaskell, §3.4 – 3.9.
- The entropy of an adiabatic system cannot decrease. It increases in an irreversible process and remains constant during a reversible process.

S of an open system can decrease at the expense of entropy increase of another system (environment)



$$dS_{tot} = dS_{sys} + dS_{env} \geq 0$$

The Second Law Again

We can reformulate the second law in the following way:

For every thermodynamic system there exist an extensive state function called entropy which can be calculated by a reversible path from an arbitrary chosen reference state by integrating the heat absorbed by the system divided by the absolute temperature.

The entropy of a system plus its surroundings (together forming “the universe” – an isolated system) **never decreases** and increases in any irreversible process.

The 3rd law of thermodynamics:

The third law of thermodynamics, states that if one could reach absolute zero temperature (all the thermal motion of atoms could be removed) **and a complete internal equilibrium**, all bodies would have the same entropy. In other words, a body at absolute zero could exist in only one possible state, which would possess a definite energy, called the zero-point energy. This state is defined as having zero entropy.

The 3rd law has been first formulated by Walter Nernst and also known as the Nernst heat theorem.

The 3rd law allows us to define absolute values of entropy at a given T:

$$dS = \int_0^T \frac{\delta q_{\text{rev}}}{T} = \int_0^T \frac{c_P}{T} dT \quad \text{thus } S_T = S_0 + \int_0^T \frac{c_P}{T} dT \quad \text{where } S_0 = 0$$

Combined statement of the 1st and 2nd laws

For a closed system and a reversible process

$dU = \delta q - \delta w$, $\delta q = TdS$, and, assuming that work due to the volume change is the only form of work performed by the system, $\delta w = PdV$

Combining these equations together we get $dU = TdS - PdV$

$$U = U(S, V) \Rightarrow dU = (\partial U / \partial S)_V dS + (\partial U / \partial V)_S dV$$

Comparing the equations we see that

$$T = (\partial U / \partial S)_V$$
$$P = - (\partial U / \partial V)_S$$

S and V are referred to as the “natural” choice of independent variables to describe the internal energy.

If the function $U(S, V)$ is known, we have all information about the system, i.e. U can be calculated directly and T and P can be calculated from the derivatives of the function.

Thus, $U = U(S, V)$ is a fundamental equation of state.

In a system with $U = \text{const}$ and $V = \text{const}$ equilibrium occurs when the entropy is maximized, $dS = 0$ – the definition of S through the second law of thermodynamics allows to predict the direction of spontaneous change in a system that initially is not in equilibrium.

Entropy calculation

Constant volume process

$$dS = \frac{\delta q}{T} \quad c_v = \left(\frac{\delta q}{dT} \right)_v \quad \Rightarrow \quad \delta q = dU = c_v dT$$

$$\boxed{dS = \frac{c_v dT}{T}} \quad \int dS = \Delta S = \int_{T_i}^{T_f} \frac{c_v}{T} dT \quad \left(\frac{\partial S}{\partial U} \right)_v = \frac{1}{T} > 0$$

Constant pressure process

$$dS = \frac{\delta q}{T} \quad c_p = \left(\frac{\delta q}{dT} \right)_p \quad \Rightarrow \quad \delta q = dH = c_p dT$$

$$\boxed{dS = \frac{c_p dT}{T}} \quad \int dS = \Delta S = \int_{T_i}^{T_f} \frac{c_p}{T} dT$$

Example: Calculate the difference in entropy between 3 moles of O₂ gas at 800 K and at 300 K. Pressure is 1 atm in each case.

