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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 α 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–α unknowns** which requires **M–α independent K_p expressions** (=number of reaction degress of freedom)

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Examples

- Mixture: H_2 and O_2
  - how many K_p required?
  - M=2, α=2 ⇒ M–α=0 K_p required

Red colored expressions - are formation reactions

- Mixture: H_2, O_2, H_2O
  - how many K_p required?
  - M=3, α=2 ⇒ M–α=1 K_p required

e.g., $H_2 + ½\ O_2 \leftrightarrow H_2O$

or $2H_2O \leftrightarrow 2H_2+O_2$

- Mixture: H_2, O_2, H_2O, OH, O, H
  - how many K_p required?
  - M=6, α=2 ⇒ M–α=4 K_p required

e.g., $H_2 + ½\ O_2 \leftrightarrow H_2O$ (1)
$½\ H_2 \leftrightarrow H$ (2)
$½\ O_2 \leftrightarrow O$ (3)
$½\ H_2 + ½\ O_2 \leftrightarrow OH$ (4)

could replace (2), (3) *or* (4) or? $H+O \leftrightarrow OH$
could replace (1), (2) *or* (4) or? $H+OH \leftrightarrow H_2O$

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Examples (con't)

- Mixture of NH_3, HCl, NH_4Cl
  - how many K_p required?
  - M=3, α=3 $\Rightarrow$ M–α=0 K_p required ??
- No!
  - for this problem, only 2 of the atom conservation equations are independent

$$\begin{array}{ll} \text{N:} & dn_{NH_3} + dn_{NH_4Cl} = 0 \qquad 3\times \\ \text{Cl:} & dn_{HCl} + dn_{NH_4Cl} = 0 \qquad +\ 1\times \\ \text{H:} & 3dn_{NH_3} + dn_{HCl} + 4dn_{NH_4Cl} = 0 \qquad = \end{array}$$

Number of independent equilibrium expressions required is M–α* where α* is number of INDEPENDENT atom conservation equations

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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