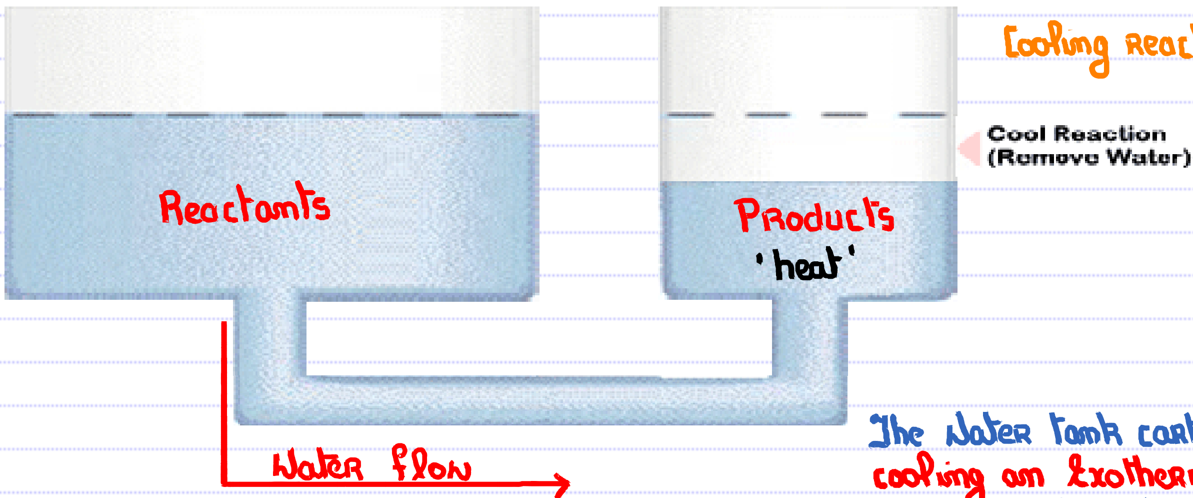
15.4 Disturbing a Chemical Equilibrium: Le Chatelier's Principle

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 ?

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

K must be T dependant.

Cooling an exothermic equilibrium reaction results in K↑

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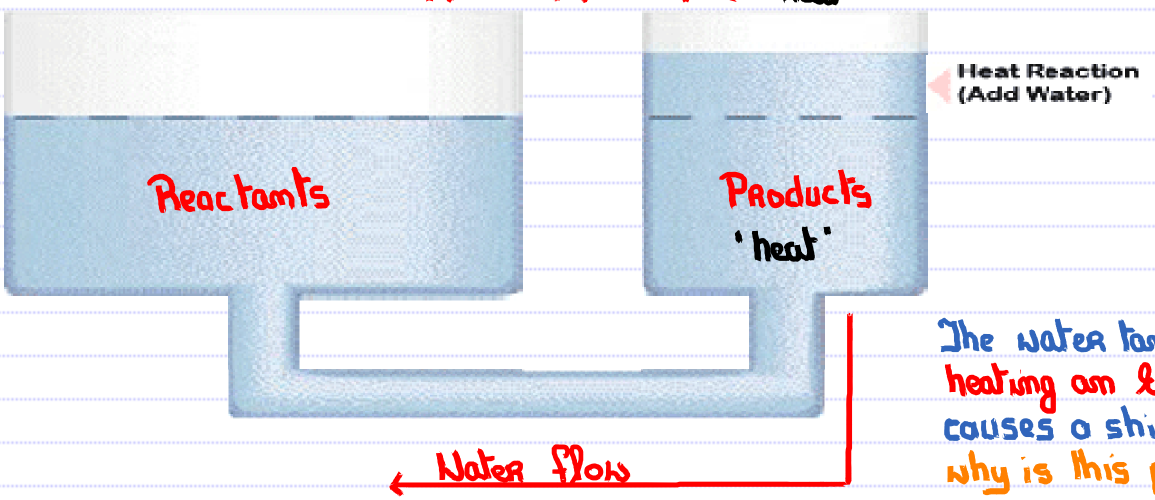

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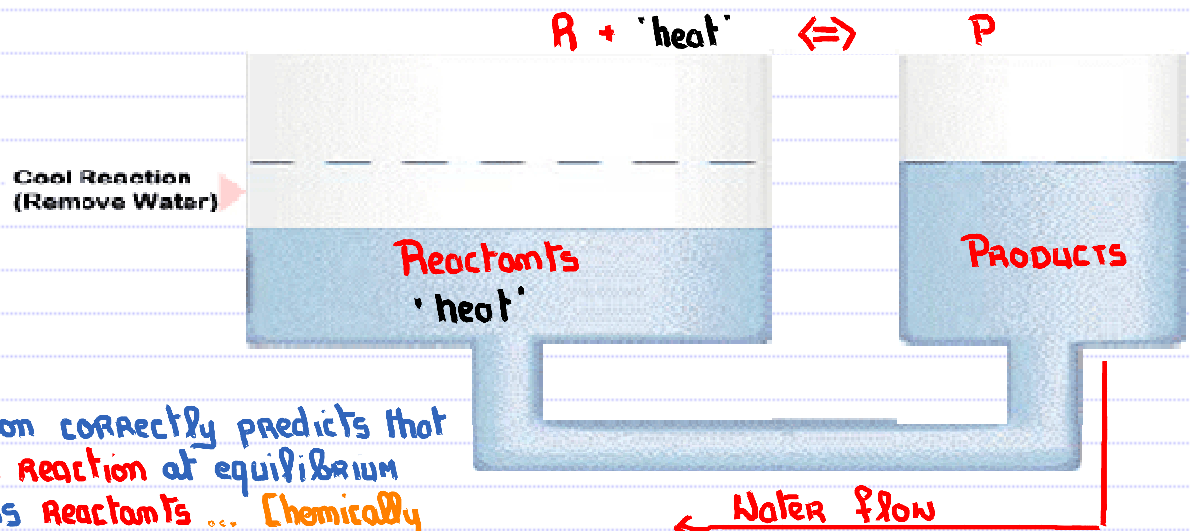

