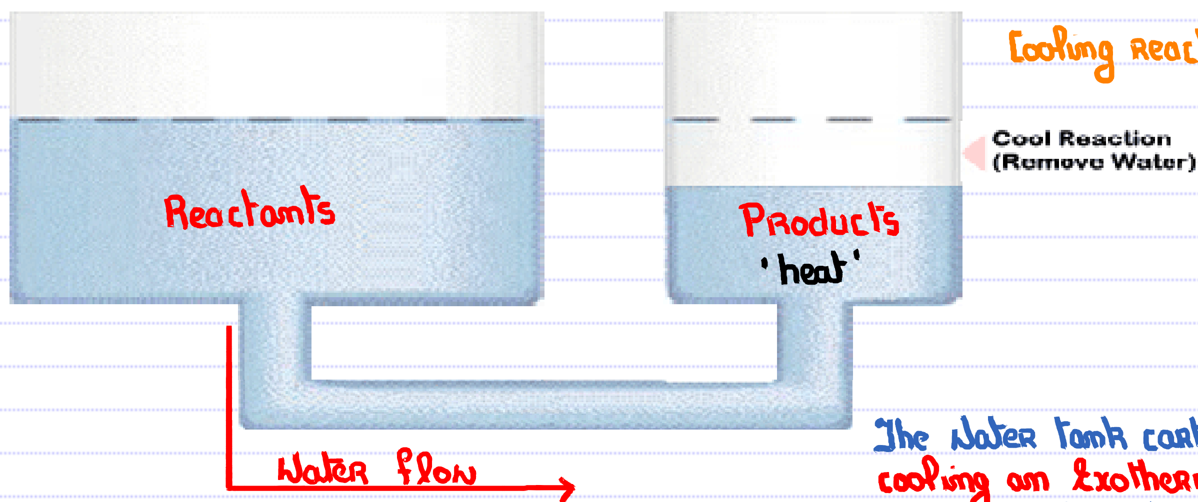
15.4 Disturbing a Chemical Equilibrium: Le Chatelier's Principle

Change in Temperature – Exothermic Reactions

Chemistry Interactive: LeChatelier's Principle - The Water Tank Analogy

R <=> P + 'heat'



Cooling Reaction = Removing a product

The water tank cartoon correctly predicts that cooling an exothermic reaction at equilibrium causes a shift towards products.. Chemically why is this prediction correct ?

$$K = \frac{[\text{Producrs}]}{[\text{Reactants}]}$$ No 'heat' in the equation.

K must be T dependant.

Cooling an exothermic equilibrium reaction Results in K↑

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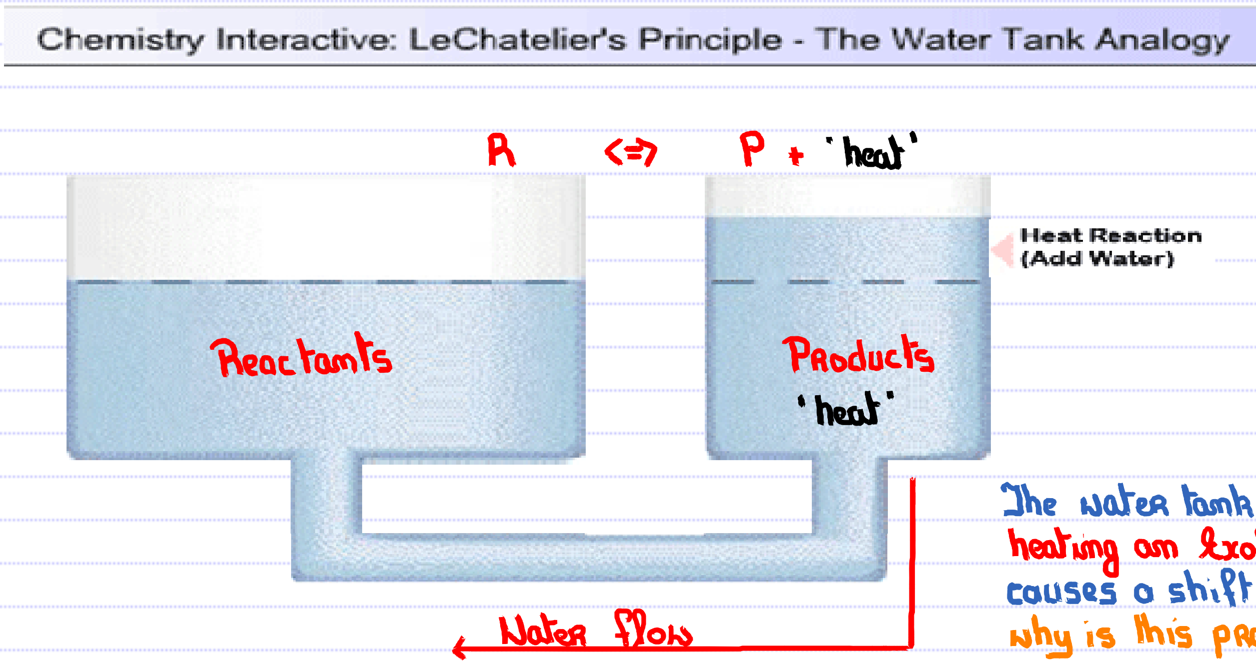

