Chemical Thermodynamics

1 Overview

Chemical thermodynamics is a branch of physical chemistry that studies the relationships between heat, work, and chemical reactions. It's built upon principles derived from classical thermodynamics, which is a broader field that describes the behavior of matter and energy on a macroscopic scale. Chemical thermodynamics applies these principles specifically to chemical systems and helps us understand how energy is transferred during chemical reactions.

2 Equilibrium Requirement

Recall the conditions for equilibrium:

$$\sum \mu_i dn_i \leq 0 \tag{1}$$

and:

$$dG \leq 0 \tag{2}$$

Therefore, we need to minimize Gibbs energy to reach equilibrium.
Recall that:

$$G = \sum_i n_i \mu_i = \sum_i n_i (\mu_i^o + \bar{R}T \ln p_i) \tag{3}$$

The first term represents G for **simple 'mixing' (put together) of LHS + RHS.** The second term represents ΔG for **'mixing' (actual mix) entropy of LHS and RHS.** When these two terms are overall balance, then the reaction reaches equilibrium.

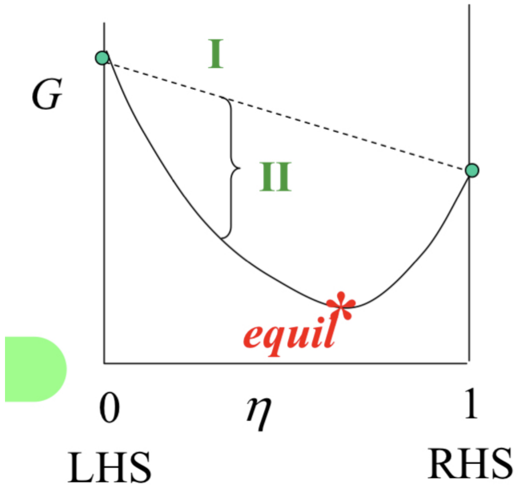

Figure 1: Minimum G

3 Equilibrium Constant

3.1 Van't Hoff Relation (Second Step)

Recall the first step Van't Hoff relation:

$$\frac{\partial(G/T)}{\partial T}|_{p,n_i} = -\frac{H}{T^2} \tag{4}$$

Change this to partial molar property:

$$\frac{\partial(\bar{g}_i/T)}{\partial T}|_{p,n_i} = -\frac{\bar{h}_i}{T^2} \tag{5}$$

Recall that:

$$\bar{g}_i = \mu_i^o + \bar{R}T \ln p_i \tag{6}$$

$$\bar{h}_i = \hat{h}_i \tag{7}$$

Then we have:

$$\frac{\partial(\mu_i^o/T)}{\partial T} = -\frac{\bar{h}_i}{T^2} = -\frac{\hat{h}_i}{T^2} \tag{8}$$

Now we introduce the definition of **equilibrium constant in pressure** K_p. Recall that at equilibrium:

$$\sum_i \mu_i v_i = \sum_i^{o} \mu_i^o v_i + \bar{R}T \sum_i v_i \ln p_i = 0 \tag{9}$$

Then we have:

$$-\frac{\sum_i v_i \mu_i^o}{\bar{R}T} = \sum_i v_i \ln p_i = \sum_i \ln {p_i}^{v_i} = \ln \prod_i p_i^{v_i} \tag{10}$$

We define:

$$K_p = \prod_i p_i^{v_i} \tag{11}$$

Therefore we have:

$$\ln K_p = -\frac{\sum_i v_i \mu_i^o}{\bar{R}T} \tag{12}$$

We know the equilibrium constant for a given reaction expression is a function of temperature only. Now we want to get the temperature dependence:

$$\frac{d}{dT}(\ln K_p) = \frac{d}{dT}(-\frac{1}{\bar{R}} \sum_i v_i \frac{\mu_i^o}{T}) = -\frac{1}{\bar{R}} \sum_i v_i \frac{d}{dT}(\frac{\mu_i^o}{T}) \tag{13}$$

Finally we have:

$$\frac{d}{dT}(\ln K_p) = \frac{1}{\bar{R}} \sum_i v_i \frac{\hat{h}_i}{T^2} \tag{14}$$

Here we define the **standard heat of reaction** as:

$$\Delta \hat{H}_R^o = \hat{H}_{RHS}^o - \hat{H}_{LHS}^o = \sum_i v_i \hat{h}_i \tag{15}$$

And we define $\Delta \hat{H}_R^o$:

1. < 0: Exothermic
2. > 0: Endothermic

Then we get the **Van't Hoff's Equation**:

$$\frac{d}{dT}(\ln K_p) = \frac{\Delta \hat{H}_R(T)}{\bar{R}T^2} \tag{16}$$

4 K_p Temperature Dependence

Based on K_p definition, it could also expressed as:

$$K_p = \frac{X_{RHS}^{|v_i|}}{X_{LHS}^{|v_i|}} p^{\sum_i v_i} \tag{17}$$

Therefore, for **exothermic reaction**, if temperature **increases**, based on **le chatelier's principle**, the reaction is tending to move towards LHS, so K_p will **decrease**.

