

## Lecture Presentation

## Chapter 14 Chemical Equilibrium

$$
\begin{aligned}
& 14.1,14.2,14.3,14.4, \\
& \text { 14.7, 14.9, 14.10, 14.11, } \\
& \text { 14.12, 14.14, 14.15, 14.19, } \\
& \text { 14.23, 14.24, 14.25, 14.27, } \\
& \text { 14.31, 14.34, 14.50, 14.52, } \\
& \text { 14.54, 14.56, 14.58, 14.60. } \\
& 14.68,14.74,14.88,14.98, \\
& 14.100,14.110
\end{aligned}
$$

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## The Equilibrium State (kinetic chapter no reversible rxx this chapter all reversible rxn)

Chemical Equilibrium: The state reached when the concentrations of reactants and products remain constant over time (dynamic equilibrium $\rightleftarrows$ ) (dynamic equilibrium: rxn to product $=r \times n$ to reactant)

This Chapter: How far forward does the reaction go ? NOT how fast but the ratio of products and reactants

Liquid bromine in dynamic equilibrium with gaseous bromine.

## The Equilibrium State

## $\mathrm{N}_{2} \mathrm{O}_{4}(g) \rightleftharpoons 2 \mathrm{NO}_{2}(g)$ <br> Colorless Brown



## The Equilibrium State

$\mathrm{N}_{2} \mathrm{O}_{4}(g) \rightleftharpoons 2 \mathrm{NO}_{2}(g)$

Experiment 1: forward rxn start with only $\mathrm{N}_{2} \mathrm{O}_{4}(g)$
(a) Only $\mathrm{N}_{2} \mathrm{O}_{4}$ is present initially.


Experiment 2: backward rxn Start with only $\mathrm{NO}_{2}(\mathrm{~g})$
(b) Only $\mathrm{NO}_{2}$ is present initially.


Both experiments end with exactly the same concentration of the $\mathrm{N}_{2} \mathrm{O}_{4}$ and $\mathrm{NO}_{2}$

## The Equilibrium State rate forward rxn = rate backward rxn

figure for rxn Starting from $\mathrm{N}_{2} \mathrm{O}_{4}$

$\mathrm{N}_{2} \mathrm{O}_{4}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NO}_{2}(\mathrm{~g})$

Time $\longrightarrow$
When the two rates become equal, an equilibrium state is attained and there are no further changes in concentrations.

## The Equilibrium Constant $K_{\mathrm{c}}$

$\mathrm{N}_{2} \mathrm{O}_{4}(g) \rightleftharpoons 2 \mathrm{NO}_{2}(g)$

## TABLE 14.1 Concentration Data at $25^{\circ} \mathrm{C}$ for the Reaction $\mathrm{N}_{2} \mathrm{O}_{4}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NO}_{2}(\mathrm{~g})$

| Experiment | Initial <br> Concentrations (M) |  | Equilibrium <br> Concentrations (M) |  | Equilibrium <br> Constant Expression |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | [ $\mathrm{N}_{2} \mathrm{O}_{4}$ ] | [ $\mathrm{NO}_{2}$ ] | [ $\mathrm{N}_{2} \mathrm{O}_{4}$ ] | [ $\mathrm{NO}_{2}$ ] | $\left[\mathrm{NO}_{2}\right]^{2} /\left[\mathrm{N}_{2} \mathrm{O}_{4}\right]$ |
| 1 | 0.0400 | 0.0000 | 0.0337 | 0.0125 | $4.64 \times 10^{-3}$ |
| 2 | 0.0000 | 0.0800 | 0.0337 | 0.0125 | $4.64 \times 10^{-3}$ |
| 3 | 0.0600 | 0.0000 | 0.0522 | 0.0156 | $4.66 \times 10^{-3}$ |
| 4 | 0.0000 | 0.0600 | 0.0246 | 0.0107 | $4.65 \times 10^{-3}$ |
| 5 | 0.0200 | 0.0600 | 0.0429 | 0.0141 | $4.63 \times 10^{-3}$ |

Elementary Reaction Mechanism Step
rate $=\mathrm{k}_{1}\left[\mathrm{~N}_{2} \mathrm{O}_{4}\right]$
rate $($ back $)=\mathrm{k}_{2}\left[\mathrm{NO}_{2}\right]^{2}$

## Why?

Equilibrium
state

The Equilibrium Constant $K_{\mathrm{c}}$
$\mathrm{K}_{\mathrm{c}}$ is the same at the same temperature no matter how much of each reactant or product you have

For a general reversible reaction: $a \mathrm{~A}+b \mathrm{~B} \rightleftharpoons c \mathrm{C}+d \mathrm{D}$

Equilibrium constant expression
For the following reaction: $\mathrm{N}_{2} \mathrm{O}_{4}(g) \rightleftharpoons 2 \mathrm{NO}_{2}(g)$

$$
K_{\mathrm{c}}=\frac{\left[\mathrm{NO}_{2}\right]^{2}}{\left[\mathrm{~N}_{2} \mathrm{O}_{4}\right]}=4.64 \times 10^{-3}\left(\text { at } 25^{\circ} \mathrm{C}\right)
$$

## HW 14.1: The Equilibrium Constant $K_{\mathrm{c}}$

 Write the equilibrium constant expression for the following reactions. ( $\mathrm{K}_{\mathrm{p}}=$ equilibrium constants with amounts given by pressure of each component)(if gas is in solution use $\mathrm{K}_{\mathrm{c}}$, if gas is in gas state use $\mathrm{K}_{\mathrm{p}}$ )$$
a \mathrm{~A}+b \mathrm{~B} \rightleftharpoons c \mathrm{C}+d \mathrm{D} \quad K_{\mathrm{c}}=\frac{[\mathrm{C}]^{c}[\mathrm{D}]^{d}}{[\mathrm{~A}]^{a}[\mathrm{~B}]^{b}}
$$

