

## 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.

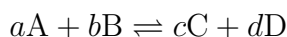
We can substitute this result into  $\left( \frac{\partial G}{\partial T} \right)_p - \frac{G}{T} = -\frac{H}{T}$  and, after dividing both sides by  $T$ , we obtain:

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

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  $a_{\text{X}}$  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  $\nu_i$  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  $\mu_i$  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  $\nu_i$  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:

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