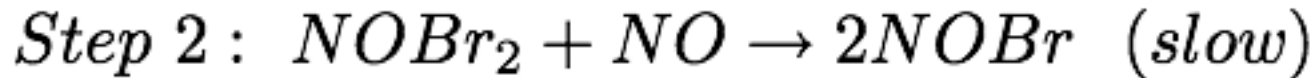
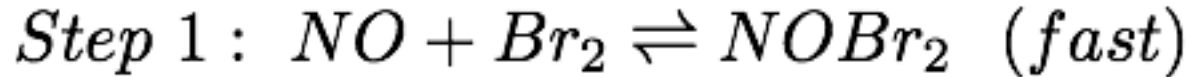


Chemical Equilibrium

Fast Initial Step



- Because $\text{Rate}_f = \text{Rate}_r$,

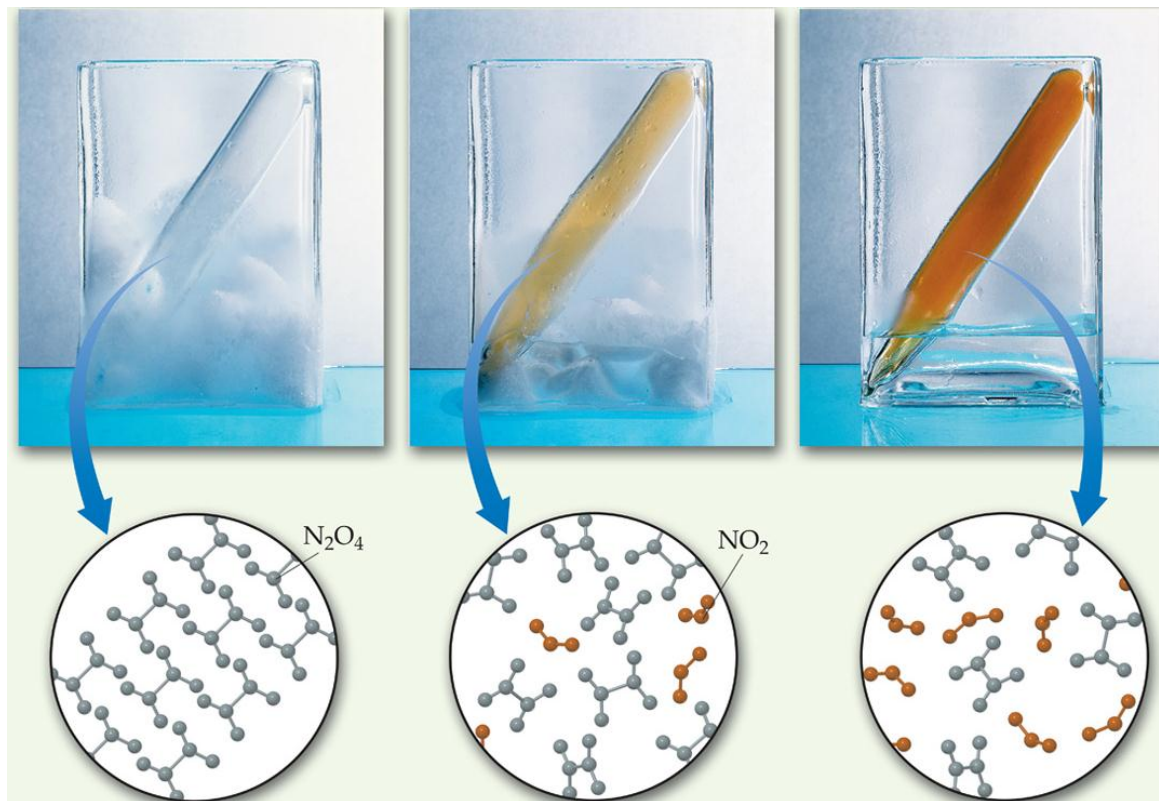
$$k_1 [\text{NO}] [\text{Br}_2] = k_{-1} [\text{NOBr}_2]$$

Solving for $[\text{NOBr}_2]$ gives us

$$\frac{k_1}{k_{-1}} [\text{NO}] [\text{Br}_2] = [\text{NOBr}_2]$$

Can also write as:
$$\frac{k_1}{k_{-1}} = \frac{[\text{NOBr}_2]}{[\text{NO}] [\text{Br}_2]}$$

