

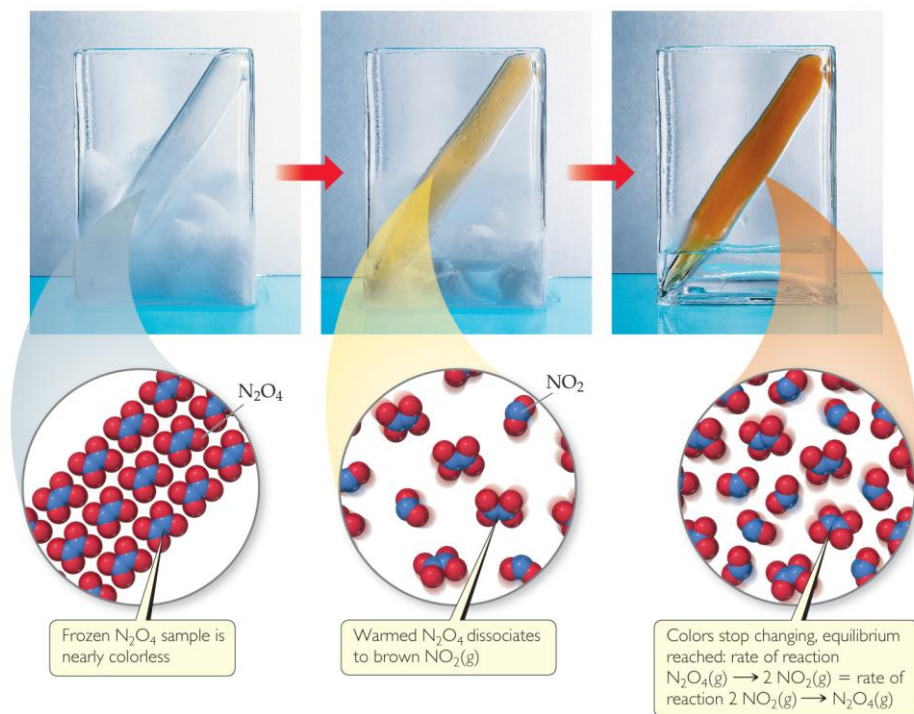
Lecture Presentation

Chapter 15

Chemical Equilibrium

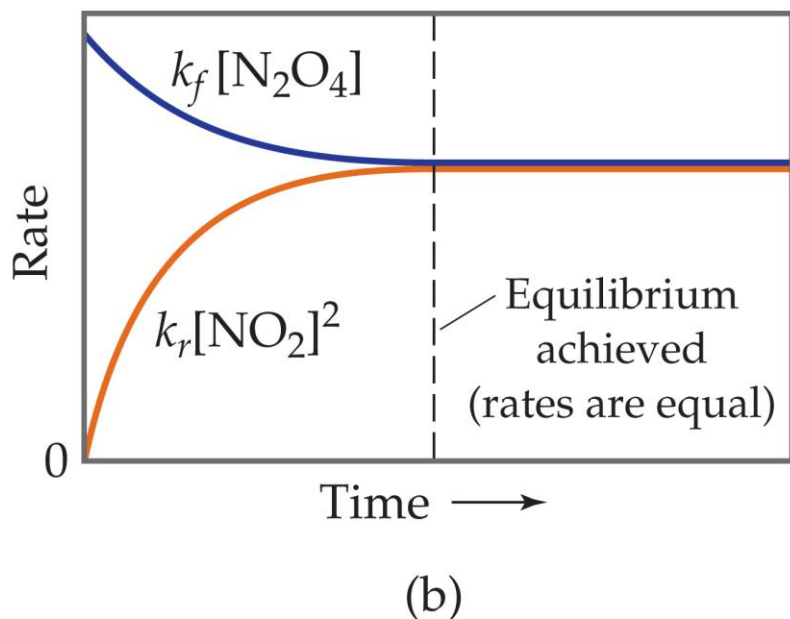
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The Concept of Equilibrium



Chemical equilibrium occurs when a reaction and its reverse reaction proceed at the same rate.

The Concept of Equilibrium

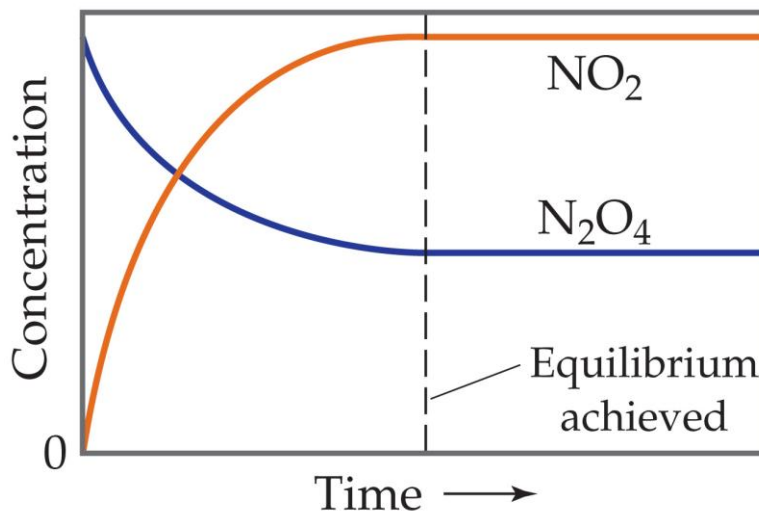


- As a system approaches equilibrium, both the forward and reverse reactions are occurring.
- At equilibrium, the forward and reverse reactions are proceeding *at the same rate*.

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A System at Equilibrium

Once equilibrium is achieved, the *amount* of each reactant and product remains constant.



