3.5 The Helmholtz and Gibbs energies

Key points

1. The Clausius inequality: criteria for spontaneous change under a variety of conditions
2. Helmholtz energy: a spontaneous process at constant $T$ and $V$
3. The change in the Helmholtz energy = the maximum work
4. Gibbs energy: a spontaneous process at constant $T$ and $P$
5. The change in the Gibbs energy = the maximum non-expansion work
3.5 The Helmholtz and Gibbs energies

(a) Criteria for spontaneity

\[ dS - \frac{dq}{T} \geq 0 \] : The Clausius inequality

- Let’s consider heating at constant volume.
- \( dq_V = dU \) in absence of the non-expansion work

\[ dS - \frac{dU}{T} \geq 0 \]

\[ TdS \geq dU \] (constant V, no additional work)

\[ dS_{U,V} \geq 0 \]
\[ dU_{S,V} \leq 0 \]
3.5 The Helmholtz and Gibbs energies

(a) Criteria for spontaneity

\[ dS_{U,V} \geq 0 \]

- Entropy increases in a spontaneous process in a system at a constant \( V \) and \( U \) (an isolated system)

\[ dU_{S,V} \leq 0 \]

- Internal energy decreases in a spontaneous process in a system at a constant \( V \) and \( S \)
- The entropy of the system is unchanged and then there must be an increase in entropy of the surroundings
- The entropy of the surrounding is increased only if the energy of the system decreases as energy flows out as heat
3.5 The Helmholtz and Gibbs energies

(a) Criteria for spontaneity

\[ dS - \frac{dq}{T} \geq 0 \quad : \text{The Clausius inequality} \]

- Let’s consider heating at constant pressure
- \( dq_p = dH \) in absence of the non-expansion work

\[ dS - \frac{dH}{T} \geq 0 \]

\[ TdS \geq dH \quad (\text{constant } p, \text{ no additional work}) \]

\[ dS_{H,p} \geq 0 \quad dH_{S,p} \leq 0 \]
3.5 The Helmholtz and Gibbs energies

(a) Criteria for spontaneity

Helmholtz energy, \( A \)
\[
A = U - TS
\]

Gibbs energy, \( G \)
\[
G = H - TS
\]

At constant \( T \),
\[
dA = dU - TdS \\
dG = dH - TdS
\]

The criteria of spontaneous change
\[
dA_{T,V} \leq 0 \\
dG_{T,p} \leq 0
\]

All the symbols in these two definitions refer to the system!!
3.5 The Helmholtz and Gibbs energies

(b) Some remarks on the Helmholtz energy

- The criterion of equilibrium

\[ dA_{T,V} = 0 \]

- Systems move spontaneously toward states of lower A if a path is available

- The system is in equilibrium when neither the forward nor reverse process has a tendency to occur

- The form of \( dA \) may give the impression that systems favor lower energy, but that is misleading
  - \( dS \) is the entropy change of the system
  - \( -dU/T \) is the entropy change of the surroundings

\[ dA = dU - TdS \]
3.5 The Helmholtz and Gibbs energies

(c) Maximum work

The change in the Helmholtz function is equal to the maximum work accompanying a process at constant $T$

$$dw_{\text{max}} = dA$$

$$w_{\text{max}} = \Delta A$$

$$\Delta A = \Delta U - T\Delta S$$

- $A = U - TS$: $A$ is the total internal energy of the system, $U$, less a contribution that is stored as energy of thermal motion (the quantity $TS$).
- Because energy stored in random thermal motion cannot be used to achieve uniform motion in the surroundings, only the part of $U$ that is not stored in that way, the quantity $U - TS$, is available for conversion into work.
3.5 The Helmholtz and Gibbs energies

(c) Maximum work

The process is spontaneous if overall the entropy of the system and its surroundings increase.

The entropy of the system decreases, so that of the surroundings must increase, which means that energy must pass from to the surrounding as heat.