(s) or (1)
(a) 2 BrCl (soln) $\underset{\leftarrow}{\underset{ }{\rightarrow}} \mathrm{Br}_{2}$ (soln) $+\mathrm{Cl}_{2}$ (soln)
(b) $2 \mathrm{~N}_{2}(\mathrm{~g})+2 \mathrm{O}_{2}(\mathrm{~g}) \underset{\leftarrow}{\rightarrow} 4 \mathrm{NO}(\mathrm{g})\left(\right.$ give $\left.\mathrm{K}_{\mathrm{p}}\right)$
(c) $\mathrm{BaSO}_{4}(\mathrm{~s}) \underset{\leftarrow}{\rightarrow} \mathrm{Ba}^{2+}(\mathrm{aq})+\mathrm{SO}_{4}{ }^{2-}(\mathrm{aq})$
(d) $\mathrm{Fe}_{2} \mathrm{O}_{3}(\mathrm{~s})+3 \mathrm{CO}(\mathrm{g}) \underset{\leftarrow}{\rightarrow} 2 \mathrm{Fe}(\mathrm{s})+3 \mathrm{CO}_{2}(\mathrm{~g})$

HW 14.1: The Equilibrium Constant $K_{c}$
Write the equilibrium constant expression for the
following reactions. ( $\mathrm{K}_{\mathrm{p}}=$ equilibrium constants with amounts are given by pressure of each component)(if gas is in solution use $\mathrm{K}_{\mathrm{c}}$, if gas is in gas state use $\mathrm{K}_{\mathrm{p}}$ )

$$
a \mathrm{~A}+b \mathrm{~B} \rightleftharpoons c \mathrm{C}+d \mathrm{D} \quad K_{\mathrm{c}}=\frac{[\mathrm{C}]^{[ }[\mathrm{D}]^{d}}{[\mathrm{~A}]^{2}[\mathrm{~B}]^{b}} \quad \begin{aligned}
& \text { (s) or }(\mathrm{l}) \\
& \text { leave out of } \\
& \text { K expression }
\end{aligned}
$$


(b) $2 \mathrm{~N}_{2}(\mathrm{~g})+2 \mathrm{O}_{2}(\mathrm{~g}) \underset{\leftarrow}{\rightarrow} 4 \mathrm{NO}(\mathrm{g}) \quad\left(\right.$ give $\left.\mathrm{K}_{\mathrm{p}}\right)$

$$
K_{p}=\frac{\left(\mathrm{P}_{\mathrm{NO}}\right)^{4}}{\left(\mathrm{P}_{\mathrm{N} 2}\right)^{2}\left(P_{\mathrm{O} 2}\right)^{2}}
$$

(c) $\mathrm{BaSO}_{4}(\mathrm{~s}) \underset{\leftarrow}{\underset{ }{*}} \mathrm{Ba}^{2+}(\mathrm{aq})+\mathrm{SO}_{4}{ }^{2-(\mathrm{aq})} \quad K_{\mathrm{c}}=\left[\mathrm{Ba}^{2+}\right]\left[\mathrm{SO}_{4}{ }^{2}\right]$
(d) $\mathrm{Fe}_{2} \mathrm{O}_{3}(\mathrm{~s})+3 \underset{\leftarrow}{\underset{\leftarrow}{\mathrm{CO}(\mathrm{g})}} 2 \mathrm{Fe}(\mathrm{s})+3 \mathrm{CO}_{2}(\mathrm{~g}) \underset{\text { 2/28 Friday }}{ } \quad K_{p}=\frac{\left(\mathrm{P}_{\mathrm{CO2}}\right)^{3}}{\left(\mathrm{P}_{\mathrm{co}}\right)^{3}}$

## The Equilibrium Constant $K_{\mathrm{c}}$

TABLE 14.1 Concentration Data at $25^{\circ} \mathrm{C}$ for the Reaction $\mathrm{N}_{2} \mathrm{O}_{4}(g) \rightleftharpoons 2 \mathrm{NO}_{2}(g)$

|  | Initial <br> Concentrations (M) |  | Equilibrium <br> Concentrations (M) |  | Equilibrium <br> Constant Expression |
| :--- | :---: | :---: | :---: | :---: | :---: |
| Experiment | $\left[\mathrm{N}_{2} \mathrm{O}_{4}\right]$ | $\left[\mathrm{NO}_{2}\right]$ | $\left[\mathrm{N}_{2} \mathrm{O}_{4}\right]$ | $\left[\mathrm{NO}_{2}\right]$ | $\left[\mathrm{NO}_{2}\right]^{2} /\left[\mathrm{N}_{2} \mathrm{O}_{4}\right]$ |
| 1 | 0.0400 | 0.0000 | 0.0337 | 0.0125 | $4.64 \times 10^{-3}$ |
| 2 | 0.0000 | 0.0800 | 0.0337 | 0.0125 | $4.64 \times 10^{-3}$ |
| 3 | 0.0600 | 0.0000 | 0.0522 | 0.0156 | $4.66 \times 10^{-3}$ |
| 4 | 0.0000 | 0.0600 | 0.0246 | 0.0107 | $4.65 \times 10^{-3}$ |
| 5 | 0.0200 | 0.0600 | 0.0429 | 0.0141 | $4.63 \times 10^{-3}$ |

$$
K_{\mathrm{c}}=\frac{\left[\mathrm{NO}_{2}\right]^{2}}{\left[\mathrm{~N}_{2} \mathrm{O}_{4}\right]} \quad \frac{\text { Experiment 1 }}{\frac{(0.0125)^{2}}{0.0337}=4.64 \times 10^{-3}} \quad \frac{(0.0141)^{2}}{0.0429}=4.63 \times 10^{-3}
$$