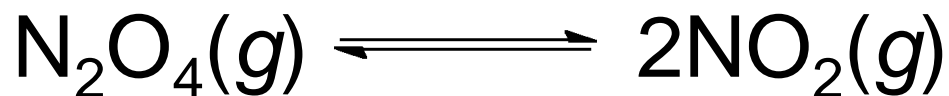
(a)

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Equilibrium

Depicting Equilibrium

Since, in a system at equilibrium, both the forward and reverse reactions are being carried out, we write its equation with a double arrow:

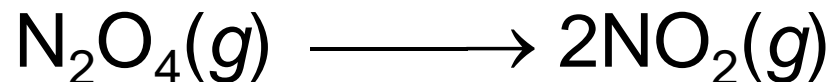


The Equilibrium Constant



The Equilibrium Constant

- Forward reaction:



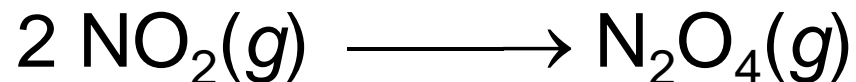
- Rate law:

$$\text{Rate} = k_f[\text{N}_2\text{O}_4]$$



The Equilibrium Constant

- Reverse reaction:



- Rate law:

$$\text{Rate} = k_r[\text{NO}_2]^2$$



The Equilibrium Constant

- Therefore, at equilibrium

$$\text{Rate}_f = \text{Rate}_r$$

$$k_f[\text{N}_2\text{O}_4] = k_r[\text{NO}_2]^2$$

- Rewriting this, it becomes

$$\frac{k_f}{k_r} = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$



The Equilibrium Constant

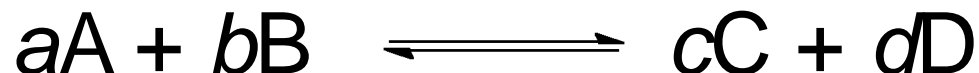
The ratio of the rate constants is a constant at that temperature, and the expression becomes

$$K_{\text{eq}} = \frac{k_f}{k_r} = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$



The Equilibrium Constant

- Consider the generalized reaction



- The equilibrium expression for this reaction would be

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$



The Equilibrium Constant

Since pressure is proportional to concentration for gases in a closed system, the equilibrium expression can also be written

$$K_p = \frac{(P_C^c) (P_D^d)}{(P_A^a) (P_B^b)}$$



Relationship Between K_c and K_p

- From the ideal-gas law we know that

$$PV = nRT$$

- Rearranging it, we get

$$P = \frac{n}{V} RT$$



Relationship Between K_c and K_p

Plugging this into the expression for K_p , for each substance, the relationship between K_c and K_p becomes

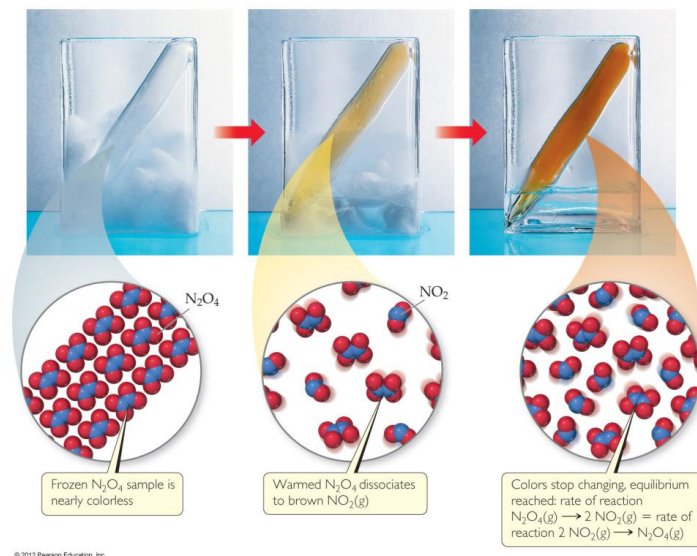
$$K_p = K_c (RT)^{\Delta n}$$

where

$\Delta n = (\text{moles of gaseous product}) - (\text{moles of gaseous reactant})$



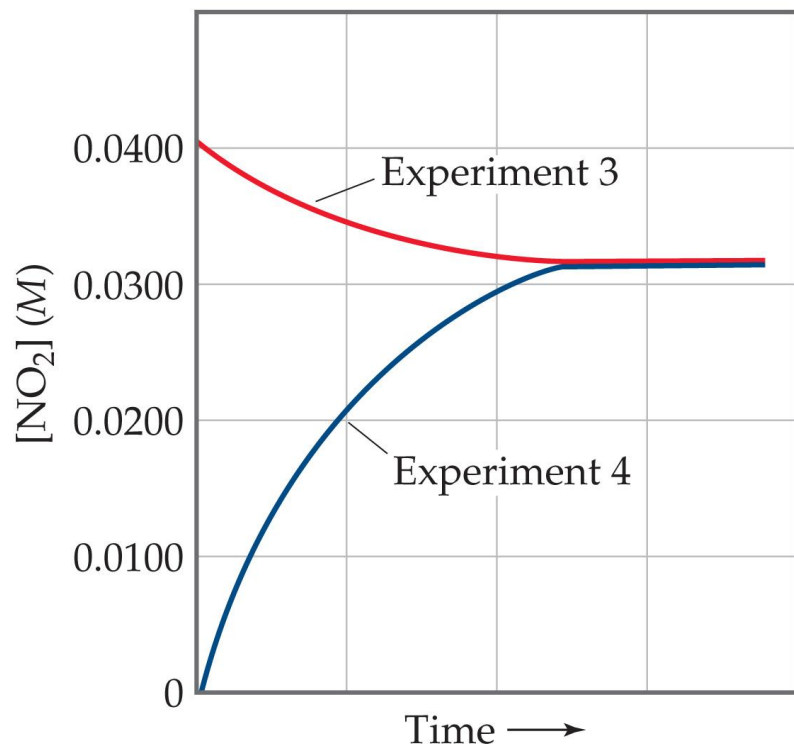
Equilibrium Can Be Reached from Either Direction



As you can see, the ratio of $[\text{NO}_2]^2$ to $[\text{N}_2\text{O}_4]$ remains constant at this temperature no matter what the initial concentrations of NO_2 and N_2O_4 are.



