

Spontaneous processes : Entropy & Energy

- o 2nd Law - various forms
 - transport of entropy & relation to heat & temperature
 - key role of entropy production ('inside' system)
 - ↙ still applies
- o Energy versions & application to different systems types, & to multiple processes/steps.
 - ↳ Helmholtz free energy
 - Cubbs free energy
 - Enthalpy

2nd law for
non-isolated
systems, in
terms of energy
potentials.



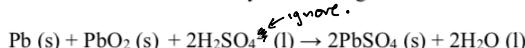
- Questions — calculate free energy/enthalpy (from table etc)
 — state: spontaneous? exothermic? Exergonic?

2018
 (Summer school)

29) Given the table of standard Gibbs free energies of formation below:

| Substance | Phase | Chemical Formula | ΔG_f° (kJ.mol ⁻¹) |
|----------------|--------|--------------------------------|--|
| Water | liquid | H ₂ O | -237.14 |
| Water | gas | H ₂ O | -228.61 |
| Oxygen | gas | O ₂ | 0 |
| Hydrogen | gas | H ₂ | 0 |
| Carbon dioxide | gas | CO ₂ | -394.39 |
| Lead | solid | Pb | 0 |
| Lead sulfate | solid | PbSO ₄ | -813.2 |
| Lead oxide | solid | PbO ₂ | -215.48 |
| Sulfuric acid | liquid | H ₂ SO ₄ | -744.63 |

- a. Determine the overall change in Gibbs free energy for the following lead acid battery reaction under standard conditions. Show your working.

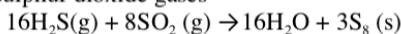


(3 marks)

- b. Does this reaction take place spontaneously under standard conditions? Justify your answer.
 (1 mark)

Answer: _____

- 34) Solid sulphur is commonly formed at the vents of volcanoes in a reaction between hydrogen sulphide and sulphur dioxide gases



The enthalpy change $\Delta H = -1876 \text{ kJ/mol}$

The entropy change $\Delta S = -3.424 \text{ kJ/mol}^\circ\text{K}$

- a. Is this reaction exothermic or endothermic?

(1 mark)

Answer: _____

- b. Why is the entropy change for this reaction negative?

(1 mark)

Answer:

- c. Is this reaction exergonic or endergonic at temperature T = 298K? Justify your answer.
 (2 marks)

Answer:

- d. Does this reaction take place spontaneously at 298K? Justify your answer. (1 mark)

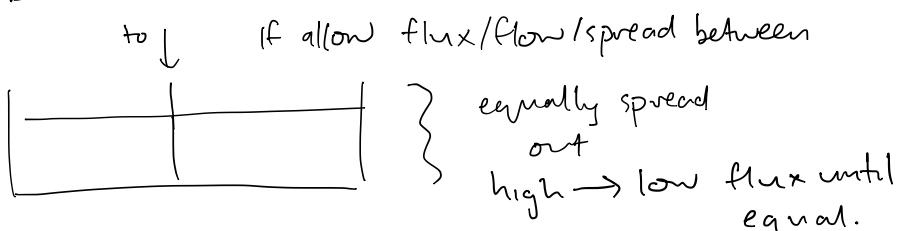
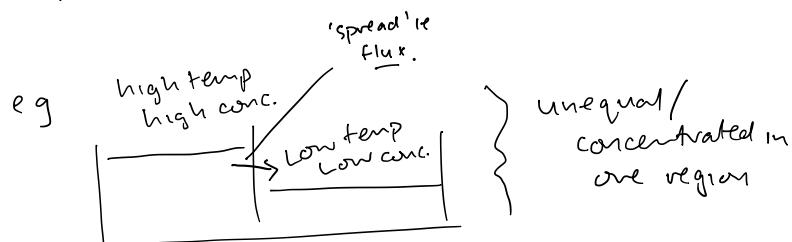
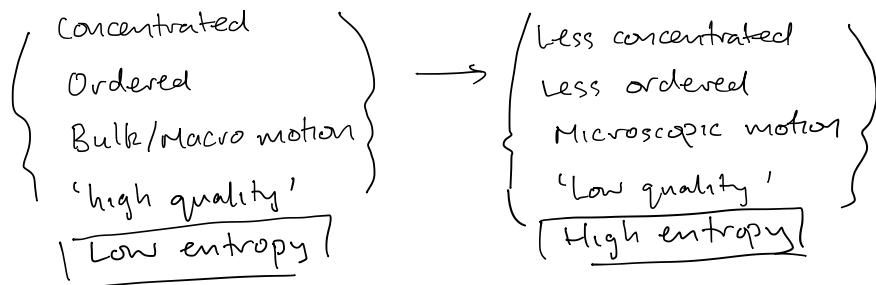
Answer:

Entropy & 2nd Law : a summary (mainly for interest/guidance)

2nd Law short version:

'without assistance' (*)

Things (energy, mass etc) tend to 'naturally'
'spread out' as much as possible



(*) Key is the 'extra' entropy 'production' inside system, over } ie once
& above any added/subtracted by external transport } interaction
is accounted for.

