Sharif University of Technology
School of Mechanical Engineering
Center of Excellence in Energy Conversion

Advanced Thermodynamics

Lecture 28

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$T\ ,\ P$

Mix.

A, B, C, D

Equil. Comp. $n_A\ ,\ n_B\ ,\ n_C\ ,\ n_D$

Change or Reaction Eq. $n_A A + n_B B \qquad n_C C + n_D D$

n_i (i=A, B, C or D) are stoichiometery coefficient and are fixed constants. These are different from No. of mole.

$$dG_{T\ ,\ P} = -\cancel{SdT}_0 + \cancel{VdP}_0 + \sum \bar{G}_i dn_i$$

- From Mass Conservation Law:

$$A + n_B B \qquad n_C C + n_D D$$

$$\frac{\Delta n_A}{n_A} = \frac{\Delta n_B}{n_B} = -\frac{\Delta n_C}{n_C} = -\frac{\Delta n_D}{n_D} = -de$$

- e : degree of reaction, it can be arbitrary positive or negative.

$$dG_{T\ ,\ P} = (n_C \bar{G}_C + n_D \bar{G}_D - n_A \bar{G}_A - n_B \bar{G}_B)\ de$$

$$dG_{T,P} = (n_C\bar{G}_C + n_D\bar{G}_D - n_A\bar{G}_A - n_B\bar{G}_B)\, de$$

$$\left.\begin{aligned} \underset{\text{mix. T,P}}{\bar{G}_i} &= \bar{g}_i^{\,*} + \bar{R}T\,\ln\left(\frac{\bar{f}_i}{P^*}\right) \\ \underset{\text{comp. T,P}}{\bar{G}_i} &= \underset{T,P}{\bar{g}_i^{\,0}} + \bar{R}T\,\ln\left(\frac{\bar{f}_i}{P^0}\right) \end{aligned}\right\} \quad \text{Reference states:} \begin{cases} * = \text{I.G.} \\ 0 = \text{I.G. \& P=0.1 MPa} \end{cases}$$

- **Definition:** Activity $= a_i = \dfrac{\bar{f}_i}{f_i^{\,0}} \xrightarrow{I.G.} \dfrac{\bar{f}_i}{P^0}$

- Models for Chemical Equilibrium:

  - Ideal Solution Model: I.S.M. $\rightarrow a_i = \dfrac{y_i f_i}{P^0}$

  - Mixture at Chemical Equilibrium State of Ideal Gas: This is a special case of I.S.M. $\rightarrow a_i = \dfrac{y_i P}{P^0}$

Equilibrium Constant

- I.S.M.:

$$\Delta G = \underbrace{(n_C \bar{g}_C^0 + n_D \bar{g}_D^0 - n_A \bar{g}_A^0 - n_B \bar{g}_B^0)}_{\Delta G^0 = f(T)} + \bar{R}T \ln \underbrace{\left(\frac{a_C{}^{n_C} a_D{}^{n_D}}{a_A{}^{n_A} a_B{}^{n_B}} \right)}_{K = \text{Equil. Cpnst.}}$$

$$\ln K = \frac{-\Delta G^0}{\bar{R}T} = f(T)$$

- $\ln K$ is tabulated for different reactions (usually at 0.1 MPa).

To calculate ΔG^0: $\Delta G^0 = \Delta H^0 - T\,\Delta S^0$ or $\bar{g}_i^0 = \bar{g}_{f_i}^0 + \Delta \bar{g}_{T_0 \to T}^0$

$$K = \frac{a_C{}^{n_C} a_D{}^{n_D}}{a_A{}^{n_A} a_B{}^{n_B}} \xrightarrow{\text{I.S.M.}} K = \frac{y_C{}^{n_C} y_D{}^{n_D}}{y_A{}^{n_A} y_B{}^{n_B}} \left(\frac{P}{P_0} \right)^{n_C + n_D - n_A - n_B} \left[\frac{\left(f/P\right)_C^{n_C} \left(f/P\right)_D^{n_D}}{\left(f/P\right)_A^{n_A} \left(f/P\right)_B^{n_B}} \right]$$

For I.G.M. $\left(f/P\right) = 1$

- Dissociation: at high temperature.

$$N_2 \quad 2N$$

- Ionization: at very high temperature (electrical arc) and usually at low pressure (like in higher layers of the atmosphere).

