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Equilibrium Constant

- **Goal**
  - find equilibrium composition for "single reaction" $\sum_i \nu_i M_i = 0$
  - for TPG mixture $\sum_i \nu_i \mu_i = \sum_i \nu_i \left(\mu_i^o + \bar{R}T \ln p_i\right)$
  - at equilibrium $= 0$

*equilibrium composition values denoted by **

$$-\frac{\sum_i \nu_i \mu_i^o}{\bar{R}T} = \sum_i \nu_i \ln p_i^* = \sum_i \ln\left(p_i^*\right)^{\nu_i}$$

sum of ln's is ln of product $= \ln \prod_i p_i^{*\nu_i}$

$= \ln K_p$

  - **Equilibrium Constant** $K_p \equiv \prod_i p_i^{*\nu_i}$

constrains equilibrium composition of TPG mixture in terms of partial pressures

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Law of Mass Action

- From previous expression $K_p = e^{-\sum_i \nu_i \mu_i^o / \bar{R}T}$
  - K_p solely a function of T for a TPG mixture, or $K_p = K_p(T)$
  - one form of what is known as **Law of Mass Action**
- Example: $O_2 + N_2 \leftrightarrow 2NO$

2 possible chemical "states" for our system: 1) only O_2 and N_2; 2) only NO

$$K_p = \frac{\left(p_{NO}^*\right)^2}{p_{O_2}^* p_{N_2}^*} = e^{\frac{-1}{\bar{R}T}\left(2\mu_{NO}^o - \mu_{O_2}^o - \mu_{N_2}^o\right)}$$

unless T=0, 0<K_p<∞
⇒ some finite amount of ALL three species

unitless

- Example: $O_2 \leftrightarrow 2O$

$$K_p = \frac{\left(p_O^*\right)^2}{p_{O_2}^*} = e^{\frac{-1}{\bar{R}T}\left(2\mu_O^o - \mu_{O_2}^o\right)}$$

has pressure units?

because we dropped p^o (=1 ?) from ln(p/p^o) in μ expression for TPG

- Standard Gibbs Free Energy (change) for given "reaction", ΔG^o or ΔG_T^o (it is function of T)

$$\Delta G_T^o \equiv \sum_i \nu_i \mu_i^o$$

$$K_p(T) = e^{-\Delta G_T^o / \bar{R}T}$$

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Mole Fractions and Concentrations

- Can write equilibrium constant expression in terms of **mole fractions** $K_p(T)=\prod_i p_i^{*\nu_i}=\prod_i(\chi_i^* p)^{\nu_i}=p^{\sum_i \nu_i}\prod_i \chi_i^{*\nu_i}$
  - since K_p not function of p, then RHS of expression is a constant for given T
    - e.g., if $p^{\sum_i \nu_i}\uparrow$ then $\prod_i \chi_i^{\nu_i}\downarrow$

$O_2 \leftrightarrow 2O$

$$K_p = p\frac{(\chi_O^*)^2}{\chi_{O_2}^*}$$

mole fractions will tend to increase as p increases on "side" of reaction with less moles

- Equil. constant for **concentrations** $K_c(T)\equiv\prod_i [M_i]^{*\nu_i}=\frac{K_p(T)}{(\bar{R}T)^{\sum_i \nu_i}}$
  - $[M]\equiv n_M/V$
    e.g., moles/cm^3

$[M_i]=p_i/\bar{R}T$

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Imperfect Gases

- For imperfect gases, can follow similar approach to perfect gases, but use fugacity to define an equilibrium constant
  - as before for a given "reaction" $\sum_i \nu_i M_i = 0$

$$0=\sum_i \nu_i\mu_i^* \Rightarrow -\frac{\sum_i \nu_i\mu_i^o}{\bar{R}T}=\sum_i \nu_i \ln f_i^*$$

  - equilibrium constant

$$K_f\equiv\prod_i f_i^{*\nu_i} \qquad K_f(T)=e^{-\sum_i \nu_i\mu_i^o/\bar{R}T}=e^{-\Delta G_T^o/\bar{R}T}$$

  - note: if we used p, K_p for imperfect gases,
    - would get $K_p=K_p(T,p)$
    - not as useful since p, T dependence not separated