**Spontaneity**

**Entropy and Free Energy**

**WHAT DRIVES A REACTION TO BE SPONTANEOUS?**

**ENTROPY ($\Delta S$)**

- disorder of a system (more disorder is favored) Nature tends toward chaos! Think about your room at the end of the week!

- Your mom will love this law.

**Spontaneous reactions** are those that occur without outside intervention. They may occur fast OR slow (that is kinetics).

Some reactions are very fast (like combustion of hydrogen) other reactions are very slow (like graphite turning to diamond)
ENTROPY  
The Second Law of Thermodynamics

- The universe is constantly increasing disorder.
- Rudolph Clausius (you'll hear lots about him later when we study vapor pressures) ‘discovered’ it and gave it its symbol.)

ENTROPY  
The Third Law of Thermodynamics

- The entropy of a perfect crystal at 0 K is zero.
- not a lot of perfect crystals out there so, entropy values are RARELY ever zero—even elements

So what?

This means the absolute entropy of a substance can then be determined at any temperature higher than 0 K.

(Handy to know if you ever need to defend why G & H for elements = 0... BUT S does not!)
In general, the greater the number of arrangements, the higher the entropy of the system!

Statistical Thermodynamics

This is a way to use a particulate level view of matter to help understand the nature of entropy/disorder in terms of the concept of microstates.

Statistical Thermodynamics

Let's consider a sample of an ideal gas in a container at a given temperature and pressure.

If we look at the distribution of particles in terms of position and energy, we can get a better idea of the concept of a microstate.

A snapshot of the sample can be considered a microstate.
**Statistical Thermodynamics**

Boltzmann developed the relationship between entropy (S) and the number of microstates (W)

\[ S = k \ln W \]

**Statistical Thermodynamics**

Boltzmann developed the relationship between entropy (S) and the number of microstates (W)

\[ \Delta S = k \ln \frac{W_{\text{final}}}{W_{\text{initial}}} \]

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For a change of condition ΔS is positive if the final condition has more microstates than the initial condition.

**Predicting the entropy of a system based on physical evidence:**

Which container is the system more disordered? Has the highest entropy? In which are there more possible position, and energy states?
Predicting the entropy of a system based on physical evidence:

- Entropy is largest for gases, then liquids, and finally solids;
- Reactions increasing the number of moles of particles often increase entropy;
- Entropy generally increases with increasing molecular complexity (crystal structures); KBr vs. CaCl₂ since there are more moving electrons!
- When a gas molecule escapes from a solvent, the entropy increases.

Exercise 2
Predicting Entropy Changes

Predict the sign of the entropy change for each of the following processes.

A: Solid sugar is added to water to form a solution.

B: Iodine vapor condenses on a cold surface to form crystals.

Solution:

A: $+\Delta S$
B: $-\Delta S$
Sample Problem A

Which of the following has the largest increase in entropy?

a) CO₂(s) → CO₂(g)
b) H₂(g) + Cl₂(g) → 2 HCl(g)
c) KNO₃(s) → KNO₂(l)
d) C\text{(diamond)} → C\text{(graphite)}

Answer:

a) the substance changes from a highly organized state to a more disorganized state.

Calculating Entropy from tables of standard values:

Just the same as calculating the enthalpy earlier.
BIG MAMMA, verse 2

\[ \Delta S^\circ_{\text{rxn}} = \Sigma S^\circ_{\text{(products)}} - \Sigma S^\circ_{\text{(reactants)}} \]

S is + when disorder increases (favored)
S is − when disorder decreases

Units are usually J/K·mol (not kJ ---tricky!)
Note: the entropy values for products and reactants are absolute, not Δ (change) in entropy!

