## EQUILIBRIUM CONTANTS

## MEANING OF VALUES

$$
\begin{array}{r}
2 \mathrm{H}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g})<2 \mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) \\
\mathrm{K}_{\mathrm{c}}=\frac{\left[\mathrm{H}_{2} \mathrm{O}\right]^{2}}{\left[\mathrm{H}_{2}\right]^{2}\left[\mathrm{O}_{2}\right]}=\frac{9.1 \times 10^{80}}{1}
\end{array}
$$

Very little reactant relative to product.
Requires $200,000 \mathrm{~L}$ of water vapor to locate $2 \mathrm{H}_{2}$ and $1 \mathrm{O}_{2}$ molecules.

$$
\mathrm{N}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g})<=>2 \mathrm{NO}(\mathrm{~g})
$$

$$
\mathrm{K}_{\mathrm{c}}=\frac{[\mathrm{NO}]^{2}}{\left[\mathrm{~N}_{2}\right]\left[\mathrm{O}_{2}\right]}=4.8 \times 10^{-31}=\frac{4.8}{10^{31}}
$$

Very little product relative to reactant.

In general for either $\mathrm{K}_{\mathrm{c}}$ or $\mathrm{K}_{\mathrm{p}}$

K value very large Reaction far toward completion
K value close to 1
K value very small

Reactant and product concentrations nearly same Hardly any products formed

## EQUILIBRIUM EXPRESSION

Equilibrium Expression for General Reaction

$$
\mathrm{aA}+\mathrm{bB}<=>\mathrm{cC}+\mathrm{dD} \quad \mathrm{~K}_{\mathrm{c}}=\frac{[\mathrm{C}]^{\mathrm{c}}[\mathrm{D}]^{\mathrm{d}}}{[\mathrm{~A}]^{\mathrm{a}}[\mathrm{~B}]^{\mathrm{b}}}
$$

Also termed "mass action quotient" or "reaction quotient"
For reverse reaction $\quad c C+d D \Leftrightarrow a A+b B \quad K_{c}^{-1}=\frac{[A]^{a}[B]^{b}}{[C]^{c}[D]^{d}}$
If double reaction, all coefficients are twice original value so $\left(\mathrm{K}_{\mathrm{c}}\right)^{2}$ If $1 / 2$ reaction, all coefficients are $1 / 2$ original value so $\left(\mathrm{K}_{\mathrm{c}}\right)^{1 / 2}$

If add two reactions

$$
\begin{gathered}
2 \mathrm{~A} \Leftrightarrow \mathrm{C} \\
\frac{3 \mathrm{~B}}{2 \mathrm{~A}+\mathrm{B} \Leftrightarrow 3 \mathrm{D}} \quad \begin{array}{c}
K_{1}=\frac{[C]}{[A]^{2}} \\
\mathrm{~K}=\mathrm{K}_{1} \mathrm{~K}_{2}=\frac{[\mathrm{C}]}{[\mathrm{A}]^{2}} \times \frac{[\mathrm{D}]^{3}}{[\mathrm{~B}]}=\frac{[\mathrm{C}][\mathrm{D}]^{3}}{[\mathrm{~A}]^{2}[\mathrm{~B}]}
\end{array} . \begin{array}{c}
{[D]^{3}} \\
{[B]} \\
\hline
\end{array}
\end{gathered}
$$

## EQUILIBRIUM EXPRESSIONS

Relationship of $\mathrm{K}_{\mathrm{p}}$ and $\mathrm{K}_{\mathrm{c}}$
For a gaseous reaction the ratio of products to reactants in terms of pressure (atm) is $\mathrm{K}_{\mathrm{p}}$
$\mathrm{aA}+\mathrm{bB}<=>\mathrm{cC}+\mathrm{dD}$
$K_{c}=\frac{[C]^{\mathrm{c}}[\mathrm{D}]^{\mathrm{d}}}{[\mathrm{A}]^{\mathrm{a}}[\mathrm{B}]^{\mathrm{b}}}$ and $\mathrm{K}_{\mathrm{p}}=\frac{\mathrm{P}_{\mathrm{C}}{ }^{\mathrm{c}} \mathrm{P}_{\mathrm{D}}{ }^{\mathrm{d}}}{\mathrm{P}_{\mathrm{A}}{ }^{\mathrm{a}} \mathrm{P}_{\mathrm{B}}{ }^{\mathrm{b}}}$
$\mathrm{PV}=\mathrm{nRT}$ so $\quad \mathrm{P}=\frac{\mathrm{n}}{\mathrm{V}} \mathrm{RT}=\mathrm{MRT}$
$K_{p}=\frac{P_{C}{ }^{c} P_{D}{ }^{d}}{P_{A}{ }^{a} P_{B}{ }^{b}}=\frac{\left(M_{C} R T\right)^{c}\left(M_{D} R T\right)^{d}}{\left(M_{A} R T\right)^{a}\left(M_{B} R T\right)^{b}}$

