Chapter 17
Thermodynamics: Directionality of Chemical Reactions

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Chemical Reactions & Dispersal of Energy

"Energy will spread out (disperse) unless it is hindered from doing so".

Most exothermic reactions are product favored.
  • \( E \) is transferred to the surroundings.
  • Bond (potential) \( E \) dispersed into many more atoms and molecules.

Dispersal of energy is probability driven:
  • \( E \) is more likely to spread over many atoms than over just a few.

Probability and Dispersal of Energy

What are the possible outcomes if 2 excited atoms make contact with 2 more atoms?

Excited atoms \((A, B)\) + \(C, D\) → Unexcited atoms

\[ \begin{align*}
  A^* B^* + C D & \rightarrow A B C D \\
  A^* B C D & \rightarrow A B C^* D \\
  A B^* C D & \rightarrow A B C D^* \\
  A B C D & \rightarrow A B C D^* \\
  A B C D^* & \rightarrow A B C^* D \\
  A B^* C^* D & \rightarrow A B C D^* \\
  A B C D & \rightarrow A B C D^* \\
  A B C D^* & \rightarrow A B C^* D \\
  A B C^* D & \rightarrow A B C D^* \\
  A B C^* D & \rightarrow A B C D^* \\
  A B C^* D & \rightarrow A B C D^*
\end{align*} \]

\( E \) stays with original atoms in only 3 (of 10) cases:
  • 70% chance that \( E \) will disperse.
  • More atoms: \( E \) concentration is much less likely.

Dispersal of Matter

\( E \) is dispersed when a system expands.
  • Gases expand to fill a container.
  • Quantum theory: \( E \)-levels for gas motion get closer together when volume expands.
  • More \( E \)-levels become accessible at a given \( T \).
  • \( E \) will disperse over more levels.

Measuring Dispersal of \( E \): Entropy

In summary:
Processes are product favored if \( E \) is dispersed from a few levels into many levels.

This typically occurs during:
• exothermic reactions (bond \( E \) dispersal).
• processes in which matter is dispersed.

In thermodynamics, nanoscale \( E \) dispersal is measured by the Entropy \((S)\) of a system.
At constant $T$: 
\[ \Delta S = S_{\text{final}} - S_{\text{initial}} = \frac{q_{\text{rev}}}{T} \]

“rev”: Only applies to reversible changes.

A reversible process:
- can be reversed by a slight change in conditions.
- e.g. ice melting at 0.0°C and 1 atm is reversible.
  - small decrease in $T$ will cause it to refreeze.

**Absolute Entropy Values**

A perfect crystal, at absolute zero (0 K) has:
- Minimum molecular motion (min. $E$ dispersal).

\[ S = 0 \] (perfect crystal at 0 K)

(The 3rd law of thermodynamics)

Measure the heat to change from 0 K $\to$ room- $T$ (reversibly). Gives $\Delta S$ and the absolute $S$ at room $T$.

\[ \Delta S = S_{\text{final}} - S_{\text{initial}} = \frac{q_{\text{rev}}}{T} \]

$S_{\text{room }T} = \Delta S - S_{\text{initial}} = \Delta S$

**Measuring Dispersal of $E$: Entropy**

Calculate $\Delta S$ when 25.0 g of Al(s) melts at its normal melting point (660.3 °C; 1 atm). $\Delta H_{\text{fus}}(\text{Al}) = 10.7 \text{ kJ mol}^{-1}$

\[
\Delta S = \frac{q_{\text{rev}}}{T} = \frac{\Delta H_{\text{fus}}}{T} \\
T = 660.3 ^\circ \text{C} = 933.5 \text{ K} \\
q_{\text{rev}} = \frac{25.0 \text{ g}}{26.98 \text{ g mol}^{-1}} = 0.9266 \text{ mol} \\
\Delta S = \frac{0.9266 \text{ mol}(10.7 \text{ kJ mol}^{-1})}{933.5 \text{ K}} = 0.01062 \text{ kJ K}^{-1} \\
\Delta S = 10.6 \text{ J K}^{-1}
\]

**Absolute Entropy Values**

Standard molar entropies ($S^\circ$), are measured by heating 1 mol of substance from 0 K to:
- A specified $T$ (often 25°C = 298.15 K)
- At constant $P = 1$ bar

$S^\circ$ has J K$^{-1}$mol$^{-1}$ units.

$S^\circ$ is always positive, for all materials.