Sample Problem B

Calculate the entropy change at 25°C, in J/K·mol for:
2 SO\(_2\)(g) + O\(_2\)(g) → 2 SO\(_3\)(g)

Given the following absolute entropy data:
SO\(_2\)(g) 248.1 J/K·mol
O\(_2\)(g) 205.3 J/K·mol
SO\(_3\)(g) 256.6 J/K·mol

Solution:

2 SO\(_2\)(g) + O\(_2\)(g) → 2 SO\(_3\)(g)

\[ \Delta S^\circ_{\text{rxn}} = \Sigma S^\circ_{\text{(products)}} - \Sigma S^\circ_{\text{(reactants)}} \]
\[ \Delta S^\circ_{\text{rxn}} = 2\times 256.6 \text{ J/K·mol} - [2\times 248.1 \text{ J/K·mol} + 205.3 \text{ J/K·mol}] \]
\[ \Delta S^\circ_{\text{rxn}} = 513.2 \text{ J/K·mol} - 741.5 \text{ J/K·mol} \]
\[ \Delta S^\circ_{\text{rxn}} = -188.3 \text{ J/K·mol} \]
SUMMARY

ENTROPY:

\[ \Delta S = + \text{ MORE DISORDER} \]
(FAVORED CONDITION)

\[ \Delta S = - \text{ MORE ORDER} \]

PREICTING ENTROPY CHANGES

a) \( H_2O(s) \rightarrow H_2O(l) \)

b) \( 2Mg(s) + O_2(g) \rightarrow 2MgO(s) \)

c) \( Ba(OH)_2 \cdot 8H_2O(s) + 2NH_4Cl(s) \rightarrow BaCl_2(aq) + 10H_2O(l) + 2NH_3(aq) \)

d) \( H_2(g) + 1/2O_2(g) \rightarrow H_2O(l) \)

e) \( CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) \)

f) \( Al(s) + 3/2Br_2(l) \rightarrow AlBr_3(s) \)

PREICTING ENTROPY CHANGES

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Sign ( \Delta S )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H_2O(g) \rightarrow H_2O(l) )</td>
<td>+</td>
</tr>
<tr>
<td>( 2Mg(s) + O_2(g) \rightarrow 2MgO(s) )</td>
<td>-</td>
</tr>
<tr>
<td>( Ba(OH)_2 \cdot 8H_2O(s) + 2NH_4Cl(s) \rightarrow BaCl_2(aq) + 10H_2O(l) + 2NH_3(aq) )</td>
<td>+</td>
</tr>
<tr>
<td>( H_2(g) + 1/2O_2(g) \rightarrow H_2O(l) )</td>
<td>-</td>
</tr>
<tr>
<td>( CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) )</td>
<td>(-)</td>
</tr>
<tr>
<td>( Al(s) + 3/2Br_2(l) \rightarrow AlBr_3(s) )</td>
<td>(-)</td>
</tr>
</tbody>
</table>
First law of thermodynamics demands that this energy is transferred from the system to the surroundings so...

\[-\Delta H_{\text{system}} = \Delta H_{\text{surroundings}}\]

or

\[-(-483.6 \text{ kJ/mol}) = +483.6 \text{ kJ/mol}\]
\[ \Delta S^\circ_{\text{surroundings}} = \]

\[ \frac{\Delta H^\circ_{\text{surroundings}}}{T} = +483.6 \text{ kJ} \]

\[ T = 298 \text{ K} \]

\[ = 1620 \text{ J/K} \]

Now we can find \( \Delta S^\circ_{\text{universe}} \)

\[ \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = \Delta S_{\text{universe}} \]

\[ (-88.9 \text{ J/K}) + (1620 \text{ J/K}) = 1530 \text{ J/K} \]

Even though the entropy of the system declines, the entropy change for the surroundings is SOOO large that the overall change for the universe is positive.