→ different systems (open, closed, isolated) allow
different external transport/interactions

→ allow different simplifications of } reformulations of
the same 'law' } same thing.

→ law focuses on the 'not due to interactions/transport' } 'natural' part.

↳ 'entropy production' ≥ 0 .

2.7 Spontaneous processes: entropy and energy

L10

As mentioned, the second law extends far beyond just steam engines. Here we look at the ideas in more generality. Later in the course we will see how to apply them to help us understand biological processes!

always about:
the
entropy
production

Warning: You may find some of the following material difficult - most do, including me! - the key takeaways are simple, however: know what sorts of processes are natural in which types of system and know how to calculate free energy or enthalpy changes in given processes.

2.7.1 The second law of thermodynamics

While the 'interpretation' of the second law of thermodynamics is subtle and relates to order/disorder, probability, the arrow of time etc, it's relatively simple to state verbally:

traditional

The second law of thermodynamics: The entropy of an isolated system is non-decreasing. That is, the change in entropy in any process is ≥ 0 .

It's also relatively simple to state mathematically:

$$\delta Q \leq T dS$$

where δQ is a 'small amount' of heat added, T is the absolute temperature and dS is a small change in entropy. This equation applies to any system, isolated or not: note that when $\delta Q = 0$ (isolated system) it becomes $dS \geq 0$ ($T \geq 0$ since it is the absolute temperature).

what about non-isolated?

idea: entropy transport assoc. with energy (heat) transfer:
 $\delta J = \delta Q/T$: heat transfers less entropy.
 $dS > \frac{\delta Q}{T}$
 in general.

Entropy is a state variable which is why we use a normal 'd' to represent a differential (small difference) in state space while δ just represents a small change of any quantity, not necessarily a state quantity.

For reversible processes we have

$\frac{\delta Q}{T}$
 Net external supply
 (due to heat flow at temp T)

$dS = \frac{\delta Q}{T}$
 $\delta Q \stackrel{\text{rev}}{=} T dS$
 internal 'production' of entropy
 entropy increases 'naturally'
 unlike energy

$$ds = \frac{\delta Q}{T} = \delta J$$

total entropy = entropy change of system. (rev) transported via heat

Heatwork¹: $TdS \sim \text{force} \times \text{displacement}$.

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internal entropy changes,
excluding
transport.

Oliver Maclaren

Note the analogy to e.g. PdV work. This equality condition can actually be taken as the **definition of a reversible process**. Another way of making this clear is to introduce the **entropy production** $\delta^i S$ via:

$$dS = \delta^r S + \delta^i S$$

↑ transported ↗ internal
where

$$TdS = T(\delta^r S + \delta^i S) = T\delta^r S + T\delta^i S$$

Total change = Transport + Internal source

'transported'

$$\delta Q = T\delta^r S, \quad \delta^i S \geq 0$$

internal 'source' or production
of entropy
(natural decay)

Reversibility corresponds to

$$dS - \frac{\delta Q}{T} = \delta^i S \geq 0$$

$$T\delta^i S^{rev} = 0$$

i.e. a reversible process is one in which there is no entropy production.
 Entropy production can be thought of as 'extra internal disorder' created during a process, over and above that introduced by external heat addition. Real processes are irreversible processes and have positive entropy production.

To 'integrate' or 'add up' a δ during an arbitrary, finite process we need to follow a *specific path*, while to determine a d change we just need to know the difference in start and end states: state variable differences are *path independent*. For finite heat transfers Q we can write

emphasise analogy to $w = \int pdV$ etc

$$w = \int \delta Q$$

(energy version)

'force \times distance'

$$Q \leq \int_{S_1}^{S_2} TdS$$

This is usually written in the form of the *Clausius inequality*:

emphasise $\delta Q/T$ as entropy transport

(entropy version)

$$\Delta S = S_2 - S_1 \geq \int_C \frac{\delta Q}{T}$$

Total increase in entropy \geq amount transported in

where the integral is a *path/line integral* that requires a specific path of integration to be given (and is denoted here by C). Note that we use Δ for the changes in a state variable but not for process variables like Q or W .

