

Problem Set: Chapter 16 questions 25, 27, 33, 35, 43, 71

## Examples of Equilibrium

 Water can exists simultaneously in the gas and liquid phase. The vapor pressure of $\mathrm{H}_{2} \mathrm{O}$ at a given temperature is a property associated with an equilibrium condition. $\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} \longleftrightarrow \mathrm{H}_{2} \mathrm{O}_{(\mathrm{g})}$
$\mathrm{I}_{2}$ originally dissolved in water (left) will partition between the $\mathrm{CCl}_{4}$ and $\mathrm{H}_{2} \mathrm{O}$ liquids such that $\left[I_{2}\right]_{\mathbf{C C l 4}} /\left[I_{2}\right]_{\mathbf{H 2 O}}=86$. The distribution coefficient of a solute between two immiscible liquids is an equilibrium property.

(a)
$\mathrm{N}_{2} \mathrm{O}_{4(\mathrm{~g}) \text { (colourless) }}$ decomposes to give 2 molecules of $\mathrm{NO}_{2(\mathrm{~g}) \text { (brown gas) }}$. At low T, we have mostly $\mathrm{N}_{2} \mathrm{O}_{4}$. At high temperatures we have mostly $\mathrm{NO}_{2}$. Under a given set of conditions, the concentration of each is in equilibrium.

## Dynamic Equilibrium

Equilibrium is a "dynamic" condition. Even though the system does not appear to be changing, on a microscopic level it is constantly changing.

In each case shown previously, the forward and reverse processes are occurring at equal rates, such that the macroscopic system appears to be "static".

We symbolize this equilibrium by the double arrow,

reminding us that the forward and reverse reactions are proceeding at equal rates, resulting in a balanced chemical system.

## Proof of Dynamic Equilibrium


$\mathbf{A g I}_{(\mathrm{s})} \longleftrightarrow \mathbf{A g}^{+}{ }_{(\mathrm{aq})}+\mathbf{I}_{(\mathrm{aq})}^{-}$ $\mathbf{A g}^{131} \mathbf{I}_{(\mathrm{s})} \longleftrightarrow \mathbf{A g}^{+}{ }_{(\mathrm{aq})}+{ }^{131} \mathbf{I}_{(\mathrm{aq})}^{-}$

Add saturated solution made from radioactive Ag $^{131}$ I to saturated nonradioactive AgI

- solution is radioactive, should solid be?
- gradual appearance of radioactivity in the solid AgI is proof that ${ }^{131} I$ is incorporated into solid. That is the equilibrium is dynamic


## Approach to Equilibrium

Example: Methanol production using the "synthesis" reaction

$$
\mathrm{CO}_{(\mathrm{g})}+2 \mathrm{H}_{2(\mathrm{~g})} \longleftrightarrow \mathrm{CH}_{3} \mathrm{OH}_{(\mathrm{g})}
$$



$t_{\mathrm{e}}=$ time for equilibrium to be reached
$-\mathrm{mol} \mathrm{CO}$
$-\mathrm{mol} \mathrm{H}_{2}$
$-\mathrm{mol} \mathrm{CH}_{3} \mathrm{OH}$

- regardless of our initial starting conditions, change in the system slows down and appears to come to equilibrium.
- there does not appear to be a consistent final condition, i.e. - a relationship between concentrations
....but there is!!


## Final state for Synthesis reaction

| TABLE 16.1 Three Approaches to Equilibrium in the Reaction ${ }^{\text {a }}$ $\mathrm{CO}(\mathrm{g})+2 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons \mathrm{CH}_{3} \mathrm{OH}(\mathrm{g})$ |  |  |  | $\frac{\left[\mathrm{CH}_{3} \mathrm{OH}\right]}{[\mathrm{CO}]\left[\mathrm{H}_{2}\right]^{2}}$ |
| :---: | :---: | :---: | :---: | :---: |
|  | $\mathrm{CO}(\mathrm{g})$ | $\mathrm{H}_{2}(\mathrm{~g})$ | $\mathrm{CH}_{3} \mathrm{OH}(\mathrm{g})$ |  |
| Experiment 1 |  |  |  |  |
| Initial amounts, mol | 1.000 | 1.000 | 0.000 |  |
| Equilibrium amounts, mol | 0.911 | 0.822 | 0.0892 | 14.5 |
| Equilibrium concentrations, mol/L | 0.0911 | 0.0822 | 0.00892 |  |
| Experiment 2 |  |  |  |  |
| Initial amounts, mol | 0.000 | 0.000 | 1.000 |  |
| Equilibrium amounts, mol | 0.753 | 1.506 | 0.247 | 14 |
| Equilibrium concentrations, mol/L | 0.0753 | 0.151 | 0.0247 | 14.4 |
| Experiment 3 |  |  |  |  |
| Initial amounts, mol | 1.000 | 1.000 | 1.000 |  |
| Equilibrium amounts, mol | 1.380 | 1.760 | 0.620 |  |
| Equilibrium concentrations, mol/L | 0.138 | 0.176 | 0.0620 | 14.5 |
| The concentrations printed in blue are used in the calculations in Table 16.2. ${ }^{\text {a }}$ Reaction carried out in a 10.0 - flask at 483 K . |  |  |  |  |