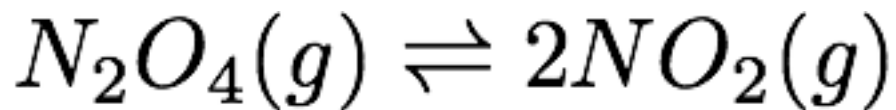
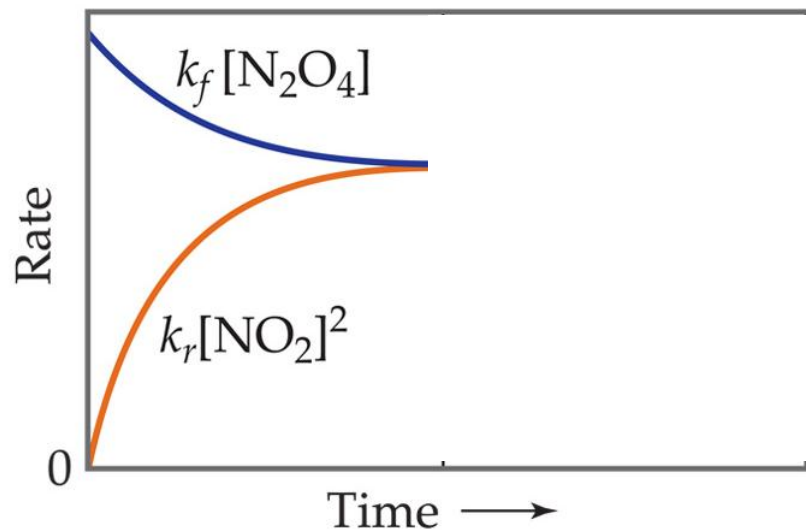
The Concept of Equilibrium



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

Equilibrium

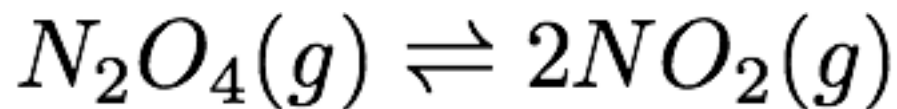
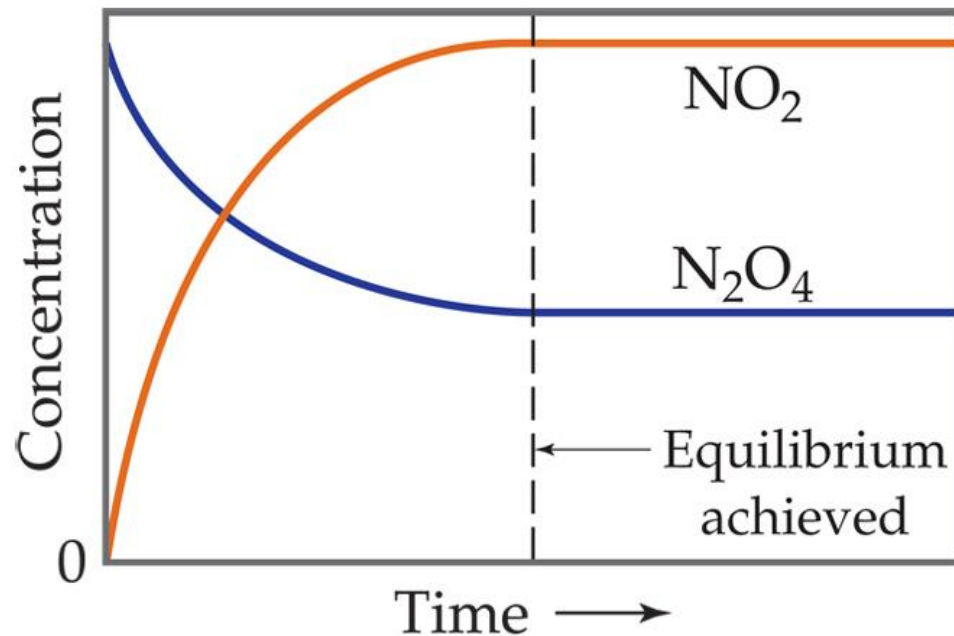
The Concept of Equilibrium



- 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.