$$c_p = 30 + 4.18 \times 10^{-3} T - 17 \times 10^4 T^{-2} \quad [\text{Jmol}^{-1}\text{K}^{-1}]$$

$$\begin{aligned} \int dS = \Delta S &= 3 \int_{300}^{800} \frac{c_p}{T} dT = 3 \int_{300}^{800} \left(\frac{30}{T} + 4.18 \times 10^{-3} - \frac{17 \times 10^4}{T^3} \right) dT = \\ &= 3 \left(30 \ln \left[\frac{800}{300} \right] + 4.18 \times 10^{-3} [800 - 300] + 8.5 \times 10^4 \left[\frac{1}{800^2} - \frac{1}{300^2} \right] \right) = \\ &= 94 \text{ J K}^{-1} \end{aligned}$$

Entropy production – reversible phase transformation

Example: One mole of liquid lead at its equilibrium freezing temperature, 600°K freezes slowly/reversibly at 1 atm pressure to solid state. Calculate the entropy production.

$$c_p(\text{liquid}) = 32.4 - 3.1 \times 10^{-3} T \text{ [Jmol}^{-1}\text{K}^{-1}\text{]}$$

$$c_p(\text{solid}) = 23.6 + 9.75 \times 10^{-3} T \text{ [Jmol}^{-1}\text{K}^{-1}\text{]}$$

$$\Delta H_m = 4810 \text{ Jmol}^{-1} - \text{latent heat of melting}$$

Entropy created/produced:

$$\Delta S = S_{\text{solid}}^{\text{Pb}} + S_{\text{final}}^{\text{th.res.}} - (S_{\text{liquid}}^{\text{Pb}} + S_{\text{initial}}^{\text{th.res.}}) = \Delta S^{\text{Pb}} + \Delta S^{\text{th.res.}}$$

$$\Delta S^{\text{Pb}} = \frac{q^{\text{Pb}}}{T} = -\frac{4810}{600} \quad \text{negative – heat is removed}$$

$$\Delta S^{\text{th.res.}} = \frac{q^{\text{th.res.}}}{T} = \frac{4810}{600} \quad \text{positive - heat flows into reservoir}$$

$$\Delta S = \Delta S^{\text{Pb}} + \Delta S^{\text{th.res.}} = 0$$

There **is** change in entropy in both lead and the thermal reservoir. The **sum**, however, is zero in reversible process.

Entropy production – irreversible process

Example: One mole of supercooled liquid lead spontaneously freezes at 590°K and 1 atm pressure to the solid state. Calculate the entropy production.

$$C_p(\text{liquid}) = 32.4 - 3.1 \times 10^{-3} T \text{ [Jmol}^{-1}\text{K}^{-1}\text{]}$$

$$C_p(\text{solid}) = 23.6 + 9.75 \times 10^{-3} T \text{ [Jmol}^{-1}\text{K}^{-1}\text{]}$$

$$\Delta H_m = 4810 \text{ Jmol}^{-1} - \text{latent heat of melting}$$

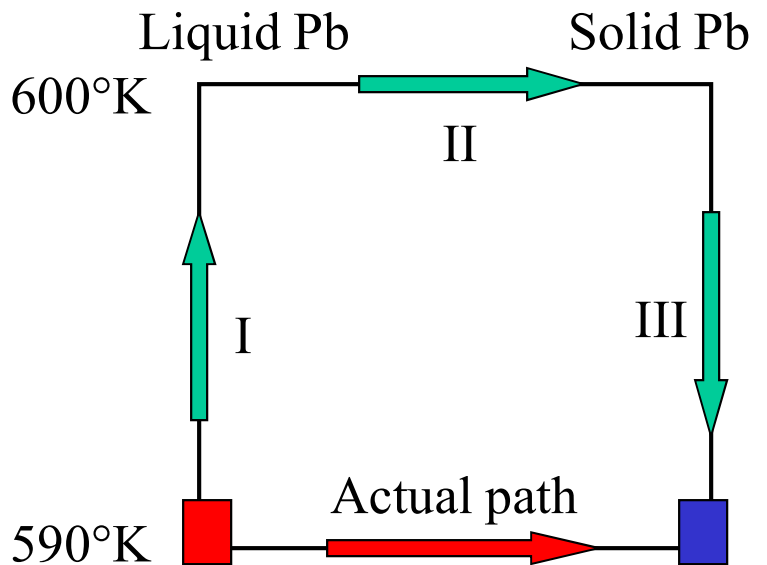
Entropy created/produced:

