Module 2, Lecture 2
Chemical Thermodynamics
Part 2

Learning Objectives:

- Understand the concept of entropy being related to the number of possible arrangements of particles in a system.
- Qualitatively predict entropy changes.
- Carry out calculations using S^o

Textbook: Chapter 19

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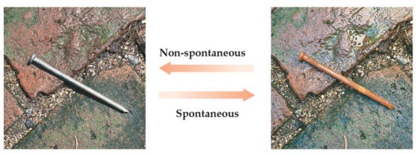
Spontaneous processes

- A **spontaneous process** is one which, once started, will continue without any help.



- Originally thought that only exothermic processes were spontaneous as they would lead to a lowering in energy.

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But…

Cold soft drinks warm up on standing - endothermic

Ice cubes melting - endothermic
ΔH^o = +6 kJ mol^{-1}

Dissolving NH_4NO_3 in water - endothermic
ΔH^o = +26 kJ mol^{-1}

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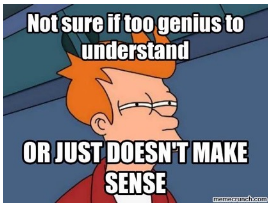
Entropy



Must also consider **entropy** *(S).*

Several definitions of entropy

- **A measure of the number of possible arrangements of particles in a system**
- A measure of the distribution of energy over available states in a system
- *(The number of available microstates - CHEM201/physics/books)*
- A measure of randomness.
- **A measure of disorder?**

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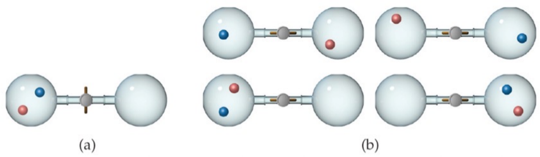
Entropy

Possible arrangements of two gas molecules in two flasks:



Result	Entropy	Chance
2 molecules in left flask	low	1/4
2 molecules in right flask	low	1/4
1 molecule in each flask	high	2/4

Which result has the highest entropy?
Two molecules in each flask has higher entropy because more possible arrangements of the particles OR the system is more disordered/random.

Which result is more likely after the tap is opened?
Ordered system is very unlikely – 1 in 4 chance of both being in left flask

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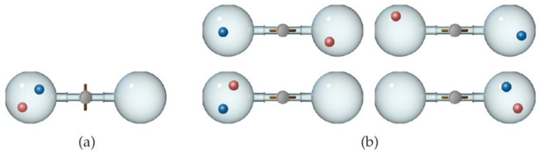
Entropy

Which result is more likely?



If 4 molecules, then just 0.5^4 = 6.25% - a 1 in 16 chance of both being in the left flask..

If 1 mole of molecules, just $0.5^{6.023 \times 10^{23}}$ chance – less than 1 in 10^{100}

Very small chance of an ordered system, system spontaneously becomes more disordered :

– increase in entropy

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ordered

small # of possible arrangements of sheep

disordered

large # of possible arrangements of sheep

Increase in entropy

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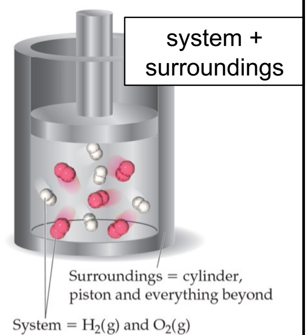
The second law of thermodynamics

"Whenever a spontaneous event takes place in our universe, the ***total*** *entropy of the universe increases"*



- In thermodynamics, the universe consists of the system of interest, plus the surroundings. Because of this, the entropy of a system *can* decrease during a spontaneous process, as long as the entropy of the surroundings increases by a larger amount.

- The **enthalpy** of the universe is **constant**; the **entropy** of the universe is **increasing**. The available energy is constantly being dispersed throughout the universe.

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The second law of thermodynamics

*"Whenever a spontaneous event takes place in our universe, the **total** entropy of the universe increases"*

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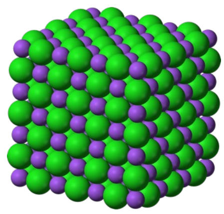
Measuring entropy

- Unlike enthalpy, it is possible to measure absolute values of entropy for a substance.



- This is because the **third law of thermodynamics** states:

  "*at absolute zero, the entropy of a perfectly ordered pure crystalline substance is zero"*

  (i.e. there is NO disorder at all)

- A value measured at 1 bar is called a ***standard entropy (S^o)***. Units are J mol^{-1} K^{-1}.

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Entropy

- Solids have the lowest entropies, followed by liquids, with gases having the highest.

  S^o (H_2O, s) = 41 **J** mol^{-1} K^{-1}

  S^o (H_2O, l) = 70 **J** mol^{-1} K^{-1}

  S^o (H_2O, g) = 189 **J** mol^{-1} K^{-1}

Careful!
- S^o small values note J not kJ
- Note the "K^{-1}" in the unit.

