

Chemistry 2000 Slide Set 9: Entropy and the second law of thermodynamics

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Thermodynamics: not just heat

- As its name suggests, thermodynamics started out as the science of heat.
- Specifically, the founders of the discipline were concerned with **heat engines**, machines that convert heat into work.
- Along the way, they discovered fundamental principles encoded in the **laws of thermodynamics** that go far beyond describing the function of heat engines.

The thermodynamic description of matter

- In **classical thermodynamics**, we describe the state of a system by **macroscopic** variables that can be measured using ordinary lab equipment.

Macroscopic variables include

- the number of moles of each chemical component in a system
- the temperature
- the total pressure
- the volume
- ...

- We typically only need to know a few of the macroscopic variables since they are connected by **equations of state**.

Examples:

- $PV = nRT$ for an ideal gas.

- $$V = \frac{V^\circ}{1 - \alpha(T - T^\circ) + \kappa(P - P^\circ)}$$
for solids or liquids with (T, P) near a reference state (T°, P°) .

The mechanical description of matter

- We can also describe matter by its **microscopic state**.

The **microscopic state** includes

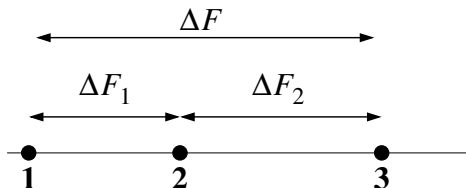
- positions of all particles
- momenta of all particles
($p = mv$)
- occupation of all energy levels of the atoms or molecules
- The microscopic state (or just **microstate**) includes an extraordinarily large number of variables.

Microstate vs macrostate

Each macroscopic state corresponds to a huge number of microscopic states.

State functions

- A **state function** is a quantity that depends only the macroscopic state of a system, and not on how the system was brought to that state
- State functions are **additive**.



$$\Delta F_1 = F_2 - F_1$$

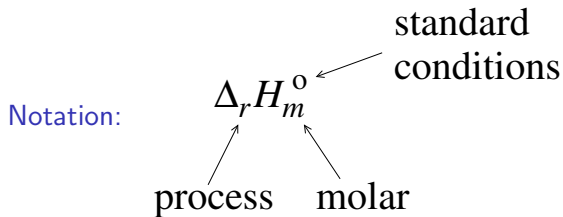
$$\Delta F_2 = F_3 - F_2$$

$$\Delta F = F_3 - F_1 = \Delta F_1 + \Delta F_2$$

Review of enthalpy

(with a few new ideas thrown in)

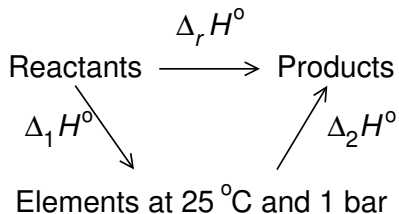
Enthalpy (H) is a state function that was **designed** so that ΔH gives the heat at constant pressure.



Standard conditions: **25 °C and 1 bar (10⁵ Pa)**

Standard enthalpies of formation

- For any reaction, we can imagine several different paths from reactants to products. In particular,



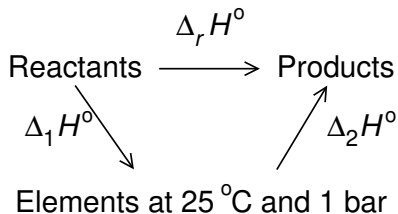
- Because enthalpy is a state function,

$$\Delta_r H = \Delta_1 H + \Delta_2 H$$

Standard enthalpies of formation (continued)

- Define the **formation reaction** for a compound as
elements in most stable forms at STP \rightarrow **1** compound
- The **standard enthalpy of formation** of a compound is the enthalpy change in the formation reaction, symbolized $\Delta_f H^\circ$.
- By definition, the enthalpy of formation of an **element** in its standard state is **zero**.