## A General Expression for $\mathbf{K}_{\mathbf{c}}$

For the general reaction

$$
\mathbf{a A}+\mathbf{b B}+\mathbf{c} \mathbf{C} \rightleftarrows \mathbf{g G}+\mathbf{h} \mathbf{H}+\mathbf{i I}
$$

The equilibrium constant expression has the form


- " c " denotes that concentrations are expressed as molarities.
- the equilibrium constant is temperature dependent
- do not confuse the general expression for equilibrium with the general expression for the rate law....here the concentrations ARE raised to the stoichiometric coefficients. Remember this was not true in general for the kinetic rate law.


## Thermodynamic Equilibrium Constant, $\mathbf{K}_{\mathrm{eq}}$

The thermodynamic equilibrium constant is slightly different than what we just described...

For the general reaction

$$
\begin{gathered}
\mathbf{a A}+\mathbf{b B}+\mathbf{c} \mathbf{C} \rightleftarrows \mathbf{g G}+\mathbf{h} \mathbf{H}+\mathbf{i I} \\
\mathrm{K}_{\mathrm{eq}}=\frac{\left(\mathrm{a}_{\mathrm{G}}\right)^{\mathrm{g}}\left(\mathrm{a}_{\mathrm{H}}\right)^{\mathrm{h}}\left(\mathrm{a}_{\mathrm{I}}\right)^{\mathrm{i}}}{\left(\mathrm{a}_{\mathrm{A}}\right)^{\mathrm{a}}\left(\mathrm{a}_{\mathbf{B}}\right)^{\mathrm{b}}\left(\mathrm{a}_{\mathrm{C}}\right)^{\mathrm{c}}} \\
\mathbf{a}_{\mathbf{A}}=\text { unitless "activiy" of } \mathbf{A} \\
\mathbf{a}_{\mathbf{B}}=\text { unitless "activiy" of } \mathbf{B}, \text { etc. }
\end{gathered}
$$

## Activities and $K_{e q}$

- activities are unitless
(by definition $\mathbf{a}=\gamma \times$ conc./stand. refer. conc.) stand. refer. conc. is typically chosen as 1 M
- activities are defined such that activities of dilute solutes in solution are generally numerically equivalent to their concentrations expressed as molarities ( $\gamma=1$ )
- activities of gases are approximately equal to their partial pressure expressed in atmospheres.
- activities of pure solids and pure liquids are defined to be unity (i.e. $a_{\text {pure liquid }}=a_{\text {pure solid }}=1.00$ )
- thermodynamic equilibrium constants are unitless.


## Working with Equilibrium Constants

The equilibrium constant for a reverse reaction is given by the inverse of the forward reaction equilibrium constant...
example

$$
K_{c, \text { reverse }}=\left(K_{c}\right)^{-1}=\frac{1}{K_{c}}
$$

$\mathrm{N}_{2}+3 \mathrm{H}_{2} \rightleftarrows 2 \mathbf{N H}_{3}$

$$
\begin{gathered}
\mathrm{K}_{\mathrm{c}}=\frac{\left[\mathrm{NH}_{3}\right]^{2}}{\left[\mathrm{~N}_{2}\right]\left[\mathrm{H}_{2}\right]^{3}}=3.6 \times 10^{8} \mathrm{M}^{-2} \\
\mathbf{2} \mathbf{N H}_{\mathbf{3}} \rightleftarrows \mathbf{N}_{\mathbf{2}}+\mathbf{3 \mathbf { H } _ { \mathbf { 2 } }} \\
\mathrm{K}_{\mathrm{c}, \text { reverse }}=\frac{\left[\mathrm{N}_{2}\right]\left[\mathrm{H}_{2}\right]^{3}}{\left[\mathrm{NH}_{3}\right]^{2}}=\frac{1}{\mathrm{~K}_{\mathrm{c}}}=\frac{1}{3.6 \times 10^{8}}=2.8 \times 10^{-9} \mathrm{M}^{2}
\end{gathered}
$$

## cont'd

The equilibrium constant for a reaction that has been multiplied through by constant, $x$, is given by :

$$
\mathbf{K}_{\mathbf{c}}^{\prime}=\left(\mathbf{K}_{\mathbf{c}}\right)^{\mathbf{x}}
$$