Now we can find \( \Delta S^\circ_{\text{universe}} \)

\[ \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = \Delta S_{\text{universe}} \]

\[ \Delta S_{\text{system}} - \Delta H_{\text{system}}/T = \Delta S_{\text{universe}} \]

Multiply through by \(-T\) we get:

\[ -T\Delta S_{\text{system}} + \Delta H_{\text{system}} = -T\Delta S_{\text{universe}} \]

Rename \(-T\Delta S^\circ_{\text{universe}}\) as \( \Delta G^\circ_{\text{system}} \)

\[ -T\Delta S^\circ_{\text{system}} + \Delta H_{\text{system}} = \Delta G^\circ \]
Now we can find $\Delta S^\circ_{\text{universe}}$

$-T\Delta S^\circ_{\text{system}} + \Delta H^\circ_{\text{system}} = \Delta G^\circ$

Rearrange:

$\Delta H^\circ_{\text{system}} - T\Delta S^\circ_{\text{system}} = \Delta G^\circ$

So if we can calculate $\Delta H^\circ$ and $\Delta S^\circ$ for a reaction we can determine if the reaction is spontaneous.

Check out the signs: $\Delta H^\circ$ is $-$ and $\Delta S^\circ$ is $+$ then $\Delta G^\circ$ is $-$...spontaneous reaction.

### Predicting Free Energy CHANGES

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H^\circ$ (kJ/mol)</th>
<th>$\Delta S^\circ$ (J/mol K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2O(s) \rightarrow H_2O(l)$</td>
<td>+6.01</td>
<td>+39</td>
</tr>
<tr>
<td>$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$</td>
<td>-1202</td>
<td>-213</td>
</tr>
<tr>
<td>$Ba(OH)_2 \cdot 8H_2O(s) + 2NH_4Cl(s) \rightarrow BaCl_2(aq) + 10H_2O(l) + 2NH_4(aq)$</td>
<td>+78</td>
<td>+428</td>
</tr>
<tr>
<td>$H_2(g) + 1/2O_2(g) \rightarrow H_2O(l)$</td>
<td>-286</td>
<td>-163</td>
</tr>
<tr>
<td>$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$</td>
<td>-803</td>
<td>-4</td>
</tr>
<tr>
<td>$Al(s) + 3/2Br_2(l) \rightarrow AlBr_3(s)$</td>
<td>-526</td>
<td>-72</td>
</tr>
</tbody>
</table>

### FREE ENERGY

$H_2O(s) \rightarrow H_2O(l)$

$\Delta H^\circ = 6.01 \text{ kJ/mol}$

$\Delta S^\circ = 39 \text{ J/mol K} = 0.039 \text{ kJ/mol K}$

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

$\Delta G^\circ = 6.01 \text{ kJ/mol} - 298 K \times 0.039 \text{ kJ/mol K} = 6.01 \text{ kJ/mol} - 11.5 \text{ kJ/mol}$

$\Delta G^\circ = -5.53 \text{ kJ/mol}$ spontaneous
FREE ENERGY

- Calculation of Gibb’s free energy is what ultimately decides whether a reaction is spontaneous or not.
- **NEGATIVE** $\Delta G$’s are spontaneous.

$\Delta G$ can be calculated one of several ways:

Big Mamma, verse 3:

$$\Delta G^\circ_{\text{rxn}} = \sum \Delta G^\circ \text{(products)} - \sum \Delta G^\circ \text{(reactants)}$$

This works the same way as enthalpy and entropy from tables of standard values!

Standard molar free energy of formation

Same song, 3rd verse.

$$\Delta G^\circ_f = 0$$

for elements in standard state
GRAND Daddy:

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

This puts together all information thus far!

By far, one of the most beneficial equations to learn!

BIG MAMMA, verse 3:

$\Delta G^{\circ}_{\text{rxn}} = \sum \Delta G^{\circ}_{\text{products}} - \sum \Delta G^{\circ}_{\text{reactants}}$

Sample Problem C:

Find the free energy of formation for the oxidation of water to produce hydrogen peroxide.