A System at Equilibrium

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

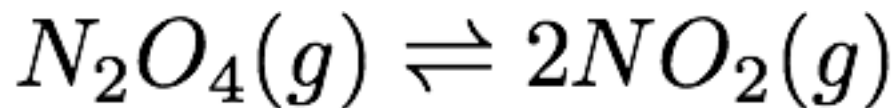
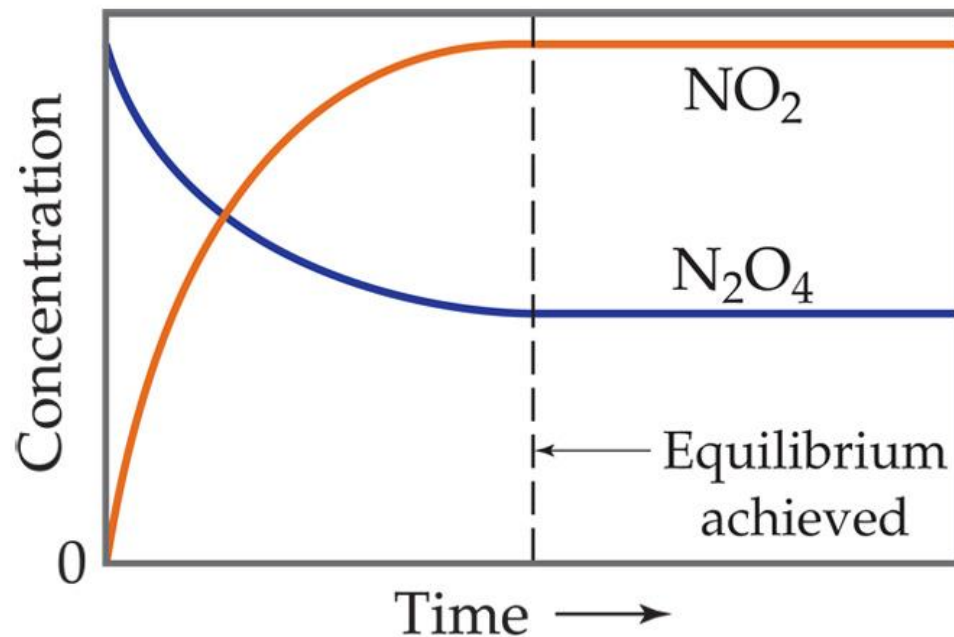
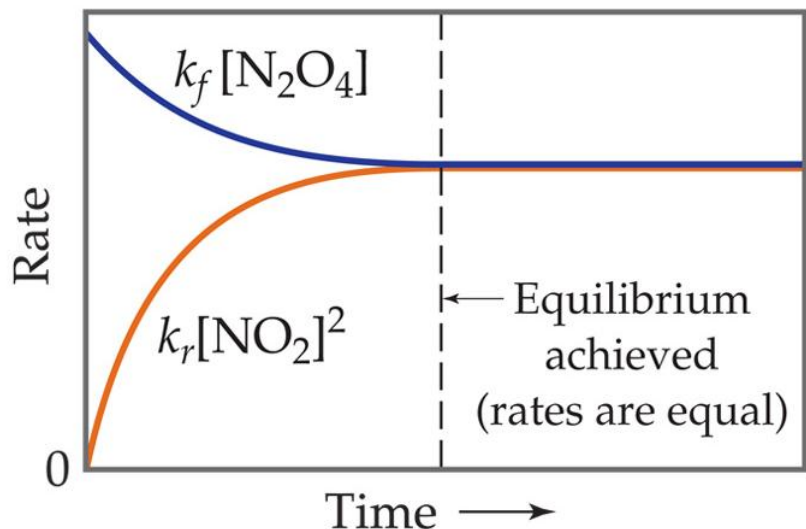


Equilibrium

A System at Equilibrium

Rates become equal

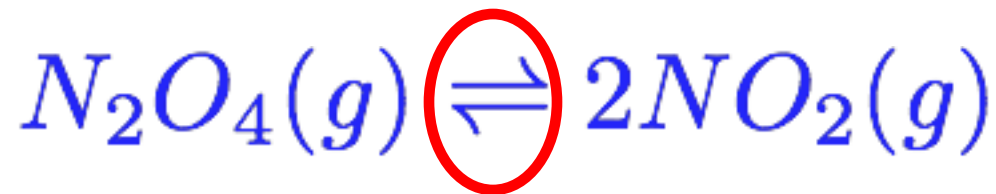
Concentrations become constant



Equilibrium

Depicting Equilibrium

In a system at equilibrium, both the forward and reverse reactions are running simultaneously. We write the chemical equation with a double arrow:



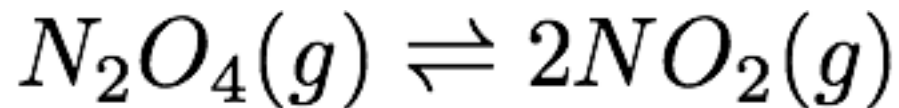


Equilibrium



The Equilibrium Constant

The Equilibrium Constant



Forward reaction:



Reverse reaction:



Rate law

$$rate = k_f [N_2O_4]$$

Rate Law

$$rate = k_r [NO_2]^2$$

The Equilibrium Constant

At equilibrium

$$rate_f = rate_b$$

$$k_f [N_2O_4] = k_r [NO_2]^2$$

Rearranging gives:

$$\frac{k_f}{k_r} = \frac{[NO_2]^2}{[N_2O_4]}$$

Equilibrium

The Equilibrium Constant

The ratio of the rate constants is a constant (as long as T is constant).