Example - multiply eq from previous example
$\mathrm{N}_{2}+3 \mathrm{H}_{2} \rightleftarrows 2 \mathrm{NH}_{3}$
by $1 / 2$ to produce only 1 mole of ammonia

$$
\begin{aligned}
& \frac{\mathbf{1}}{\mathbf{2}} \mathbf{N}_{\mathbf{2}}+\frac{\mathbf{3}}{\mathbf{2}} \mathbf{H}_{\mathbf{2}} \rightleftarrows \mathbf{N H}_{\mathbf{3}} \\
& \mathrm{K}_{\mathrm{c}}{ }^{\prime}=\frac{\left[\mathrm{NH}_{3}\right]}{\left[\mathrm{N}_{2}\right]^{1 / 2}\left[\mathrm{H}_{2}\right]^{3 / 2}}=\left(\frac{\left[\mathrm{NH}_{3}\right]^{2}}{\left[\mathrm{~N}_{2}\right]\left[\mathrm{H}_{2}\right]^{3}}\right)^{1 / 2}=\left(\mathrm{K}_{\mathrm{c}}\right)^{1 / 2}= \\
& \left(3.6 \times 10^{8}\right)^{1 / 2}=1.9 \times 10^{4} \mathrm{M}^{-1}
\end{aligned}
$$

## Equilibria with Gases

- Mixtures of gases are in many ways analogous to mixtures in solution. Concentrations of gases can be expressed as molarities OR by partial pressure due to the ideal behaviour of gases.

$$
[\mathrm{G}]=\frac{\mathrm{n}_{\mathrm{G}}}{\mathrm{~V}}=\frac{\mathrm{P}_{\mathrm{G}}}{\mathrm{RT}} \quad(\text { recall that } \mathrm{PV}=\mathrm{nRT})
$$

- Equilibrium constants for reactions involving gases are often expressed as $K_{p}$, where the subscript $p$ denotes the use of pressure units.

> For the general reaction

$$
\begin{gathered}
\mathbf{a} \mathbf{A}_{(\mathrm{g})}+\mathbf{b B} \mathbf{B}_{(\mathrm{g})}+\mathbf{c C _ { ( g ) }} \rightleftarrows \mathbf{g G}_{(\mathrm{g})}+\mathbf{h H _ { ( g ) }}+\mathbf{i I}_{(\mathrm{g})} \\
\mathbf{K}_{\mathrm{p}}=\frac{\mathbf{P}_{\mathrm{G}}{ }^{\mathrm{g}} \mathbf{P}_{\mathrm{H}}^{\mathrm{h}} \mathbf{P}_{\mathrm{I}}^{\mathrm{i}}}{\mathbf{P}_{\mathrm{A}}{ }^{\mathrm{a}} \mathbf{P}_{\mathrm{B}}{ }^{\mathbf{b}} \mathbf{P}_{\mathrm{C}}{ }^{\mathbf{c}}}
\end{gathered}
$$

## Relationship between $\mathbf{K}_{\mathrm{C}}$ and $\mathbf{K}_{\mathrm{p}}$

$$
\begin{aligned}
& K_{p}=K_{\mathbf{c}}(\mathbf{R T})^{\Lambda \mathrm{n}}
\end{aligned}
$$

where:
$\Delta \mathbf{n}$ is the difference in stoichiometric coefficients of products and reactants ( $\Delta \mathbf{n}=\mathbf{g}+\mathbf{h}+\mathbf{i}-\mathbf{a}-\mathbf{b}-\mathbf{c}$ )
$R$ is the gas constant $\left(0.08206 \mathrm{~L}\right.$ atm $\left.\mathrm{mol}^{-1} \mathrm{~K}^{-1}\right)$

## Equilibria with Pure Liquids or Solids

- Equilibrium constant expressions do NOT contain terms for solids or liquid phases of a single component (not a mixture).
- Why?

1) concentrations of single-component solids and liquids do not change.
2) "activities" of pure liquids and solids are defined to be 1 Example: $\mathrm{C}(\mathrm{s})+\mathrm{H}_{2} \mathrm{O} \rightleftarrows \mathrm{CO}(\mathrm{g})+\mathrm{H}_{2}(\mathrm{~g})$
coal vapour


$$
\xrightarrow{\mathbf{K}_{\mathrm{eq}}}=\frac{\mathbf{a}_{\mathrm{CO}} \mathbf{a}_{\mathrm{H}_{2}}}{\mathbf{a}_{\mathrm{C}} \mathbf{a}_{\mathrm{H}_{2} \mathrm{O}}}=\frac{\mathbf{a}_{\mathrm{CO}} \mathbf{a}_{\mathrm{H}_{2}}}{1 \times \mathbf{a}_{\mathrm{H}_{2} \mathrm{O}}}=\frac{\mathbf{a}_{\mathrm{CO}} \mathbf{a}_{\mathrm{H}_{2}}}{\mathbf{a}_{\mathrm{H}_{2} \mathrm{O}}}
$$