You will likely cover the details of these ideas in future courses. For now we will only need the basics!

2.7.2 Spontaneous processes - isolated systems

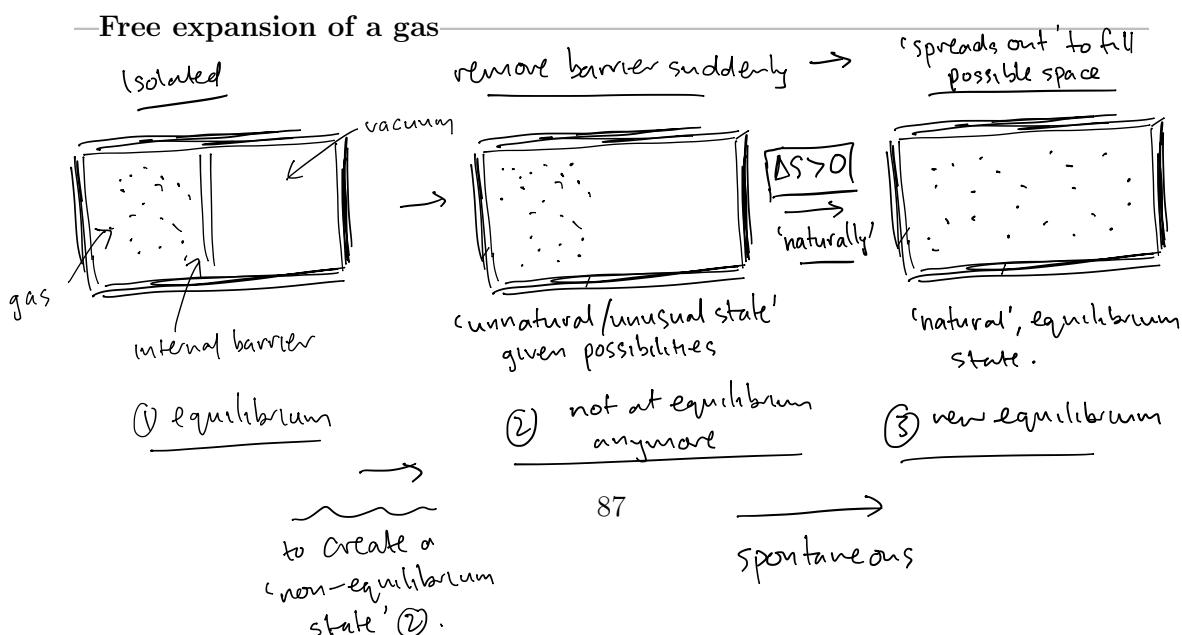
As mentioned above, all 'real' macroscopic processes are associated with a positive entropy production. A spontaneous process is one for which $\delta^i S \geq 0$. This applies whether the system is isolated or not because we account for the contribution of (reversible) heat transport.

Isolated systems

It's helpful to think about spontaneous processes in the context of isolated systems (indeed as we have seen the second law is usually stated for isolated systems). Here spontaneous processes are 'natural' or 'probable' processes that are likely to occur in isolated systems, i.e. without needing any mass or energy input. In the case of isolated systems the second law corresponds to $\Delta S \geq 0$ since $\delta Q = 0$ by definition.

You can thus imagine, when considering isolated systems, that these processes are 'driven' by entropy differences (in a similar way to how energy differences provide driving potentials for mechanical processes). Importantly, an isolated system will continue to undergo spontaneous processes that increase the entropy until the system maximises its entropy: thus thermodynamic equilibrium in an isolated system occurs at maximum entropy.