The Equilibrium Constant $K_{\mathrm{c}}$
The equilibrium constant and the equilibrium constant expression are for the chemical equation as written.

$$
a \mathrm{~A}+b \mathrm{~B} \rightleftharpoons c \mathrm{C}+d \mathrm{D} \quad K_{\mathrm{c}}=\frac{[\mathrm{C}]^{c}[\mathrm{D}]^{d}}{[\mathrm{~A}]^{a}[\mathrm{~B}]^{b}}
$$

End 2/28F A section
(a) $\mathrm{N}_{2}(g)+3 \mathrm{H}_{2}(g) \rightleftharpoons 2 \mathrm{NH}_{3}(g) \quad K_{\mathrm{c}}=\frac{\left[\mathrm{NH}_{3}\right]^{2}}{\left[\mathrm{~N}_{2}\right]\left[\mathrm{H}_{2}\right]^{3}}$ double rxn
(b) $2 \mathrm{NH}_{3}(g) \rightleftharpoons \mathrm{N}_{2}(g)+3 \mathrm{H}_{2}(g)$ reversed rxn (a) - turn K upside down
(c) $2 \mathrm{~N}_{2}(g)+6 \mathrm{H}_{2}(g) \rightleftharpoons 4 \mathrm{NH}_{3}(g)$ doubled rxn (a) - square all terms reverse rxn

$$
K_{\mathrm{c}}^{\prime}=\frac{\left[\mathrm{N}_{2}\right]\left[\mathrm{H}_{2}\right]^{3}}{\left[\mathrm{NH}_{3}\right]^{2}}=\frac{1}{K_{\mathrm{c}}}
$$

(c) $\mathrm{N}_{2}(\mathrm{~g})+6 \mathrm{H}_{2}(\mathrm{~g}) \xrightarrow{(\mathrm{C}}$

$$
K_{\mathrm{c}}^{\prime}=\frac{\left[\mathrm{NH}_{3}\right]^{4}}{\left[\mathrm{~N}_{2}\right]^{2}\left[\mathrm{H}_{2}\right]^{6}}=K_{\mathrm{c}}^{2}
$$

## HW 14.2: The Equilibrium Constant $K_{\mathrm{c}}$

Give the (a) equilibrium constant expression and the (b) numerical value of the equilibrium constant expression for the following reactions given the reaction. (assume dissolved in solvent)

$$
\begin{aligned}
& \mathrm{N}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \underset{\leftarrow}{\rightarrow} 2 \mathrm{NO}(\mathrm{~g}) \\
& (1) 2 \mathrm{NO}(\mathrm{~g}) \underset{\leftarrow}{\underset{~}{\leftarrow}} \mathrm{~N}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g})
\end{aligned}
$$

(2) $2 \mathrm{~N}_{2}(\mathrm{~g})+2 \mathrm{O}_{2}(\mathrm{~g}) \underset{\leftarrow}{\rightarrow} 4 \mathrm{NO}(\mathrm{g})$

# HW 14.2: The Equilibrium Constant $K_{c}$ 

 Give the (a) equilibrium constant expression and the (b) numerical value of the equilibrium constant expression for the following reactions given the reaction.$$
\begin{array}{ll}
\mathrm{N}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \underset{\leftarrow}{\underset{\leftarrow}{*}} 2 \mathrm{NO}(\mathrm{~g}) \quad \mathrm{Kc}=7.5 \times 10^{-9} \\
(1) 2 \mathrm{NO}(\mathrm{~g}) \underset{\leftarrow}{\underset{\leftarrow}{*}} \underset{\mathrm{~N}}{\mathrm{~N}}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \quad K_{\mathrm{c}}=\frac{\left[\mathrm{N}_{2}\right]\left[\mathrm{O}_{2}\right]}{\left[\mathrm{NO}^{2}\right.} & \\
\mathrm{Kc}=1 / 7.5 \times 1 \mathrm{NO}^{2} \\
{\left[\mathrm{~N}_{2}\right]\left[\mathrm{O}_{2}\right]} \\
(2) 2 \mathrm{~N}_{2}(\mathrm{~g})+2 \mathrm{O}_{2}(\mathrm{~g}) \underset{\leftarrow}{\rightarrow} 4 \mathrm{NO}(\mathrm{~g}) & K_{\mathrm{c}}=\frac{\left[\mathrm{NO}^{4}\right.}{\left[\mathrm{N}_{2}\right]^{2}\left[\mathrm{O}_{2}\right]^{2}} \\
\mathrm{Kc}=\left(7.5 \times 10^{-9}\right)^{2}=5.6 \times 10^{-17} &
\end{array}
$$

## The Equilibrium Constant $K_{\mathrm{c}}\left(\mathrm{K}_{\mathrm{p}}\right)$

$$
\begin{aligned}
& \mathrm{N}_{2} \mathrm{O}_{4}(g) \rightleftharpoons 2 \mathrm{NO}_{2}(g) \\
& K_{\mathrm{p}}=\frac{\left(P_{\mathrm{NO}_{2}}\right]^{2}}{P_{\mathrm{N}_{2} \mathrm{O}_{4}}}
\end{aligned}
$$

$\boldsymbol{P}$ is the partial pressure of that component.

