15.4 Disturbing a Chemical Equilibrium: Le Chatelier's Principle

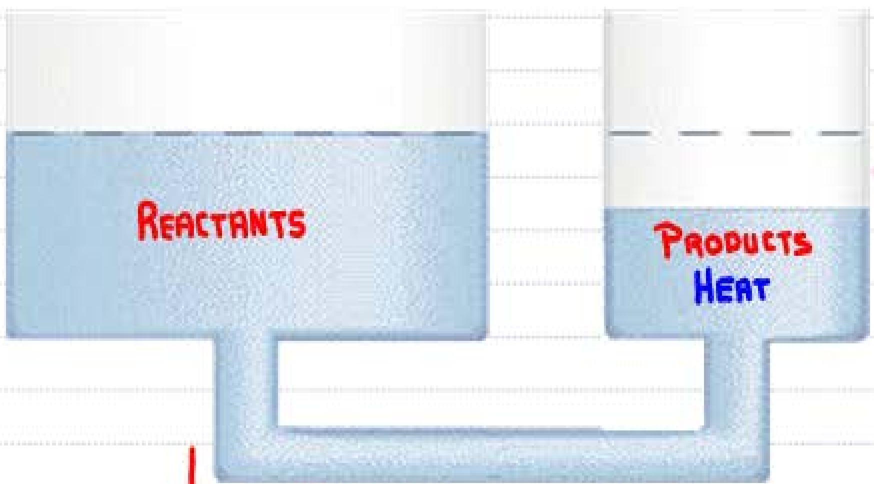
Change in Temperature – Exothermic Reactions

K is temperature dependant.

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

R ⇔ P + 'heat'

Cooling reaction = 'removing product'



→ Water flow.

Shift from Reactants to Products.

Why?

$$K = \frac{[\text{Products}]}{[\text{Reactants}]}$$

Cooling an exothermic reaction results in K↑, thus a shift towards products

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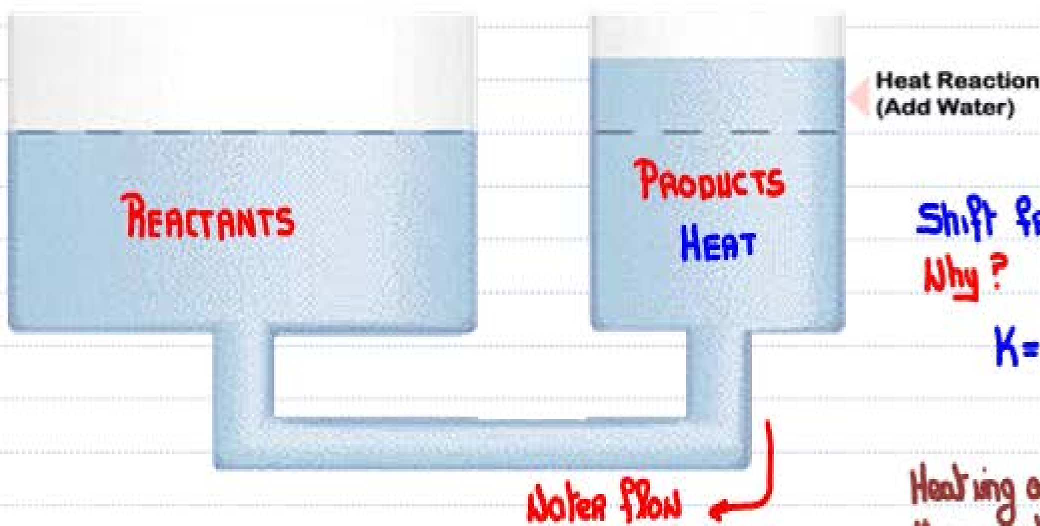
R ⇔ P + heat



Heating reaction = 'adding product'

Shift from Products to Reactants

Why?

$$K = \frac{[Products]}{[Reactants]}$$

Heating an exothermic reaction results in K↓ ...
thus a shift towards Reactants.

