

Outline

- Second Law of Thermodynamics
- Entropy
- Reversible and Irreversible Processes
- Entropy Calculations
- Equilibrium
- Third Law of Thermodynamics
- Physical Meaning of Entropy

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Reversible and Irreversible Processes

• Wood will burn spontaneously in air if ignited, but the reverse process (*i.e. the spontaneous recombination of the combustion products to wood and oxygen*) does not occur in nature.

• Ice at 1 atm and above 0°C always melts spontaneously, but the reverse (water at 1 atm and above 0°C \rightarrow ice) never occurs.

A process, which involves the spontaneous change of a system from a state to some other state, is called or natural process. As such a process cannot be reversed without help of an external force, the process is called

• As a result of the irreversible or spontaneous process, the system has degraded (*the internal energy was converted to <u>heat</u> and this energy is no longer available for external use*).

• The system will arrive to the equilibrium state when the energy available for doing useful work is completely <u>consumed</u>.

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Equilibrium

• The equilibrium state is a state of rest. Once at equilibrium, a system will not move away from equilibrium unless some external force acts on it.

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

• A process during which the system is never away from equilibrium is called a process.

• Since the definition of reversible process contradicts that of equilibrium, the reversible process is an *imaginary* one.

• If a process proceeds with an infinitesimally small driving force in such a way that the system is never more than an infinitesimal distance from equilibrium, a condition which is virtually indistinguishable from equilibrium, then the process can be regarded as a reversible process. Hence, for a reversible process to take place it must be infinitely slow.



Reversible and Irreversible Processes

How to predict which process will proceed spontaneously?

1st law indicates that U and H are state functions. Therefore, $\Delta U(A \rightarrow B) = -\Delta U(B \rightarrow A)$ or $\Delta H(A \rightarrow B) = -\Delta H(B \rightarrow A)$

A AH B

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

- By Intuition we would expect that systems would proceed towards a state with lower energy. *So the process would release heat for example.*
- Indeed, often spontaneous changes are exothermic,

e.g. H_2 (gas) + $\frac{1}{2}$ O₂ (gas) -> H₂O (liquid) $\Delta H = -286$ kJ/mol

• <u>But</u>, sometimes endothermic reactions occur spontaneously, e.g. H₂O (liquid,105°C) \rightarrow H₂O (gas,105°C) Δ H = +44 kJ/mol

A negative sign of Δ H favors but does not guarantee spontaneity

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Reversible and Irreversible Processes

Reversible process in thermodynamics is one that is reversed by an infinitesimal modification of the conditions of the surroundings.



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Quantification of Irreversibility

The energy alone is not sufficient, for example:

Sn^{white} \rightarrow Sn^{grey} @ room temp. Δ H=-2100 J/mol

However, the fact is that white tin is stable at room temp.

Therefore, 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 $\tau \rho \sigma \pi \eta$ = transformation in Greek), was introduced by Clausius in 1850.

So, What is entropy? *To answer this question we need to introduce the second law*

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2nd Law of Thermodynamics

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 $dS = \delta q_{rev}/T$ and for all irreversible processes is such that $dS > \delta q/T$ or in general, $dS \geq \delta q/T$

Why q/T ?

To answer this question, Let us consider two irreversible processes:

- 1. Conversion of work (mechanical energy) into heat
- 2. Flow of heat down a temperature gradient
- 3. A combination of the above processes

These are three processes with different degree of

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Degree of Irreversibility: Example 1

But before discussing an example involving mechanical work, let us consider the following case, the includes only heat conversion, first.





Degree of Irreversibility: Example 1



Whenever a system undergoes a change in state and the amount of work done by the system is less than the maximum possible amount of work, then there is a net entropy production.

2nd Law of Thermodynamics

 $\frac{q_r - q}{r} = 0$

 $dS_{tot} = \frac{\delta q_r - \delta q}{\delta q_r} = 0$

 $dS_{sur} = \frac{-\delta q}{T}$

 $dS_{tot} = \frac{\delta q_r - \delta q}{T} > 0$



2nd Law of Thermodynamics

The second law states that entropy is a state function and – if added up for all parts of the system – never

 $\Delta S \ge \frac{q}{T} \qquad \qquad \Delta S_{total} = \Delta S_{sys} + \Delta S_{sur}$

This turns out to be incredibly useful, since if we want to find the conditions at which a system stops changing (i.e., equilibrium) then the entropy of the entire system is as **large** as possible.

There are many different ways to state the 2nd law and they all sound quite different from each other. This fact is not very interesting, but the ability to show that all the differing statements are consistent is very enlightening.

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Combination of the 1st and 2nd Laws

For a closed system and a reversible process:





Entropy

Show that entropy is a state function?!