Equilibrium Can Be Reached from Either Direction

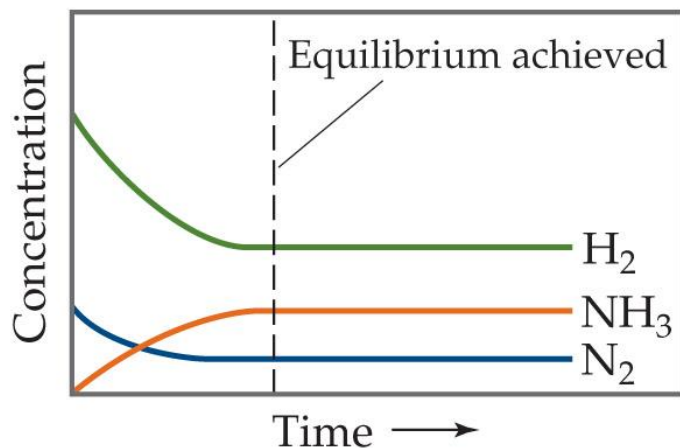


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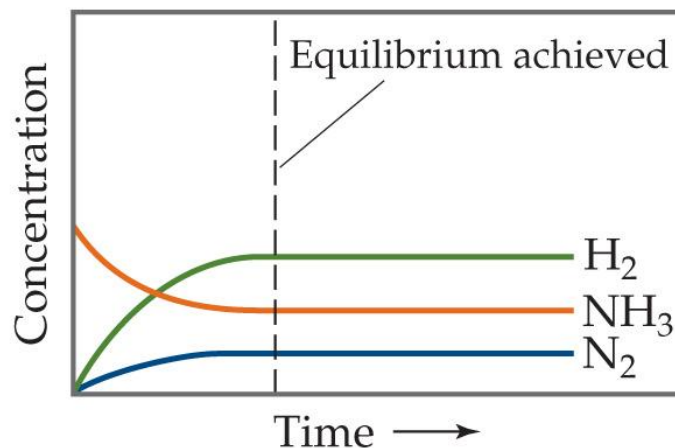
These are the data from the last two trials from the table on the previous slide.



Equilibrium Can Be Reached from Either Direction

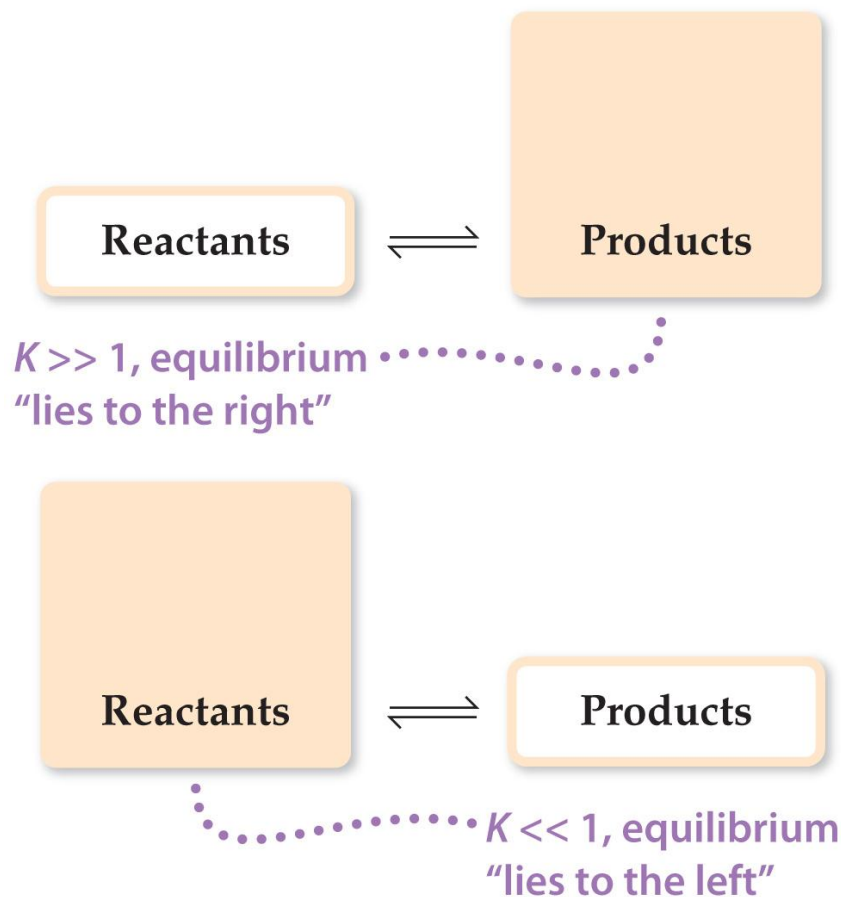


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It doesn't matter whether we start with N_2 and H_2 or whether we start with NH_3 , we will have the same proportions of all three substances at equilibrium.

What Does the Value of K Mean?

