

Thermodynamics

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Lecture 4

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:

$$dG = V dp - S dT$$

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:

$$\frac{df}{dx} = g \frac{dh}{dx} + h \frac{dg}{dx}$$

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.

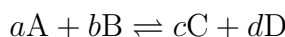
We can substitute this result into $\left(\frac{\partial G}{\partial T} \right)_p - \frac{G}{T} = -\frac{H}{T}$ and, after dividing both sides by T , we obtain:

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

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

The equilibrium constant and the 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:



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 if i is a reactant. If the system has a nearly ideal behaviour we can approximate the constant of equilibrium to

$$K_c = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

In the case of a gas phase reaction the activity of each species i can be replaced by the ratio f_i/f_i^\ominus , where f_i is the fugacity of species i (which could be thought of as an effective partial pressure) and f_i^\ominus is the fugacity in the standard state. However, we choose the standard state as the pure ideal gas at the pressure of 1 bar, and $f_i^\ominus = 1$ bar. The equilibrium constant for a gas phase reaction can be expressed as:

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

If the pressure in the system is low, the equilibrium constant can be approximated to:

$$K_p = \frac{p_{\text{C}}^c p_{\text{D}}^d}{p_{\text{A}}^a p_{\text{B}}^b}$$

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:

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

where μ_i is the chemical potential of species i , \bar{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, for simplicity, we focus our attention on a low-pressure gas phase reaction at equilibrium, we can approximate the activity of each species with its partial pressure, so that the previous equation becomes:

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

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

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

We can calculate the difference of free energy between the products and the reactants. In the case of the initial $aA + bB \rightleftharpoons cC + dD$ this would give:

$$(c\bar{G}_C - c\bar{G}_C^\ominus) + (d\bar{G}_D - d\bar{G}_D^\ominus) - (a\bar{G}_A - a\bar{G}_A^\ominus) - (b\bar{G}_B - b\bar{G}_B^\ominus) = \\ RT \ln p_C^c + RT \ln p_D^d - RT \ln p_A^a - RT \ln p_B^b$$

The left hand term can be expressed as $\Delta G_r - \Delta G_r^\ominus$, while the right hand side can be expressed as $RT \ln \frac{p_C^c p_D^d}{p_A^a p_B^b}$ or $RT \ln K_p$. Therefore:

$$\Delta G_r - \Delta G_r^\ominus = RT \ln K_p$$

However, we are in a state of equilibrium and $\Delta G_r = 0$ and as a consequence:

$$\Delta G_r^\ominus = -RT \ln K_p$$

The equation we derived for a gas phase reaction at low pressure can be extended to any reaction by replacing K_p with the exact value K_{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 $dG = V dp - S dT$, which led us to the conclusion that $\left(\frac{\partial G}{\partial T}\right)_p = -S$. Therefore for a generic reaction we can write:

$$\left(\frac{\partial \Delta G_r^\ominus}{\partial T}\right)_p = -\Delta S_r^\ominus$$

We also know that $\Delta G_r^\ominus = \Delta H_r^\ominus - T \Delta S_r^\ominus$, which we can rearrange as $\Delta S_r^\ominus = \frac{\Delta H_r^\ominus - \Delta G_r^\ominus}{T}$. Therefore:

$$\left(\frac{\partial \Delta G_r^\ominus}{\partial T}\right)_p = -\Delta S_r^\ominus = \frac{\Delta G_r^\ominus - \Delta H_r^\ominus}{T}$$

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

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

Therefore:

$$\cancel{-R \ln K_{\text{eq}}} - RT \frac{\partial \ln K_{\text{eq}}}{\partial T} = \frac{\cancel{\Delta G_r^\ominus} - \Delta H_r^\ominus}{T}$$

from which:

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

and finally:

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

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:

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

The effect of pressure on chemical equilibrium

The **Le Chatelier's principle** states: if the conditions under which an equilibrium is established are changed, the system will respond by shifting the equilibrium in a way that will minimise the effect of the changes.

How does this general principle apply to a gas phase chemical equilibrium subject to a change of pressure? The value of the equilibrium constant does not change with pressure, being dependent on temperature only; however, the composition at equilibrium can change: it could shift towards the reactants, favouring the reverse reaction, or it could shift towards the products, favouring the forward reaction.

An implication of the Le Chatelier's principle is that an increase in pressure, will cause the equilibrium to shift towards the side of the reaction with fewer moles of gas, counteracting the change of pressure of the system. Similarly, when there is a decrease in pressure, the equilibrium will shift towards the side of the reaction with more moles of gas. If a reaction occurs with no change in the number of moles of gas, the change in pressure will have no effect on the composition at equilibrium.