⟨Element Potential⟩

At equilibrium ⟹ minimum Gibbs Function G

$$G = \sum_i N_i \, g_i$$

Atom balance

$$\sum_i n_{ij} N_i = a_j = \text{total \# of moles of } j \text{ atoms in the system}$$

$\Downarrow$

number of j atoms in species i

e.g.) $CH_4 + 2CO_2 \Rightarrow a_C = 1 \times 1 + 1 \times 2 = 3.$ $\left(n_{CH_4,\,C} = 1,\ n_{CO_2,\,C} = 1. \atop N_{CH_4} = 1,\ N_{CO_2} = 2. \right)$

$$G = G(T, P, N_i)$$

$$dG_{(T,P)} = \sum_i g_i \, dN_i$$

T, P constant.

$\left[\begin{array}{l} - \sum_i n_{ij} \, dN_i = da_j = 0 \quad (\text{atom conservation}) \\[1em] \circledcirc \text{Method of Lagrange Multipliers.} \\[1em] \hookrightarrow \text{We will have } j \text{ eqns } (j \text{ constraints}) \end{array}\right.$

e.g.) $CH_4 + 2CO_2$

there are 3 constraints (C, H, O) from atom balance

multiplier λ_j represents jth constraint to drop out N_i.

at equilibrium $\quad dG_{T,P} = 0 = \underbrace{dG_{T,P}}_{\sum_i g_i \, dN_i} - \sum_j \lambda_j \underbrace{\sum_i n_{ij} \, dN_i}_{= da_j = 0}$

$$\Rightarrow \sum_i \left(g_i - \sum_j n_{ij} \lambda_j \right) dN_i = 0.$$

at equilibrium, coef. for dN_i should be 0

$$\therefore g_i = \sum_j n_{ij} \lambda_j$$

$$\underline{\lambda_j \equiv \text{element potential for the } j \text{ atoms}}$$
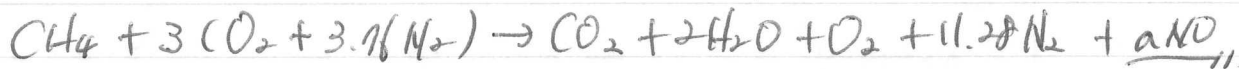
For an ideal gas.

$$g_i(T, p_i) = g_i(T, p) + \hat{R}T \ln X_i = \sum_j n_{ij} \lambda_j$$

$$\therefore \boxed{\ln X_i = -\frac{g_i(T,p)}{\hat{R}T} + \sum_j n_{ij}\left(\frac{\lambda_j}{\hat{R}T}\right)}$$

To get X_i, we need $\lambda_j s$.

$*$ ⇒ These can be derived using dominant species assumption.
then, using the element potentials ($\lambda_j s$), mole fractions
of minor product species can be estimated.

ex) Calculate the equilibrium NO mole fraction in the product of
the combustion of a lean methane/air mixture ($\phi = \frac{2}{3}$) at
1500 K, 1 bar.

$$CH_4 + 3(O_2 + 3.76 N_2) \rightarrow CO_2 + 2H_2O + O_2 + 11.28 N_2 + \underline{a NO}_{,,}$$

To estimate X_{NO}, we need element potential of N and O.

$$X_{N_2} = \frac{11.28}{1 + 2 + 1 + 11.28} = 0.738 \quad \therefore NO \text{ is minor species}$$

$$X_{O_2} = 0.0654.$$

$$\rightarrow \ln X_{N_2} = -\frac{g_{N_2}(1500K, 1 bar)}{\underbrace{8.314 \times 1500}_{=\tilde{R}}} + 2 \times \frac{\lambda_N}{8.314 \times 1500}$$

$$\ln X_{O_2} = -\frac{g_{O_2}(1500K, 1bar)}{8.314 \times 1500} + 2 \times \frac{\lambda_O}{8.314 \times 1500}$$

$$g_i = \left(h_i(T) - h_i(T_{ref})\right)_{sens} + \Delta_f H_i(T_{ref}) - T s_i(T, 1 bar)$$

on NIST-JANAF table

$$g_{N_2} = -324.4 \text{ kJ/mol}$$
$$g_{O_2} = -346.5 \text{ kJ/mol}$$
$$g_{NO} = -264.0 \text{ kJ/mol}$$

$$\left(\begin{array}{l} \lambda_N = -13.15 \times \hat{R}T \\ \lambda_0 = -15.26 \times \hat{R}T \end{array} \right)$$

$$X_{NO} = \exp\left(\frac{-g_{NO} + \lambda_N + \lambda_0}{\hat{R}T} \right) = \boxed{1.14 \times 10^{-4}} \text{ minor product.}$$