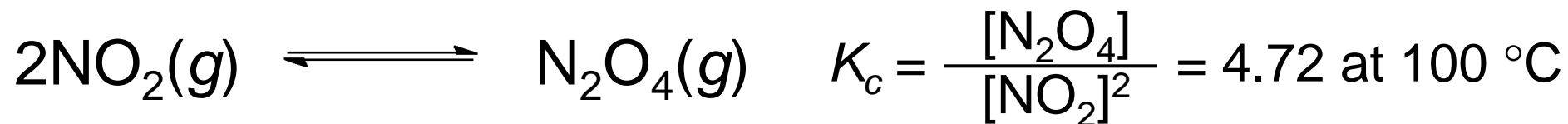
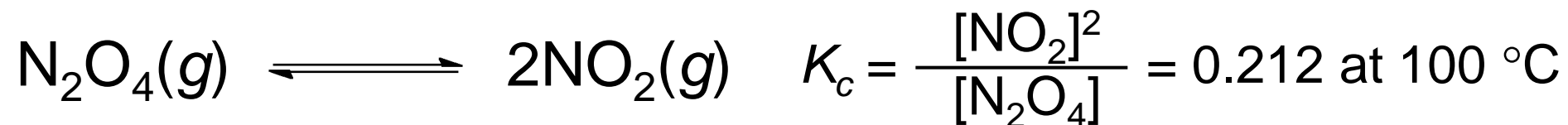


- If $K \gg 1$, the reaction is *product-favored*; product predominates at equilibrium.

- If $K \ll 1$, the reaction is *reactant-favored*; reactant predominates at equilibrium.

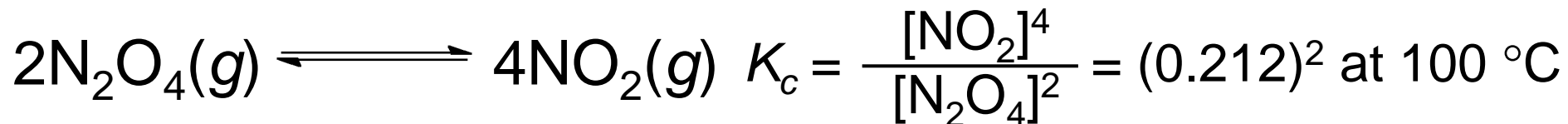
Manipulating Equilibrium Constants

The equilibrium constant of a reaction in the reverse reaction is the reciprocal of the equilibrium constant of the forward reaction:



Manipulating Equilibrium Constants

The equilibrium constant of a reaction that has been multiplied by a number is the equilibrium constant raised to a power that is equal to that number:



Manipulating Equilibrium Constants

The equilibrium constant for a net reaction made up of two or more steps is the product of the equilibrium constants for the individual steps.

Heterogeneous Equilibrium

The Concentrations of Solids and Liquids Are Essentially Constant

Both the concentrations of solids and liquids can be obtained by multiplying the density of the substance by its molar mass—and both of these are constants at constant temperature.



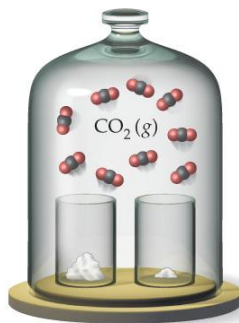
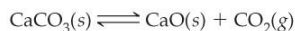
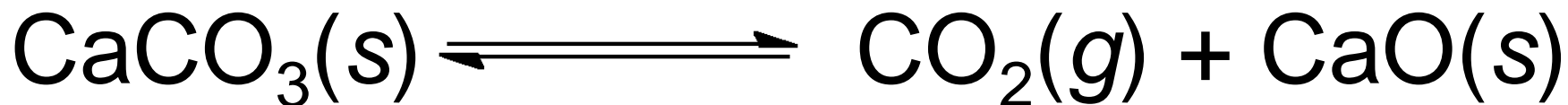
The Concentrations of Solids and Liquids Are Essentially Constant

Therefore, the concentrations of solids and liquids do not appear in the equilibrium expression.



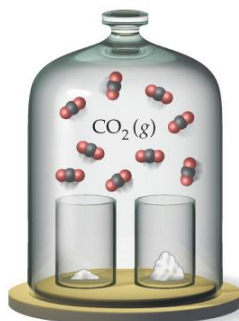
$$K_c = [\text{Pb}^{2+}] [\text{Cl}^{-}]^2$$





CaCO₃ CaO

Large amount of CaCO₃,
small amount of CaO,
gas pressure *P*



CaCO₃ CaO

Small amount of CaCO₃,
large amount of CaO,
gas pressure still *P*

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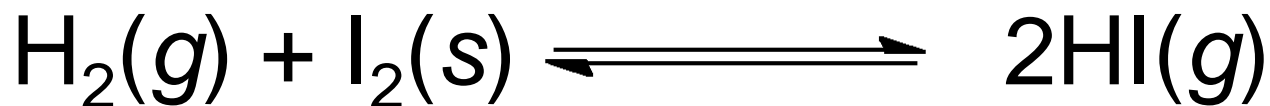
As long as *some* CaCO₃ or CaO remain in the system, the amount of CO₂ above the solid will remain the same.

Equilibrium

Equilibrium Calculations

An Equilibrium Problem

A closed system initially containing $1.000 \times 10^{-3} \text{ M H}_2$ and $2.000 \times 10^{-3} \text{ M I}_2$ at 448°C is allowed to reach equilibrium. Analysis of the equilibrium mixture shows that the concentration of HI is $1.87 \times 10^{-3} \text{ M}$. Calculate K_c at 448°C for the reaction taking place, which is



What Do We Know?

	$[\text{H}_2], M$	$[\text{I}_2], M$	$[\text{HI}], M$
Initially	1.000×10^{-3}	2.000×10^{-3}	0
Change			
At equilibrium			1.87×10^{-3}



[HI] Increases by $1.87 \times 10^{-3} \text{ M}$

	$[\text{H}_2], \text{ M}$	$[\text{I}_2], \text{ M}$	$[\text{HI}], \text{ M}$
Initially	1.000×10^{-3}	2.000×10^{-3}	0
Change			$+1.87 \times 10^{-3}$
At equilibrium			1.87×10^{-3}



Stoichiometry tells us $[\text{H}_2]$ and $[\text{I}_2]$ decrease by half as much.