The expression becomes

$$K_{eq} = \frac{k_f}{k_r} = \frac{[NO_2]^2}{[N_2O_4]}$$

The Equilibrium Constant

To generalize, the reaction:



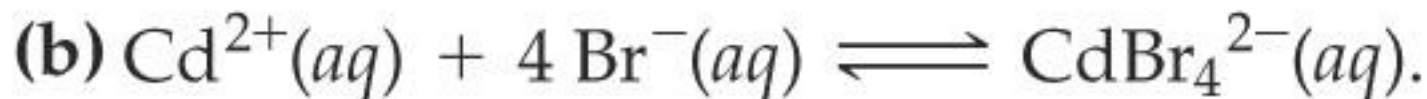
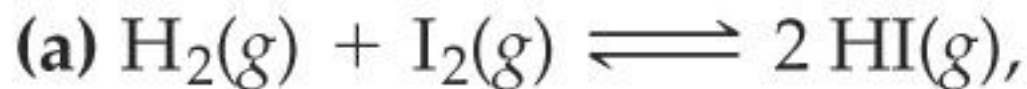
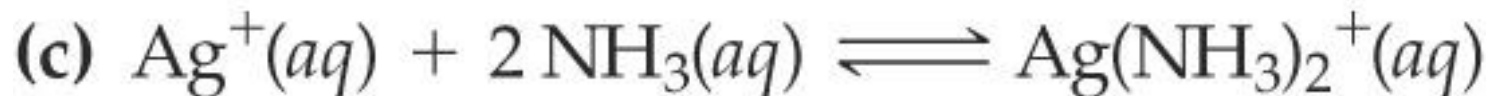
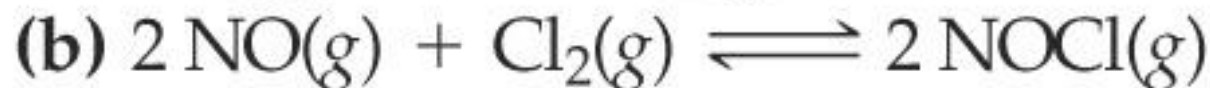
Has the equilibrium expression:

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

This expression is true even if you don't know the elementary reaction mechanism.

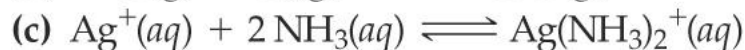
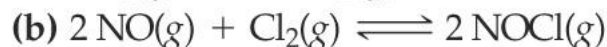
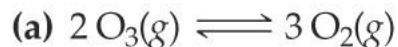
SAMPLE EXERCISE 15.1 Writing Equilibrium-Constant Expressions

Write the equilibrium expression for K_c for the following reactions:



SAMPLE EXERCISE 15.1 Writing Equilibrium-Constant Expressions

Write the equilibrium expression for K_c for the following reactions:



Solution

Analyze: We are given three equations and are asked to write an equilibrium-constant expression for each.

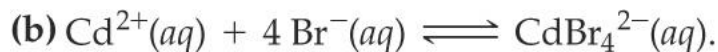
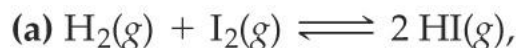
Plan: Using the law of mass action, we write each expression as a quotient having the product concentration terms in the numerator and the reactant concentration terms in the denominator. Each term is raised to the power of its coefficient in the balanced chemical equation.