## HW 14.3: The Equilibrium Constant $K_{c}$

$\mathrm{CO}(\mathrm{g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{g}) \underset{\leftarrow}{\leftarrow} \mathrm{CO}_{2}(\mathrm{~g})+\mathrm{H}_{2}(\mathrm{~g})$
$\leftarrow$
What is the value of $\mathrm{K}_{\mathrm{p}}$ at 700 K if the partial pressure in an equilibrium mixture at 700 K are 1.31 atm of $\mathrm{CO}, 10.0 \mathrm{~atm}$ of $\underline{H}_{2} \underline{O}, \underline{6.12 \mathrm{~atm} \text { of } \mathrm{CO}_{2}-}$ and $\underline{20.3 \mathrm{~atm} \text { of } \mathrm{H}_{2}-? ~}$

## HW 14.3: The Equilibrium Constant $K_{c}$

$\mathrm{CO}(\mathrm{g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{g}) \underset{\leftarrow}{\underset{\leftarrow}{\leftarrow}} \mathrm{CO}_{2}(\mathrm{~g})+\mathrm{H}_{2}(\mathrm{~g})$
What is the value of $\mathrm{K}_{\mathrm{p}}$ at 700 K if the partial pressure in an equilibrium mixture at 700 K are 1.31 atm of $\mathrm{CO}, 10.0 \mathrm{~atm}$ of $\mathrm{H}_{2} \mathrm{O}, 6.12 \mathrm{~atm}$ of $\mathrm{CO}_{2}$ and 20.3 atm of $\mathrm{H}_{2}$ ?

$$
\mathrm{K}_{\mathrm{p}}=\frac{\mathrm{P}_{\mathrm{CO} 2} \mathrm{P}_{\mathrm{H} 2}}{\mathrm{P}_{\mathrm{CO}} \mathrm{P}_{\mathrm{H} 2 \mathrm{O}}}=\frac{(6.12 \mathrm{~atm})(20.3 \mathrm{~atm})}{(1.31 \mathrm{~atm})(10.0 \mathrm{~atm})}=9.48
$$

## The Equilibrium Constant $K_{c}$

$K_{\mathrm{p}}=K_{\mathrm{c}}(R T)^{\Delta n} \quad \boldsymbol{R}$ is the gas constant, $0.08206 \frac{\mathrm{~L} \text { atm }}{\mathrm{K} \mathrm{mol}}$.
$\boldsymbol{T}$ is the absolute temperature (kelvin).
$\Delta n=\#$ moles of gaseous products minus \# moles of gaseous reactants.

## The Equilibrium Constant $K_{\mathrm{c}}$ $K_{\mathrm{p}}=K_{\mathrm{c}}(R T)^{\Delta n} \boldsymbol{R}$ is the gas constant, $0.08206 \frac{\mathrm{Latm}}{\mathrm{Kmol}}$. $\Delta \mathrm{n}=(\mathrm{c}+\mathrm{d})-(\mathrm{a}+\mathrm{b})$

$\begin{aligned} 2 \mathrm{NO}(\mathrm{g})+\mathrm{O}_{2}(\mathrm{~g}) & \rightarrow 2 \mathrm{NO}_{2}(\mathrm{~g}) \\ & \leftarrow\end{aligned}$

If $\mathrm{K}_{\mathrm{c}}=6.9 \times 10^{5}$ at $227^{\circ} \mathrm{C}$, what is the value of $\mathrm{K}_{\mathrm{p}}$ ?
$K_{p}=K_{c}(R T)^{\Delta n}$
$\Delta n=(2)-(2+1)=-1$
$K_{p}=\left(6.9 \times 10^{5}\right)[(0.08206 \mathrm{Latm} / \mathrm{mol} \mathrm{K})(227+273.15)]^{-1}$
$K_{p}=16811.9=1.7 \times 10^{4}$

## HW 14.4: The Equilibrium Constant $K_{\mathrm{c}}$

 $K_{\mathrm{p}}=K_{\mathrm{c}}\left(R T T^{\Delta n} \quad \boldsymbol{R}\right.$ is the gas constant, $0.08206 \frac{\mathrm{Latm}}{\mathrm{K} \text { mol }}$. $\Delta \mathrm{n}=(\mathrm{c}+\mathrm{d})-(\mathrm{a}+\mathrm{b})$$\mathrm{H}_{2} \mathrm{O}(\mathrm{g})+\mathrm{CH}_{4}(\mathrm{~g}) \underset{\leftarrow}{\underset{\leftarrow}{\leftarrow}} \mathrm{CO}(\mathrm{g})+3 \mathrm{H}_{2}(\mathrm{~g})$
If $\mathrm{K}_{\mathrm{c}}=3.8 \times 10^{-3}$ at 1000 K , what is the value of $\mathrm{K}_{\mathrm{p}}$ ?

