Equilibrium for Reacting Gases

- **Basic issue**
  - how to determine the equilibrium conditions for a reacting mixture of gases, i.e., how to find the equilibrium **state**
- **State requirement**
  - for a simple compressible substance, recall it takes 2 independent, intensive variables for a "*known* substance" to define a TD state
    - for a gas, common independent property pairs include: (u, v), (h, p) and (T, p)
    - since we generally don't know the composition, i.e., χ_i, **how do we define the "substance"?**

Mass (Atom) Conservation

- **Example problem statements**
  1. Determine equilibrium product composition after known initial set of gases react
     - NH_3:N_2O in mole ratio of 5:8 → Equil. Prod. Comp.
     - since can't create or destroy nuclei (except in nuclear reactions), mass conservation requires products to have same number of each atomic nuclei as reactants
  2. Determine equilibrium composition of gas mixture with specified relative amounts of atoms/nuclei
     - N:H:O = 21:15:8 → Equilibrium Composition
- Both problems have same ratio of atom/nuclei types
  - *specifying atom ratios sufficient to define "substance"*

[NH_3:N_2O✓] → [χ_i=?]

[N:H:O✓ χ_i=?]

Equilibria of Reactions Involving Gases

- With substance defined and 2 intensive state properties specified, can now find equilibrium composition (χ_i) of our mixture
- Recall, this requires finding composition such that $\sum_i \mu_i dn_i = 0$
- Also recall for a known T and p, this is equivalent to minimizing G of the mixture
  - in general, minimization of general functions can be done numerically
  - here we will explore analytic approach based on writing "reactions"
    - provides useful insights into parameters that influence equilibrium composition

Chemical Reaction Formalism: Review

- Recall general reaction equation $\sum_i \nu_i M_i = 0$
  - e.g., $2HI \leftrightarrow H_2 + I_2$
    LHS **RHS**
    defines 2 possible chemical systems/states for mixture containing HI, H_2 *and* I_2
  - mathematically
    - ν_i: stoich. coeff. for i[th] species (+) RHS; (–) LHS
    - M_i: i[th] species
- Defined progress variable $d\eta = \dfrac{dn_i}{\nu_i}$ $\quad d\eta \begin{cases} > 0 & \rightarrow \\ < 0 & \leftarrow \end{cases}$
- Requirement for chem. equilibrium between these two systems/states at known (T, p)
  - min. $G = \sum_i n_i \mu_i$ or $0 \geq \sum_i \mu_i dn_i = \left(\sum_i \nu_i \mu_i\right) d\eta$

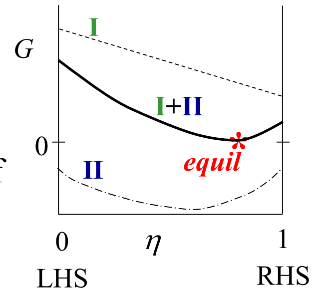
Minimum G: Interpretation

- Where does minimum exist for $G = \sum_i n_i \mu_i$
- Example, thermally perfect gas

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

  – for simplicity, let's fix T and let p=1 (really p=p^o)

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



- I: G for "simple mixing" of LHS+RHS (min. @ lowest G^o)
- II: ΔG from entropy increase of mixing (all components)
- Balance ⇒ equil. composition