




Module 2: Thermodynamics of Combustion

Lecture 11: Chemical Equilibrium

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Lecture 11: Chemical Equilibrium

Chemical Equilibrium

Note: Chemical composition won't change unless there is a change in pressure and temperature

$$dS_{sys} \geq \frac{\delta Q}{T}$$

Chemical reaction proceeds in the direction of increasing entropy

$$dS_{sys} \geq 0$$

If the system is not adiabatic, we have to invoke Gibbs free energy, G

$$G = H - TS$$

$$dG = dH - TdS - SdT$$

$$H = U + PV$$

$$dH = dU + PdV + VdP$$

From 1st Law,

At constant pressure and temperature,

$$dG = dU + PdV - TdS$$

$$\delta Q = dU + PdV$$

$$dG = \delta Q - TdS$$

From 2nd Law, of Thermodynamic

$$dG = \delta Q - TdS$$

$$(dG)_{T,P,n} = 0$$

The reaction will attain its chemical equilibrium when Gibbs function attains minimum value
 $(dG)_{T,P,n} = 0$

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Procedure for Determining Equilibrium Composition

Equilibrium products can be estimated by adopting the following steps

Step 1: Identify probable equilibrium species

Step 2: Identify equilibrium reactions scheme

Step 3: Find out equilibrium constant

Step 4: Strike balance for elemental conservation

Step 5: Strike overall mass conservation

Step 6: Solve all equations by iterative method (Newton- Raphson Method)

For a ideal gas mixture, Gibbs function of i^{th} species is given by

$$g_{i,T} = g_{i,T}^{\circ} + R_u T \ln\left(\frac{p_i}{p^{\circ}}\right)$$

$g_{i,T}^{\circ}$ -Gibbs function per mole of i^{th} species.

Gibbs function for a ideal gas mixture

p_i -Partial pressure of i^{th} species.

T -Temperature

R_u -Universal gas constant

$$G_{mix} = \sum n_i g_{i,T} = \sum n_i \left[g_{i,T}^{\circ} + R_u T \ln\left(\frac{p_i}{p^{\circ}}\right) \right]$$

At equilibrium,

$$dG_{mix} = 0 \quad \sum dn_i \left[g_{i,T}^{\circ} + R_u T \ln\left(\frac{p_i}{p^{\circ}}\right) \right] + \sum n_i d \left[g_{i,T}^{\circ} + R_u T \ln\left(\frac{p_i}{p^{\circ}}\right) \right] = 0$$

In the above equation, $d(\ln p_i) = \frac{dp_i}{p_i} = 0$ (Since pressure remains constant)

$$dG_{mix} = \sum dn_i \left[g_{i,T}^{\circ} + R_u T \ln\left(\frac{p_i}{p^{\circ}}\right) \right] = 0$$

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Consider the reaction



Where, a, b, c and d are stoichiometric coefficients

Change in number of moles of each species is given by,

$$dn_A = -ka$$

$$dn_B = -kb$$

$$dn_C = kc$$

$$dn_D = kd$$

Substituting above equation in Gibbs function, We can get,

$$\begin{aligned} & -a \left[g_{A,T}^\circ + R_u T \ln \left(\frac{p_A}{p^\circ} \right) \right] - b \left[g_{B,T}^\circ + R_u T \ln \left(\frac{p_B}{p^\circ} \right) \right] \\ & + c \left[g_{C,T}^\circ + R_u T \ln \left(\frac{p_C}{p^\circ} \right) \right] + d \left[g_{D,T}^\circ + R_u T \ln \left(\frac{p_D}{p^\circ} \right) \right] = 0 \end{aligned}$$

$$\Rightarrow \Delta G_T^\circ = c g_{C,T}^\circ + d g_{D,T}^\circ - a g_{A,T}^\circ - b g_{B,T}^\circ = -R_u T \ln \left[\frac{\left(\frac{p_D}{p^\circ} \right)^d \left(\frac{p_C}{p^\circ} \right)^c}{\left(\frac{p_A}{p^\circ} \right)^a \left(\frac{p_B}{p^\circ} \right)^b} \right]$$

$$\Delta G_T^\circ = -R_u T \ln K_p \quad K_p = e^{\left(\frac{-\Delta G_T^\circ}{R_u T} \right)} = \left[\frac{\left(\frac{p_D}{p^\circ} \right)^d \left(\frac{p_C}{p^\circ} \right)^c}{\left(\frac{p_A}{p^\circ} \right)^a \left(\frac{p_B}{p^\circ} \right)^b} \right]$$

In terms of mole fraction,

$$K_p = \frac{X_C^c X_D^d}{X_A^a X_B^b} \left(\frac{P}{p^\circ} \right)^{(c+d)-(a+b)}$$

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Summary

- The basic thermodynamic principles are useful in estimation of properties related to combustion.
- Stoichiometric calculations are useful in estimation of fuel-air requirements for a combustion process.
- Adiabatic flame temperature indicates maximum possible temperature in combustion process.
- Thermodynamic relations can be used to relate the change in Gibbs free energy with equilibrium constant.
- Equilibrium composition can be used to calculate adiabatic flame temperature using an iterative procedure.

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