$2 \text{H}_2\text{O}(l) + \text{O}_2(g) \rightarrow 2 \text{H}_2\text{O}_2(l)$

Given the following information:

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\Delta G^{\circ}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{O}(l)$</td>
<td>-285</td>
</tr>
<tr>
<td>$\text{O}_2(g)$</td>
<td>0</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2(l)$</td>
<td>-113.8</td>
</tr>
</tbody>
</table>
Solution:

\[ 2 \text{H}_2\text{O(l)} + \text{O}_2(g) \rightarrow 2 \text{H}_2\text{O}_2(l) \]

\[ \Delta G^\circ_{\text{rxn}} = \Sigma \Delta G^\circ_{\text{products}} - \Sigma \Delta G^\circ_{\text{reactants}} \]

\[ \Delta G^\circ_{\text{rxn}} = 2\Delta G^\circ(\text{H}_2\text{O}_2(l)) - [2\Delta G^\circ(\text{H}_2\text{O}(l)) + \Delta G^\circ(\text{O}_2(g))] \]

\[ \Delta G^\circ_{\text{rxn}} = 2\times(-114 \text{ kJ/mol}) - [2\times(-286 \text{ kJ/mol} + 0)] \]

\[ \Delta G^\circ_{\text{rxn}} = 344 \text{ kJ/mol} \]

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Exercise 9 (GRAND Daddy: \( \Delta G = \Delta H - T\Delta S \))

Calculating \( \Delta H^\circ, \Delta S^\circ, \) and \( \Delta G^\circ \)

Consider the reaction:

\[ 2 \text{SO}_2(g) + \text{O}_2(g) \rightarrow 2 \text{SO}_3(g) \]

carried out at 25°C and 1 atm.

---

Calculate \( \Delta H^\circ, \Delta S^\circ, \) and \( \Delta G^\circ \) using the following data:

<table>
<thead>
<tr>
<th>Substance</th>
<th>( \Delta H^\circ (\text{kJ/mol}) )</th>
<th>( S^\circ (\text{J/K} \cdot \text{mol}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{SO}_2(g)</td>
<td>-297</td>
<td>248</td>
</tr>
<tr>
<td>\text{SO}_3(g)</td>
<td>-396</td>
<td>257</td>
</tr>
<tr>
<td>\text{O}_2(g)</td>
<td>0</td>
<td>205</td>
</tr>
</tbody>
</table>
Solution:

\[ \Delta H^\circ = -198 \text{ kJ/mol} \]
\[ \Delta S^\circ = -187 \text{ J/K \cdot mol} \]
\[ \Delta G^\circ = -142 \text{ kJ/mol} \]

Exercise 10 (Hess’s law of summation) Calculating \( \Delta G^\circ \)

Using the following data (at 25°C):

\[ \text{C}_\text{diamond}(s) + \text{O}_2(g) \rightarrow \text{CO}_2(g) \quad \Delta G^\circ = -397 \text{ kJ/mol} \]
\[ \text{C}_\text{graphite}(s) + \text{O}_2(g) \rightarrow \text{CO}_2(g) \quad \Delta G^\circ = -394 \text{ kJ/mol} \]

Calculate \( \Delta G^\circ \) for the reaction:
\[ \text{C}_\text{diamond}(s) \rightarrow \text{C}_\text{graphite}(s) \]

Solution:

\[ \Delta G^\circ = -3 \text{ kJ/mol} \]
SUMMARY OF FREE ENERGY:

\[ \Delta G = + \text{ NOT SPONTANEOUS} \]

\[ \Delta G = - \text{ SPONTANEOUS} \]

Conditions of $\Delta G$:

<table>
<thead>
<tr>
<th>$\Delta H$</th>
<th>$\Delta S$</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>neg</td>
<td>pos</td>
<td>spontaneous at all temps</td>
</tr>
<tr>
<td>pos</td>
<td>pos</td>
<td>spontaneous at high temps</td>
</tr>
<tr>
<td>neg</td>
<td>neg</td>
<td>spontaneous at low temps</td>
</tr>
<tr>
<td>pos</td>
<td>neg</td>
<td>not spontaneous, ever</td>
</tr>
</tbody>
</table>