

Thermal Equilibrium



Reading
15-1 → 15-6

Problems

Criterion for a Reacting Mixture

In general, the thermodynamic state of any mixture capable of heat transfer, expansion work and chemical reaction can be fixed by the specification of its internal energy, volume and composition.

$$S = S(U, V, n_1, n_2, \dots, n_k)$$

Recalling the fundamental definition of T , P and $\bar{\mu}_i$, where $\bar{m}\bar{\mu}_i$ is the molar electro chemical potential of the i^{th} component per mole of the i^{th} component.

$$dS = \underbrace{\left(\frac{\partial S}{\partial U}\right)_{V, n_i} dU}_{\equiv \frac{1}{T}} + \underbrace{\left(\frac{\partial S}{\partial V}\right)_{U, n_i} dV}_{\equiv \frac{P}{T}} + \underbrace{\left(\frac{\partial S}{\partial n_1}\right)_{U, V, n_j, j \neq 1} dn_1}_{\equiv -\frac{\bar{\mu}_1}{T}} + \dots + \underbrace{\left(\frac{\partial S}{\partial n_k}\right)_{U, V, n_j, j \neq k} dn_k}_{\equiv -\frac{\bar{\mu}_k}{T}}$$

Using the above relation, the Gibb's function for a mixture can be written as

$$TdS = dU + PdV - \sum_{i=1}^k \bar{\mu}_i dn_i \quad (1)$$

Noting the Gibb's function (free energy used to predict the spontaneity of a chemical reaction) is defined as

$$G = H - TdS = U + PV - TS$$

$$dG = dU + PdV + vdP - TdS - SdT$$

or when combined with Eq. (1)

$$dG = VdP - SdT + \sum_{i=1}^k \bar{\mu}_i dn_i \quad (2)$$

For the general equilibrium condition, consider the reacting mixture as the system

From a 1st law balance

$$dU = dQ - dW = dQ - PdV \quad (3)$$

From a 2nd law balance

$$dS \frac{dQ}{T} \geq 0 \quad (4)$$

Combining (1), (3) and (4)

$$\sum_{i=1}^k \bar{\mu}_i \, d\mathbf{n}_i \leq 0 \quad (5)$$

This is the product of the chemical potential and the change in composition.

As the reactions continue, some species will be formed ($d\mathbf{n}_i > \mathbf{0}$) and others will be depleted ($d\mathbf{n}_i < \mathbf{0}$), such that

$$\sum \bar{\mu}_i \, d\mathbf{n}_i < 0$$

Eventually the reactions will be completed and there will be no further change in the composition of the mixture

$$\sum \bar{\mu}_i \, d\mathbf{n}_i = 0$$

This is the *Equilibrium criterion*.

Notice that for the common case of combustion at constant \mathbf{T} and \mathbf{P} , Eq. (5) yields

$$dG_{T,P} \leq 0$$

When equilibrium is finally obtained

$$dG_{T,P} = 0$$

A reaction can take place spontaneously as long as Gibb's function decreases.

Examining the mixture more closely

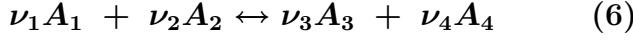
$$\begin{array}{ll}
 \mathbf{n}_1 \text{ moles of } \mathbf{A}_1 \\
 \mathbf{n}_2 \text{ moles of } \mathbf{A}_2 \\
 \vdots \\
 \mathbf{n}_k \text{ moles of } \mathbf{A}_k
 \end{array}$$

where

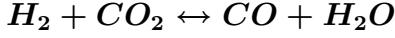
$\mathbf{A}_1 = \text{chemical constituents}$

$\nu_i = \text{stoichiometric coefficients}$

Therefore a chemical equation of reactants and products can be written as



For example:



$$\nu_{\mathbf{H}_2} = 1, \quad ; \quad \nu_{\mathbf{CO}_2} = 1, \quad ; \quad \nu_{\mathbf{CO}} = 1, \quad ; \quad \nu_{\mathbf{H}_2\mathbf{O}} = 1$$

As a result of reaction (6), the composition of the mixture will change by

$$\begin{aligned}
 d\mathbf{n}_2 &= \frac{\nu_2}{n\mathbf{u}_1} d\mathbf{n}_1 \Rightarrow \frac{d\mathbf{n}_2}{\nu_2} = \frac{d\mathbf{n}_1}{\nu_1} \\
 d\mathbf{n}_3 &= -\frac{\nu_3}{n\mathbf{u}_1} d\mathbf{n}_1 \Rightarrow \frac{d\mathbf{n}_1}{\nu_1} = -\frac{d\mathbf{n}_3}{\nu_3} \\
 d\mathbf{n}_4 &= -\frac{\nu_4}{n\mathbf{u}_1} d\mathbf{n}_1 \Rightarrow \frac{d\mathbf{n}_1}{\nu_1} = -\frac{d\mathbf{n}_4}{\nu_4}
 \end{aligned}$$

From Eq. (5)

$$\sum \bar{\mu}_i d\mathbf{n}_i \leq 0$$

we obtain

$$\left[\underbrace{(\bar{\mu}_1 \nu_1 + \bar{\mu}_2 \nu_2)}_{EP_{LHS}} - \underbrace{(\bar{\mu}_3 \nu_3 + \bar{\mu}_4 \nu_4)}_{EP_{RHS}} \right] d\mathbf{n}_1 \leq 0$$

If $EP_{LHS} > EP_{RHS}$ then $d\mathbf{n}_1 < \mathbf{0}$ and A_1 is being depleted, i.e. the reaction proceeds to the right.

