LE CHATLIER’S PRINCIPLE

If an equim condition is disturbed, a shift in the balance of reactants and products will occur to minimize the effect of the disturbance.

\[ Q \rightarrow K \]
CONSIDER THE EQUILIBRIUM

4 \text{HBr(g)} + \text{O}_2(g) \rightleftharpoons 2 \text{H}_2\text{O(g)} + 2 \text{Br}_2(g)

Initial conditions: 4.0 mol \text{HBr}, 1.0 mol \text{O}_2 in 1.00 L vessel at 500 K.

At equm: \([\text{HBr}] = 1.0 \text{ M}\) \quad [\text{O}_2] = 0.25 \text{ M}
\[\text{[H}_2\text{O]} = 1.5 \text{ M}\] \quad [\text{Br}_2] = 1.5 \text{ M}

\[\Delta H_{\text{rxn}} = -466 \text{ kJ/mol}\]

QUESTIONS

1. What is \(K_c\)?
2. What will happen to [\text{Br}_2] if 4.0 mol \text{HBr} are added to the system at equm?
3. What if volume is decreased to 0.5 L?
4. What if we add 5.0 mol of inert gas?
5. What if we increase the T to 1000 K?
Add 4.0 mol HBr at equum

\[ [\text{HBr}] = 1.0 + 4.0 = 5.0 \text{ M} \]
\[ [\text{O}_2] = 0.25 \text{ M} \]
\[ [\text{H}_2\text{O}] = 1.5 \text{ M} \]
\[ [\text{Br}_2] = 1.5 \text{ M} \]

\[ Q = \frac{(1.5)^2 (1.5)^2}{(5.0)^4 (0.25)} = 0.032 \]

\[ Q < K_c \]
\[ 0.032 < 20 \]

System will increase numerator, decrease denominator to make \( Q \rightarrow K_c \)

Reaction will go toward right

**Principle**: At equum, added reactant or product will cause concs to shift and consume part of the added material.
Decrease the volume to 0.5 L

\[ \text{in } 1.0 \text{ L} \quad \text{in } 0.5 \text{ L} \]

\[
\begin{array}{l}
[HBr] \quad 1.0 \quad 2.0 \\
[O_2] \quad 0.25 \quad 0.5 \\
[H_2O] \quad 1.5 \quad 3.0 \\
[Br_2] \quad 1.5 \quad 3.0 \\
\end{array}
\]

at equm \hspace{1cm} \text{init conditions after P - V change}

\[
Q = \frac{(3.0)^2 (3.0)^2}{(2.0)^4 (0.5)} = 10 \quad Q < K_c
\]

\[
10 < 20
\]

To increase numerator, decrease denom

\[ Q \rightarrow K_c \]

Reaction goes to right
Add 5.0 mol of inert gas

\[ \text{\[ \text{[ ]} = \frac{n}{V} \text{ same} \quad P = \text{[ ] RT same} \] } \]

<table>
<thead>
<tr>
<th>Species</th>
<th>At equm</th>
<th>With inert gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>[HBr]</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>[O_2]</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>[H_2O]</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>[Br_2]</td>
<td>1.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>

No change in concentrations
No pressure-volume change
Partial pressures of species not changed

System still at equilibrium
**SUMMARY SO FAR**

Changing a concentration or pressure-volume puts stress on the reaction.

These stresses do not change K.

Q is changed, systems shifts to reestablish equim $Q \rightarrow K$.

**NEXT STEP**

A temp change **does** change K.

How K changes depends on whether the reaction is endothermic or exothermic.
Increase in temperature

4 HBr(g) + O_2(g) \rightleftharpoons 2 H_2O(g) + 2 Br_2(g) + \text{HEAT}  
(466 \text{ kJ/mol})

K_c' = \frac{[H_2O]^2[Br_2]^2 \text{ (heat)}}{[HBr]^4 [O_2]}

Exothermic reaction
Raising the temp will cause shift to left

**Principle**: When heat added to system at equim, the reaction shifts in the direction that absorbs heat.
EQUILIBRIUM
DEMONSTRATION

CoCl$_2$

CoCl(H$_2$O)$_5$$^+$ (aq) + Cl$^-$ (aq) + heat $\rightleftharpoons$ CoCl$_2$(H$_2$O)$_2$(aq) + 3 H$_2$O

pink octahedral

blue tetrahedral

Endothermic reaction, $\Delta H > 0$.
Think of heat as a reactant.

Cool with liquid $N_2$, removes heat which is on the reactant side, watch blue CoCl$_2$(H$_2$O)$_2$ solution shift toward pink CoCl(H$_2$O)$_5$$^+$ solution.
CONTROLLING CHEMICAL REACTIONS

Using Le Chatlier’s principle to advantage

Example: Haber-Bosch Process

\[ N_2(g) + 3 \, H_2(g) \rightleftharpoons 2 \, NH_3(g) \]

Exothermic reaction
Decrease in entropy
Use high pressure (200 atm)
Remove product from reaction
Use catalyst
Optimum T is 450 °C

Process has been studied and tuned
Ammonia is cheap
Haber-Bosch Process

\[ \text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g) \]
EQUILIBRIUM QUESTIONS

\[ \text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g}) + \text{heat} \]

What will happen to \([\text{NH}_3]\) if:

- add \(\text{N}_2\) ?
- remove \(\text{H}_2\) ?
- raise \(T\) ?
- increase \(P\) ?
- decrease \(V\) ?
- add catalyst ?
For this reaction at equilibrium, which of the changes will **not** have any effect on the equilibrium concentrations of reactants or products?

\[
5 \text{CO(g)} + \text{I}_2\text{O}_5(s) \rightleftharpoons \text{I}_2(g) + 5 \text{CO}_2(g)
\]

\[\Delta H^\circ = -1175 \text{ kJ}\]

A. adding more CO(g) to the mixture
B. increasing the pressure by decreasing the volume of the container
C. removing some of the I₂(g)
D. raising the temperature of the mixture
E. adding more I₂O₅(s)
Consider this equilibrium

\[ \text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g}) \]

\[ K_c = 160 \text{ at } 500 \text{ K} \]

A mixture of these gases in a closed container at 500 K has $[\text{H}_2] = 4.8 \times 10^{-3} \text{ M}$, $[\text{I}_2] = 2.4 \times 10^{-3} \text{ M}$ and $[\text{HI}] = 2.4 \times 10^{-3} \text{ M}$. Which one of these statements is true?

A. the total pressure of the mixture must increase for the system to reach equilibrium
B. the $[\text{H}_2]$ concentration must increase for the mixture to reach equilibrium
C. the $[\text{HI}]$ concentration must increase for the mixture to reach equilibrium
D. the total pressure must decrease for the system to reach equilibrium
E. the concentrations will not change because the system is at equilibrium