$$\Delta S = S_{\text{solid}}^{\text{Pb}} + S_{\text{final}}^{\text{th.res.}} - (S_{\text{liquid}}^{\text{Pb}} + S_{\text{initial}}^{\text{th.res.}}) = \Delta S^{\text{Pb}} + \Delta S^{\text{th.res.}}$$

First, let's calculate change in entropy for Pb

The entropy changes along the actual path is unknown - the process is irreversible.

But since entropy is a state function, we can calculate the entropy change along a reversible path.



$$\Delta S^{\text{Pb}} = \Delta S^{\text{I}} + \Delta S^{\text{II}} + \Delta S^{\text{III}}$$

Entropy change in the piece of lead, ΔS^{Pb} :

(I) isobaric reversible heating

$$\Delta S^I =$$

(II) isothermal isobaric process of freezing

$$\Delta S^{II} =$$

(III) isobaric reversible cooling

$$\Delta S^{III} =$$

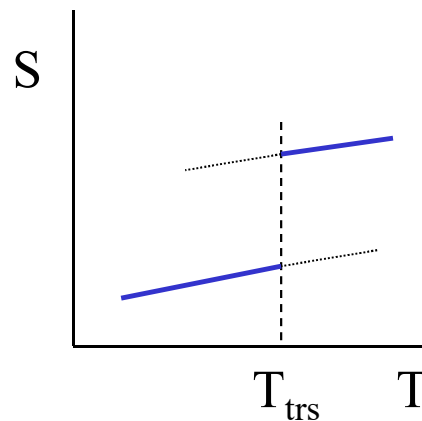
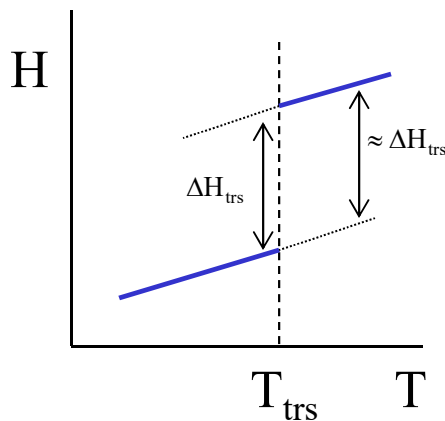
$$\Delta S^{Pb} = \Delta S^I + \Delta S^{II} + \Delta S^{III} =$$

There is also a change in entropy in the surroundings. This relates to the heat transfer to the constant temperature reservoir at constant pressure.

$$\Delta S^{th.res.} =$$

Entropy and phase transformations

The example considered above shows that **the entropy change in “the universe” is positive** if a low-temperature phase converts into a high-temperature phase at a temperature above the equilibrium transition temperature. Or if the high-T phase converts to a low-T one at T below the transition temperature. Otherwise it is negative and the transition is prohibited by the 2nd law of thermodynamics – will not go spontaneously.



$$\Delta S_{\text{trs}} = \frac{\Delta H_{\text{trs}}}{T_{\text{trs}}}$$

$$\left(\frac{dH}{dT} \right)_P = c_P$$

$$\left(\frac{dS}{dT} \right)_P = \frac{c_P}{T}$$

Summary

Make sure you understand terminology and concepts:

- Spontaneous/irreversible processes
- The direction of spontaneous change
- Entropy – quantitative measure of irreversibility
- 2nd law of thermodynamics
- Entropy in a reversible process
- Fundamental equation: $U = U(S, V)$ $dU = TdS - PdV$
- Calculation of entropy in isochoric and isobaric processes
- Calculation of entropy in reversible and irreversible processes