**Standard Molar Entropies (298.15 K)**

<table>
<thead>
<tr>
<th>Compound</th>
<th>$S^\circ$ (J K$^{-1}$ mol$^{-1}$)</th>
<th>Compound</th>
<th>$S^\circ$ (J K$^{-1}$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (graphite)</td>
<td>5.740</td>
<td>CCl$_2$(g)</td>
<td>223.066</td>
</tr>
<tr>
<td>C(g)</td>
<td>158.096</td>
<td>Br$_2$(g)</td>
<td>152.231</td>
</tr>
<tr>
<td>CH$_4$(g)</td>
<td>186.264</td>
<td>I$_2$(s)</td>
<td>116.135</td>
</tr>
<tr>
<td>C$_2$H$_6$(g)</td>
<td>229.60</td>
<td>HCl(g)</td>
<td>186.908</td>
</tr>
<tr>
<td>C$_2$H$_4$(g)</td>
<td>269.9</td>
<td>H$_2$O(g)</td>
<td>188.825</td>
</tr>
<tr>
<td>C$_2$H$_6$(g)</td>
<td>219.4</td>
<td>H$_2$O(l)</td>
<td>69.91</td>
</tr>
<tr>
<td>CH$_3$OH(l)</td>
<td>126.8</td>
<td>NaCl(s)</td>
<td>72.13</td>
</tr>
<tr>
<td>CO(g)</td>
<td>197.674</td>
<td>KOH(s)</td>
<td>78.9</td>
</tr>
<tr>
<td>CO$_2$(g)</td>
<td>213.74</td>
<td>NaCl(aq)</td>
<td>115.5</td>
</tr>
<tr>
<td>F$_2$(g)</td>
<td>202.78</td>
<td>KOH(aq)</td>
<td>91.6</td>
</tr>
</tbody>
</table>

**Qualitative Guidelines for Entropy**

$S_{\text{gas}} >> S_{\text{liquid}} > S_{\text{solid}}$

Solid molecules vibrate about fixed lattice points. Liquid molecules can slide past each other. Gas molecules have few restrictions on motion.

More motion = higher $S$

<table>
<thead>
<tr>
<th>$S^\circ$ (J K$^{-1}$ mol$^{-1}$)</th>
<th>gas</th>
<th>liquid</th>
<th>solid</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S^\circ$(I$_2$)</td>
<td>261</td>
<td>-</td>
<td>116</td>
</tr>
<tr>
<td>$S^\circ$(Br$_2$)</td>
<td>245</td>
<td>152</td>
<td>-</td>
</tr>
<tr>
<td>$S^\circ$(Cl$_2$)</td>
<td>223</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Larger, more complex, molecules have larger $S$: $S^{\circ}_{\text{complex molecule}} > S^{\circ}_{\text{simple molecule}}$

<table>
<thead>
<tr>
<th>Species type</th>
<th>$S^{\circ}$ (J K$^{-1}$ mol$^{-1}$)</th>
<th>Species mass $S^{\circ}$ (J K$^{-1}$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$ alkane</td>
<td>186</td>
<td>Ar 40 155</td>
</tr>
<tr>
<td>C$_2$H$_6$ alkane</td>
<td>230</td>
<td>CO$_2$ 44 214</td>
</tr>
<tr>
<td>C$_3$H$_8$ alkane</td>
<td>270</td>
<td>C$_3$H$_8$ 44 270</td>
</tr>
</tbody>
</table>

Larger molecules have more ways to distribute $E$ (more bonds to hold potential and kinetic $E$).

### Qualitative Guidelines for Entropy

**Solid or liquid dissolving**

Larger matter dispersal. $S$ usually* increases:

<table>
<thead>
<tr>
<th>Substance</th>
<th>$S^{\circ}$ (pure)</th>
<th>$S^{\circ}$ (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$COOH(ℓ)</td>
<td>160</td>
<td>179</td>
</tr>
<tr>
<td>NH$_4$NO$_3$(s)</td>
<td>151</td>
<td>260</td>
</tr>
</tbody>
</table>

J K$^{-1}$ mol$^{-1}$ units

*Strong solvation may increase order. $\Delta S < 0$ is possible.

### Qualitative Guidelines for Entropy

**Gas dissolving**

Gas-molecule motion becomes restricted. $\Delta S < 0$.

<table>
<thead>
<tr>
<th>Substance</th>
<th>$S^{\circ}$ (gas)</th>
<th>$S^{\circ}$ (aq, soln)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>214</td>
<td>118</td>
</tr>
<tr>
<td>H$_2$</td>
<td>131</td>
<td>58</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>240</td>
<td>133</td>
</tr>
</tbody>
</table>

J K$^{-1}$ mol$^{-1}$ units

### Predicting Entropy Changes

CaCO$_3$(s) $\rightarrow$ CaO(s) + CO$_2$(g)  $\Delta S = 161$ J K$^{-1}$mol$^{-1}$

Large entropy increase:
- Solid $\rightarrow$ gas, $\Delta S > 0$.
- 1 molecule $\rightarrow$ 2 molecules, $\Delta S > 0$.