## Examples of Equilibrium Constants

## TABLE 16.3 Equilibrium Constants of Some Common Reactions

## Reaction

$$
\begin{aligned}
& 2 \mathrm{H}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \\
& \mathrm{CaCO}_{3}(\mathrm{~s}) \rightleftharpoons \mathrm{CaO}(\mathrm{~s})+\mathrm{CO}_{2}(\mathrm{~g}) \\
& 2 \mathrm{SO}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{SO}_{3}(\mathrm{~g}) \\
& \mathrm{C}(\mathrm{~s})+\mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) \rightleftharpoons \mathrm{CO}(\mathrm{~g})+\mathrm{H}_{2}(\mathrm{~g})
\end{aligned}
$$

Equilibrium constant, $\boldsymbol{K}_{\mathrm{p}}$
$1.4 \times 10^{83}$ at 298 K
$1.9 \times 10^{-23}$ at 298 K
1.0 at about 1200 K
3.4 at 1000 K
$1.6 \times 10^{-21}$ at 298 K
10.0 at about 1100 K

- A reaction is often said to go to completion if the numerical value of the equilibrium constant is very large (i.e. $K>\mathbf{1 0}^{\mathbf{1 0}}$ )

Note: that large $K$ is consistent with a large value in the numerator (products) and/or a small value in the denominator (reactants).
$\mathbf{2} \mathbf{H}_{\mathbf{2}(\mathrm{g})}+\mathrm{O}_{\mathbf{2}(\mathrm{g})} \rightarrow \mathbf{2} \mathbf{H}_{2} \mathrm{O}_{(\mathrm{l})}$ (written with single arrow)

## Example

- A few liters of liquid water are added to the largest experimental container that can be found in the chemistry department at York (CAC smog chamber; $9.0 \mathrm{~m}^{3}$ ) at 298 K . If we waited a large period of time such that the system comes to equilibrium (or add a hypothetical catalyst to speed up the reaction), what would be the equilibrium concentration of $\mathrm{H}_{2}$ and $\mathrm{O}_{2}$ ? How many molecules of $\mathrm{H}_{2}$ and $\mathrm{O}_{2}$ would exist?

$$
\mathbf{2} \mathbf{H}_{\mathbf{2}} \mathbf{0}_{(\mathrm{l})} \rightleftarrows \mathbf{2} \mathbf{H}_{\mathbf{2 ( g )}}+\mathbf{O}_{\mathbf{2}(\mathrm{g})} \quad \mathrm{K}_{\mathrm{p}}=\frac{\mathrm{P}_{\mathrm{H}_{2}}^{2} \mathrm{P}_{\mathrm{O}_{2}}}{1}=\left(1.4 \times 10^{83}\right)^{-1}=
$$

$$
\text { Let } \mathbf{P}_{\mathbf{O} 2}=\mathbf{x} ; \mathbf{P}_{\mathbf{H} 2}=2 \mathbf{x}
$$

$$
K_{p}=(2 x)^{2} x=4 x^{3}=7.1 \times 10^{-84}
$$

$$
\mathrm{n}=\frac{\mathrm{PV}}{\mathrm{RT}}=\frac{\left(1.21 \times 10^{-28} \mathrm{~atm}\right)(9000 \mathrm{~L})}{\left(0.08206 \mathrm{Latm} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}\right)(298 \mathrm{~K})}=4.46 \times 10^{-26} \mathrm{~mol}
$$

$$
\# O_{2}=n \times N_{A}=\left(4.46 \times 10^{-26} \mathrm{~mol}\right)\left(6.022 \times 10^{23} \mathrm{~mol}^{-1}\right)=0.027 \text { molecules }
$$

Conclusion - at equilibrium, only a fraction of a molecule of $\mathrm{O}_{2}$ will exist. Since this is physically impossible, we conclude the reaction lies completely to the right and does not proceed to the left to any meaningful extent.

$$
2 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} \longleftrightarrow 2 \mathrm{H}_{2(\mathrm{~g})}+\mathrm{O}_{2(\mathrm{~g})}
$$

## The Reaction Quotient (kwo:shent)

- Often we would like to predict the direction of chemical change for a system that is not at equilibrium.
- This prediction is trivial for the cases of systems in which we have only reactants or only products. But what about an intermediate case in which we start with a mixture of reactants and products?
- To make this prediction, we use the reaction quotient, $Q_{c}$ or $Q_{p}$ or $Q_{\text {eq. }}$. For the 'general reaction' :
$Q_{c}=\frac{[G]_{\text {init }}^{\mathrm{g}}[H]_{\text {init }}^{\mathrm{h}}[I]_{\text {init }}^{\mathrm{i}}}{[A]_{\text {init }}^{\mathrm{a}}[B]_{\text {init }}^{\mathrm{b}}[C]_{\text {init }}^{c}}$
where "init" implies initial concentrations for the nonequilibrium system