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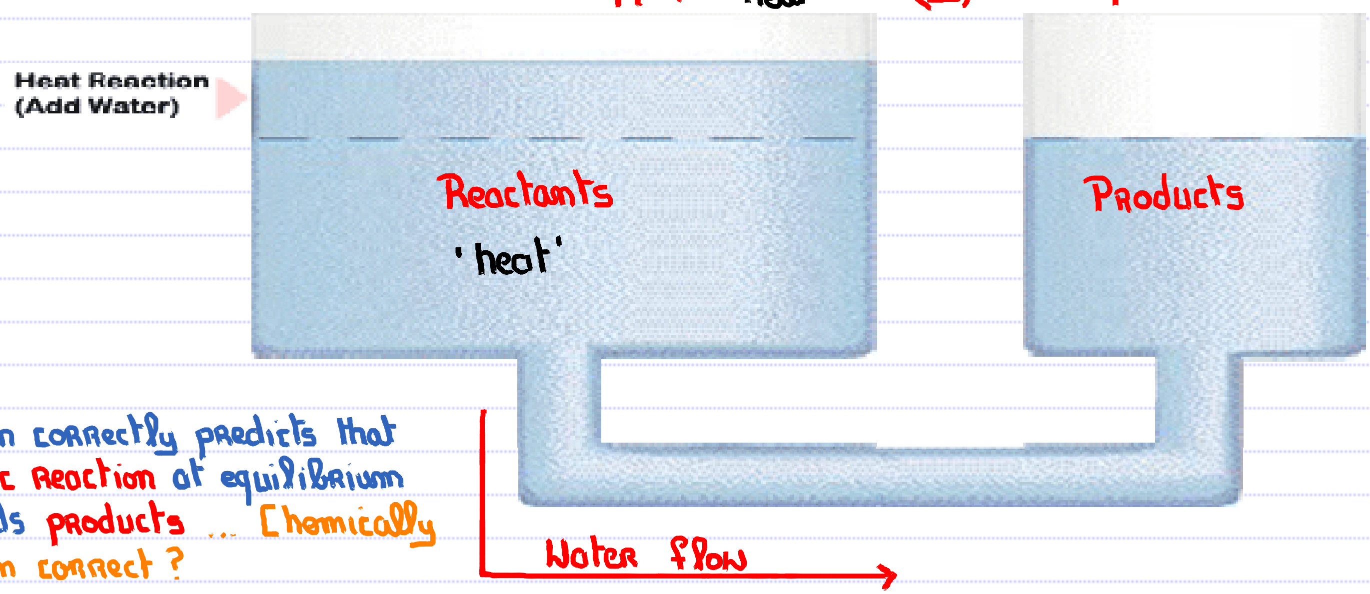

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Change in Temperature

The production of ammonia is an exothermic process –

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

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

a) Heat the reaction

b) Cool the reaction ✓

c) Leave it as is

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

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

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Change in Temperature – van't Hoff Equation

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

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

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

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

$K_1 = 3.5 \times 10^8$ $\quad T_1 = 298$ K

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

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

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

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

$$\ln K_2 - \ln(3.5 \times 10^8) = 13387(-1.9726 \times 10^{-3})$$

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

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

$$\ln K_2 = -6.7338$$

$K_2 = 1.19 \times 10^{-3}$ @ 723K

→ Ouch … a ~10" drop.

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

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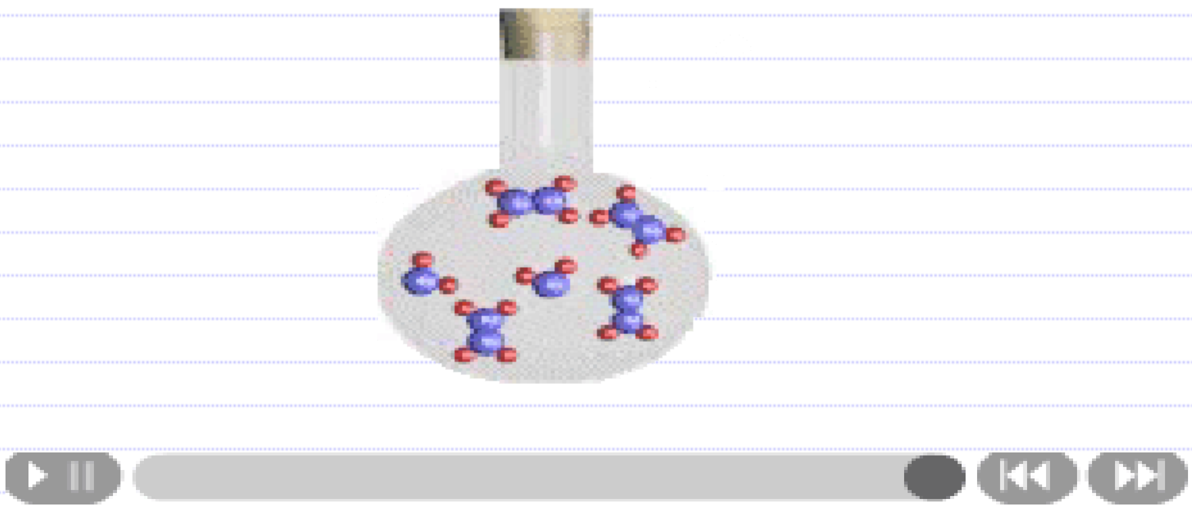
Change in the Volume of the System

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.