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Heating an exothermic equilibrium reaction results in K ↓

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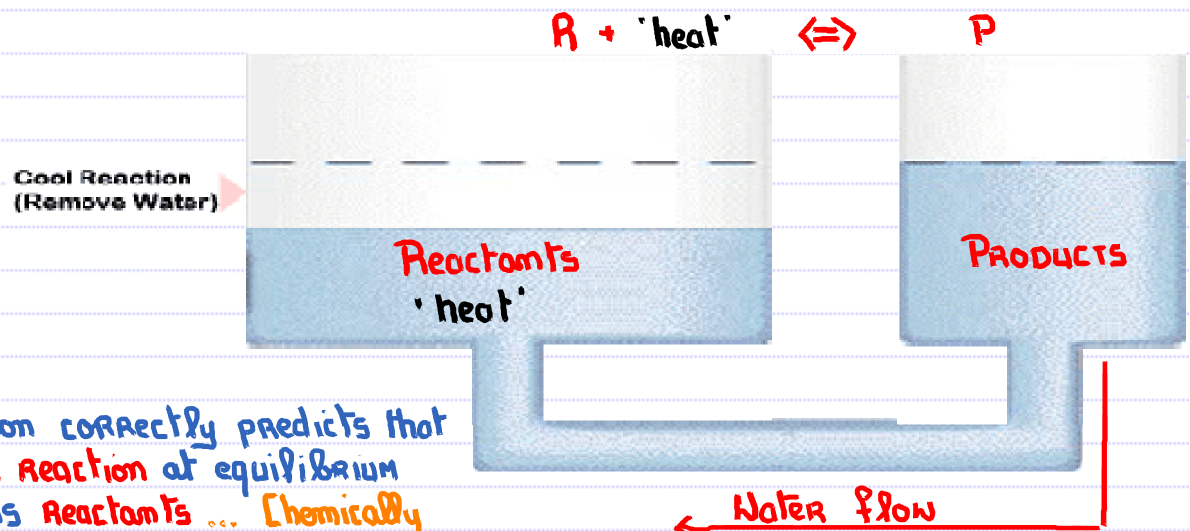

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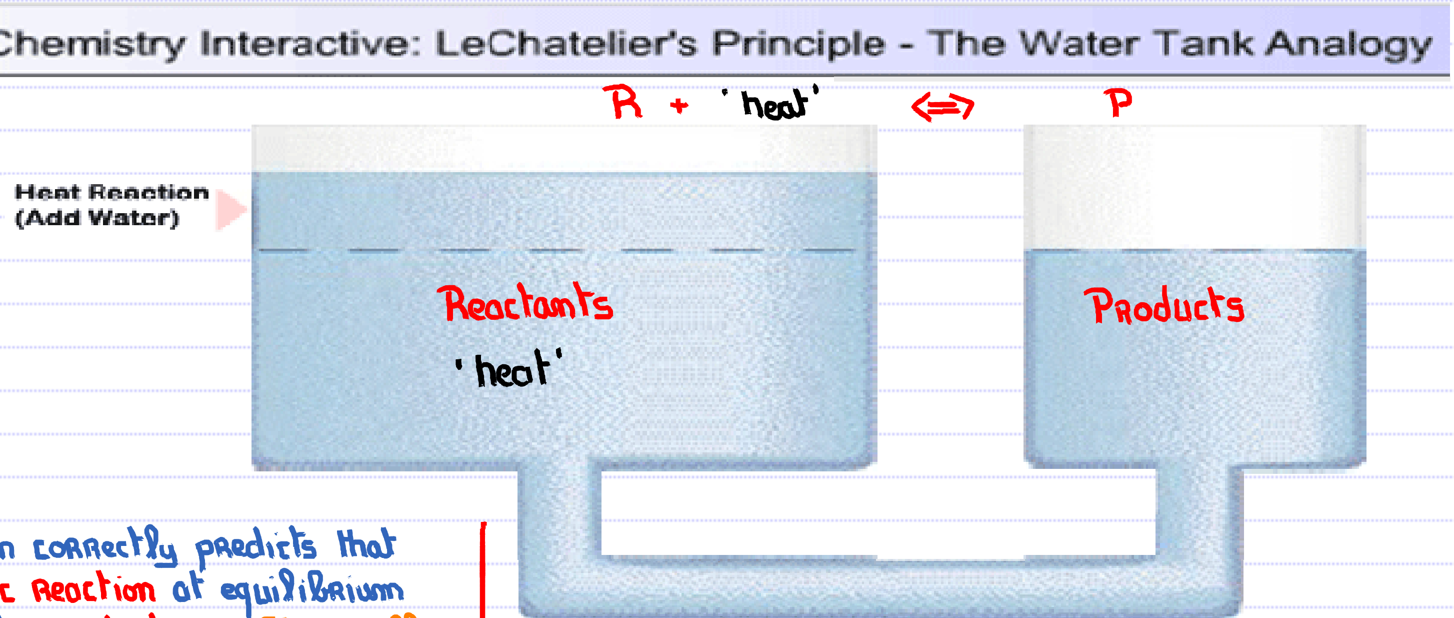
Change in Temperature – Endothermic Reactions