Note: $dS < 0$ can be true as long as have enough net low entropy flux.

$$\text{ie : } dS - \frac{\delta Q}{T} = \underbrace{\delta^i S}_{\substack{\text{extra} \\ \text{internal entropy} \\ \text{increase}}} \geq 0$$


Spontaneous: move from non-equilibrium to equilibrium.

eg 'remove barrier' (see 'activation energy' later)

Often: equilibrium + perturbation \rightarrow non-equilibrium

then non-equilibrium \rightarrow new equilibrium

$$\Delta S|_{\text{isolated}} \geq 0 \quad \left. \begin{array}{l} \text{Key is still} \\ \text{entropy production} \geq 0 \end{array} \right\}$$

actually easier to use this!
basic principle

2.7.3 Energy functions for spontaneous processes in non-isolated systems

equations
where $G = H - TS$
 $\Delta G < 0$ spontaneous

What about non-isolated systems? Again we could consider entropy production; however, just as it is helpful to think of entropy (not just entropy production) as providing the 'potential' or 'natural direction' for spontaneous processes in isolated systems, we can define 'natural potentials' for spontaneous process in different types of system.

translate

These can be specified either in terms of 'entropy-like' functions or in terms of 'energy-like' functions. Energy-type functions are most common, however. With this in mind we first translate the tendency of isolated systems to move towards the state of maximum entropy into an equivalent minimum energy principle. — Key is: what is held fixed?

diff. systems {

Maximum entropy, minimum energy

System state: U, N, V

↑
internal energy
↑
number particles
↑
volume

write:
 $S = S(U, N, V)$
 (entropy is state function.)

Entropy of a constant energy, workless system increases to max

Entropy production > 0 & isolated

88 Equilibrium:
 maximise S
 subject to constant U, N, V } isolated
 $\hookrightarrow dS \geq 0$ spontaneous

Internal energy of a workless, constant entropy system decreases to min \rightarrow net heat flux out
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$$\frac{SQ^{\text{in}}}{T} \rightarrow \boxed{\uparrow} \rightarrow \frac{SQ^{\text{out}}}{T} \quad SQ^{\text{out}} > SQ^{\text{in}} \text{ if } \Delta S = 0$$

+ prod. Oliver Maclarens

Energy version: Minimum internal energy

Entropy production ≥ 0 & constant total entropy, N, volume

Equilibrium:

$$\begin{aligned} &\text{minimise } U(S, N, V) \\ &\text{st. constant } S, N, V \end{aligned}$$

swap S, V roles.

1st-2nd:

$$\text{eq: } \boxed{dU - TdS = SW - TS^i S} \quad \text{when: } \boxed{SW = 0, dS = 0}$$

$dU < 0$ spontaneous

$$\boxed{dU = -TS^i S \leq 0} \quad \text{for } \boxed{SW = 0} \quad \boxed{dS = 0}$$

Other systems

For other types of system it can be shown that **other 'energy-like' functions are minimised at equilibrium**. We won't discuss the details here but deriving these make use of the important mathematical concept of a **Legendre transformation**. These show up in many mechanics and thermodynamics applications.

all just disguised version of the 2nd Law

In particular we find that the **Helmholtz free energy**, the **enthalpy** and the **Gibbs free energy** are each natural potentials for different types of system. We discuss these, and the types of system for which they are natural, below. In this course the enthalpy and the Gibbs free energy will be the most useful to us.

not so imp. here.

Helmholtz free energy

Defⁿ: $F = F(N, V, T)$ { N, V, T are 'natural' state vars

$$\text{where } \boxed{F = U - TS}$$

$$\begin{aligned} &\text{swap } S, T \\ &U(N, V, S) \rightarrow F(N, V, T) \end{aligned}$$

[Interpretation: maximum work avail. at constant temperature

$$dF = dU - TdS + SdT$$

$$dU = SW + TdS \text{ for reversible (max work)}$$

$$\underline{dF = SW \text{ for reversible.}}$$

'Subtracting off
 $SQ = TdS$ '

slightly imp.

Enthalpy

(related to heat)

$$H = H(N, P, S)$$

$$\boxed{|H = U + PV|}$$

$$\begin{aligned} &\text{swap } P, V \\ &(U(N, V, S) \rightarrow H(N, P, S)) \end{aligned}$$

(subtract $-PdV$,
ie work on,
at constant p).

[Interpretation: heat added, at constant P & when only pdV work done.]

$$dH = dU + pdV + Vdp \rightarrow$$

$$dU = -pdV + \delta Q \quad (\text{work on} = -pdV)$$

$$dH = \delta Q \quad \text{[subtracting off pdV work']}$$

most imp.!

↳ $dH < 0$: give off heat, under $P=\text{const}$, pdV work only.