Solve:

$$\text{(a) } K_c = \frac{[\text{O}_2]^3}{[\text{O}_3]^2}, \text{ (b) } K_c = \frac{[\text{NOCl}]^2}{[\text{NO}]^2[\text{Cl}_2]}, \text{ (c) } K_c = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2}$$

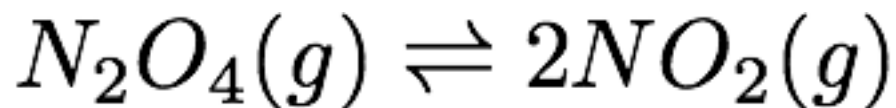
PRACTICE EXERCISE

Write the equilibrium-constant expression, K_c for



Answers: (a) $K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$; (b) $K_c = \frac{[\text{CdBr}_4^{2-}]}{[\text{Cd}^{2+}][\text{Br}^-]^4}$

Equilibrium Can Be Reached from Either Direction



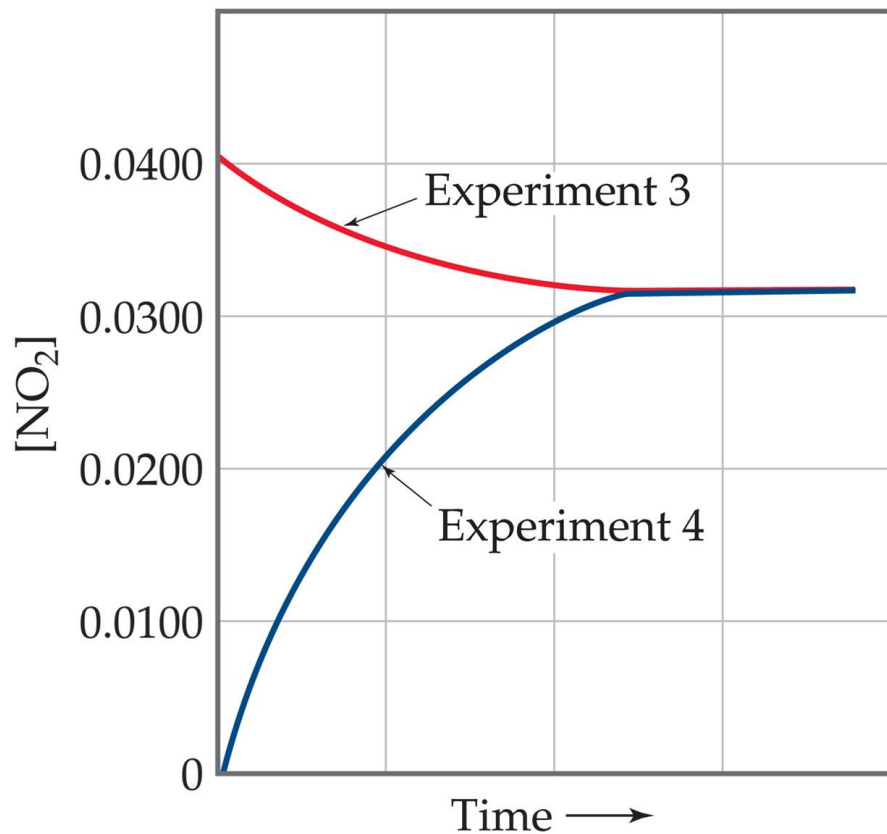
Experiment	Initial N_2O_4 Concentration (M)	Initial NO_2 Concentration (M)	Equilibrium N_2O_4 Concentration (M)	Equilibrium NO_2 Concentration (M)	K_c
1	0.0	0.0200	0.00140	0.0172	0.211
2	0.0	0.0300	0.00280	0.0243	0.211
3	0.0	0.0400	0.00452	0.0310	0.213
4	0.0200	0.0	0.00452	0.0310	0.213

K_c , the final ratio of $[NO_2]^2$ to $[N_2O_4]$, reaches a constant no matter what the initial concentrations of NO_2 and N_2O_4 are (with const T).