Standard enthalpies of formation



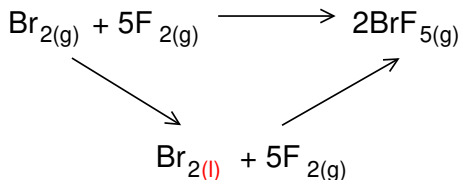
- Then

$$\Delta_2 H = \sum_{P \in \text{products}} \Delta_f H^\circ(P)$$

$$\Delta_1 H = - \sum_{R \in \text{reactants}} \Delta_f H^\circ(R)$$

$$\therefore \Delta_r H = \sum_{P \in \text{products}} \Delta_f H^\circ(P) - \sum_{R \in \text{reactants}} \Delta_f H^\circ(R)$$

Example: Reaction of Br₂ with F₂ in the gas phase



$$\begin{aligned}
 \Delta_r H^\circ &= 2\Delta_f H^\circ(\text{BrF}_5, \text{g}) - [\Delta_f H^\circ(\text{Br}_2, \text{g}) + 5\Delta_f H^\circ(\text{F}_2)] \\
 &= 2(-428.72) - [30.91 + 5(0)] \text{ kJ mol}^{-1} \\
 &= -888.35 \text{ kJ mol}^{-1}
 \end{aligned}$$

This reaction **produces** 888.35 kJ of heat per mole of Br_{2(g)} used, or per 5 mol of F_{2(g)} used, or per 2 mol of BrF_{5(g)} made.

Example: Heat generated by the combustion of 1.0 L of methane at 25 °C and 1.0 bar

Assume we are burning methane in an open flame so that the water generated stays in the vapor phase once the products have returned to room temperature.

Data:

Species	$\Delta_f H^\circ / \text{kJ mol}^{-1}$
$\text{CH}_4(\text{g})$	-74.81
$\text{CO}_2(\text{g})$	-393.51
$\text{H}_2\text{O}(\text{g})$	-241.826

Answer: -32 kJ

Statistical entropy

- **Entropy** is a key quantity in thermodynamics.
- The **statistical entropy** is calculated by

$$S = k_B \ln \Omega$$

where

k_B is Boltzmann's constant (again).

Ω is the total number of microscopic states consistent with a given macroscopic state.

- **S is a measure of our ignorance of the microscopic state at any given time.**

Example: Entropy of 25\$

- Suppose that I tell you that I have 25\$ in my pocket, all in bills.
- Your ignorance of how this 25\$ is composed could be considered a form of entropy.
- Possible “microstates” of 25\$ consistent with the constraint (no coins):

- In **information theory**, we use the base-2 logarithm and set $k_B = 1$ (corresponds to a change of units for the entropy).
- Then we would have

$$\begin{aligned} S_{\text{inf}}(25\$) &= \log_2 4 \\ &= \log_2(2^2) \\ &= 2. \end{aligned}$$

- Note that this is the number of yes/no questions you would have to ask to figure out the microstate, i.e. the number of bits of information (as computer scientists would say):
 - 1 Are there any 10\$ bills?
 - 2 Is there more than one 5\$ bill?
- **Entropy measures the amount of information needed to reconstruct the microstate.**
- Note that extra information (e.g. “no coins”) reduces the entropy because it increases the information we have.

Orientational entropy of solid CO

- CO has a small dipole moment.
- As a result, there is only a very small energy difference between lining up CO molecules CO-CO vs CO-OC or OC-CO.
- When we freeze CO, the molecules line up more-or-less randomly.
- As we cool the crystal, because of the lack of rotational freedom, the CO molecules are “stuck” in the orientations they originally crystallized in.