In an ideal gas undergoing reversible process $\delta q_{rev} = dU + PdV = c_V dT + PdV = c_V dT + \frac{RT}{V} dV$

and, dividing by T, $\frac{\delta q_{rev}}{T} = \frac{c_V}{T} dT + \frac{R}{V} dV$ T

It is possible to integrate this equation over segments of dT (at V = const) and dV (at T = const) and, therefore, over any path in the (T,V) space

 \therefore The integral of $\delta q_{rev}/T$ depends only on its end points (T,V) and has the properties of state function.

$$\int_{A}^{B} \frac{dq_{rev}}{T} = \int_{A}^{B} dS = S_{B} - S_{A}$$
$$dS = \left(\frac{\partial S}{\partial T}\right)_{V} dT + \left(\frac{\partial S}{\partial V}\right)_{T} dV \qquad \left(\frac{\partial S}{\partial T}\right)_{V} = \frac{C_{V}}{T} \qquad \left(\frac{\partial S}{\partial V}\right)_{T} = \left(\frac{\partial P}{\partial T}\right)_{V} = \frac{R}{V}$$

Summary

Entropy is a state function.

> Entropy is not conserved except in the hypothetical limiting case of a reversible process.

> Entropy is not directly measurable. However, the change in entropy is calculated from measurable quantities such as T, P, V and heat capacity.

> When the weight-heat reservoir system, discussed earlier, undergoes a spontaneous process which causes the adsorption of heat q at a constant temperature, 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

- > All real processes involve some degree of irreversibility \rightarrow all real process lead to an increase in the <u>total entropy</u> ($\Delta S_{total} = \Delta S_{svs} + \Delta S_{suv}$)
- > The total entropy can never decrease. It can only increase.

➤ The increase in entropy due to an irreversible process, arises from the degradation of energy potentially available for useful work into heat.

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Summary

> 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.

> The entropy of an adiabatic system cannot decrease. It increases in an irreversible, spontaneous or natural processes and remains constant during a reversible process.

> Entropy is a measure of disorder \rightarrow Things left to themselves proceed to a state of maximum possible disorder.

or "mixed-up-ness" (Gibbs)

When the entropy has reached its, the process will cease to proceed further.



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Calculation of Entropy

 $dS = \frac{\delta q}{T}$ and $c_v = \left(\frac{\delta q}{dT}\right)_v \Rightarrow \delta q = c_v dT \Rightarrow dS = \frac{c_v dT}{T} \Rightarrow \int dS = \Delta S = \int_{T}^{t_f} \frac{c_v}{T} dT$

 $dS = \frac{\delta q}{T}$ and $c_p = \left(\frac{\delta q}{dT}\right)_p \Rightarrow \delta q = c_p dT \Rightarrow dS = \frac{c_p dT}{T} \Rightarrow \int dS = \Delta S = \int_{-\infty}^{T_r} \frac{c_p}{T} dT$

Example: Calculate the difference in entropy for 3 moles of O_2 gas at atmospheric pressure if it is cooled from 800K to 300K. $c_p = 30 + 100$

The 2nd Law - Again

The second law can be reformulated in the following way:

For every thermodynamic system there exist an **extensive** state function called the 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 (total entropy) never decreases and increases in any irreversible process.

As you can see again, there are many different ways to state the second law and they all sound quite different from each other. This fact is not very interesting, but the ability to show that all the differing statements are consistent is very important.

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Solution:

Constant volume process

Constant Pressure process

4.18×10⁻³ T - 17×10⁴ T⁻² J/mol.K



Calculation of Entropy

Example: One mole of liquid lead at its equilibrium freezing temperature (600K) freezes slowly/reversibly at 1 atm pressure to solid state. Calculate the entropy production. Given that $c_p(liquid) = 32.4 - 3.1 \times 10^{-3} \text{ T J/mol.K}$, $c_p(solid) = 23.6 + 9.75 \times 10^{-3} \text{ T J/mol.K}$ and $\Delta H_m = 4810 \text{ J/mol}$ (*latent heat of melting*)

Solution:



Calculation of Entropy

Example: One mole of supercooled liquid lead spontaneously freezes at 590K and 1 atm pressure to the solid state. Calculate the entropy production if you know that $c_p(liquid) = 32.4 - 3.1 \times 10^{-3} \text{ T J/mol.K}$, $c_p(solid) = 23.6 + 9.75 \times 10^{-3} \text{ T J/mol.K}$ and $\Delta H_m = 4810 \text{ J/mol.}$ Can the freezing be carried out reversibly?



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Entropy and Phase Transformations



The example considered earlier shows that the change in the total entropy is positive if a high-temperature phase converts into a low-temperature phase at a temperature below the equilibrium transition temperature. Or if the low-temp phase converts to a high-temp one at higher than the transition temperature. Otherwise, it is negative and the transition is prohibited by the 2nd law of thermodynamics.

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Actual path

590°

Solid Ph

Ш

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Entropy of Formation of a Compound: Example

Compute the entropy change during the formation of alumina from aluminum and oxygen at 298 K.