H$_2$(g) + F$_2$(g) $\rightarrow$ 2 HF(g)  $\Delta S = 14$ J K$^{-1}$mol$^{-1}$

- All gases, $S$ = constant.
- 2 reactant gases, 2 product gases, $S$ = constant.

Actual $\Delta S$ shows a small increase.
Entropy is a state function (like \( H \)). For a reaction:

\[
\Delta S^\circ = \sum (n_{\text{product}} S^\circ_{\text{product}}) - \sum (n_{\text{reactant}} S^\circ_{\text{reactant}})
\]

**Example**

Methanol is a common fuel additive. Calculate \( \Delta S^\circ \) at 298 K for its combustion:

\[
2 \text{ CH}_3\text{OH}(l) + 3 \text{ O}_2(g) \rightarrow 2 \text{ CO}_2(g) + 4 \text{ H}_2\text{O}(l)
\]

Look up \( S^\circ \) values (J K\(^{-1}\) mol\(^{-1}\)):

- \( \text{CH}_3\text{OH}(l) = 126.8 \) J K\(^{-1}\) mol\(^{-1}\)
- \( \text{O}_2(g) = 205.138 \) J K\(^{-1}\) mol\(^{-1}\)
- \( \text{CO}_2(g) = 213.74 \) J K\(^{-1}\) mol\(^{-1}\)
- \( \text{H}_2\text{O}(l) = 69.91 \) J K\(^{-1}\) mol\(^{-1}\)

Calculating \( \Delta S^\circ \):

\[
\Delta S^\circ = \sum (n_{\text{product}} S^\circ_{\text{product}}) - \sum (n_{\text{reactant}} S^\circ_{\text{reactant}})
\]

\[
= (2 \times 213.74) + 4 \times 69.91 \]  
- \( 2 \times 126.8 + 3 \times 205.14 \) 

\[
= 707.12 - 869.02 
\]

\[
= -161.90 \text{ J K}^{-1} \text{ mol}^{-1}
\]

Entropy decreases as expected: 3 gas + 2 \( l \) \( \rightarrow \) 2 gas + 4 \( l \)

**Entropy & the 2\(^{nd} \) Law of Thermodynamics**

Energy dispersal is accompanied by an increase in disorder of a system:

- Increased disorder = increased \( S \)

Second Law of Thermodynamics

“The total entropy of the universe is continuously increasing.”

- The universe is slowly becoming more disordered.

**Entropy & the 2\(^{nd} \) Law of Thermodynamics**

Calculate \( \Delta S^\circ_{\text{univ}} \) for the combustion of octane in air:

\[
2 \text{ C}_8\text{H}_{18}(g) + 25 \text{ O}_2(g) \rightarrow 16 \text{ CO}_2(g) + 18 \text{ H}_2\text{O}(l)
\]

For the reaction \( \Delta H^\circ = -11,024 \text{ kJ} \) and \( \Delta S^\circ = -1383.9 \) J/K at 298.15 K.

\[
\Delta S^\circ_{\text{univ}} = \Delta S^\circ_{\text{sys}} + \Delta S^\circ_{\text{surr}}
\]

\[
\Delta S^\circ_{\text{univ}} = \Delta S^\circ_{\text{sys}} + \Delta S^\circ_{\text{surr}} \quad \text{given} \quad \Delta H^\circ / T
\]

\[
\Delta S_{\text{univ}} = -1383.9 \text{ J/K} + (+11,024 \times 10^3 \text{ J})/298.15 \text{ K}
\]

\[
= -1383.9 \text{ J/K} + 36.975 \text{ kJ/K}
\]

\[
= +35,591 \text{ J/K}
\]

**Gibbs Free Energy**

Neither entropy (\( S \)), nor enthalpy (\( H \)), alone can predict whether a reaction is product favored. Spontaneous (product favored) reactions can:

- Be exothermic or endothermic.
- Increase or decrease the \( S_{\text{system}} \).

The Gibbs free energy (\( G \)), combines \( H \) and \( S \).

\( \Delta G \) does predict if a reaction is product favored or not.
The Gibbs Free Energy is equal to:

\[ \Delta G = \Delta H - T \Delta S \]

If \( G \):
- Decreases \( (\Delta G < 0) \) a reaction is product favored (at constant \( P \) and \( T \)).
- Increases \( (\Delta G > 0) \) a reaction is reactant favored.

\( \Delta G \) can be calculated from \( \Delta H \) and \( \Delta S \) values…

or from Gibbs free energies of formation \( (\Delta G^\circ_f) \):

\[ \Delta G^\circ = \sum (n_{product} \Delta G^\circ_{f, product}) - \sum (n_{reactant} \Delta G^\circ_{f, reactant}) \]

\( \Delta G^\circ \) equals:
- \( \Delta G \) to make 1 mol of compound from its elements.
- 0 for an element in its most stable state (like \( \Delta H^\circ \)).

