

## Chemical Equil: Number of $K_p$ Eqns.

- How many equilibrium stoichiometric reactions ( $K_p$ 's) are required to determine equilibrium composition of chosen set of species?
- Assume mixture of  $m$  species having  $\alpha$  kinds of atoms (nuclei)
- Generally  $m+2$  unknowns (2 intensive TD props.)
- IF we specify the 2 TD properties (e.g,  $T,p$  or  $h,p$ ) AND the number/ratio of atomic nuclei
  - that leaves  **$m-\alpha$  unknowns** which requires  **$m-\alpha$  independent  $K_p$  expressions** (=number of reaction degrees of freedom)

## Examples

- Mixture of  $H_2$  and  $O_2$ 
  - how many  $K_p$  required?
  - $m=2, \alpha=2 \Rightarrow m-\alpha=0$   $K_p$  required
- Mixture of  $H_2, O_2, H_2O$ 
  - how many  $K_p$  required?
  - $m=3, \alpha=2 \Rightarrow m-\alpha=1$   $K_p$  required
- Mixture of  $H_2, O_2, H_2O, OH, O, H$ 
  - how many  $K_p$  required?
  - $m=6, \alpha=2 \Rightarrow m-\alpha=4$   $K_p$  required

## Examples (con't)

- Mixture of  $\text{NH}_3$ ,  $\text{HCl}$ ,  $\text{NH}_4\text{Cl}$ 
  - how many  $K_p$  required?
  - $m=3, \alpha=3 \Rightarrow m-\alpha=0$   $K_p$  required ??
- No!
  - for this problem, only 2 of the atom conservation equations are independent

$$\begin{array}{rcl}
 N: & dn_{\text{NH}_3} + dn_{\text{NH}_4\text{Cl}} = 0 & 3\times \\
 Cl: & dn_{\text{HCl}} + dn_{\text{NH}_4\text{Cl}} = 0 & + 1\times \\
 H: & 3dn_{\text{NH}_3} + dn_{\text{HCl}} + 4dn_{\text{NH}_4\text{Cl}} = 0 & =
 \end{array}$$

*SO, number of independent equilibrium expressions required is  $m-\alpha^*$  where  $\alpha^*$  is #of independent conservation equations*

## Number of Independent Reactions

- How do you determine how many of the atom conservation equations are independent?
  - linear algebra can be used
  - atomic formation reaction approach
    1. write a reaction forming each non-monatomic species from its atoms
    2. combine equations to eliminate any atom not actually a species in chosen composition