Equilibria of Reactions Involving Gases

- **Basic issue**
  – how to determine the equilibrium conditions for a reacting mixture of gases
- **Example problem statements**
  1. how to find the product composition after an initial “well-defined” set of gases are “allowed” to react
     - NH_3:N_2O (5:8) $\rightarrow$ Equilibrium Products
  2. how to find the equilibrium composition of gas mixture containing specified relative amounts of atomic elements
     - N:H:O (21:15:8) $\rightarrow$ Equilibrium Composition

Chemical Reaction Formalism

- Recall general reaction equation $\sum_i \nu_i M_i = 0$
  – e.g., $2HI \leftrightarrow H_2 + I_2$
  LHS RHS
  – mathematically
    - ν_i: stoich. coeff. for i[th] species (+) RHS; (–) LHS
    - M_i: mass of i[th] species
- Defined progress variable $d\eta = \frac{dn_i}{\nu_i}$ $\quad d\eta \begin{cases} >0 & \rightarrow \\ <0 & \leftarrow \end{cases}$
- General requirement for reaction (chemical) equilibria
  – min. $G = \sum_i n_i \mu_i$ or $0 \geq \sum_i \mu_i dn_i = \left(\sum_i \nu_i \mu_i \right) d\eta$

Minimum G

- Why does minimum exist for $G = \sum_i n_i \mu_i$
- Example, P.G.

  $$G = \sum_i n_i \left(\mu_i^o + \bar{R}T \ln p + \bar{R}T \ln \chi_i \right)$$

  – for simplicity, fix T and p=1

  $$G = \underbrace{\sum_i n_i \mu_i^o}_{\text{I}} + \underbrace{\sum_i n_i \bar{R}T \ln \chi_i}_{\text{II}}$$

- I: G for simple "mixing" of LHS+RHS
- II: ΔG associated with "mixing" entropy of LHS,RHS
- Overall balance ⇒ equil.