## HW 14.4: The Equilibrium Constant $K_{\mathrm{c}}$

 $K_{\mathrm{p}}=K_{\mathrm{c}}(R T)^{\Delta n} \quad \boldsymbol{R}$ is the gas constant, $0.08206 \frac{\mathrm{Latm}}{\mathrm{Kmol}}$.$\Delta \mathrm{n}=(\mathrm{c}+\mathrm{d})-(\mathrm{a}+\mathrm{b})$

$$
\mathrm{H}_{2} \mathrm{O}(\mathrm{~g})+\mathrm{CH}_{4}(\mathrm{~g}) \underset{\leftarrow}{\leftarrow} \mathrm{CO}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g})
$$

End 3/2 Monday A section

If $\mathrm{K}_{\mathrm{c}}=3.8 \times 10^{-3}$ at 1000 K , what is the value of $\mathrm{K}_{\mathrm{p}}$ ?
$\mathrm{K}_{\mathrm{p}}=\mathrm{K}_{\mathrm{c}}(\mathrm{RT})^{\Delta \mathrm{n}}$
$\Delta \mathrm{n}=(1+3)-(1+1)=2$
$\mathrm{K}_{\mathrm{p}}=\left(3.8 \times 10^{-3}\right)[(0.08206 \mathrm{Latm} / \mathrm{mol} \mathrm{K})(1000 \mathrm{~K})]^{2}$
$\mathrm{K}_{\mathrm{p}}=25.588=26$

## Heterogeneous Equilibria

$$
\mathrm{CaCO}_{3}(s) \rightleftharpoons \mathrm{CaO}(s)+\mathrm{CO}_{2}(g)
$$

Limestone Lime
$K_{\mathrm{c}}=\frac{[\mathrm{CaO}]\left[\mathrm{CO}_{2}\right]}{\left[\mathrm{CaCO}_{3}\right]}=\frac{(1)\left[\mathrm{CO}_{2}\right]}{(1)}=\left[\mathrm{CO}_{2}\right]$
Pure solids and pure liquids are not included in equilibrium expression.

$$
K_{\mathrm{c}}=\left[\mathrm{CO}_{2}\right] \quad K_{\mathrm{p}}=P_{\mathrm{CO}_{2}}
$$

Molarity
If dissolved.

Pressure
If just gas - no solvent.

## Using the Equilibrium Constant

$2 \mathrm{H}_{2} \mathrm{O}(\mathrm{g}) \rightleftharpoons 2 \mathrm{H}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g})$
(at 500 K ) $K_{\mathrm{c}}=4.2 \times 10^{-48}$

The larger the value of the equilibrium constant $K_{\mathrm{c}}$

$\mathrm{H}_{2}(\mathrm{~g})+\mathrm{I}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{HI}(\mathrm{g})$
(at 700 K ) $K_{\mathrm{c}}=57.0$
$2 \mathrm{H}_{2}(g)+\mathrm{O}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{H}_{2} \mathrm{O}(\mathrm{g})$
(at 500 K ) $K_{\mathrm{c}}=2.4 \times 10^{47}$

## Using the Equilibrium Constant

$$
a \mathrm{~A}+b \mathrm{~B} \rightleftharpoons c \mathrm{C}+d \mathrm{D}
$$

Reaction quotient: $\quad Q_{\mathrm{c}}=\frac{[\mathrm{C}]_{t}^{c}[\mathrm{D}]_{t}^{d}}{[\mathrm{~A}]_{t}^{a}[\mathrm{~B}]_{t}^{b}}$
The reaction quotient, $Q_{C}$, is defined in the same way as the equilibrium constant, $K_{\mathrm{c}}$, except that the concentrations in $Q_{\mathrm{c}}$ are not necessarily equilibrium values. (value of mixed reaction before equilibrium)

## Using the Equilibrium Constant

- If $Q_{\mathrm{c}}<K_{\mathrm{c}}$ net reaction goes from left to right (reactants to products, $\rightarrow$ ).
- If $Q_{c}>K_{c}$ net reaction goes from right to left (products to reactants, $\leftarrow$ ).
- If $Q_{\mathrm{c}}=K_{\mathrm{c}}$ no net reaction occurs.
(at equilibrium)

> End 3/3 Tuesday
> C section

## HW 14.5: Using the Equilibrium Constant

- If $Q_{\mathrm{c}}<K_{\mathrm{c}}$ net reaction goes from left to right (reactants to products, $\rightarrow$ ).
- If $Q_{\mathrm{c}}>K_{\mathrm{c}}$ net reaction goes from right to left (products to reactants, $\leftarrow$ ).
- If $Q_{\mathrm{c}}=K_{\mathrm{c}}$ no net reaction occurs. (at equilibrium)

If the equilibrium constant $\mathrm{K}_{\mathrm{c}}=2.78 \times 10^{-10}$ and you have a reaction $\mathrm{A}+2 \mathrm{~B} \rightarrow 3 \mathrm{C}+\mathrm{D}$ and $[\mathrm{A}]=1.78 \times 10^{-4}, \quad[\mathrm{~B}]=1.1 \times 10^{-5}$ and $[\mathrm{C}]=1.23 \times 10^{-6},[\mathrm{D}]=7.8 \times 10^{-8}$ does the reaction go forward to produce more products or backwards to produce more reactant or stay in equilibrium?

## HW 14.5: Using the Equilibrium Constant

- If $Q_{\mathrm{c}}<K_{\mathrm{c}}$ net reaction goes from left to right (reactants to products, $\rightarrow$ ).
- If $Q_{\mathrm{c}}>K_{\mathrm{c}}$ net reaction goes from right to left (products to reactants, $\leftarrow$ ).
- If $Q_{\mathrm{c}}=K_{\mathrm{c}}$ no net reaction occurs. (at equilibrium)

If the equilibrium constant $\mathrm{K}_{\mathrm{c}}=2.78 \times 10^{-10}$ and you have a reaction $\mathrm{A}+2 \mathrm{~B} \rightarrow 3 \mathrm{C}+\mathrm{D}$ and $[\mathrm{A}]=1.78 \times 10^{-4}, \quad[\mathrm{~B}]=1.1 \times 10^{-5}$ and $[\mathrm{C}]=1.23 \times 10^{-6},[\mathrm{D}]=7.8 \times 10^{-8}$ does the reaction go forward to produce more products or backwards to produce more reactant or stay in equilibrium?

$$
\mathrm{Kc}=\frac{[\mathrm{C}]^{3}[\mathrm{D}]}{[\mathrm{A}][\mathrm{B}]^{2}} \quad \mathrm{Q}=\frac{\left[1.23 \times 10^{-6}\right]^{3}\left[7.8 \times 10^{-8}\right]}{\left[1.78 \times 10^{-4}\right]\left[1.1 \times 10^{-5}\right]^{2}}
$$

$$
Q=6.74 \times 10^{-12} \quad \& \quad 6.74 \times 10^{-12}<2.78 \times 10^{-10}
$$

Reaction goes forward until equilibrium is reached.