$$K_{eq} = \frac{[NO_2]^2}{[N_2O_4]}$$

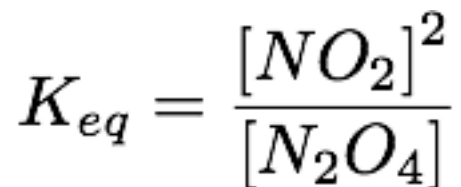
Equilibrium

Equilibrium Can Be Reached from Either Direction



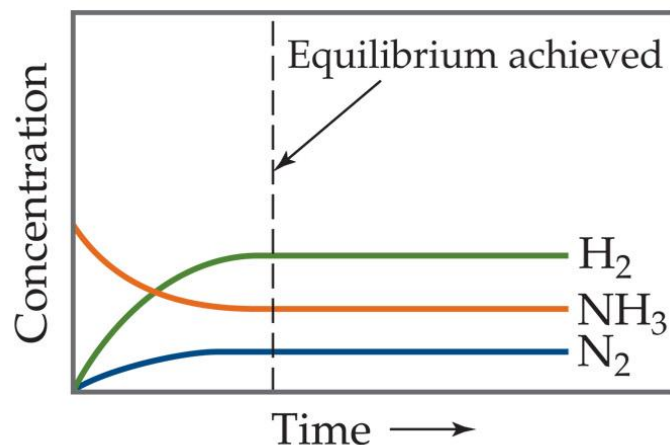
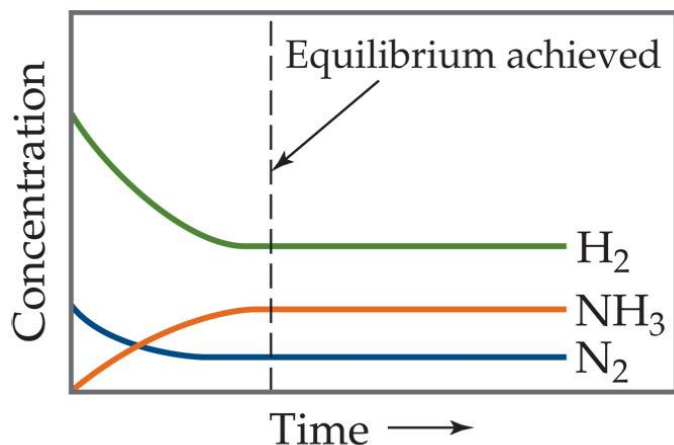
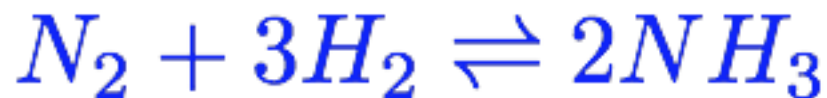
This graph shows data from the last two trials from the table.

QuickTime™ and
TIFF (LZW) decompre:
e needed to see this pi



Equilibrium

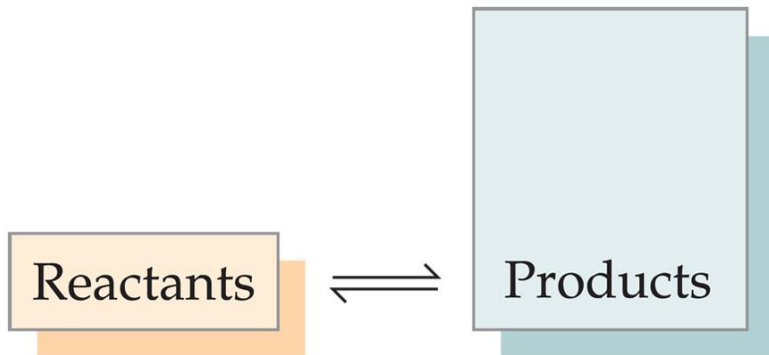
Equilibrium Can Be Reached from Either Direction



It does not 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 is the equilibrium expression?

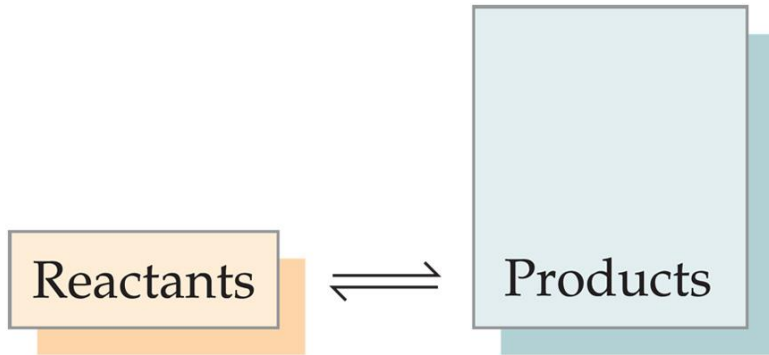
What Does the Value of K Mean?



(a) $K \gg 1$

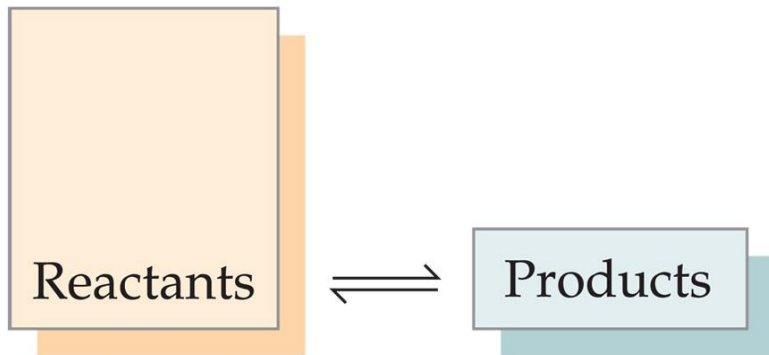
- If $K \gg 1$, the reaction is *product-favored*; product predominates at equilibrium.