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$$K = \frac{[\text{Products}]}{[\text{Reactants}]}$$ } No 'heat' in the equation.

K must be temperature dependant

Heating an endothermic equilibrium reaction results in $K\uparrow$

15.4 Disturbing a Chemical Equilibrium: Le Chatelier's Principle

Change in Temperature

The production of ammonia is an exothermic process –

$$N_2(g) + 3\,H_2(g) \Leftrightarrow 2\,NH_3(g) \qquad Kc = 3.5\times10^{8} \text{ @ } 25^{o}C$$

To maximize the $[NH_3]$ at equilibrium it is best to

a) Heat the reaction

b) Cool the reaction ✓

c) Leave it as is

$$N_2(g) + 3\,H_2(g) \Leftrightarrow 2\,NH_3(g) + \text{'heat'}$$

→ To maximize $NH_3(g)$, Remove a product ... Remove heat by cooling the reaction.

Change in Temperature – van't Hoff Equation

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$N_2(g) + 3\,H_2(g) \Leftrightarrow 2\,NH_3(g)$$

At 25°C, $\Delta H^\circ = -91.8$ kJ.mol^{-1}, K = 3.5×10^{8} – however at this temperature the reaction is extremely slow.

With the help of a catalyst, the optimum temperature for the reaction is 450°C. $\Delta H^\circ = -111.3$kJ.mol^{-1} at this temperature. What is the value for K at this temperature?

$K_1 = 3.5\times10^{8}$ $\quad T_1 = 298$ K

$K_2 = ?$ $\quad T_2 = 723$ K

$\Delta H^\circ = -111{,}300$ J.mol^{-1}

$R = 8.314$ J.mol^{-1}.K^{-1}

$$\ln \frac{K_2}{K_1} = -\left(\frac{-111{,}300}{8.314}\right)\left(\frac{1}{723} - \frac{1}{298}\right)$$

$$\ln K_2 - \ln(3.5\times10^{8}) = 13387(-1.9726\times10^{-3})$$

$$\ln K_2 - 19.6734 = -26.4072$$

$$\ln K_2 = -26.4072 + 19.6734$$

$$\ln K_2 = -6.7338$$

$K_2 = 1.19\times10^{-3}$ @ 723K

→ Ouch … a ~ 10^{11} drop

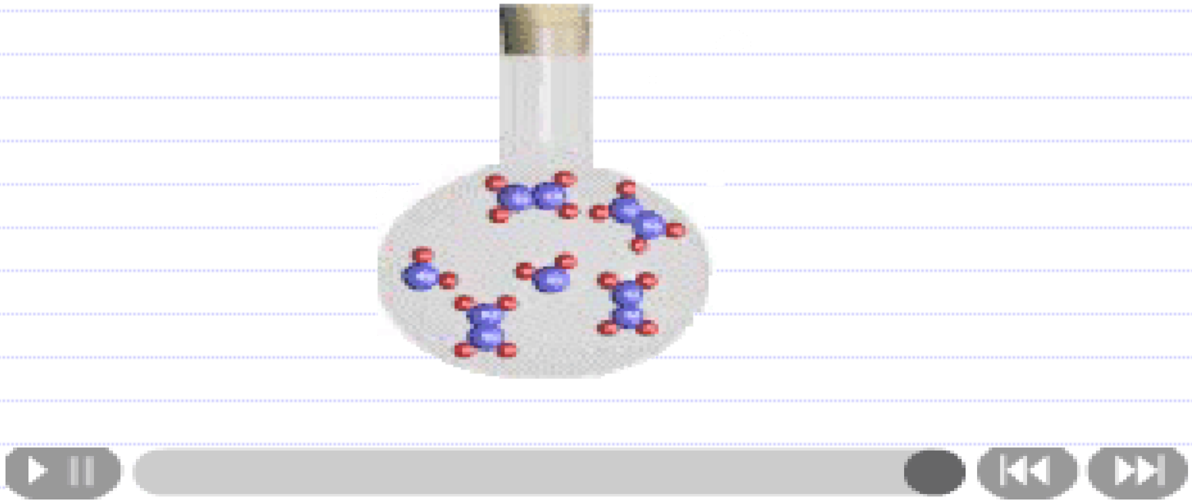
While the decrease in K was expected since the process involved heating an exothermic equilibrium, this decrease is dramatic.