End 3/2/20
Monday section A

## Using the Equilibrium Constant - ICE method [Initial, Change, Equilibrium] (given K \& initial concentrations, calculate equilibrium concentrations)

At $700 \mathrm{~K}, 0.500 \mathrm{~mol}$ of HI is added to a 2.00 L container and allowed to come to equilibrium. Calculate the equilibrium concentrations of $\mathrm{H}_{2}, \mathrm{I}_{2}$, and $\mathrm{HI} . K_{\mathrm{c}}$ is 57.0 at 700 K

Initial: Zero<br>of reactants

$\mathrm{H}_{2}(g)+\mathrm{I}_{2}(g) \rightleftharpoons 2 \mathrm{HI}(g)$

## Using the Equilibrium Constant

Set up a table: Initial, Change, Equilibrium

| $\mathrm{H}_{2}(g)+\mathrm{I}_{2}(g) \rightleftharpoons 2 \mathrm{HI}(g)$ |
| :--- |
| 0 0 0.250 <br> $+x$ $+x$ $-2 x$ <br>  Initial 0.500 mol in 2 <br> L is 0.250 M <br> $x$ $x$ $0.250-2 x$ |
| Change <br> Equilibrium |

Substitute values into the equilibrium expression:

$$
K_{\mathrm{c}}=\frac{[\mathrm{HI}]^{2}}{\left[\mathrm{H}_{2}\right]\left[\mathrm{I}_{2}\right]} \quad 57.0=\frac{(0.250-2 x)^{2}}{x^{2}}
$$

## Using the Equilibrium Constant

Solve for " $x$ ":

$$
\begin{aligned}
& \sqrt{57.0}=\sqrt{\frac{(0.250-2 x)^{2}}{x^{2}}} \quad x=0.0262 \\
& 7.55=\frac{0.250-2 x}{x} \quad 7.55 \mathrm{x}=0.250-2 \mathrm{x} \\
& 9.55 \mathrm{x}=0.250 \quad \mathrm{x}=0.250 / 9.55=0.0262
\end{aligned}
$$

Determine the equilibrium concentrations:

$$
\begin{aligned}
& \mathrm{H}_{2}=\mathrm{x}=0.0262 \mathrm{M} \\
& \mathrm{I}_{2}=\mathrm{x}=0.0262 \mathrm{M} \\
& \mathrm{HI}=0.250-2 \mathrm{x}=0.250-2(0.0262)=0.198 \mathrm{M}
\end{aligned}
$$

## HW 14.6: Using the Equilibrium Constant

For $\mathrm{H}_{2}(\mathrm{~g})+\mathrm{l}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{HI}(\mathrm{g})$, for initial concentrations of $\mathrm{H}_{2}(0.00623 \mathrm{M}), \mathrm{l}_{2}$ ( 0.00414 M ) and $\mathrm{HI}(0.0224 \mathrm{M})$. Calculate the concentrations at equilibrium given $K_{\mathrm{c}}$ (54.3) assuming forward rxn.
(a) Set up the ICE table. (where $\mathrm{x}=$ change of $\mathrm{H}_{2}$ )
(b) show the expression for Kc
(c) If your solution to Kc gives $x=0.00156$, calculate the concentration of HI .

$K \mathbf{c}=$

Solution $\mathrm{x}=0.00156$
$[\mathrm{Hl}]=$ $\qquad$

## HW 14.6: Using the Equilibrium Constant

For $\mathrm{H}_{2}(\mathrm{~g})+\mathrm{l}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{HI}(\mathrm{g})$, for initial concentrations of $\mathrm{H}_{2}(0.00623 \mathrm{M}), \mathrm{l}_{2}$ ( 0.00414 M ) and $\mathrm{HI}(0.0224 \mathrm{M})$. Calculate the concentrations at equilibrium given $K_{\text {c }}$ (54.3) assuming forward rxn.
(a) Set up the ICE table. (where $x=$ change of $\mathrm{H}_{2}$ )
(b) show the expression for Kc
(c) If your solution to Kc gives $x=0.00156$, calculate the concentration of HI .
$\mathrm{H}_{2}(g)+\mathrm{I}_{2}(g) \rightleftharpoons 2 \mathrm{HI}(g)$

| 0.00623 | 0.00414 | 0.0224 |
| :---: | :---: | :---: |
| Initial |  |  |
| $-x$ | $-x$ | $+2 x$ |
| Change |  |  |
| $0.00623-x$ | $0.00414-x$ | $0.0224+2 x$ |
| Equilibrium |  |  |
|  |  |  |
| $\mathrm{Kc}=\frac{[0.0224+2 \mathrm{x}]^{2}}{[0.00623-\mathrm{x}][0.00414-\mathrm{x}]}=54.3$ |  |  |