Therefore, for **endothermic reaction**, if temperature **increases**, based on **le chatelier's principle**, the reaction is tending to move towards RHS, so K_p will **increase**.

5 K_C Temperature Dependence

Here we introduce **the equilibrium constant in concentration K_C.** Based on the definition of concentration:

$$C_i = \frac{n_i}{V} \tag{18}$$

Where n_i is the moles of i^{th} component, V is the volume. Then we define:

$$K_C = \prod_i C_i^{v_i} \tag{19}$$

Therefore:

$$K_p = \prod_i p_i^{v_i} = \prod_i (\frac{n_i \bar{R}T}{V})^{v_i} = \prod_i C_i^{v_i} \prod_i (\bar{R}T)^{\sum_i v_i} = (\bar{R}T)^{v_i} K_C \tag{20}$$

Recall that:

$$\sum_i v_i = \Delta n_R \tag{21}$$

$$\ln K_C = \ln K_p - \Delta n_R \ln \bar{R}T \tag{22}$$

Now we also want to know the temperature dependence of K_C. Take the derivative:

$$\begin{aligned}
\frac{d}{dT}\ln K_C &= \frac{d}{dT}\ln K_p - \Delta n_R \frac{d}{dT}\ln \bar{R}T \\
&= \frac{\Delta \hat{H}_R(T)}{\bar{R}T^2} - \Delta n_R \frac{1}{T} \\
&= \frac{\Delta \hat{H}_R(T) - \Delta n_R \bar{R}T}{\bar{R}T^2} \\
&= \frac{\Delta \hat{H}_R(T) - \Delta(pV)}{\bar{R}T^2} \\
&= \frac{\Delta \hat{U}_R}{\bar{R}T^2}
\end{aligned} \tag{23}$$

6 Equilibrium Calculation

6.1 Overall Reactions

Assume we have more than one reaction:

$$A + B \rightarrow C \tag{24}$$

$$C + D \rightarrow E + F \tag{25}$$

And the overall reaction:

$$A + B + D \rightarrow E + F \tag{26}$$

Then we have the equilibrium constants:

$$K_{p_1} = \frac{p_c}{p_A p_B} \tag{27}$$

$$K_{p_2} = \frac{p_E p_F}{p_C p_D} \tag{28}$$

$$K_{p_3} = \frac{p_E p_F}{p_A p_B p_D} \tag{29}$$

Therefore we have:

$$K_{p_3} = K_{p_1} K_{p_2} \tag{30}$$

Overall K_p equals to the product of individual K_p.

6.2 Composition Calculation

The classic question is to calculate the chemical composition at specified T and p. Assume the reaction as:

$$CO_2 \rightarrow CO + \frac{1}{2}O_2 \tag{31}$$

We have **3 unknowns, so we need 3 equations.**

Notice that we can calculate the overall K_p using the individual step K_p, here we can use the formation reactions constant K_{p_f}. Therefore we have the **first equation:**

$$K_p = \frac{p_{CO} p_{O_2}^{1/2}}{p_{CO_2}} = \frac{K_{p_{f,CO}} K_{p_{f,O_2}}^{1/2}}{K_{p_{f,CO_2}}} \tag{32}$$

Here all the K_ps are the function of temperature. Then we can relate this to the mole fractions:

$$K_p = \frac{(pX_{CO})(pX_{O_2})^{1/2}}{(pX_{CO_2})} \tag{33}$$

We also need to specify the atomic ratios, so we have:

$$n^C = n_{CO} + n_{CO_2},\ n^O = n_{CO} + 2n_{CO_2} + 2n_{O_2} \tag{34}$$

So we can introduce the **second equation:**

$$\frac{n^C}{n^O} = \frac{X_{CO} + X_{CO_2}}{X_{CO} + 2X_{CO_2} + 2X_{O_2}} \tag{35}$$

Also we have the **third equation:**

$$X_{CO} + X_{CO_2} + X_{O_2} = 1 \tag{36}$$

Finally we can calculate each composition.

6.3 Number of K_p Equations

Another important question is that **How many equilibrium stoichiometric reactions are required to determine equilibrium composition?**

Assume the mixture of **m** species having α kinds of atoms, then:

1. Generally we have m+2 unknowns (2 intensive TD properties)
2. **If we specify the 2TD properties (usually T, p), AND the number/ratio of atomic nuclei**, then we only have $m - \alpha$ **unknowns**, so we need $m - \alpha$ independent K_p expressions.

Example: if we have a mixture of H_2, O_2, H_2O, OH, O, H, then we have $m = 6$ species and $\alpha = 2$ atoms (O, H), so we need $6 - 2 = 4K_p$.