Note: we can also write analogous equations for $Q_{p}$ using partial pressures and $Q_{e q}$ using activities

## Predicting the Direction of Change

- We compare the reaction CALCULATED quotient to the KNOWN equilibrium constant to predict the direction of chemical change in a reaction.
- If $\mathbf{Q}_{\mathrm{c}}<\mathrm{K}_{\mathrm{c}}$ the reaction will proceed to the right
- If $Q_{c}>K_{c}$ the reaction will proceed to the left
- If $\mathbf{Q}_{\mathbf{c}}=\mathbf{K}_{\mathbf{c}}$ the reaction is at equilibrium



## Le Chatelier's Principle

When an equilibrium system is subject to some change in conditions, the system will respond by minimizing the effect of that change.

Petrucci states it as:

When an equilibrium system is subjected to a change in temperature, pressure, or concentration of a reacting species, the system responds by attaining a new equilibrium that partially offsets the impact of the change.

## Effect of Change in Amount

If the amount of one species in an equilibrium system is increased, the system will try to decrease it according to the Le Chatelier's Principle
Indeed the equilibrium will shift in the direction that favours the removal of that species.
Alternatively, if the amount of the species is decreased, the equilibrium shifts in the direction that increases the amount of that species.
Example: recall the synthesis reaction

$$
\mathrm{CO}_{(\mathrm{g})}+2 \mathrm{H}_{2(\mathrm{~g})} \longleftrightarrow \mathrm{CH}_{3} \mathrm{OH}_{(\mathrm{g})} \quad \mathrm{K}_{\mathrm{c}}=14.5
$$

What would happen to the equilibrium system if we added a cold finger to the reaction vessel, allowing us to condense out methanol? Let us presume that we can remove $80 \%$ of the gaseous methanol as liquid, in each of several condensation steps. Start with experiment 1 conditions.

Effect of Incremental removals of $\mathrm{CH}_{3} \mathrm{OH}$

|  | $\begin{aligned} & {[\mathrm{CO}]_{\mathrm{g}}} \\ & \mathrm{~mol} / \\ & \mathrm{L} \end{aligned}$ | $\begin{aligned} & {\left[\mathrm{H}_{2}\right]_{\mathrm{g}}} \\ & \mathrm{~mol} / \\ & \mathrm{L} \end{aligned}$ | $\begin{aligned} & {\left[\mathrm{CH}_{3} \mathrm{OH}\right]_{\mathrm{g}}} \\ & \mathrm{~mol} / \mathrm{L} \end{aligned}$ | $\mathbf{Q}_{\text {c }}$ | $-\mathrm{CH}_{3} \mathrm{OH}$ <br> moles* | Comment |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Exp 1 Start | . 0911 | . 0822 | . 00892 | 14.5 |  | $\mathrm{Q}_{\mathrm{c}}=\mathrm{K}_{\mathrm{c}}$, equilib |
| Condense 80\% | . 0911 | . 0822 | . 00178 | 2.90 | -0.0714 | $\mathbf{Q}_{\mathbf{c}}<K_{c}$; must shift right |
| Shift right | . 0863 | . 0726 | . 00659 | 14.5 |  | $\mathrm{Q}_{\mathrm{c}}=\mathrm{K}_{\mathrm{c}}$, equilib. |
| Condense 80\% | . 0863 | . 0726 | . 00132 | 2.90 | -0.0527 | $\mathbf{Q}_{\mathbf{c}}<K_{c}$; must shift right again |
| Shift right | . 0825 | . 0651 | . 00507 | 14.5 |  | $\mathrm{Q}_{\mathrm{c}}=\mathrm{K}_{\mathrm{c}}$, equilib. |
| Condense $80 \%$ | . 0825 | . 0651 | . 00101 | 2.90 | -0.0405 | $\mathbf{Q}_{\mathrm{c}}<\mathrm{K}_{\mathrm{c}}$; must shift right again |
| Shift right | . 0795 | . 0591 | . 00402 | 14.5 |  | $\mathrm{Q}_{\mathrm{c}}=\mathrm{K}_{\mathrm{c}}$, equilib. |

Each time we condense liquid methanol, we remove gaseous methanol, making $Q_{c}<K_{c .}$ The equilibrium condition is re-established by a shift of the reaction to the right, such that $\boldsymbol{Q}_{c}=K_{c}$ again.
*Incremental amount of liquid methanol removed in moles (calculated).