If $EP_{LHS} < EP_{RHS}$ then $d\mathbf{n}_1 > \mathbf{0}$ and the reaction proceeds to the left.

Hence equilibrium is attained when

$$(\bar{\mu}_1\nu_1 + \bar{\mu}_2\nu_2) - (\bar{\mu}_3\nu_3 + \bar{\mu}_4\nu_4) = 0 \quad (7)$$

or in general

$$\sum_{R \text{ (LHS)}} \bar{\mu}_i \nu_i = \sum_{P \text{ (RHS)}} \bar{\mu}_i \nu_i \quad (8)$$

In a perfect gas, $\bar{\mu}$ for the *i'th* species is given by

$$\bar{g}_i = \bar{\mu}_i = \bar{g}_i^o(T, P_0) + \mathcal{R}T \ln \left(\frac{P_i}{P_0} \right) \quad (9)$$

where $P_0 = 1 \text{ atm}$ is the reference pressure and \bar{g}_i^o is Gibb;s function of components *i* evaluated at T and $P = 1 \text{ atm}$.

Note that

$$\frac{P_i}{P} = \frac{n_i}{n}$$

The molal Gibb's function is

$$\bar{g}_i^o = \bar{g}_i(T, P_0) = \text{function of } T \text{ only}$$

$$\bar{g}_i^o = \bar{h}_{f_i}^o - T \bar{s}_i^o$$

Substitute Eq. (9) into (7), noting that the products and the reactants must be at a constant T .

$$\begin{aligned} (\mu_1 \bar{g}_1^o + \mu_2 \bar{g}_2^o) - (\mu_3 \bar{g}_3^o + \mu_4 \bar{g}_4^o) &= \mathcal{R}T \ln \left[\frac{\left(\frac{P_3}{P_0} \right)^{\nu_3} \left(\frac{P_4}{P_0} \right)^{\nu_4}}{\left(\frac{P_1}{P_0} \right)^{\nu_1} \left(\frac{P_2}{P_0} \right)^{\nu_2}} \right] \\ &= -\Delta G^o = -\Delta G(T, P_0) \end{aligned}$$

Therefore

$$\underbrace{\left(\frac{P_3^{\nu_3} P_4^{\nu_4}}{P_1^{\nu_1} P_2^{\nu_2}} \right) \left(\frac{1}{P_0} \right)^{\nu_3 + \nu_4 - \nu_1 - \nu_2}}_{\equiv K(T)} = \exp \left[-\frac{\Delta G^o}{RT} \right] \quad (10)$$

where $K(T)$ is the equilibrium constant for reactions.

The JANAF tables list $\ln K$ with $P_0 = 1 \text{ atm}$ for various reactions of substances.

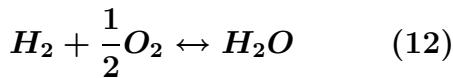
Note that

$$P_i = P \left(\frac{n_i}{n} \right)$$

Therefore

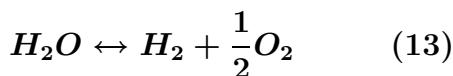
$$K(T) = \left(\frac{n_3^{\nu_3} n_4^{\nu_4}}{n_1^{\nu_1} n_2^{\nu_2}} \right) \left(\frac{P}{nP_0} \right)^{\nu_3 + \nu_4 - \nu_1 - \nu_2}$$

Example:



$$K_{12} = \left(\frac{n_{H_2O}}{n_{H_2} n_{O_2}^{1/2}} \right) \left(\frac{P}{nP_0} \right)^{1-1-1/2}$$

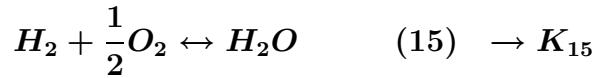
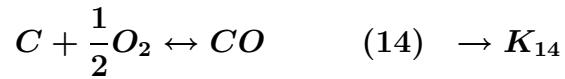
Note that K depends on the way the equation is written



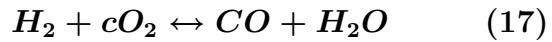
Then

$$K_{13} = \frac{1}{K_{12}} \Rightarrow \ln K_{13} = -\ln K_{12}$$

The K' s can be combined when the reactions are combined



Equations (14) + (15) - (16) gives



$$K_{17} = \frac{n_{CO} n_{H_2O}}{n_{H_2} n_{CO_2}} = \frac{K_{14} K_{15}}{K_{16}}$$