Solution $\mathrm{x}=0.00156 \quad[\mathrm{Hl}]=\mathbf{0 . 0 2 2 4}+\mathbf{2}(\mathbf{0 . 0 0 1 5 6})=\mathbf{0 . 0 2 5 5} \mathbf{M}$ Step 2: The equilibrium constant is

$$
54.3=\frac{(0.0224+2 \mathrm{x})^{2}}{(0.00623-x)(0.00414-x)}
$$

$$
54.3=\frac{5.02 \times 10^{-4}+0.0448 x+0.0448 x+4 x^{2}}{\left(2.58 \times 10^{-5}-0.00623 x-0.00414 x+x^{2}\right)}
$$

$54.3\left(2.58 \times 10^{-5}-0.0104 x+x^{2}\right)=5.02 \times 10^{-4}+$ $0.0896 x+4 x^{2}$
$1.40 \times 10^{-3}-0.56472 \mathrm{x}+54.3 \mathrm{x}^{2}=5.02 \times 10^{-4}+0.089 \mathrm{x}$ $+4 x^{2}$

$$
50.3 x^{2}-0.654 x+8.98 \times 10^{-4}=0
$$

## Using the Equilibrium Constant - showing the math not responsible for on exam - too long for quiz/exam

For equation: $\quad 50.3 x^{2}-0.654 x+8.98 \times 10^{-4}=0$
This is a quadratic equation of the form $\mathrm{a} x^{2}+b x+c=0$. The solution for a quadratic equation (see Appendix 4) is

$$
x=\frac{-b \pm \sqrt{b^{2}-4 a c}}{2 a}
$$

Here we have $\mathrm{a}=50.3, b=-0.654$, and $c=8.98 \times 10^{-4}$

$$
\begin{gathered}
x=\frac{0.654 \pm \sqrt{(-0.654)^{2}-4(50.3)\left(8.98 \times 10^{-4}\right)}}{2 \times 50.3} \\
x=0.0114 \mathrm{M} \quad \text { or } \quad x=0.00156 \mathrm{M}
\end{gathered}
$$

The first solution is physically impossible because the amounts of $\mathrm{H}_{2}$ and $\mathrm{l}_{2}$ reacted would be more than those originally present. The second solution gives the correct answer. Note that in solving quadratic equations of this type, one answer is always physically impossible, so choosing a value for $x$ is easy.

## At equilibrium, the concentrations are

$$
\begin{gathered}
{\left[\mathrm{H}_{2}\right]=(0.00623-0.00156) M=\mathbf{0 . 0 0 4 6 7} \mathbf{M}} \\
{\left[\mathrm{I}_{2}\right]=(0.00414-0.00156) M-\mathbf{0 . 0 0 2 5 8} \mathbf{M}} \\
{[\mathrm{HI}]=(0.0224+2 \times 0.00156) M=\mathbf{0 . 0 2 5 5} \mathbf{M}}
\end{gathered}
$$

## Le Châtelier's Principle

Le Châtelier's Principle: If a stress is applied to a reaction mixture at equilibrium, net reaction occurs in the direction that relieves the stress. (possible changes) (equilibrium shifts to undo stress applied to system)

- concentration of reactants or products
- pressure and volume only effect for rxn with gases, otherwise not much effect of P \& V for liquid \& solids
- temperature can be changed. (can predict only if given enthalpy) $\quad(-\Delta \mathrm{H}$ exo $\rightarrow$ lower T$)$


## Altering an Equilibrium Mixture: Changes in Concentration

In general, when an equilibrium is disturbed by the addition or removal of any reactant or product, Le Châtelier's principle predicts that

- the concentration stress of an added reactant or product is relieved by net reaction in the direction that consumes the added substance.
- the concentration stress of a removed reactant or product is relieved by net reaction in the direction that replenishes the removed substance.


## Altering an Equilibrium Mixture: Changes in Concentration

$$
\mathrm{N}_{2}(g)+3 \mathrm{H}_{2}(g) \rightleftharpoons 2 \mathrm{NH}_{3}(g) \text { at } 700 \mathrm{~K}, K_{\mathrm{c}}=0.291
$$

An equilibrium mixture of $0.50 \mathrm{M} \mathrm{N}_{2}, 3.00 \mathrm{M} \mathrm{H}_{2}$, and $1.98 \mathrm{M} \mathrm{NH}_{3}$ is disturbed by increasing the $\mathrm{N}_{2}$ concentration to 1.50 M .

$$
Q_{\mathrm{c}}=\frac{\left[\mathrm{NH}_{3}\right]^{2}}{\left[\mathrm{~N}_{2}\right]\left[\mathrm{H}_{2}\right]^{3}}=\frac{(1.98)^{2}}{(1.50)(3.00)^{3}}=0.0968<K_{\mathrm{c}}
$$

Since $Q_{\mathrm{c}}<K_{\mathrm{c}}$, more reactants will be consumed and the net reaction will be from left to right.

# Altering an Equilibrium Mixture: Changes in Concentration 


add reactant, rxn goes $\rightarrow$ add product, rxn goes $\leftarrow$
subtract reactant, rxn goes $\leftarrow$ subtract product, rxn goes $\rightarrow$

## End Quiz 6 End Test 3

## Altering an Equilibrium Mixture: Changes in Pressure \& Volume

## $\mathrm{N}_{2}(g)+3 \mathrm{H}_{2}(g) \rightleftharpoons 2 \mathrm{NH}_{3}(g)$

(a) A mixture of gaseous $\mathrm{N}_{2}$, $\mathrm{H}_{2}$, and $\mathrm{NH}_{3}$ at equilibrium ( $Q_{\mathrm{c}}=K_{\mathrm{c}}$ ).
(b) When the pressure is increased by decreasing the volume, the mixture is no longer at equilibrium $\left(Q_{\mathrm{c}}<K_{\mathrm{c}}\right)$.
(c) Net reaction occurs from reactants to products, decreasing the total number of gaseous molecules until equilibrium is re-established $\left(Q_{\mathrm{c}}=K_{\mathrm{c}}\right)$.