- In contrast to $\Delta_f H^o$, S^o for an element in its standard state is **not zero**

  S^o (H_2, g, 298 K) = 130.6 J mol^{-1} K^{-1}

  S^o (O_2, g, 298 K) = 205.0 J mol^{-1} K^{-1}

This is because the reference point is the pure crystalline solid at 0 K.

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Standard entropy of reaction

Can write $\Delta_r S^o$ just like for $\Delta_r H^o$:

$\Delta_r S^o$ = sum of entropy of products – sum of entropy of reactants

$$\Delta_r S^o = \sum[S^o \text{ (products)}] - \sum[S^o \text{ (reactants)}]$$

(taking account of stoichiometry)

Can often **qualitatively** predict ΔS for a chemical reaction from the states of the substances involved.

- A reaction which results in the formation of a gas from a solid or liquid will very likely have ΔS +ve
- A reaction having fewer moles of products than reactants (all in the same phase) will very likely have ΔS –ve.

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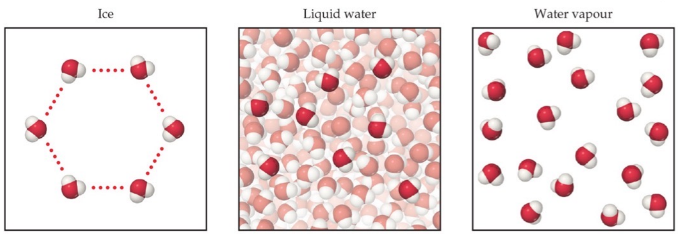
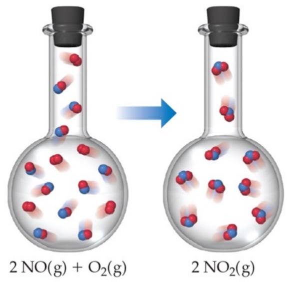
Effect of phase/number of particles





Increase in entropy

Decrease in entropy

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Qualitative example

- What is the expected sign of $\Delta_r S$ for the following reactions?

(1) $\mathbf{N_2(l) \rightarrow N_2(g)}$ https://www.youtube.com/watch?v=th43nMgN578

(2) $\mathbf{N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)}$

For (1), we have 1 mole of liquid being converted to 1 mole of gas. Molecules of gaseous N_2 are less constrained than liquid molecules, therefore have more possible arrangements. **$\Delta_r S$ will be +ve.**

For (2), we have 4 moles of gas reacting to give 2 moles of gas. Fewer possible arrangements of the product molecules, therefore **$\Delta_r S$ will be –ve.**

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Quantitative example

- Calculate $\Delta_r S^o$ for the hydrolysis of urea:

$CO(NH_2)_2(s) + H_2O(l) \rightarrow CO_2(g) + 2NH_3(g)$

given
$S^o [CO(NH_2)_2(s)] = 173.8$ J mol^{-1} K^{-1}
$S^o [H_2O(l)] = 69.96$ J mol^{-1} K^{-1}
$S^o [CO_2(g)] = 213.6$ J mol^{-1} K^{-1}
$S^o [NH_3(g)] = 192.5$ J mol^{-1} K^{-1}

$\Delta_r S^o = [213.6 + (2\times192.5)] - [173.8 + 69.96]$ J mol^{-1} K^{-1}
$= 354.8$ J mol^{-1} K^{-1}

Sanity check?
The large positive value is consistent with the formation of 3 moles of gas from an aqueous solution.

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So what determines spontaneity?

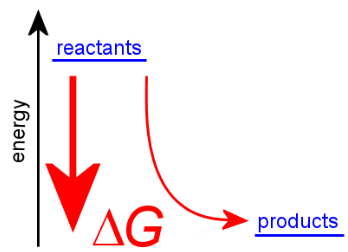
- A positive value of ΔS for a particular process is no guarantee that the process will be spontaneous

- e.g. the melting of ice at -10 ^{o}C is nonspontaneous despite ΔS being positive.

- So what determines spontaneity?

- A combination of ΔH and ΔS

Gibbs energy



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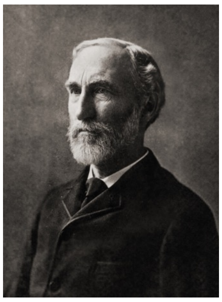
Gibbs energy



Josiah Willard Gibbs

- Gibbs energy (***G***) is defined as follows

$$G = H - TS$$

- ***H*** is the enthalpy of the system
- ***S*** is the entropy of the system
- ***T*** is the temperature in Kelvin (0 °C = 273 K)

- Can't measure absolute values of *G*, so always talk about the ***change*** in *G* for a process, ΔG

$$\Delta G = \Delta H - T\Delta S$$

- When referring to a chemical reaction (rather than a physical change) we use the usual terminology

$$\Delta_r G = \Delta_r H - T\Delta_r S$$

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✱ Homework ✱

Chemistry – the central science 15th Ed

Brown *et al.*

Problems 19.81, 19.82, 19.87

Answers on Blackboard

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