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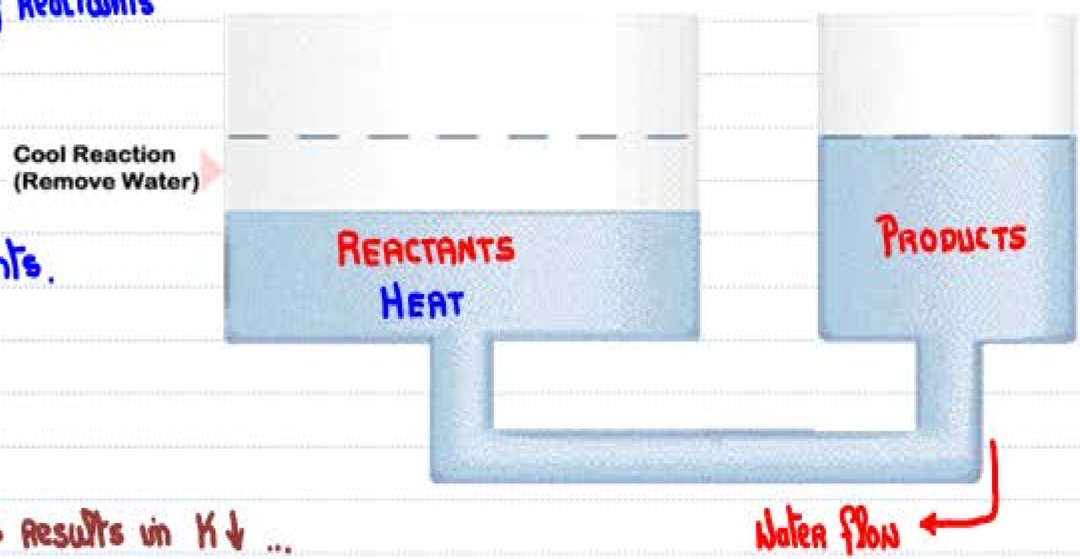
Change in Temperature – Endothermic Reactions

K is temperature dependant

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

R + 'heat' ⇔ P

Cooling reaction = 'Removing reactants'



Shift from products to reactants.
Why?

$$K = \frac{[\text{Products}]}{[\text{Reactants}]}$$

Cooling an endothermic reactions results in K↓ ...
thus a shift towards reactants.

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Change in Temperature – Endothermic Reactions

K is temperature dependant.

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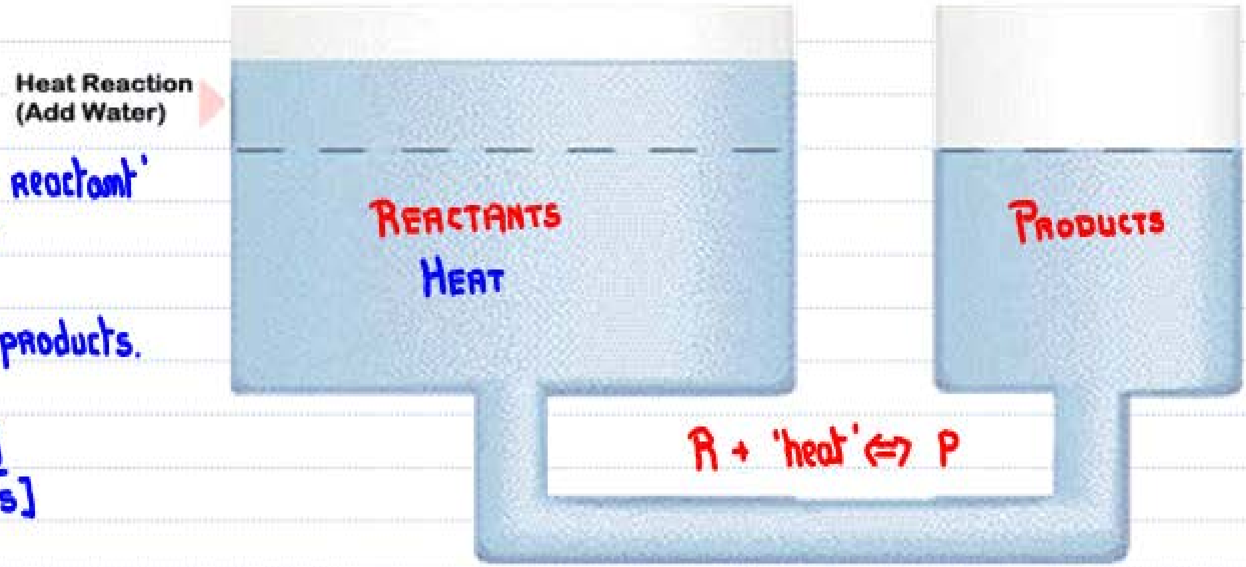


Heating reaction = 'adding reactant'

Shift from reactants to products.