What Does the Value of K Mean?



(a) $K \gg 1$

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

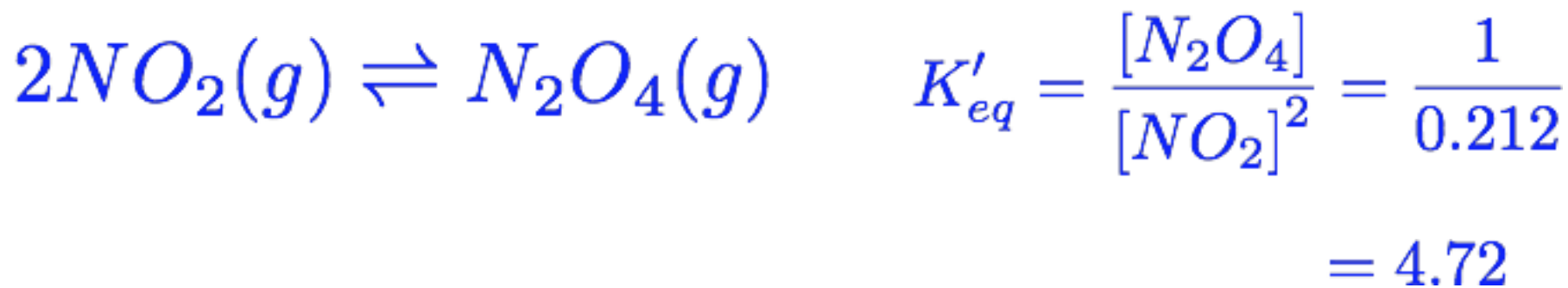
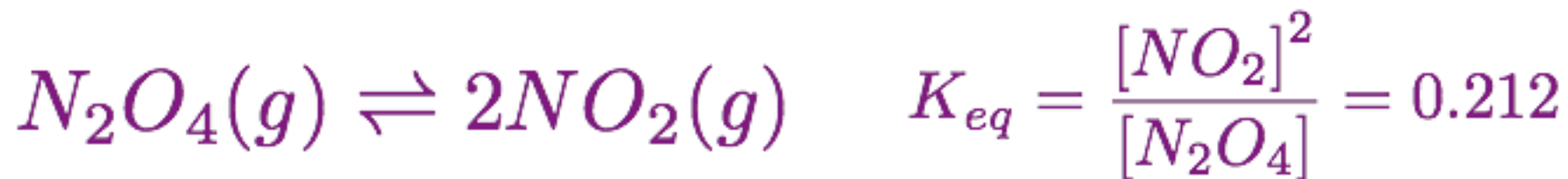


(b) $K \ll 1$

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

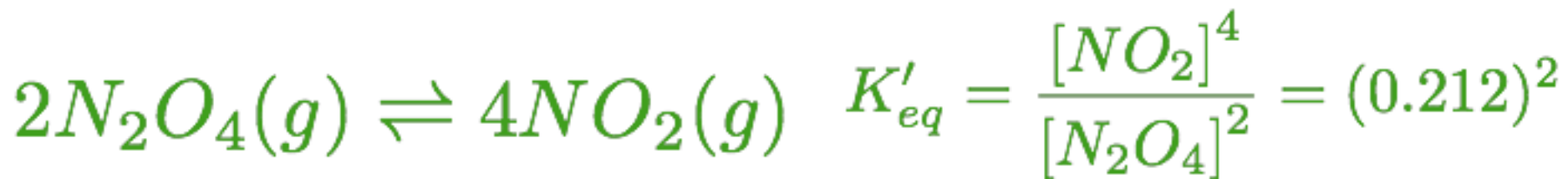
Manipulating Equilibrium Constants

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



Manipulating Equilibrium Constants

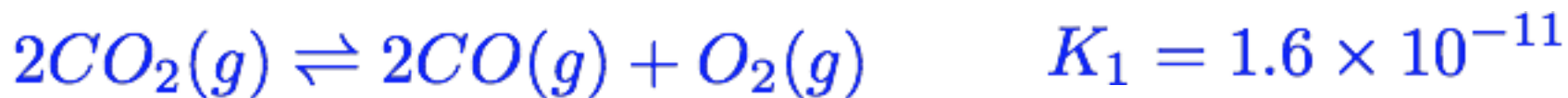
The equilibrium constant of a reaction that has been multiplied by a number is the equilibrium constant raised to a power that is equal to that number.



