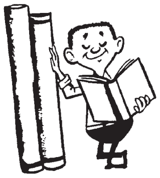
Thermal Equilibrium



Reading	**Problems**
15-1 → 15-6	

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.

$$\boldsymbol{S = S(U, V, n_1, n_2, \ldots n_k)}$$

Recalling the fundamental definition of $\boldsymbol{T, P}$ and $\boldsymbol{\overline{\mu}_i}$, where $\boldsymbol{\overline{mu}_i}$ is the molar electro chemical potential of the $\boldsymbol{i'th}$ component per mole of the $\boldsymbol{i'th}$ component.

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

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

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

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

$$\begin{aligned} G &= H - tdS = U + PV - TS \\ dG &= dU + PdV + vdP - TdS - SdT \end{aligned}$$

or when combined with Eq. (1)

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

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

From a 1st law balance

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

From a 2nd law balance

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

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

$$\sum_{i=1}^{k} \overline{\mu}_i \, dn_i \leq 0 \qquad (5)$$

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

As the reactions continue, some species will be formed ($dn_i > 0$) and others will be depleted ($dn_i < 0$), such that

$$\sum \overline{\mu_i} \, dn_i < 0$$

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

$$\sum \overline{\mu_i} \, dn_i = 0$$

This is the *Equilibrium criterion*.

Notice that for the common case of combustion at constant T and 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

$$\begin{array}{c} n_1 \text{ moles of } A_1 \\ n_2 \text{ moles of } A_2 \\ \vdots \\ n_k \text{ moles of } A_k \end{array}$$

where

$$\begin{aligned} A_1 &= chemical\, constituents \\ \nu_i &= stoichiometric\, coefficients \end{aligned}$$

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

$$\nu_1 A_1 \;+\; \nu_2 A_2 \leftrightarrow \nu_3 A_3 \;+\; \nu_4 A_4 \qquad\qquad (6)$$

For example:

$$H_2 + CO_2 \leftrightarrow CO + H_2O$$

$$\nu_{H_2} = 1, \quad ; \quad \nu_{CO_2} = 1, \quad ; \quad \nu_{CO} = 1, \quad ; \quad \nu_{H_2O} = 1$$

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

$$\begin{aligned} dn_2 &= \frac{\nu_2}{nu_1} dn_1 \quad \Rightarrow \quad \frac{dn_2}{\nu_2} = \frac{dn_1}{\nu_1} \\ dn_3 &= -\frac{\nu_3}{nu_1} dn_1 \quad \Rightarrow \quad \frac{dn_1}{\nu_1} = -\frac{dn_3}{\nu_3} \\ dn_4 &= -\frac{\nu_4}{nu_1} dn_1 \quad \Rightarrow \quad \frac{dn_1}{\nu_1} = -\frac{dn_4}{\nu_4} \end{aligned}$$

From Eq. (5)

$$\sum \overline{\mu}_i \, dn_i \leq 0$$

we obtain

$$\left[\underbrace{(\overline{\mu}_1 \nu_1 + \overline{\mu}_2 \nu_2)}_{EP_{LHS}} - \underbrace{(\overline{\mu}_3 \nu_3 + \overline{\mu}_4 \nu_4)}_{EP_{RHS}} \right] \; dn_1 \leq 0$$

If $EP_{LHS} > EP_{RHS}$ then $dn_1 < 0$ and A_1 is being depleted, i.e. the reaction proceeds to the right.

If $EP_{LHS} < EP_{RHS}$ then $dn_1 > 0$ and the reaction proceeds to the left.

Hence equilibrium is attained when

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

or in general

$$\sum_{R\ (LHS)} \overline{\mu}_i\nu_i = \sum_{P\ (RHS)} \overline{\mu}_i\nu_i \qquad (8)$$

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

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

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

Note that

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

The molal Gibb's function is

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

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

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

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

Therefore

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

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

The JANAF tables list $\ln K$ with $P_0 = 1\ atm$ for various reactions fo 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:

$$H_2 + \frac{1}{2}O_2 \leftrightarrow H_2O \qquad (12)$$

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

Note that K depends on the way the equation is written

$$H_2O \leftrightarrow H_2 + \frac{1}{2}O_2 \qquad (13)$$

Then

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

The $\boldsymbol{K's}$ can be combined when the reactions are combined

$$\boldsymbol{C + \frac{1}{2}O_2 \leftrightarrow CO \qquad (14) \quad \rightarrow K_{14}}$$

$$\boldsymbol{H_2 + \frac{1}{2}O_2 \leftrightarrow H_2O \qquad (15) \quad \rightarrow K_{15}}$$

$$\boldsymbol{C + O_2 \leftrightarrow CO_2 \qquad (16) \quad \rightarrow K_{16}}$$

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

$$\boldsymbol{H_2 + cO_2 \leftrightarrow CO + H_2O \qquad (17)}$$

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