Why?

$$K = \frac{[\text{PRODUCTS}]}{[\text{REACTANTS}]}$$

Heating an endothermic reaction results in K↑ ...
thus a shift towards products.

15.4 Disturbing a Chemical Equilibrium: Le Chatelier's Principle

Change in Temperature

The production of ammonia is an exothermic process –

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

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

Desire a shift towards products

↳ Remove product, remove heat, cool the reaction.

15.4 Disturbing a Chemical Equilibrium: Le Chatelier's Principle

Change in Temperature – van't Hoff Equation

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

Arrhenius Equation.
Looks similar to Clausius-Clapeyron Equation.

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

At 25°C, $\Delta H^\circ = -91.8$ kJ.mol^{-1}, $K = 3.5\times10^8$ – 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?

$K_1 = 3.5\times10^8$ $T_1 = 298K$
$K_2 = ?$ $T_2 = 723K$
$\Delta H^\circ = -111.3$ kJ. mol^{-1}

$$\ln \frac{K_2}{K_1} = -\left(\frac{-111300}{8.314}\right)\left(\frac{1}{723} - \frac{1}{298}\right)$$

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

$$\ln K_2 - 19.6734 = -26.4072$$
$$\ln K_2 = -26.4072 + 19.6734$$
$$\ln K_2 = -6.7338$$

$$K_2 = 1.19\times10^{-3}$$

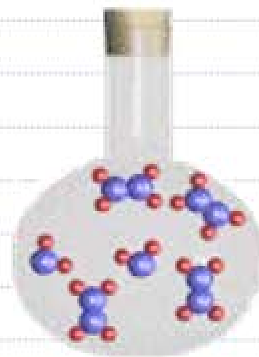
↳ 'Ouch! ... But a decrease in K was expected for an exothermic reaction in which T was increased.

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

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



See Class Web Site.

15.4 Disturbing a Chemical Equilibrium: Le Chatelier's Principle

Change in the Volume of the System

Reactants (g) ⇐⇒ Products (g)

Δn = mol of gas products - mol of gas reactants

Δn : = 0, > 0, or < 0

Action:	Equilibrium Shift:
Volume ↑, Pressure ↓	Towards the side with the greater number of gas molecules ... trying to increase the pressure ... if it can?
Volume ↓, Pressure ↑	Towards the side with the fewest number of gas molecules ... trying to reduce the pressure ... if it can?

15.4 Disturbing a Chemical Equilibrium: Le Chatelier's Principle

Change in the Volume of the System – A Summary

1. $O_3(g) + NO(g) \rightleftharpoons O_2(g) + NO_2(g)$ ● + ● ⇌ ● + ● $\Delta n = 0$

Action	Equilibrium Shift	Why
V↑, P↓	No shift	$\Delta n = 0$, Q is unaffected.
V↓, P↑	No shift	$\Delta n = 0$, Q is unaffected.

2. $2\,NOCl(g) \rightleftharpoons 2\,NO(g) + Cl_2(g)$ ● + ● ⇌ ● + ● + ● $\Delta n > 0$

Action	Equilibrium Shift	Why
V↑, P↓	Towards products	$\Delta n > 0$, $Q > K$
V↓, P↑	Towards reactants	$\Delta n > 0$, $Q < K$

3. $N_2(g) + 3H_2(g) \rightleftharpoons 2\,NH_3(g)$ ● + ● + ● + ● ⇌ ● + ● $\Delta n < 0$

Action	Equilibrium Shift	Why
V↑, P↓	Towards reactants	$\Delta n < 0$, $Q < K$
V↓, P↑	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 –

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

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

a) Increase the volume

b) ✓ Decrease the volume — Increase the pressure.

c) Leave it as is

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

• + • + • + • ⇔ • + •

Less gas molecules on the NH_3 side.

$\Delta n < 0$