Factor out RT
$K_{p}=(R T)^{\Delta n_{g s s}}\left(\frac{M_{C}^{c} M_{D}^{d}}{M_{A}^{a} M_{B}^{b}}\right)$
Therefore
$\mathrm{K}_{\mathrm{p}}=(\mathrm{RT})^{\Delta \mathrm{n}_{\mathrm{gas}}} \mathrm{K}_{\mathrm{c}} \quad$ where $\Delta \mathrm{n}_{\mathrm{gas}}=(\mathrm{c}+\mathrm{d})-(\mathrm{a}+\mathrm{b})$

## EQUILIBRIUM EXPRESSIONS

For the reaction: $2 \mathrm{NO}(\mathrm{g})+\mathrm{Cl}_{2}(\mathrm{~g})<=>2 \mathrm{ClNO}(\mathrm{g})$, write the $\mathrm{K}_{\mathrm{c}}$ and $\mathrm{K}_{\mathrm{p}}$ equilibrium expressions.

$$
\begin{aligned}
\mathrm{K}_{\mathrm{C}} & =\frac{[\mathrm{ClNO}]^{2}}{[\mathrm{NO}]^{2}\left[\mathrm{Cl}_{2}\right]} \\
\mathrm{K}_{\mathrm{P}} & =\frac{\mathrm{P}_{\mathrm{ClNO}}{ }^{2}}{\mathrm{P}_{\mathrm{NO}}{ }^{2} \mathrm{P}_{\mathrm{Cl} 2}}
\end{aligned}
$$

At 500 K , an equilibrium mixture contained $0.242 \mathrm{~atm} \mathrm{NO}, 0.605 \mathrm{~atm} \mathrm{Cl}_{2}$, and 1.38 atm CINO. Determine the $\mathrm{K}_{\mathrm{p}}$ and $\mathrm{K}_{\mathrm{c}}$ values.
To calculate $K_{c}$ the relationship $K_{p}=K_{c}(R T)^{\Delta n}$ is used.

$$
\begin{aligned}
& \mathrm{K}_{\mathrm{P}}=\frac{\mathrm{P}_{\mathrm{ClNO}}}{\mathrm{P}_{\mathrm{NO}}{ }^{2} \mathrm{P}_{\mathrm{C} 12}}=\frac{(1.38 \mathrm{~atm})^{2}}{(0.242 \mathrm{~atm})^{2}(0.605 \mathrm{~atm})}=53.7 \mathrm{~atm}^{-1} \\
& \mathrm{~K}_{\mathrm{P}}=\mathrm{K}_{\mathrm{C}}(\mathrm{RT})^{\text {angas }} \\
& 53.7 \mathrm{~atm}^{-1}=\mathrm{K}_{\mathrm{C}}(0.08206 \mathrm{~L} \cdot \mathrm{~atm} / \mathrm{mol} \bullet \mathrm{~K} * 500 \mathrm{~K})^{-1} \\
& \mathrm{~K}_{\mathrm{C}}=2.20 \times 10^{3} \mathrm{M}^{-1}
\end{aligned}
$$

## HETEROGENEOUS EQUILIBRIA

Pure solids or pure liquids do not appear in equilibrium expression since their concentration is constant.

$$
\begin{gathered}
\text { EXAMPLE: } \quad \underset{\text { density }=2.71 \mathrm{~g} / \mathrm{cm}^{3}}{\mathrm{CaCO}_{3}(\mathrm{~s})} \begin{array}{c}
\mathrm{CaO}(\mathrm{~s}) \\
\text { density }=3.25 \mathrm{~g} / \mathrm{cm}^{3}
\end{array}+\mathrm{CO}_{2}(\mathrm{~g}) \\
{\left[\mathrm{CaCO}_{3}\right]=\left(\frac{2.71 \mathrm{~g}}{\mathrm{~cm}^{3}}\right)\left(\frac{1 \mathrm{~mol}}{100.1 \mathrm{~g}}\right)\left(\frac{1000 \mathrm{~cm}^{3}}{1 \mathrm{~L}}\right)=27.1 \mathrm{~mol} / \mathrm{L}} \\
{[\mathrm{CaO}]=} \\
\left(\frac{3.25 \mathrm{~g}}{\mathrm{~cm}^{3}}\right)\left(\frac{1 \mathrm{~mol}}{56.1 \mathrm{~g}}\right)\left(\frac{1000 \mathrm{~cm}^{3}}{1 \mathrm{~L}}\right)=57.9 \mathrm{~mol} / \mathrm{L}
\end{gathered}
$$

$$
\mathrm{K}=\frac{[\mathrm{CaO}]\left[\mathrm{CO}_{2}\right]}{\left[\mathrm{CaCO}_{3}\right]}
$$

$$
\frac{\mathrm{K}^{*}\left[\mathrm{CaCO}_{3}\right]}{[\mathrm{CaO}]}=\left[\mathrm{CO}_{2}\right] \quad \text { So } \mathrm{K}_{\mathrm{c}}=\left[\mathrm{CO}_{2}\right] \quad \text { and } \quad \mathrm{K}_{\mathrm{p}}=\mathrm{P}_{\mathrm{CO} 2}
$$