Gibbs free energy

$$G = G(N, P, T) \quad \text{swap } v, P, S, T$$

$$G = U + PV - TS \quad \left\{ \begin{array}{l} \text{Spontaneous processes.} \\ \Delta G < 0 \text{ for constant } P, T \end{array} \right.$$

OR

$$\Rightarrow G = H - TS \quad \left\{ \begin{array}{l} \text{i.e.} \\ \text{+ve entropy production.} \end{array} \right.$$

[Interpretation: maximum chemical work at constant P, T:]

$$dG = dU + pdV + Vdp - Tds - SdT$$

rev. { $dU = -pdV + \mu dN + Tds \quad \left\{ \begin{array}{l} u = u(v, N, S) \\ dG = \mu \cdot dN \end{array} \right.$

→ 'chemical work' \leftarrow in chemical pot./pressure
 dN displacement of number of molecules.

Terminology

For Gibbs free energy and enthalpy, respectively, we introduce the following terminology.

— Gibbs free energy: exergonic or endergonic?

- **Exergonic** — positive energy from system to surroundings → $\boxed{\Delta G < 0}$ (for constant P, T)

- **Endergonic** — negative energy from system to surroundings → $\boxed{\Delta G > 0}$ (for constant P, T)

— Heat/enthalpy: exothermic or endothermic?

- (system \rightarrow surroundings)
- Exothermic — release of heat $\rightarrow \boxed{\Delta H < 0}$
 - Endothermic — absorption of heat $\rightarrow \boxed{\Delta H > 0}$
(constant pressure)

Importantly, we can also apply these energy functions to cases involving multiple processes/steps.

— Free energy in multiple processes or steps

$$\boxed{\Delta G^{\text{overall}} = \underbrace{\Delta G^{\text{products}}}_{\text{add up}} - \underbrace{\Delta G^{\text{reactants}}}_{(\text{add up})}}$$

examples
→

The Tables 2-3 will be helpful for our examples.

| Substance | Phase | Chemical Formula | ΔG_f° (kJ.mol ⁻¹) |
|----------------|--------|--------------------------------|--|
| Water | liquid | H ₂ O | -237.14 |
| Water | gas | H ₂ O | -228.61 |
| Oxygen | gas | O ₂ | 0 |
| Hydrogen | gas | H ₂ | 0 |
| Carbon dioxide | gas | CO ₂ | -394.39 |
| Lead | solid | Pb | 0 |
| Lead sulfate | solid | PbSO ₄ | -813.2 |
| Lead oxide | solid | PbO ₂ | -215.48 |
| Sulfuric acid | liquid | H ₂ SO ₄ | -744.63 |

Table 2: Examples of standard Gibbs free energy of formation, which is the Gibbs free energy that accompanies the formation of 1 mole of a substance in its standard state from its constituent elements in their standard state. Given at 298 K and 1 atm. (From notes by Thor Besier.)

Example Problems 9: Gibbs free energy

- Calculate the energy released if you oxidised the entire glucose content of a 65g chocolate bar. Assume the glucose content of the bar is 70g per 100g. Gibbs free energy of glucose is -2870 kJ/mol. The molecular weight of glucose is 180.16 g/mol.
- A typical lead acid battery undergoes the following chemical reaction to produce energy:



Given the values for Gibbs free energy of formation in the table above, determine

| Substance | Phase | Chemical Formula | ΔH_f° (kJ.mol ⁻¹) |
|----------------|--------|--------------------------------|--|
| Water | liquid | H ₂ O | -285.83 |
| Water | gas | H ₂ O | -241.8 |
| Oxygen | gas | O ₂ | 0 |
| Hydrogen | gas | H ₂ | 0 |
| Carbon dioxide | gas | CO ₂ | -393.5 |
| Lead | solid | Pb | 0 |
| Lead sulfate | solid | PbSO ₄ | -919.94 |
| Lead oxide | solid | PbO ₂ | -274.47 |
| Sulfuric acid | liquid | H ₂ SO ₄ | -909.27 |

Table 3: Examples of enthalpy of formation values. Given at 298 K and 1 atm. (From notes by Thor Besier.)

the electrochemical work produced at 298 K.

Answers

$$l. \frac{65 \text{ g bar}}{100 \text{ g bar}} \times \frac{70 \text{ g glucose}}{180.16 \text{ g}} \times \frac{1 \text{ mol}}{180.16 \text{ g}} = \frac{65 \times 0.7 \text{ mol}}{180.16 \text{ g glucose}}$$

$$\Delta G = \left(\frac{65 \times 0.7 \text{ mol}}{180.16} \right) \times \left(-2870 \frac{\text{kJ}}{\text{mol}} \right) \approx -725 \text{ kJ}$$