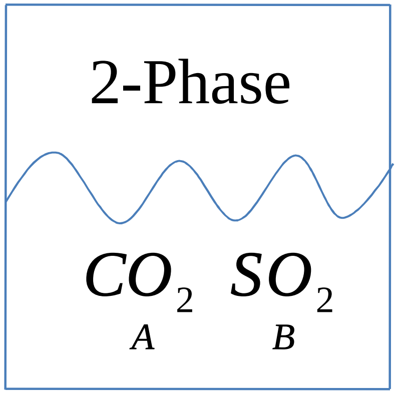
$$N \rightarrow N^+ + e^-$$

- Plasma State: special case of ionization with unequal distribution of temperature due to difference in heat transfer rate with surrounding.

$$A \quad A^+ + e^-$$

$$K = \frac{y_{A^+} y_{e^-}}{y_A}\left(\frac{P}{P_0}\right), \ \ln K = \frac{-\Delta G^0}{\bar{R}T} \text{ and } \Delta G^0 = \bar{g}^0_{A^+} + \bar{g}^0_{e^-} - \bar{g}^0_A$$

Example 1



$$\left.\begin{aligned} T &= 30^0 C \\ P &= 4\ MPa \end{aligned}\right\} \rightarrow \text{ Find } x_A,\ x_B,\ y_A,\ y_B$$

$$T_{CA} = 304.2\ K,\ T_{CB} = 430.7\ K$$

$$P_{CA} = 7.34\ MPa,\ P_{CB} = 7.88\ MPa$$

$$I.S.M. \rightarrow \begin{cases} y_A f_A^v = x_A f_A^l \\ y_B f_B^v = x_B f_B^l \end{cases} \text{ and } \begin{cases} x_A + x_B = 1 \\ y_A + y_B = 1 \end{cases}$$

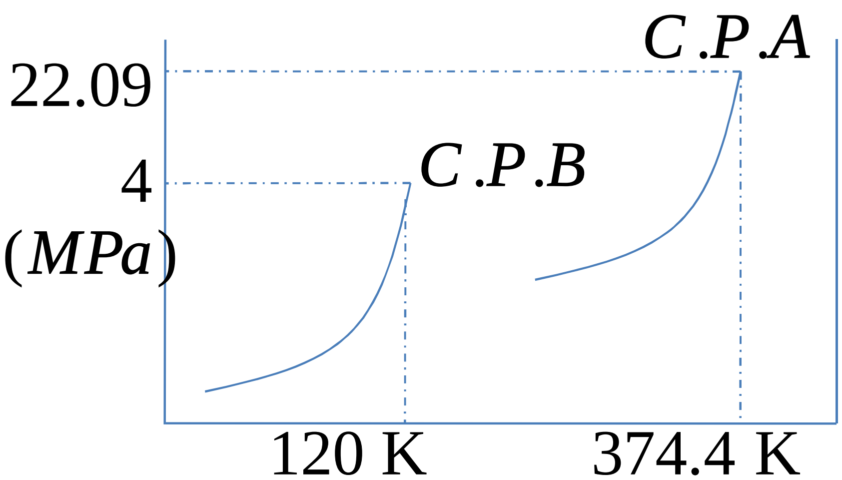
$$T_{rA} = 0.997,\ P_{rA} = 0.541 \rightarrow \underbrace{f_A^l}_{\text{hypoth.etical}} = 1.3 \times 4 = 5.2,\ \underbrace{f_A^v}_{\text{Real}} = 0.83 \times 4$$

$$T_{rB} = 0.704,\ P_{rB} = 0.508 \rightarrow \underbrace{f_B^l}_{\text{Real}} = 0.14 \times 4 = 5.2,\ \underbrace{f_B^v}_{\text{hypoth.etical}} = 0.6 \times 4$$

$$\Rightarrow x_A = 0.575,\ x_B = 0.425,\ y_A = 0.099,\ y_B = 0.901$$

Example 2

Air and vapor water at $T = 50^0 C$ & $P = 3.5\ MPa$ $\rightarrow$ Find $y_A\ (H_2O)$



$$x_A \approx 1,\ \bar{f}_A^{\,l} \approx \bar{f}_A^{\,v}$$

a) Rault-I.G. Model:

$$f_A^l \approx f_A^{sat.} \approx P_A^{sat.} = 12.349\ KPa$$

$$f_A^v \approx y_A P = 3500 y_A$$

$$\rightarrow y_A = 0.00353$$

b) I. S. Model:

$$T_{rA} = \frac{323.2}{642.3} = 0.5,\ P_{rA} = \frac{3.5}{22.04} = 0.158,\ f_A^v \quad 0.73 \times 3500 = 2555$$

$$P_{rA}^{sat.} = \frac{12.349}{22000} << 0.01 \rightarrow f_A^{sat.} \approx P_A^{sat.} = 12.349\ KPa$$

$$\ln \frac{f_A^l}{f_A^{sat.}} = \frac{0.001012(3500 - 12.349)}{\underbrace{0.46152}_{K} \times 523.2} \rightarrow f_A^l = 12.645 \quad \therefore y_A = \frac{f_A^l}{f_A^v} = 0.00495$$