	$[\text{H}_2], M$	$[\text{I}_2], M$	$[\text{HI}], M$
Initially	1.000×10^{-3}	2.000×10^{-3}	0
Change	-9.35×10^{-4}	-9.35×10^{-4}	$+1.87 \times 10^{-3}$
At equilibrium			1.87×10^{-3}



We can now calculate the equilibrium concentrations of all three compounds

	$[\text{H}_2], M$	$[\text{I}_2], M$	$[\text{HI}], M$
Initially	1.000×10^{-3}	2.000×10^{-3}	0
Change	-9.35×10^{-4}	-9.35×10^{-4}	$+1.87 \times 10^{-3}$
At equilibrium	6.5×10^{-5}	1.065×10^{-3}	1.87×10^{-3}



and, therefore, the equilibrium constant:

$$\begin{aligned}K_c &= \frac{[\text{HI}]^2}{[\text{H}_2] [\text{I}_2]} \\&= \frac{(1.87 \times 10^{-3})^2}{(6.5 \times 10^{-5})(1.065 \times 10^{-3})} \\&= 51\end{aligned}$$

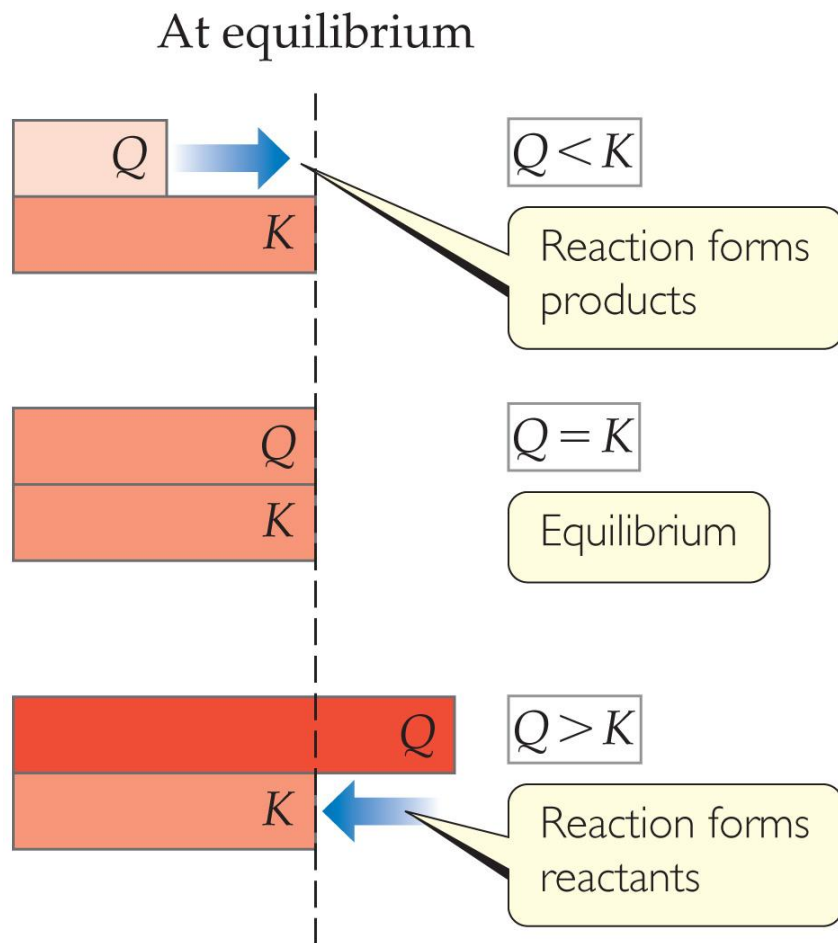


The Reaction Quotient (Q)

- Q gives the same ratio the equilibrium expression gives, but for a system that is *not* at equilibrium.
- To calculate Q , one substitutes the initial concentrations on reactants and products into the equilibrium expression.



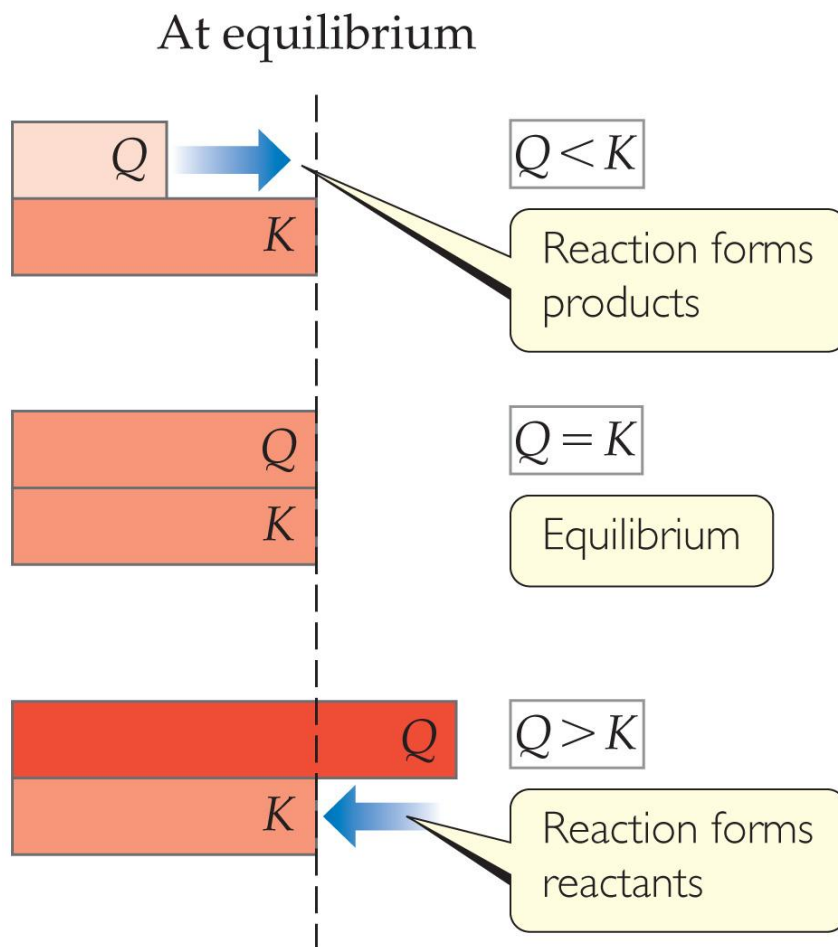
If $Q = K$, the system is at equilibrium.