$\bullet[\mathrm{CO}] \quad \bullet[\mathrm{H} 2] \quad \bullet[\mathrm{CH} 3 \mathrm{OH}]$

## Effect of Change in Pressure

If the total pressure of a chemical system is increased (or decreased) by changing the volume, the equilibrium will shift in a direction that favours a reduction (or increase) in the total pressure.
Example: $\mathbf{2} \mathbf{S O}_{\mathbf{2 ( g )}}+\mathbf{O}_{\mathbf{2 ( g )}} \rightleftarrows \mathbf{2} \mathbf{S O}_{\mathbf{3 ( g )}} \quad \mathrm{K}_{\mathrm{c}}=\mathbf{2 8 0 ( 1 0 0 0 K )}$
A decrease in volume increases the partial pressure of all gases in the system. The equilibrium is shifted in a direction that reduces the total pressure, in this case to the right, since there are fewer moles of gases on the right.


## Another Explanation

$$
\begin{aligned}
& 2 \mathrm{SO}_{2(\mathrm{~g})}+\mathrm{O}_{2(\mathrm{~g})} \rightleftarrows 2 \mathrm{SO}_{3(\mathrm{~g})} \quad \mathrm{K}_{\mathrm{c}}=280(1000 \mathrm{~K}) \\
& \mathrm{K}_{\mathrm{c}}=\frac{\left[\mathrm{SO}_{3}\right]^{2}}{\left[\mathrm{SO}_{2}\right]^{2}\left[\mathrm{O}_{2}\right]}=\frac{[0.068]^{2}}{[.032]^{2}[.016]}=282
\end{aligned}
$$

After compression to 1.0 L , and before the system can respond we have all concentration increased 10 fold: $\left[\mathrm{SO}_{3}\right]=\mathbf{0 . 6 8} \mathrm{M} ;\left[\mathrm{SO}_{2}\right]=0.32 \mathrm{M} ;\left[\mathrm{O}_{2}\right]=\mathbf{0 . 1 6 M}$

$$
\mathrm{Q}_{\mathrm{c}}=\frac{\left[\mathrm{SO}_{3}\right]^{2}}{\left[\mathrm{SO}_{2}\right]^{2}\left[\mathrm{O}_{2}\right]}=\frac{[0.68]^{2}}{[.32]^{2}[.16]}=28.2
$$

Since $\mathbf{Q}_{\mathbf{c}}<\mathbf{K}_{\mathrm{c}}$, equilibrium will shift to the right. Note that for every " x " moles of $\mathrm{O}_{2}$ consumed, " 2 x " moles of $\mathrm{SO}_{2}$ are consumed and " 2 x " moles of $\mathrm{SO}_{3}$ are produced. Thus, when equilibrium is reached we must have:

$$
\mathrm{K}_{\mathrm{c}}=\frac{\left[\mathrm{SO}_{3}\right]^{2}}{\left[\mathrm{SO}_{2}\right]^{2}\left[\mathrm{O}_{2}\right]}=\frac{[0.68+2 \mathrm{x}]^{2}}{[.32-2 \mathrm{x}]^{2}[.16-\mathrm{x}]}=282
$$

We will later discuss how to solve these problems. For now the solution is: " $x$ " $=0.0751$ moles; $\left[\mathrm{SO}_{3}\right]_{\text {final }}=0.830 \mathrm{M},\left[\mathrm{SO}_{2}\right]_{\text {final }}=0.1697 \mathrm{M},\left[\mathrm{O}_{2}\right]_{\text {final }}=$ 0.0849M,

## What We Learned So Far



## Effect of Increased Total pressure using "spectator" gases

If we increase the total pressure at constant volume by adding an inert gas or another gas not involved in the equilibrium, the partial pressure of each species in the equilibrium will not change...therefore the reaction quotient will not change.

The system will not respond to changes in total pressure achieved by adding inert gases at constant volume.

Note: In solution, dilution of a mixture by addition of water WOULD change the total volume, WOULD change the concentration of each species in an equilibrium, and therefore the reaction quotient WOULD change in general. We should expect a shift in equilibrium in this case

## Effect of Change in Temperature

To predict the effect that temperature has on an equilibrium system, we can invoke Le Chatelier's principle. If we increase the temperature, the equilibrium system responds by trying to lower the temperature (utilize the excess energy). It would do this by shifting in the direction of the endothermic reaction. If the temperature is decreased, the equilibrium shifts in the direction of the reaction that provides excess heat (ie- the exothermic reaction)
$\mathrm{N}_{\mathbf{2}} \mathrm{O}_{4(\mathrm{~g})} \rightleftarrows \quad 2 \mathrm{NO}_{2(\mathrm{~g})} \quad \Delta \mathrm{H}=+57.2 \mathrm{~kJ} \mathrm{~mol}^{-1}$
Q: Will the amount of $\mathrm{NO}_{2(g)}$ formed be greater at high or low temperature?
A: The forward reaction as written is endothermic. An increase in temperature will favour a shift to the right in equilibrium. $\mathbf{N O}_{\mathbf{2 ( g )}}$ will be higher at higher temperature.