15.4 **Disturbing a Chemical Equilibrium: Le Chatelier's Principle**

Change in the Volume of the System

Chemistry Interactive: Effect of Changing Volume on the NO_2/N_2O_4 Equilibrium

$$2\ NO_2(g) \rightleftharpoons N_2O_4(g) \qquad K = 171$$



See Class Web Site.

15.4 Disturbing a Chemical Equilibrium: Le Chatelier's Principle

Change in the Volume of the System

Reactants (g) $\rightleftharpoons$ Products (g)

Δn = mol of gas products - mol of gas reactants.

Δn : $= 0$, > 0, or < 0

Action	Equilibrium Shift
a) Volume ↑, ie Pressure ↓	Toward the side with the greater number of gas molecules ... trying to increase the pressure ... if it can*
b) Volume ↓, ie Pressure ↑	Toward the side with the fewest number of gas molecules ... trying to decrease the pressure ... if it can*

* $\Delta n = 0$: Nothing the equilibrium can do to counter any pressure changes.

15.4 **Disturbing a Chemical Equilibrium: Le Chatelier's Principle**

Change in the Volume of the System – A Summary

Action		Equilibrium Shift	Why?
a) V↑, P↓			
b) V↓, P↑			
1	$O_{3(g)} + NO_{(g)} \Leftrightarrow O_{2(g)} + NO_{2(g)}$		● + ● ⇔ ● + ●
a)		No shift	$\Delta n = 0$, Q Remains unchanged
b)		No shift	
2	$2\,NOCl_{(g)} \Leftrightarrow 2\,NO_{(g)} + Cl_{2(g)}$		● + ● ⇔ ● + ● + ●
a)		Towards products	$\Delta n > 0$, $Q > K$
b)		Towards Reactants	$\Delta n > 0$, $Q < K$
3.	$N_{2(g)} + 3\,H_{2(g)} \Leftrightarrow 2\,NH_{3(g)}$		● + ● + ● + ● ⇔ ● + ●
a)		Towards Reactants	$\Delta n < 0$, $Q < K$
b)		Towards products	$\Delta n < 0$, $Q > K$

15.4 Disturbing a Chemical Equilibrium: Le Chatelier's Principle

Change in the Volume of the System.

The production of ammonia is an exothermic process –

$N_2(g) + 3\,H_2(g) \Leftrightarrow 2\,NH_3(g)$ $K_c = 3.5\times10^8$ @ 25°C

To maximize the $[NH_3]$ at equilibrium it is best to

a) Increase the volume

b) Decrease the volume ✓ … Increases the pressure

c) Leave it as is

$N_2(g) + 3\,H_2(g) \Leftrightarrow 2\,NH_3(g)$

● + ● ● ● ⇔ ● ●

↳ less gas molecules on NH_3 side.

$\Delta n < 0$

15.4 Disturbing a Chemical Equilibrium: Le Chatelier's Principle

Production of ammonia – an equilibrium dilemma!

The production of ammonia is an exothermic process –

$N_2(g) + 3\,H_2(g) \Leftrightarrow 2\,NH_3(g)$ $K_c = 3.5\times10^8$ @ 25°C

How can we maximize the production of $[NH_3]$.

a) At room temperature, Kc is product favored
However at room temperature this reaction is extremely slow. Very high Activation Energy.
To speed it up ... heat it ... and/or use a catalyst to lower the Activation Energy

b) However the reaction is exothermic ... thus heating it will result in Kc decreasing
As we calculated previously ... even with a catalyst the process is done at ~ 450°C ...
at 450°C, $K_c = 1.19\times10^{-3}$. Thus while reaching equilibrium in a reasonable time, the equilibrium is now very reactant favored.

c) Not daunted as this gaseous reaction has $\Delta n < 0$
Therefore if P is increased, then Q becomes > Kc, thereby causing a shift towards products ... increasing the $[NH_3]$.