Orientational entropy of solid CO (continued)

- Each CO molecule has two possible orientations.
- If there are N molecules of CO, then $\Omega = 2^N$.
- Therefore, the entropy associated with this orientational freedom is $S = k_B \ln(2^N) = Nk_B \ln 2$.
- This “frozen in” entropy is called the **residual entropy** for reasons that will become clear later.

$$S = k_B \ln(2^N) = Nk_B \ln 2$$

- Divide both side by N to get the entropy per molecule, then multiply by N_A to get the molar entropy:

$$S_m = R \ln 2 = 5.76 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$(N_A k_B = R)$$

- Experimentally (using a different method than counting microstates), this contribution to the entropy of solid CO is found to be about $5 \text{ J K}^{-1} \text{ mol}^{-1}$, which is pretty good agreement. The difference (if it isn't just due to experimental error) may be due to the difference in energy between different relative orientations resulting in a not completely random distribution of orientations.

Properties of the entropy

- 1 For a given macroscopic state of a system, there is a fixed number of microscopic states, and thus a fixed value of the entropy.
 - Entropy is a state function.
- 2 If a system has Ω microstates, then doubling the size of the system would increase the number of microstates to Ω^2 , which doubles the entropy.
($\ln \Omega^2 = 2 \ln \Omega$)
 - Entropy is an extensive property.
 m , n , V , energy and enthalpy are other extensive properties.
 - Properties that **don't** depend on the size of the system (T , p , ...) are said to be **intensive**.

Reversibility

- We now turn to a classical thermodynamic approach to entropy.
- Heat and work are **path functions**, which means that the amount of heat delivered to a system or work done depends on the way in which we carry out the process.
- A special class of paths called **reversible** paths plays a special role in thermodynamics.

A **reversible process** is one during which the system and its surroundings are constantly in equilibrium.

Examples:

- During a reversible heat transfer, the system and surroundings are at the same temperature.
- During a reversible expansion of a gas, the system and surroundings are at the same pressure.

- If the system and surroundings are truly in equilibrium, no change can occur.
- Reversible processes can be thought of as the limit of a series of processes in which we allow smaller and smaller deviations from equilibrium.
- A truly reversible process **cannot** be achieved, but is a theoretically useful idea.

Thermodynamic entropy

- In the first instance, classical thermodynamics only gives a prescription for calculating **changes** in entropy.
- In general:

$$\Delta S = \int \frac{dq_{\text{rev}}}{T}$$

- For **isothermal** reversible (equilibrium) processes, this specializes to

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

- To calculate the entropy change, we need to know the heat along a reversible path.
 - In general, this is not trivial.

Example: Entropy change during a phase transition

- At the equilibrium phase transition temperature (freezing point, boiling point), two phases are in equilibrium.
- Phase transitions at the equilibrium phase transition temperature are therefore reversible.
- At 1 atm pressure, water freezes at 0°C.
The molar heat of fusion (melting) at this temperature is 6007 J/mol.
- $\Delta_{\text{fus}}S = \frac{q_{\text{rev}}}{T} = \frac{6007 \text{ J/mol}}{273.15 \text{ K}} = 21.99 \text{ J K}^{-1} \text{ mol}^{-1}$
- $\Delta_{\text{freeze}}S = \frac{-6007 \text{ J/mol}}{273.15 \text{ K}} = -21.99 \text{ J K}^{-1} \text{ mol}^{-1}$

The second law of thermodynamics

The entropy of the Universe increases in any thermodynamically allowed process.

A thermodynamically allowed process *could* occur, but may not for kinetic reasons.

Note: In many books, the word **spontaneous** is used for this concept. Unfortunately, in everyday language, spontaneous suggests something that *will* rather than something that *could* occur.

Important: It is $\Delta S_{\text{universe}}$, **not** ΔS for the system alone that must be positive.