## Effect of a Catalyst

- For a given set of reaction conditions, the equilibrium amounts of reactants and products in a reversible reaction are independent of whether the reaction is homogeneous, heterogeneous or otherwise catalysed.
- A catalyst does not change the position of equilibrium
- The catalyst only acts to decrease the amount of time it takes to get to equilibrium
- Since we know that catalysts can provide alternate reaction mechanisms, our conclusion must be that the equilibrium condition is independent of the process by which the system moves from initial to final conditions. We will learn more about this in the section on Free Energy


## Equilibrium Calculations: Example 1

## Practice Example 16.10 B:

0.100 moles $\mathrm{SO}_{2}$ and 0.100 moles $\mathrm{O}_{2}$ are introduced into an evacuated 1.52 L flask at 900 K . When equilibrium is achieved, the amount of $\mathrm{SO}_{3}$ measured is 0.0916 moles. Use this data to determine $K_{p}$ for the reaction:
$2 \mathrm{SO}_{3(\mathrm{~g})} \leftarrow \rightarrow 2 \mathrm{SO}_{2(\mathrm{~g})}+\mathrm{O}_{2(\mathrm{~g})}$

## Solution Approach:

we will use an ICE table to relate the initial and equilibrium (final) conditions. It will be convenient to start working in units of moles. Our equilibrium concentrations can then be expressed as moles $L^{-1}$. We can then calculate $K_{c}$ and finally relate it to $K_{p}$ through the known relationship; $K_{p}=K_{c}(R T)^{\Delta n}$.

## Solution: example 1

| Amounts and <br> Concentrations | $2 \mathrm{SO}_{3}$ | $\leftarrow \rightarrow$ | $2 \mathbf{S O}_{2}$ | $\mathrm{O}_{2}$ |
| :--- | :---: | :---: | :---: | :---: |
| $\mathrm{I}_{\text {nitial }}(\mathrm{mol})$ | 0 |  | 0.100 | 0.100 |
| $\mathrm{C}_{\text {hange }}(\mathrm{mol})$ | +2 x |  | -2 x | -x |
| $\mathrm{E}_{\text {quilibrium }}(\mathrm{mol})$ | $0+2 \mathrm{x}$ |  | $0.1-2 \mathrm{x}$ | $0.1-\mathbf{x}$ |
| Conc. $\mathrm{mol} \mathrm{L}^{-1}$ | $2 \mathrm{x} / \mathrm{V}$ |  | $(0.1-2 \mathrm{x}) / \mathrm{V}$ | $(0.1-\mathbf{x}) / \mathrm{V}$ |
| Conc. $\mathrm{mol} \mathrm{L}^{-1}$ | .06026 |  | .00553 | .03566 |

We are given that the equilibrium amount of $\mathrm{SO}_{\mathbf{3}}=\mathbf{0 . 0 9 1 6}$ mole
$2 \mathrm{x}=0.0916$ moles $\quad \rightarrow \quad \mathrm{x}=0.0458$ moles
Knowing that $V=1.52 \mathrm{~L}$, we can complete the last line in the table.

## Solution 1, cont'd

$$
\begin{aligned}
& \mathrm{K}_{\mathrm{c}}=\frac{\left[\mathrm{SO}_{2}\right]^{2}\left[\mathrm{O}_{2}\right]}{\left[\mathrm{SO}_{3}\right]^{2}}=\frac{[.00553]^{2}[.03566]}{[0.06026]^{2}}=3.00 \times 10^{-4} \\
& \Delta \mathrm{n}=(2+1)-2=1 \\
& \mathrm{~K}_{\mathrm{p}}=\mathrm{K}_{\mathrm{c}}(\mathrm{RT})^{\Delta \mathrm{n}} \\
& \mathrm{~K}_{\mathrm{p}} \quad=3.00 \times 10^{-4}\left(0.08206 \mathrm{~L} \mathbf{~ a t m ~} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}\right)(900 \mathrm{~K}) \\
& K_{p} \quad=0.022
\end{aligned}
$$

## Equilibrium Calculations: Example 2

## Practice Example 16.12 A:

If 0.150 moles $H_{2(g)}$ and 0.200 moles $I_{2(g)}$ are introduced into a 15.0 L flask at $445^{\circ} \mathrm{C}$ and allowed to come to equilibrium, how many moles of HI will be present?

$$
\mathrm{H}_{2(\mathrm{~g})}+\mathrm{I}_{2(\mathrm{~g})} \leftarrow \rightarrow 2 \mathrm{HI}_{(\mathrm{g})} \quad \mathrm{K}_{\mathrm{c}}=50.2\left(445^{\circ} \mathrm{C}\right)
$$

Solution Approach:
We will again use ICE table to relate the initial and equilibrium (final) conditions. In this case though, we will not know the equilibrium concentrations, but we know $K_{c}$. We use " $x$ " as the variable of change, write the equilibrium expression in terms of $x$, and then solve for $x$. We must solve a quadratic to get $x$.