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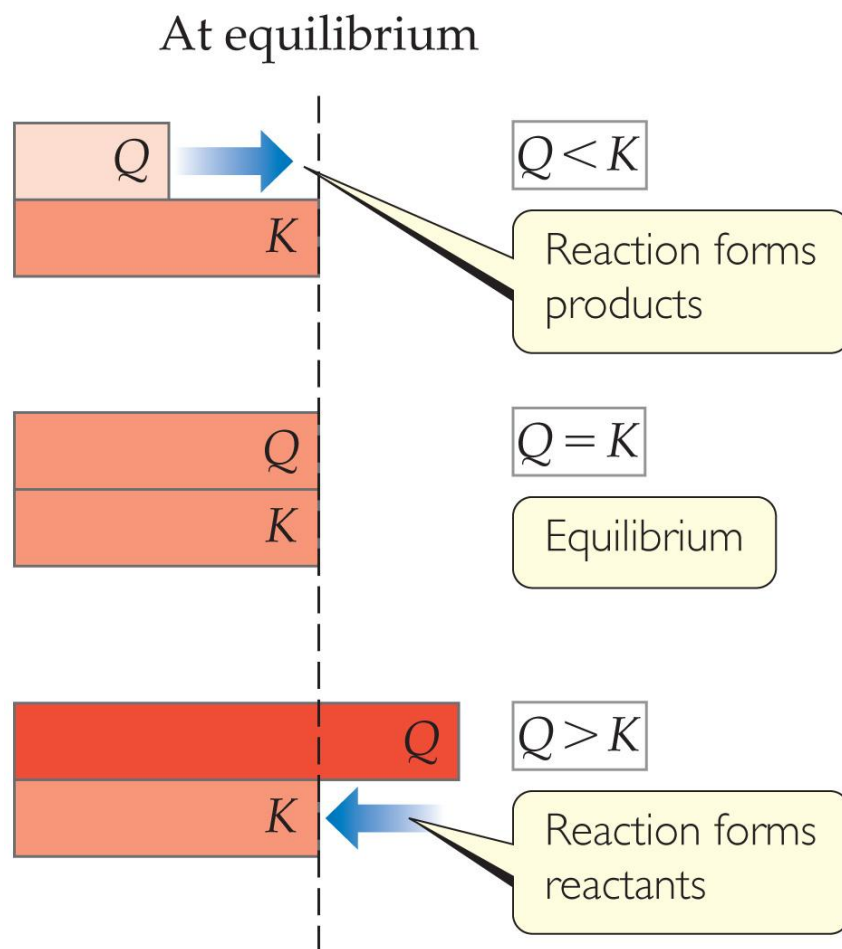
If $Q > K$, there is too much product, and the equilibrium shifts to the left.



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If $Q < K$, there is too much reactant, and the equilibrium shifts to the right.



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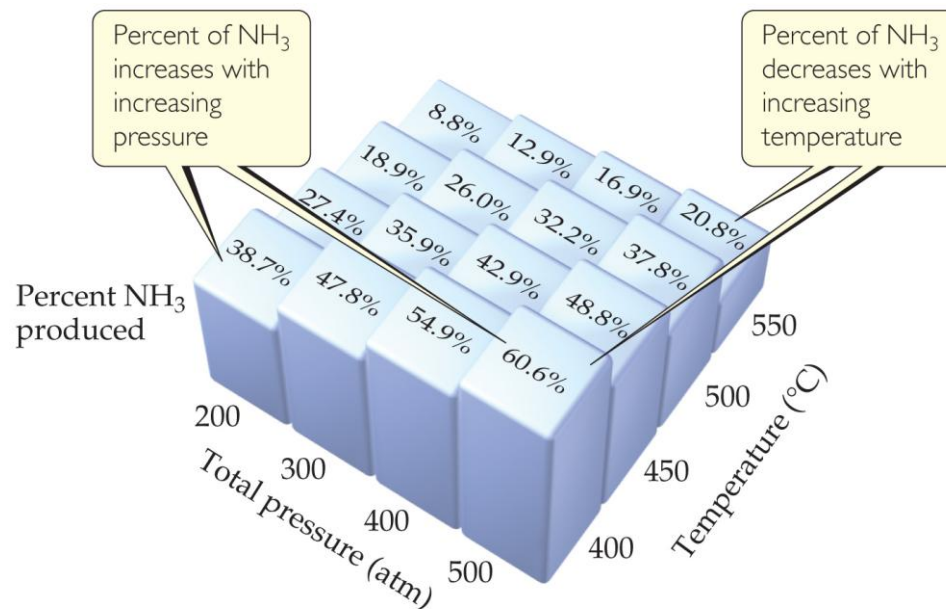
Le Châtelier's Principle

Le Châtelier's Principle

“If a system at equilibrium is disturbed by a change in temperature, pressure, or the concentration of one of the components, the system will shift its equilibrium position so as to counteract the effect of the disturbance.”

The Haber Process

The transformation of nitrogen and hydrogen into ammonia (NH_3) is of tremendous significance in agriculture, where ammonia-based fertilizers are of utmost importance.