Effect of \( T \) on Reaction Direction

Reactions go from reactant to product-favored when:

\[ \Delta G = 0 = \Delta H - T \Delta S \]

or when: \( \Delta H = T \Delta S \)

At what \( T \) will the following reaction be product favored?

\[ \text{CH}_4(g) + \text{H}_2\text{O}(g) \rightarrow \text{CO}(g) + 3 \text{H}_2(g) \]

\( \Delta H^\circ_f \) values:
- \( -74.81 \) kJ/mol
- \( -241.82 \) kJ/mol
- \( -110.53 \) kJ/mol

\( S^\circ \): (J K\(^{-1}\) mol\(^{-1}\))
- 186.26
- 188.83
- 197.67
- 130.68

\( \Delta S^\circ = [(197.67) + 3(130.68)] - [(186.26 + 188.83)] J K^{-1} \text{mol}^{-1} \)
- 214.62 J K\(^{-1}\) mol\(^{-1}\)

\( \Delta H^\circ = [(-110.53) + 3(0)] - [(-74.81) + (-241.82)] \) kJ mol\(^{-1}\)
- 206.10 kJ mol\(^{-1}\)

It will switch direction at:

\[ T = \frac{\Delta H}{\Delta S} = \frac{2.0610 \times 10^5 \text{J mol}^{-1}}{214.62 \text{J K}^{-1} \text{mol}^{-1}} = 960.30 \text{ K} \]
**Gibbs Free Energy and Equilibrium Constants**

Gibbs free energy $G$ and the equilibrium constant $K$ both show if a reaction is product-favored and are related.

\[ \Delta G^\circ = -RT \ln K^\circ \]

$K^\circ$ must be unitless.

Each quantity in the $K^\circ$ expression is divided by its standard state value:

- concentrations by 1 mol L$^{-1}$ (solids and liquids).
- pressures by 1 bar (gas reactions).

**Gibbs Free Energy & Maximum Work**

$\Delta G$ = maximum *useful* work that can be done by a reaction on its surroundings (constant $T$ and $P$).

\[ \Delta G = w_{\text{system}} = -w_{\text{max}} \]

“free” energy = available energy

For:

\[ 2 \text{H}_2(g) + \text{O}_2(g) \rightarrow 2 \text{H}_2\text{O}(g) \quad \Delta G^\circ = -474.3 \text{kJ} \]

Every 2 moles of H$_2$ consumed can do up to 474.3 kJ of work.

**Gibbs Free Energy and Equilibrium Constants**

Evaluate $K^\circ$ (298 K) for the reaction:

\[ 2 \text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g) \]

\[ \Delta G^\circ = \Delta G^\circ(\text{N}_2\text{O}_4) - 2\Delta G^\circ(\text{NO}_2) = 97.89 - 2(51.31) \text{kJ/mol} = -4.73 \text{kJ/mol} \]

\[ \ln K^\circ = \frac{-\Delta G^\circ}{RT} = -\frac{-4.73 \times 10^3 \text{J/mol}}{(8.314 \text{ J K}^{-1} \text{mol}^{-1})(298 \text{ K})} = 1.91 \]

\[ K^\circ = 6.75 \]

**Gibbs Free Energy & Maximum Work**

$\Delta G$ also equals the minimum work required to cause a reactant-favored process to occur.

\[ 2 \text{H}_2\text{O}(g) \rightleftharpoons 2 \text{H}_2(g) + \text{O}_2(g) \quad \Delta G^\circ = 474.3 \text{kJ} \]

A minimum of 474.3 kJ of work must be used to produce 2 mol of H$_2$ from liquid water.

**Thermodynamic and Kinetic Stability**

**Thermodynamically stable**

Reaction is not product-favored.

- Thermodynamically stable:
  \[ \text{Pd} + \text{O}_2 \rightarrow \text{PdO}_2 \quad \Delta G^\circ = +326 \text{kJ/mol} \]

- Thermodynamically unstable:
  \[ 4 \text{Al} + 3 \text{O}_2 \rightarrow 2 \text{Al}_2\text{O}_3 \quad \Delta G^\circ = -3164.6 \text{kJ/mol} \]

**Kinetically stable**

Product-favored, but too slow to be important.

- Diamond is thermodynamically unstable
  \[ \text{C}_{\text{diamond}} \rightarrow \text{C}_{\text{graphite}} \quad \Delta G^\circ = -2.9 \text{kJ/mol} \]

- Kinetically stable, too slow to be important.

- $E_a$ is too large