The entropy of the system increases; we can afford to lose some entropy of the surroundings. Some of their energy may be lost as heat to the system. This energy can be returned to them as work. The work done can exceed $\Delta U$. 
(d) Some remarks on the Gibbs energy

- Chemists are usually more interested in changes occurring at constant P that at constant V
- At constant T and P, chemical reactions are spontaneous in the directions of decreasing Gibbs energy

\[ dG_{T,p} \leq 0 \]

- If G decreases as the reaction proceeds, the reaction has a spontaneous tendency to convert reactants into products
- If G increases as the reaction proceeds, the reverse reaction is spontaneous
(d) Some remarks on the Gibbs energy

\[ dG = dH - TdS \]

- Endothermic reactions are driven by the increase of entropy of the system
- \( dH > 0 \); In order for the process to be spontaneous, the entropy of the system increases so much that \( TdS \) outweighs \( dH \)
- This entropy change overcomes the reduction of entropy brought about in the surroundings by the inflow of heat into the system \( (dS_{\text{sur}} = -dH/T \) at constant \( P) \)
(e) Maximum non-expansion work

At constant T and P, the maximum additional (non-expansion) work, $w_{\text{add, max}}$, is given by the change in Gibbs energy

\[
dw_{\text{add, max}} = dG
\]

\[
w_{\text{add, max}} = \Delta G
\]

This expression is particularly useful for assessing the electrical work
3.6 Standard molar Gibbs energies

Key points

1. Standard Gibbs energies of formation are used to calculate the standard Gibbs energies of reactions

2. The Gibbs energies of formation of ions may be estimated from a thermodynamic cycle and the Born equation
3.6 Standard molar Gibbs energies

The standard Gibbs energy of reaction:

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

the difference between in standard molar Gibbs energies of the products and reactants in their standard states at the temperature specified

$$\Delta_r G^\Theta = \sum_{\text{Products}} v \Delta_f G^\Theta - \sum_{\text{Reactants}} v \Delta_f G^\Theta$$

$$\Delta_r G^\Theta = \sum_{J} v_j \Delta_f G^\Theta (J)$$
3.6 Standard molar Gibbs energies

The standard Gibbs energy of formation:

\[ \Delta_f G^\Theta \]

the standard reaction Gibbs energy for the formation of a compound from its elements in their reference states.

Standard Gibbs energies of formation of the elements in their reference states are zero, because their formation is a ‘null’ reaction.

\[ \Delta_f G^\Theta (H^+, \text{aq}) = 0 \]

<table>
<thead>
<tr>
<th></th>
<th>( \Delta_f G^\Theta / (\text{kJ mol}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond, C(s)</td>
<td>2.9</td>
</tr>
<tr>
<td>Benzene, C_6H_6(l)</td>
<td>124.3</td>
</tr>
<tr>
<td>Methane, CH_4(g)</td>
<td>-50.7</td>
</tr>
<tr>
<td>Carbon dioxide, CO_2(g)</td>
<td>-394.4</td>
</tr>
<tr>
<td>Water, H_2O(l)</td>
<td>-237.1</td>
</tr>
<tr>
<td>Ammonia, NH_3(g)</td>
<td>-16.5</td>
</tr>
<tr>
<td>Sodium chloride, NaCl(s)</td>
<td>-384.1</td>
</tr>
</tbody>
</table>

* More values are given in the Data section.
3.6 Standard molar Gibbs energies

\[ \frac{1}{2} \text{H}_2(g) + \frac{1}{2} \text{X}_2(g) \rightarrow \text{H}^+(aq) + \text{X}^-(aq) \]

\[ \Delta_f G^\Theta (\text{Cl}^-, \text{aq}) = 1272 \text{kJmol}^{-1} + \Delta_{\text{solv}} G^\Theta (\text{H}^+) + \Delta_{\text{solv}} G^\Theta (\text{Cl}^-) \]

\[ \Delta_{\text{solv}} G^\Theta = -\frac{z_i^2 e^2 N_A}{8 \pi \varepsilon_0 r_i} \left(1 - \frac{1}{\varepsilon_r} \right) \quad \text{: Born equation} \]

\[ \Delta_{\text{solv}} G^\Theta = -\frac{z_i^2}{(r_i / \text{pm})} \times (6.86 \times 10^4 \text{kJ / mol}) \text{ for water} \]