Example Equilibrium Calculation

- Given mixture of CO_2, CO, O_2 at specified (T, p) *and C:O ratio*
- What is composition (intensive) at equilibrium (e.g., χ_i)?
- General approach: start with atom balances (mass conservation)
  - can write 2 equations, 1 for each nuclei type

$$n^C = n_{CO} + n_{CO_2} \qquad n^O = n_{CO} + 2n_{CO_2} + 2n_{O_2}$$

  - in terms of mole fractions

$n_i = n_{mix}\chi_i$

$$\frac{n^C}{n^O} = \frac{n_{CO} + n_{CO_2}}{n_{CO} + 2n_{CO_2} + 2n_{O_2}} = \frac{\chi_{CO} + \chi_{CO_2}}{\chi_{CO} + 2\chi_{CO_2} + 2\chi_{O_2}}$$

  - since we can't "lose" an equation, also $\chi_{CO} + \chi_{CO_2} + \chi_{O_2} = 1$

Example Equilibrium Calculation

- Given mixture of CO_2, CO, O_2 at specified (T, p) *and C:O ratio*
- What is composition (intensive) at equilibrium (e.g., χ_i)?
- After atom balances, how many equations needed?
  - 3 unknowns – 2 equations = 1 more equation needed
- Source?
  - K_p, can write chemical state relation ("reaction")
    $CO_2 \leftrightarrow CO + ½\, O_2$

$p_i = p\chi_i$

$$K_p(T) = \frac{p_{CO}\, p_{O_2}^{1/2}}{p_{CO_2}} = \frac{\chi_{CO}\,\chi_{O_2}^{1/2}}{\chi_{CO_2}}\, p^{1/2} = e^{\frac{-\sum \nu_i \hat{G}^o_{f,i}(T)}{\bar{R}T}} = \Pi\left[K_{p_{f,i}}(T)\right]^{\nu_i}$$

$$\Rightarrow \frac{\chi_{CO}\,\chi_{O_2}^{1/2}}{\chi_{CO_2}} = p^{-1/2} e^{-\left[\hat{G}^o_{f,CO}(T) - \hat{G}^o_{f,CO_2}(T)\right]/\bar{R}T} \quad \text{or} \quad \frac{\chi_{CO}\,\chi_{O_2}^{1/2}}{\chi_{CO_2}} = p^{-1/2}\frac{K_{p_{f,CO}}(T)}{K_{p_{f,CO_2}}(T)}$$

Equation Summary

- So we now have 3 equations for our 3 unknown χ_i

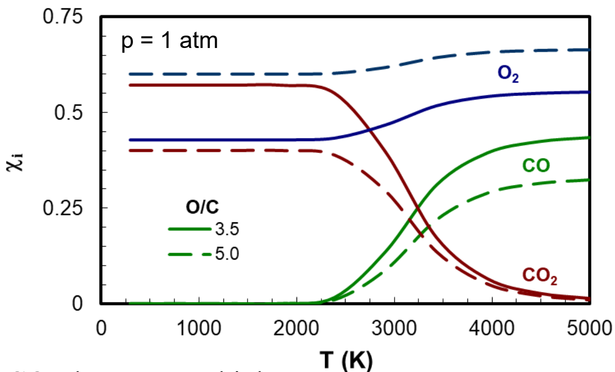
1. $$\frac{\chi_{CO}+\chi_{CO_2}}{\chi_{CO}+2\chi_{CO_2}+2\chi_{O_2}}=\frac{n^C}{n^O}$$

2. $$\chi_{CO}+\chi_{CO_2}+\chi_{O_2}=1$$

3. $$\frac{\chi_{CO}\chi_{O_2}^{1/2}}{\chi_{CO_2}}=p^{-1/2}\frac{K_{p_{f,CO}}(T)}{K_{p_{f,CO_2}}(T)}$$

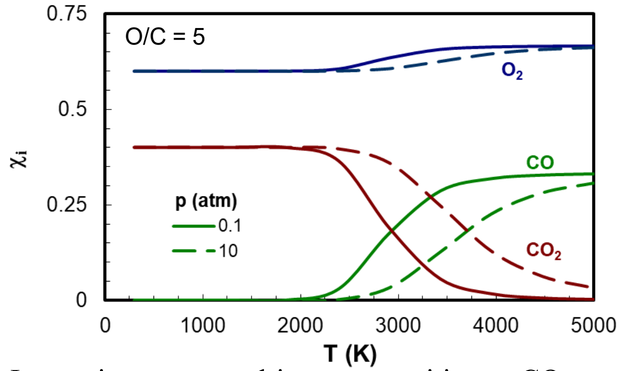
- We can solve this (nonlinear) set of equations for a given T, p and n^C/n^O if we have the necessary formation properties of our species
  - e.g., from https://janaf.nist.gov

Composition: T and O/C Dependence



- CO_2 decreases at high T
  - has low chem. energy (low Δh_f), $T\uparrow$ favors higher energy species
- Increasing O/C shifts composition from $CO \rightarrow CO_2$ ($\chi_{CO_2}/\chi_{CO}\uparrow$)

Composition: T and p Dependence



- Increasing pressure drives composition to CO_2
  - high p favors "less" moles
- At T extremes, either CO or CO_2; so weak p dependence there

Mixture (TPG) Properties

- Now that we know composition as function of T, p and atom ratios, how do we calculate other properties?
- Enthalpy?

$$\hat{h} = \sum_i \chi_i \bar{h}_i = \sum_i \chi_i \left[\left(\bar{h}_T - \bar{h}_{T_{ref}} \right)_i + \Delta \bar{h}_{f,i,T_{ref}} \right]$$

$$h = \sum_i Y_i h_i = \sum_i Y_i \left[\left(h_T - h_{T_{ref}} \right)_i + \Delta h_{f,i,T_{ref}} \right]$$

- Internal energy?

$$\hat{u} = \hat{h} - p\hat{v} = \hat{h} - \bar{R}T$$

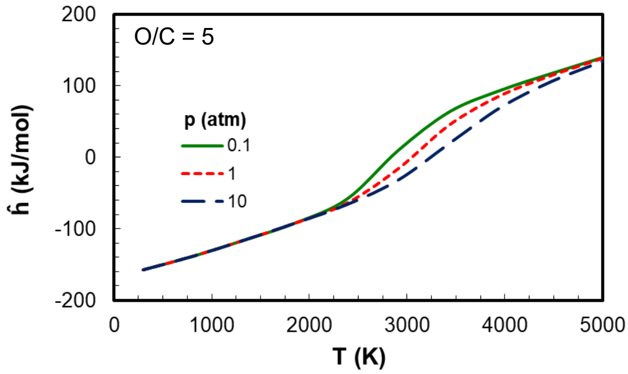
$$u = h - pv = h - RT$$

- Entropy?

$$\hat{s} = \sum_i \chi_i \bar{s}_i = \sum_i \chi_i \left[\overbrace{\int_0^T \frac{\bar{c}_{p,i}}{T} dT}^{=\bar{s}_i^o(T)} - \bar{R} \ln \frac{p_i}{p^o} \right]$$

$$s = \sum_i Y_i s_i = \sum_i Y_i \left[\overbrace{\int_0^T \frac{c_{p,i}}{T} dT}^{=s_i^o(T)} - R \ln \frac{p_i}{p^o} \right]$$

Molar Enthalpy: T and p Dependence



- Enthalpy increases monotonically with *T*
- Enthalpy of TPG mixture now depends on pressure
  - where composition is changing