## 4 moles gas reactant $\rightarrow 2$ moles gas product (this example)

* increase P or decrease V rxn goes $\rightarrow$ (toward side w less moles gas) *decrease P or increase V rxn goes $\leftarrow$ (toward side w more moles gas)


## Altering an Equilibrium Mixture: Changes in Pressure and Volume

In general, when an equilibrium is disturbed by a change in volume that results in a corresponding change in pressure, Le Châtelier's principle predicts that

- an increase in P (reducing V ) - rxn goes toward side with less moles gas
- a decrease in P (increasing $V$ ) - rxn goes toward side with more moles gas


## Altering an Equilibrium Mixture: Changes in Temperature

## $\mathrm{N}_{2}(g)+3 \mathrm{H}_{2}(g) \rightleftharpoons 2 \mathrm{NH}_{3}(g)$



As the temperature increases, the equilibrium shifts from products to reactants.
exothermic reaction $\left(-\Delta H^{\circ}\right) \mathrm{rxn}$ releases heat higher $\mathrm{T}=$ add heat xxn goes $\leqslant$ (to more reactant)

## Altering an Equilibrium Mixture: Changes in Temperature

In general, when an equilibrium is disturbed by a change in temperature, Le Châtelier's principle predicts that

- the equilibrium constant ( $\mathrm{K}=$ product /reactant) for an exothermic reaction (negative $\Delta H^{\circ}$ ) decreases (get more reactant) as the temperature increases.
- the equilibrium constant for an endothermic reaction (positive $\Delta \boldsymbol{H}^{\circ}$ ) increases (get more product) as the temperature increases.

> End $3 / 6 \mathrm{~A}, \mathrm{C}$ section

## The Effect of a Catalyst on Equilibrium

| The activation energy for the catalyzed pathway (red curve) is lower than that for the uncatalyzed pathway (blue curve) by an amount $\Delta E_{\mathrm{a}}$.


Reaction progress $\longrightarrow$
A catalyst lowers the activation energy barrier for the forward and reverse reactions by the same amount. The catalyst therefore accelerates the forward and reverse reactions by the same factor, and the composition of the equilibrium mixture is unchanged.
catalysis - no effect on equilibrium activation energy for catalyzed path is lower that for uncatalyzed -

HW 14.7: Le Châtelier's Principle: If a stress is applied to a reaction mixture at equilibrium, net reaction occurs in the direction that relieves the stress. (equilibrium shifts to undo stress applied to system)
$2 \mathrm{~A}(\mathrm{~g})+\mathrm{B}(\mathrm{g}) \rightarrow 3 \mathrm{C}(\mathrm{g})+2 \mathrm{D}(\mathrm{g}) \quad \Delta \mathrm{H}=$ negative (circle one parenthesis under which direction will equilibrium shift each letter) hint: $\Delta \mathrm{H}$ negative is exothermic $=(+$ heat, heat is product $)$
(a) add A rxn goes $[(\rightarrow)$ or $(\leftarrow)]$
(b) remove $\mathrm{B} \quad \operatorname{rxn}$ goes $[(\rightarrow)$ or $(\leftarrow)]$
(c) add C rxn goes $[(\rightarrow)$ or $(\leftarrow)]$
(d) remove C rxn goes $[(\rightarrow)$ or $(\leftarrow)]$
(e) higher $\mathrm{T} \quad$ rxn goes $[(\rightarrow)$ or $(\leftarrow)]$ end Test 3 (c) \& below
(f) higher $\mathrm{P} \quad$ rxn goes $[(\rightarrow)$ or $(\leftarrow)]$
(assume all reactants \& products in reaction are gases)
(g) higher V rxn goes $[(\rightarrow)$ or $(\leftarrow)]$
(assume all reactant \& products in reaction are gases)

HW 14.7: Le Châtelier's Principle: If a stress is applied to a reaction mixture at equilibrium, net reaction occurs in the direction that relieves the stress. (equilibrium shifts to undo stress applied to system)
$2 \mathrm{~A}(\mathrm{~g})+\mathrm{B}(\mathrm{g}) \rightarrow 3 \mathrm{C}(\mathrm{g})+2 \mathrm{D}(\mathrm{g}) \Delta \mathrm{H}=$ negative (circle one parenthesis under which direction will equilibrium shift each letter) hint: $\Delta \mathrm{H}$ negative is exothermic $=(+$ heat, heat is product $)$
(a) add $\mathrm{A} \quad$ rxn goes $[(\rightarrow)$ or $(\leftarrow)]$
(b) remove B rxn goes $[(\rightarrow)$ or $(\leftarrow)]$
(c) add C rxn goes $[(\rightarrow)$ or $(\leftarrow)]$
(d) remove C rxn goes $[(\rightarrow)$ or $(\leftarrow)]$
(e) higher $T \quad$ rxn goes $[(\rightarrow)$ or $(\leftarrow)]$ end Test $3(\mathrm{e}) \&$ below
(higher $\mathrm{T}=$ add heat)
(f) higher P rxn goes $[(\rightarrow)$ or $(\leftarrow)]$
(assume all reactants \& products in reaction are gases) (moves to fewer moles gas)
(g) higher V rxn goes $[(\rightarrow)$ or $(\leftarrow)]$
(assume all reactant \& products in reaction are gases) (moves to fewer moles gas)