## Example 2 - solution

| Amounts and <br> Concentrations | $\mathrm{H}_{2}$ | $\mathrm{I}_{2}$ | $\leftarrow \rightarrow$ | 2 HI |
| :--- | :---: | :---: | :---: | :---: |
| $\mathrm{I}_{\text {nitial }}(\mathrm{mol})$ | 0.150 | 0.200 |  | 0 |
| $\mathrm{C}_{\text {hange }}(\mathbf{m o l})$ | -x | -x |  | +2 x |
| $\mathrm{E}_{\text {quilibrium }}(\mathrm{mol})$ | $0.150-\mathrm{x}$ | $0.200-\mathrm{x}$ |  | 2 x |
| Conc. $\mathrm{mol} \mathrm{L}^{-1}$ | $(0.150-\mathrm{x}) / \mathrm{V}$ | $(0.200-\mathrm{x}) / \mathrm{V}$ | $2 \mathrm{x} / \mathrm{V}$ |  |

$\mathrm{K}_{\mathrm{c}}=\frac{[\mathrm{HI}]^{2}}{\left[\mathrm{H}_{2}\right]\left[\mathrm{I}_{2}\right]}=\frac{\left(\frac{2 x}{\mathrm{~V}}\right)^{2}}{\left(\frac{0.150-\mathrm{x}}{\mathrm{V}}\right)\left(\frac{0.200-\mathrm{x}}{\mathrm{V}}\right)}=\frac{(2 \mathrm{x})^{2}}{(0.150-\mathrm{x})(0.20-\mathrm{x})}=50.2$

This can be algebraically arranged to give:
$-46.2 x^{2}+17.57 x-1.506=0$
This is a quadratic equation... $a=-46.2, b=17.57, c-1.506$

## Solution 2, cont'd

$$
\mathbf{x}=\frac{-b \pm \sqrt{b^{2}-4 a c}}{2 a}=\frac{-17.57 \pm \sqrt{(17.57)^{2}-4(-46.2)(-1.506)}}{2(-46.2)}
$$

$\mathrm{x}=\mathbf{0 . 1 3 0 5}$ OR 0.2498
taking the + and - root respectively. Only one solution is physically realistic; $x=0.1305$. For $x=0.25$ moles we would end up with negative amounts of $H_{2}$ and $I_{2}$.

Thus $x=0.1305$ moles and at equilibrium we have $2 x$ moles of HI,

At equilibrium we have 0.261 moles of HI

## Complex Formation $\mathbf{A}+\mathbf{B} \underset{\mathbf{K}_{-1}}{\stackrel{\mathbf{k}_{1}}{\leftrightarrows}} \mathrm{AB}$

The equilibrium constant for complex formation is often called the association constant:

$$
\boldsymbol{K}_{\mathrm{a}}=\frac{[\mathrm{AB}]_{\mathrm{eq}}}{[\mathrm{~A}]_{\mathrm{eq}}[\mathrm{~B}]_{\mathrm{eq}}} \mathbf{M}^{-1}
$$

Even more often we operate with the dissociation constant:

$$
\boldsymbol{K}_{\mathrm{d}}=\frac{[\mathrm{A}]_{\mathrm{eq}}[\mathrm{~B}]_{\mathrm{eq}}}{[\mathrm{AB}]_{\mathrm{eq}}} \mathbf{M}
$$

$$
\boldsymbol{K}_{\mathrm{d}}=\frac{1}{\boldsymbol{K}_{\mathrm{a}}}
$$

## Mass Conservation Principle for Complex Formation

$$
[A]_{\text {tot }}=[A]+[A B] \quad \text { and } \quad[B]_{\text {tot }}=[B]+[A B]
$$

## Relationship between the Equilibrium

 Constant and the Rate ConstantsAt equilibrium the rate of forward reaction is equal to the rate of reverse reaction:
$\boldsymbol{k}_{1}[\mathrm{~A}]_{\mathrm{eq}}[\mathrm{B}]_{\mathrm{eq}}=\boldsymbol{k}_{-1}[\mathrm{AB}]_{\mathrm{eq}} \quad \Rightarrow \boldsymbol{k}_{-1} / \boldsymbol{k}_{1}=[\mathrm{A}]_{\mathrm{eq}}[\mathrm{B}]_{\mathrm{eq}} /[\mathrm{AB}]_{\mathrm{eq}}=K_{\mathrm{d}}$

$$
\boldsymbol{K}_{\mathrm{d}}=\frac{\boldsymbol{k}_{-1}}{\boldsymbol{k}_{1}}
$$