Solution:

The reaction is

 $2\mathrm{Al} + \frac{3}{2}\mathrm{O}_2 \rightleftharpoons \mathrm{Al}_2\mathrm{O}_3$

From appendices D and G in Dehoff's text we can find the following absolute entropies:

 $S_{A1} = 28.32 \text{ J/(mol K)}$ $S_{O_2} = 205.03 \text{ J/(mol K)}$ $S_{A1_{2O_3}} = 51.00 \text{ J/(mol K)}$ Unlike U or H, S has its absolute value



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would have the same entropy.

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 $S_T = S_0 + \int_0^T \frac{c_P}{T} dT$

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

The 3rd Law of Thermodynamics

> The 3rd law of thermodynamics, states that if one could reach

> 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

The 3rd law was first formulated by Walter Nernst and

also known as the Nernst heat theorem.

absolute zero temperature (*at which all the thermal motion of atoms could be removed*) and a complete internal equilibrium, all bodies

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The 3rd Law of Thermodynamics: *Example*

Let us consider the formation of SiC from its components.





The net entropy change in this process must be zero (*entropy is a state function*)

$$\therefore \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 = 0$$



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The 3rd Law of Thermodynamics: *Example*

Experimentally it is found that

$$\Delta S_1 + \Delta S_2 + \Delta S_3 = 0$$

This implies that one can evaluate the entropy change in step 2 without actually performing the reaction:

$$\Delta S_2 = -(\Delta S_1 + \Delta S_3)$$



Please note that ΔS_1 and ΔS_3 can be obtained using the heat capacity tabulations.

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Physical Meaning of Entropy

> Phenomenological thermodynamics explains entropy based on the analysis of possible and impossible processes. For example we know that:

- heat flows from a hot region to a cold region of a system, and
- work can be irreversibly transferred into heat.

 \succ To describe the observations, the 2nd law which states that entropy is increasing in an isolated system, was introduced.

 \succ The problem with phenomenological thermodynamics is that it only helps us to describe the observations, but does not tell us why the 2nd law works and what is the *physical* interpretation of entropy.

> In statistical thermodynamics, however, entropy is defined as a measure of

Example:



The increase in the entropy upon melting correlates with the increase in disorder. MECH6661 lecture 3/29

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Microstates and Macrostates

✓ A macroscopic state of a system can be described in terms of a few macroscopic parameters, e.g. P, T, V.

 \checkmark The system can be also described in terms of microstates,

- e.g. for a system of N particles we can specify coordinates and velocities of all atoms.

 \checkmark The 2nd law can be stated as follows:

The equilibrium state of an isolated system is the one in which the number of possible microscopic states is the largest.

As you can see again, there are many different ways to state the second law and they all sound quite different from each other.

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Understanding Microstates and Macrostates Through Dice

Macrostate = thetotal of the dice.

Each dice have 6 microstates, the system of 2 dices has $6 \times 6 = 36$ microstates, a system of N dice has 6^N microstates

• For two dices there are 6 ways/microstates to get macrostate 7. But only one microstate that correspond to 2 or 12.

• The most likely macrostate is 7. For a big number (N) of dices, the macrostate for which the number of possible microstates is a maximum is 3.5×N

• If you shake a large bag of dices and roll them it is likely that you get the total close to $3.5 \times N$



An isolated thermodynamic system is similar where thermal fluctuations do the shaking, the macrostate corresponds to the largest number of microstates.



Understanding Microstates and Macrostates Through Dice

The probability for a macrostate = the number of possible ways (possible microstates) to generate the same macrostate divided by the number of all microstates (all possible combinations of the dice. which is a constant).

Any particular arrangement of atoms where we look only on average quantities is a macrostate. Any individual arrangement defining the properties (e.g. positions and momentary velocity) of all the atoms for a given macrostate is a microstate. For a microstate, it matters what individual particles do, for the macrostate it does not.

Example - vacancies:

we just have to find how many ways (# of microstates) are there to arrange *n* vacancies (*macrostate*) in a crystal of *N* lattice sites. After we find the probability, we can use Boltzmann's equation to calculate the entropy and we can use the equilibrium condition to select the most likely macrostate - the number of vacancies in equilibrium.



Statistical Interpretation of Entropy



$S = k \log W$ By the way, Boltzman never wrote this equation in this format, Plank did!

Tombstone of Ludwig Boltzmann

$S = k_B \ln \Omega$

where Ω is the number of microstates, *k* is Boltzmann's constant (*it is the same constant that relates kinetic energy to temperature, but it was first introduced in this equation*), and *S* is the entropy.

The entropy is related to the number of ways the microstate can rearrange itself *without* affecting the macrostate.

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Statistical Interpretation of Entropy

$S = k_B \ln \Omega$

Max Planck offered another version of the 3^{rd} law

 $\lim_{T \to 0} S = 0$

Planck's hypothesis is based on the statistical thermodynamics in which the entropy is related to the number of possible energy states for a give energy or thermodynamic probability W

$S = k_B \ln W$

At absolute zero there is only one way in which the energy can be distributed in a system; i.e., atoms or molecules and electrons are all in the available quantum states therefore W=1

\therefore S = 0 at T = 0K

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Next time: Equilibrium

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