Chemical equilibrium

Gibbs-Helmholtz equation

For many processes it is useful to know the variation of Gibbs free energy with temperature. During the previous lecture we have seen the fundamental equation:

$$\mathrm{d}G = V\,\mathrm{d}p - S\,\mathrm{d}T$$

which gives:

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

Gibbs free energy G is defined as $H - TS$, which we can rearrange and express as: $S = (H - G)/T$. This equation can be also written as:

$$-S = \frac{G}{T} - \frac{H}{T}$$

Since $\left(\frac{\partial G}{\partial T}\right)_p = -S$ the previous equation can be written as:

$$\left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T} = -\frac{H}{T}$$

We can show that $\left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T} = T\left(\frac{\partial (G/T)}{\partial T}\right)_p$

A little bit of maths

If a function $f(x)$ is given by the product of 2 functions $g(x)$ and $h(x)$

$$f = gh$$

its derivative with respect to x is:

$$\frac{\mathrm{d}f}{\mathrm{d}x} = g\frac{\mathrm{d}h}{\mathrm{d}x} + h\frac{\mathrm{d}g}{\mathrm{d}x}$$

We can apply the product rule of derivatives to calculate $\left(\frac{\partial (G/T)}{\partial T}\right)_p$

$$\begin{aligned}
\left(\frac{\partial (G/T)}{\partial T}\right)_p &= \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p + G\left(\frac{\partial 1/T}{\partial T}\right)_p \\
&= \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p - G\frac{1}{T^2}
\end{aligned}$$

By multiplying both sides by T:

$$T\left(\frac{\partial(G/T)}{\partial T}\right)_p = \left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T}$$
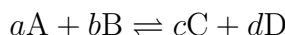
which is what we wanted to prove.

We can substitute this result into $\left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T} = -\frac{H}{T}$ and, after dividing both sides by T, we obtain:

$$\left(\frac{\partial(G/T)}{\partial T}\right)_p = -\frac{H}{T^2}$$

which is the **Gibbs-Helmholtz equation**.

Van't Hoff isotherm

The Van't Hoff isotherm correlates the Gibbs free energy of a reaction with its equilibrium constant. For a generic chemical reaction at equilibrium:

$$a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$$

the equilibrium constant is defined:

$$K_{\text{eq}} = \frac{a_{\text{C}}^c \, a_{\text{D}}^d}{a_{\text{A}}^a \, a_{\text{B}}^b}$$

where a_{X} is the activity at equilibrium of the generic X chemical species taking part to the chemical reaction. The activity of a chemical species could be thought of as an *effective concentration*. Using a more generic and compact, but maybe slightly more difficult to follow, mathematical notation we can write the equilibrium constant as:

$$K_{\text{eq}} = \prod_i a_i^{\nu_i}$$

where ν_i is the stoichiometric coefficient of species i and it's positive if i is a product and negative is i is a reactant. During lecture 2 we have seen that for each of the chemical species we can write:

$$\mu_i = \mu_i^{\ominus} + RT \ln a_i$$

or equivalently:

$$\overline{G}_i = \overline{G}_i^{\ominus} + RT \ln a_i$$

where μ_i is the chemical potential of species i, $\overline{G}_i$ is the partial molar free energy of specie i (which is by definition equivalent to its chemical potential) and the superscript $\ominus$ represents the standard conditions.

If we focus our attention to a gas phase reaction we can approximate the activity of each species with its partial pressure, so that the previous equation becomes:

$$\overline{G}_i = \overline{G}_i^{\ominus} + RT \ln p_i$$

For a certain species i with stoichiometric coefficient ν_i we can write:

$$\nu_i \overline{G}_i - \nu_i \overline{G}_i^{\ominus} = \nu_i RT \ln p_i = RT \ln p_i^{\nu_i}$$

We can calculate the difference of free energy between the products and the reactants. In the case of the initial $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$ this would give:

$$(c\overline{G}_\text{C} - c\overline{G}_\text{C}^{\ominus}) + (d\overline{G}_\text{D} - d\overline{G}_\text{D}^{\ominus}) - (a\overline{G}_\text{A} - a\overline{G}_\text{A}^{\ominus}) - (b\overline{G}_\text{B} - b\overline{G}_\text{B}^{\ominus}) =$$
$$RT \ln p_\text{C}^c + RT \ln p_\text{D}^d - RT \ln p_\text{A}^a - RT \ln p_\text{B}^b$$

The left hand term can be expressed as $\Delta G_\text{r} - \Delta G_\text{r}^{\ominus}$ while the left hand side can be expressed as $RT \ln \frac{p_\text{C}^c \ p_\text{D}^d}{p_\text{A}^a \ p_\text{B}^b}$ or $RT \ln K_\text{eq}$. Therefore:

$$\Delta G_\text{r} - \Delta G_\text{r}^{\ominus} = RT \ln K_\text{eq}$$

However, we are in a state of equilibrium and $\Delta G_\text{r} = 0$ and as a consequence:

$$\Delta G_\text{r}^{\ominus} = -RT \ln K_\text{eq}$$

Van't Hoff isochore

The Van't Hoff isochore allows us to quantify how the equilibrium constant varies with temperature. During lecture 3 we have seen that the fundamental equation can be expressed as $\text{d}G = V \, \text{d}p - S \, \text{d}T$, which led us to the conclusion that $\left(\frac{\partial G}{\partial T}\right)_p = -S$. Therefore for a generic reaction we can write:

$$\left(\frac{\partial \Delta G_\text{r}^{\ominus}}{\partial T}\right)_p = -\Delta S_\text{r}^{\ominus}$$

We also know that $\Delta G_\text{r}^{\ominus} = \Delta H_\text{r}^{\ominus} - T\Delta S_\text{r}^{\ominus}$, which we can rearrange as $\Delta S_\text{r}^{\ominus} = \frac{\Delta H_\text{r}^{\ominus} - \Delta G_\text{r}^{\ominus}}{T}$. Therefore:

$$\left(\frac{\partial \Delta G_\text{r}^{\ominus}}{\partial T}\right)_p = -\Delta S_\text{r}^{\ominus} = \frac{\Delta G_\text{r}^{\ominus} - \Delta H_\text{r}^{\ominus}}{T}$$

But from the Van't Hoff isotherm we know that $\Delta G_\text{r}^{\ominus} = -RT \ln K_\text{eq}$. Differentiating this by parts:

$$\frac{\partial \Delta G_\text{r}^{\ominus}}{\partial T} = -R \ln K_\text{eq} - RT\frac{\partial \ln K_\text{eq}}{\partial T}$$

Therefore:

$$-R \ln K_\text{eq} - RT\frac{\partial \ln K_\text{eq}}{\partial T} = \frac{\Delta G_\text{r}^{\ominus} - \Delta H_\text{r}^{\ominus}}{T}$$

from which:

$$\frac{\Delta H_\text{r}^{\ominus}}{T} = RT\frac{\partial \ln K_\text{eq}}{\partial T}$$

and finally:

$$\frac{\partial \ln K_\text{eq}}{\partial T} = \frac{\Delta H_\text{r}^{\ominus}}{RT^2}$$

which is the Van't Hoff equation.

We can integrate this differential equation and, assuming that the enthalpy change during the reaction does not depend on the value of temperature, we obtain:

$$\ln K_\text{eq,2} = \ln K_\text{eq,1} - \frac{\Delta H_\text{r}^{\ominus}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$