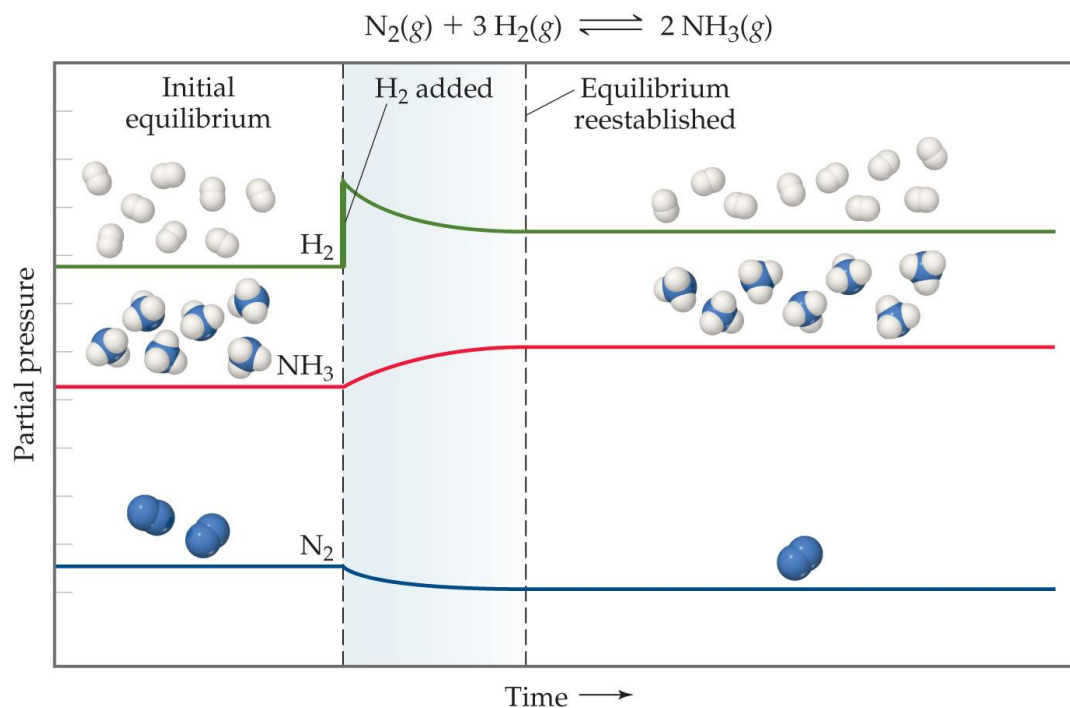


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The Haber Process

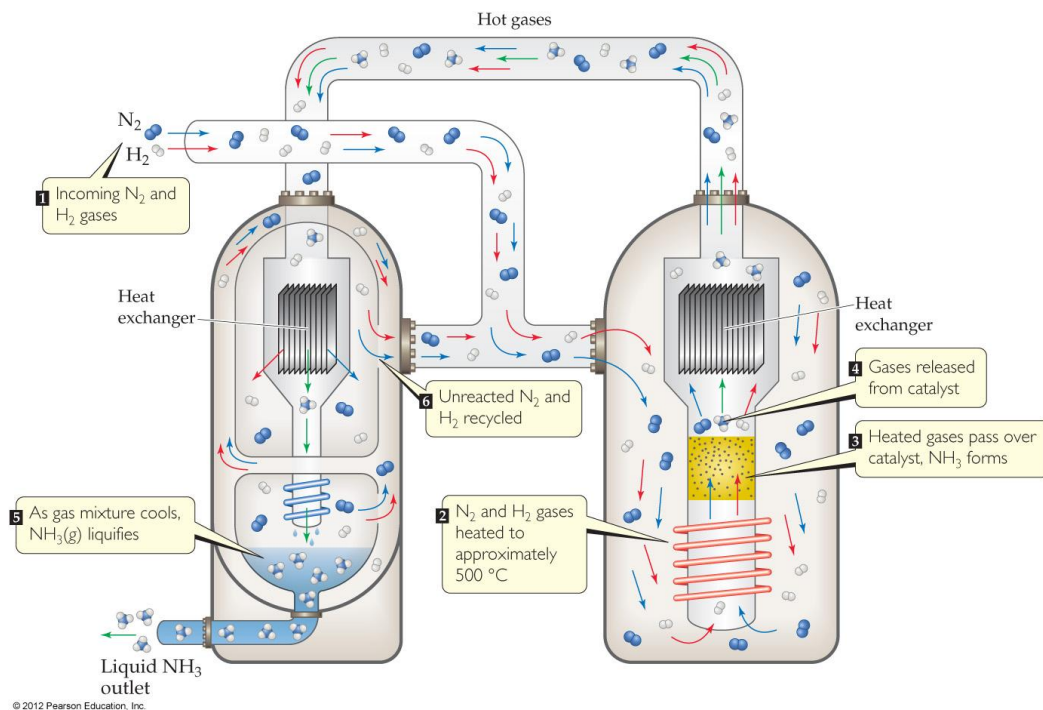


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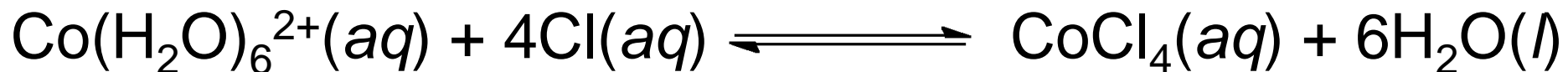
If H_2 is added to the system, N_2 will be consumed and the two reagents will form more NH_3 .

The Haber Process

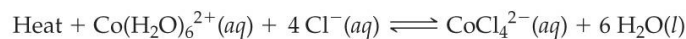
This apparatus helps push the equilibrium to the right by removing the ammonia (NH_3) from the system as a liquid.