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

Example: Freezing of ice below 0°C

- Suppose we have some liquid water in a freezer set at -20°C .
- To illustrate the principle without getting into too many details, we consider only the freezing process, not the cooling of the water to 0°C , nor the subsequent cooling of the ice.
- $\Delta S_{\text{system}} = \Delta_{\text{freeze}} S = \frac{-6007 \text{ J/mol}}{273.15 \text{ K}} = -21.99 \text{ J K}^{-1} \text{ mol}^{-1}$
- The freezer has a large heat capacity, so for reasonable amounts of water frozen, heat transfer is effectively reversible.
- $q_{\text{rev, freezer}} = 6007 \text{ J/mol}$ of water frozen.
- $\Delta S_{\text{surroundings}} = \frac{6007 \text{ J/mol}}{253.15 \text{ K}} = 23.73 \text{ J K}^{-1} \text{ mol}^{-1}$
- $\Delta S_{\text{universe}} = -21.99 + 23.73 \text{ J K}^{-1} \text{ mol}^{-1} = 1.74 \text{ J K}^{-1} \text{ mol}^{-1} > 0$,
i.e. the everyday observation of water freezing under these conditions is consistent with the second law.

The third law of thermodynamics

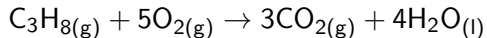
The entropy of a perfect crystal approaches zero as the temperature approaches absolute zero.

Consequences:

- This law allows us to define an **absolute entropy scale** using perfect crystals at low temperature as a reference.
- We can calculate the entropy of reaction ($\Delta_r S^\circ$) by taking the difference between the entropies of the products and reactants.

Example: Entropy of combustion of propane

- Suppose that we burn propane near room temperature, so that liquid water (rather than vapor) is one of the products.



$$\begin{aligned} \Delta_r S^\circ &= 3S^\circ_{\text{CO}_2} + 4S^\circ_{\text{H}_2\text{O}_{(\text{l})}} - (S^\circ_{\text{C}_3\text{H}_8} + 5S^\circ_{\text{O}_2}) \\ &= 3(213.7) + 4(69.940) - [269.9 + 5(205.0)] \text{ J K}^{-1}\text{mol}^{-1} \\ &= -374.0 \text{ J K}^{-1}\text{mol}^{-1}. \end{aligned}$$

Notes:

- 1 Gases have a large number of microstates compared to solids and liquids. Taking six molecules of gas and producing only 3 decreases the number of microstates significantly, hence the decrease in entropy.
- 2 We know that this reaction is spontaneous, so note again that the sign of the entropy change for the system alone **does not** tell us whether the reaction is thermodynamically allowed.
This reaction is exothermic, so q_{rev}/T for the surroundings is going to be positive and sufficiently large to cancel out the loss of entropy from the reaction.
- 3 Unlike enthalpies of formation, **absolute entropies are non-zero for all substances, including elements**, except at 0 K.

Example: Entropy of dissolution of MgF_2

- It is tempting to think that there are more microstates when we have dissociated an ionic compound into aqueous ions than in the separated solid + water, but this is not always the case.
- Consider $\text{MgF}_{2(s)} \rightarrow \text{Mg}_{(aq)}^{2+} + 2\text{F}_{(aq)}^-$:

$$\begin{aligned} \Delta_r S^\circ &= S_{\text{Mg}^{2+}}^\circ + 2S_{\text{F}^-}^\circ - S_{\text{MgF}_2}^\circ \\ &= -138.1 + 2(-13.8) - 57.24 \text{ J K}^{-1} \text{ mol}^{-1} \\ &= -222.9 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

- The decrease in entropy is due to two factors:
 - The increase in microstates of the MgF_2 itself is not as large as one might suppose due to the powerful ion-ion force.
 - The ions organize the solvent due to ion-dipole forces.

A word of caution about q_{rev}/T and chemical reactions

- In simple, isothermal and essentially reversible processes involving **only a transfer of heat** like phase changes, we can calculate the entropy change of the system by $\Delta S = q_{\text{rev}}/T$.
- We **cannot** do this for a chemical reaction because changing chemical bonds also contributes to the entropy.
Never use q_{rev}/T to try to calculate the entropy change of a chemical reaction.