Manipulating Equilibrium Constants

The equilibrium constant for a net reaction made up of two or more steps can be found from the equilibrium constants for the individual steps.

At 1565 K we have these equilibrium constants:



ans=2.9

Equilibrium

The Equilibrium Constant

Because pressure is proportional to concentration for gases, the equilibrium expression can also be written in terms of partial pressures (instead of concentration):



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

Mixed versions are also used sometimes:

$$K_{mixed} = \frac{(P_C)^c [D]^d}{[A]^a (P_B)^b}$$

Relationship between K_c and K_p

- From the ideal gas law we know that

$$PV = nRT$$

$$P = \frac{n}{V}RT \quad = \text{Pressure in terms of concentration}$$

$$P_A = \frac{n_A}{V}RT = [A] RT$$

Relationship between K_c and K_p

Substituting $P=[A]RT$ 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:

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

Hint: 'products–reactants' and 'products over reactants' is a common theme in chemistry.

Heterogeneous Equilibrium

The Concentrations of Solids and Liquids Are Essentially Constant

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

$$\frac{\textit{density}}{\textit{molar mass}} = \frac{\textit{g/L}}{\textit{g/mol}} = \frac{\textit{mol}}{\textit{L}}$$

The Concentrations of Solids and Liquids Are Essentially Constant

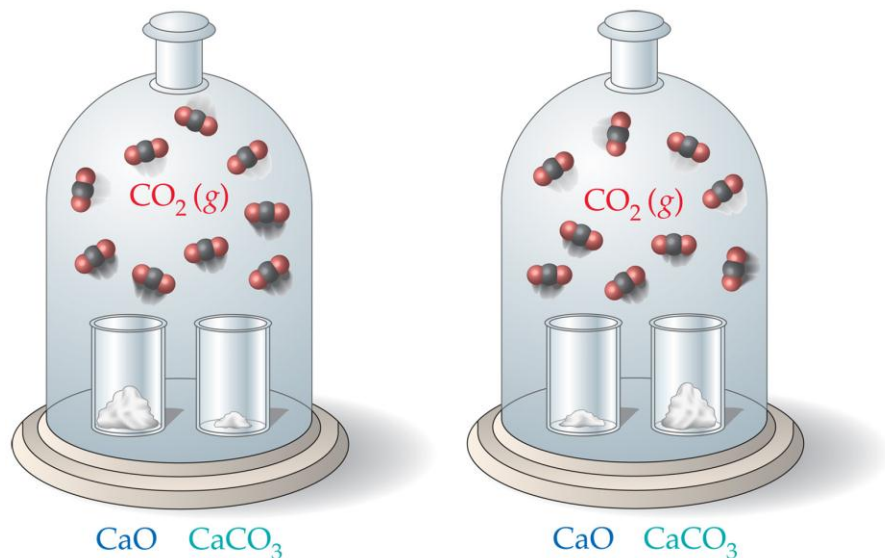
Therefore, the concentrations of solids and liquids do not appear in the equilibrium expression



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

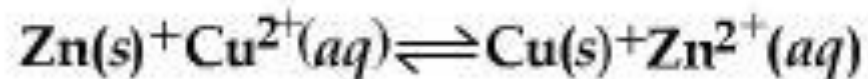
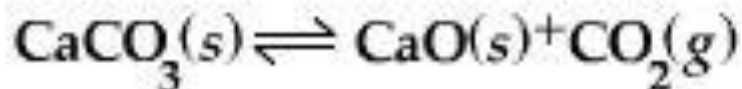
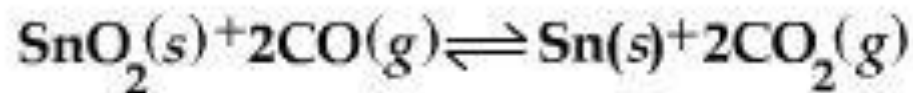


As long as some CaCO_3 or CaO remain in the system, the amount of CO_2 above the solid will remain the same.



Equilibrium

What Are the Equilibrium Expressions for These Equilibria?



The real scoop: units of equilibrium constants

Equilibrium constants are *really* defined in terms of **activity**, not concentration.

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \text{becomes:} \quad K_c = \frac{a_C^c a_D^d}{a_A^a a_B^b}$$

Activity is unitless, so K is unitless.

for pure liquids: $a = 1.0$

for pure solids: $a = 1.0$

for solutions: $a_A = [A] \gamma$

for dilute solutions: $\gamma = 1.0 \text{ M}^{-1}$