Changes in Temperature

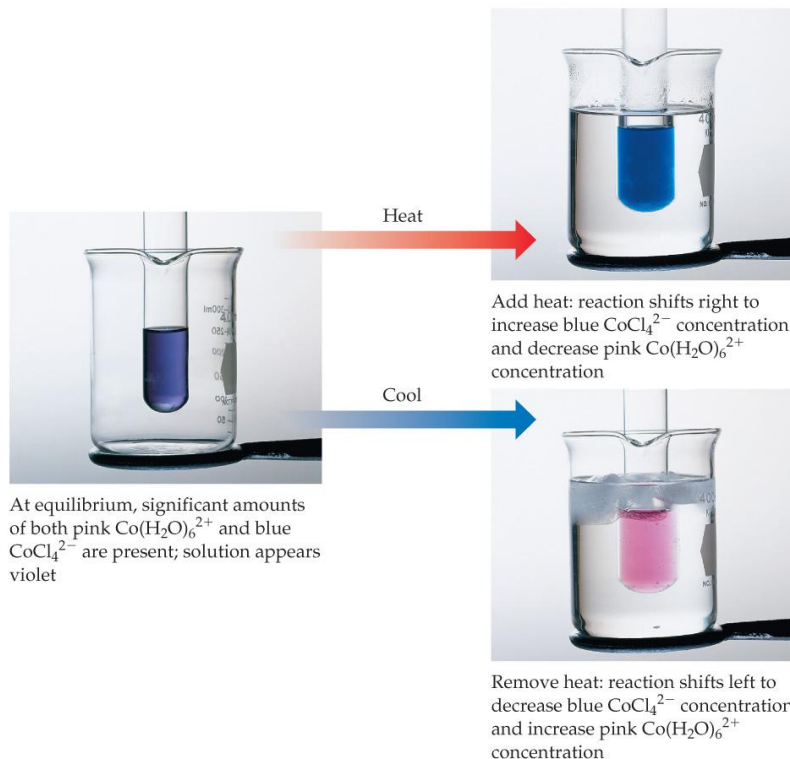


$\Delta H > 0$, endothermic reaction



Pink

Blue



Heat

Cool

At equilibrium, significant amounts of both pink $\text{Co}(\text{H}_2\text{O})_6^{2+}$ and blue CoCl_4^{2-} are present; solution appears violet

Add heat: reaction shifts right to increase blue CoCl_4^{2-} concentration and decrease pink $\text{Co}(\text{H}_2\text{O})_6^{2+}$ concentration

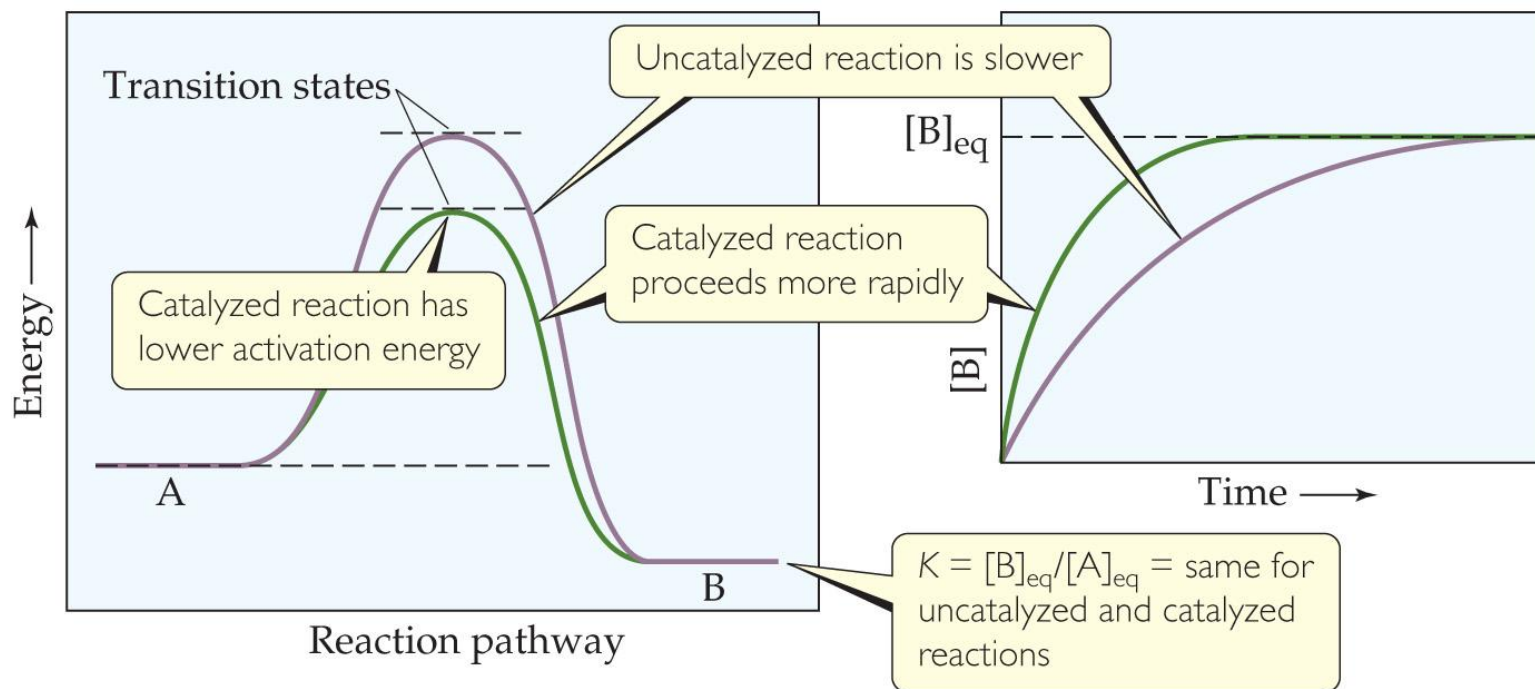
Remove heat: reaction shifts left to decrease blue CoCl_4^{2-} concentration and increase pink $\text{Co}(\text{H}_2\text{O})_6^{2+}$ concentration

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Catalysts

Catalysts

Catalysts increase the rate of both the forward *and* reverse reactions.



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Catalysts

When one uses a catalyst, equilibrium is achieved faster, but the equilibrium composition remains unaltered.

