Statistical Molecular Thermodynamics

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Video 12.1

Free Energies of Reaction
Using the ideas of reaction rates van’t Hoff described the dynamics of chemical equilibrium. This is one of the most important topics in chemistry.

van’t Hoff also published a paper early in his career that described a tetrahedral model for the carbon atom. This was not included in his thesis because it was too controversial to be accepted.

van’t Hoff was awarded the first Nobel Prize in Chemistry.
Thermodynamics and Equilibrium

Many of the most important applications of thermodynamics are to systems at chemical equilibrium.

At constant $T$ and $P$ (where most benchtop chemistry takes place) we know that the condition for equilibrium is $\Delta G = 0$. If we are not at equilibrium, we can predict whether a reaction will proceed towards equilibrium by the sign of $\Delta G$, which dictates whether a process will proceed spontaneously.

With the knowledge of thermodynamics that we have developed, we can calculate and make predictions about $G$, for example the temperature dependence. What we need in order to apply this to chemical equilibrium is to derive the relationship between $G$ and the equilibrium constant for a chemical reaction.
Start with a gas phase reaction described by a balanced chemical equation,

\[ \nu_A A(g) + \nu_B B(g) \rightleftharpoons \nu_Y Y(g) + \nu_Z Z(g) \]

Define the *extent of reaction*, \( \xi \),

**reactants**

- \( n_A = n_{A0} - \nu_A \xi \)
- \( n_B = n_{B0} - \nu_B \xi \)

**products**

- \( n_Y = n_{Y0} + \nu_Y \xi \)
- \( n_Z = n_{Z0} + \nu_Z \xi \)
Self-assessment

For the reaction:

\[ 4 \text{NH}_3 + 5 \text{O}_2 \rightleftharpoons 4 \text{NO} + 6 \text{H}_2\text{O} \]

with initial amounts of \(\text{NH}_3\), \(\text{O}_2\), \(\text{NO}\), and \(\text{H}_2\text{O}\) of 2, 2, 1, and 0 moles, respectively:

what are the amounts of \(\text{NH}_3\), \(\text{O}_2\), \(\text{NO}\), and \(\text{H}_2\text{O}\) at reaction extent \(\xi = 0.25\) moles?

what is the maximum possible reaction extent?
For the reaction:

\[ 4 \text{NH}_3 + 5 \text{O}_2 \leftrightharpoons 4 \text{NO} + 6 \text{H}_2\text{O} \]

with initial amounts of NH\(_3\), O\(_2\), NO, and H\(_2\)O of 2, 2, 1, and 0 moles, respectively:

what are the amounts of NH\(_3\), O\(_2\), NO, and H\(_2\)O at reaction extent \( \xi = 0.25 \) moles?

1, 0.75, 2, and 1.5 moles, respectively

what is the maximum possible reaction extent?

0.4 moles (at which point no O\(_2\) remains to react)
Extent of Reaction (cont.)

\[ \nu_A A(g) + \nu_B B(g) \rightleftharpoons \nu_Y Y(g) + \nu_Z Z(g) \]

\( \xi \) varies from 0 to a maximum value dictated by the stoichiometry.

For example, if \( \begin{cases} n_{A0} = \nu_A \text{ moles} \\ n_{B0} = \nu_B \text{ moles} \end{cases} \) then \( \xi \) can vary from 0 to 1 mol

(Note that in this case \( \xi \) cannot exceed 1 since \( n_A \) and \( n_B \) would become negative)

For each reactant and product:
- Reactants:
  - \( n_A = n_{A0} - \nu_A \xi \)
  - \( n_B = n_{B0} - \nu_B \xi \)
- Products:
  - \( n_Y = n_{Y0} + \nu_Y \xi \)
  - \( n_Z = n_{Z0} + \nu_Z \xi \)

Differentiate

\[ dn_A = -\nu_A d\xi \]
\[ dn_B = -\nu_B d\xi \]
\[ dn_Y = \nu_Y d\xi \]
\[ dn_Z = \nu_Z d\xi \]
Connecting to Gibbs Free Energy

\[ \nu_A A(g) + \nu_B B(g) \rightleftharpoons \nu_Y Y(g) + \nu_Z Z(g) \]

Consider \( G \), which is a function of \( T, P, n_A, n_B, n_Y, n_Z \):

\[
dG = \left( \frac{\partial G}{\partial T} \right)_{P,n_j} dT + \left( \frac{\partial G}{\partial P} \right)_{T,n_j} dP + \left( \frac{\partial G}{\partial n_A} \right)_{T,P,n_{j\neq A}} dn_A \\
+ \left( \frac{\partial G}{\partial n_B} \right)_{T,P,n_{j\neq B}} dn_B + \left( \frac{\partial G}{\partial n_Y} \right)_{T,P,n_{j\neq Y}} dn_Y + \left( \frac{\partial G}{\partial n_Z} \right)_{T,P,n_{j\neq Z}} dn_Z
\]

Using:

\[
\left( \frac{\partial G}{\partial T} \right)_P = -S \quad \left( \frac{\partial G}{\partial P} \right)_T = V \quad \mu_A = \left( \frac{\partial G}{\partial n_A} \right)_{P,T,n_{j\neq A}}
\]

\[
dG = -SdT + VdP + \mu_A dn_A + \mu_B dn_B + \mu_Y dn_Y + \mu_Z dn_Z
\]

At constant \( T \) and \( P \), (i.e., \( G \) only depends on change in \( n \)):

\[
dG = \sum_j \mu_j dn_j = \mu_A dn_A + \mu_B dn_B + \mu_Y dn_Y + \mu_Z dn_Z
\]
**Gibbs Free Energy of Reaction**

\[ dG = \mu_A \, dn_A + \mu_B \, dn_B + \mu_Y \, dn_Y + \mu_Z \, dn_Z \quad \text{(constant } T \text{ and } P) \]

Rather than having \( dG \) in terms of differentials for every component we can use stoichiometry to rewrite it in terms of the change in a single variable, \( d\xi \):

\[ dn_A = -\nu_A \, d\xi \quad dn_B = -\nu_B \, d\xi \quad dn_Y = \nu_Y \, d\xi \quad dn_Z = \nu_Z \, d\xi \]

\[ dG = \left( -\nu_A \, \mu_A - \nu_B \, \mu_B + \nu_Y \, \mu_Y + \nu_Z \, \mu_Z \right) d\xi \quad \text{(constant } T \text{ and } P) \]

\[ \Delta_r G = \left( \frac{\partial G}{\partial \xi} \right)_{T,P} = \nu_Y \, \mu_Y + \nu_Z \, \mu_Z - \nu_A \, \mu_A - \nu_B \, \mu_B \]

\( \Delta_r G \) is the change in the Gibbs energy when the extent of reaction changes by one mole. Units are energy/mol. Note that \( \Delta_r G \) only has meaning if a balanced chemical equation has been specified.
\[ dU = \delta q + \delta w \]

Next: Equilibrium Constants \( K_p, K_c, \) and \( K_a \)