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 NH₃, HCl, NH₄Cl
  - 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

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\begin{align*}
N: & \quad dn_{\text{NH}_3} + dn_{\text{NH}_4\text{Cl}} = 0 \\
Cl: & \quad dn_{\text{HCl}} + dn_{\text{NH}_4\text{Cl}} = 0 \\
H: & \quad 3dn_{\text{NH}_3} + dn_{\text{HCl}} + 4dn_{\text{NH}_4\text{Cl}} = 0
\end{align*}
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*Number of independent equilibrium expressions required is $M-\alpha^*$ where $\alpha^*$ is number of INDEPENDENT atom 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