Chapter 15
Chemical Equilibrium

Equilibrium

The Concept of Equilibrium

$$N_2O_{4\ (g)} \rightleftharpoons 2\ NO_{2\ (g)}$$
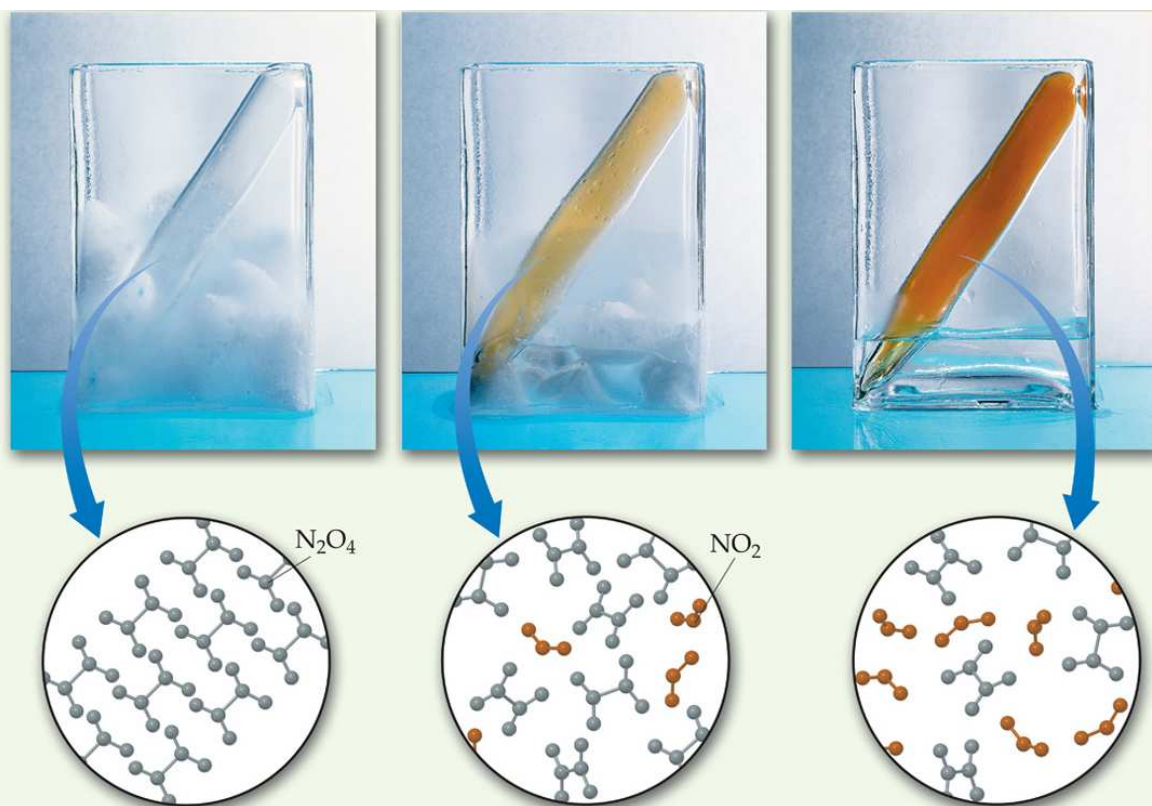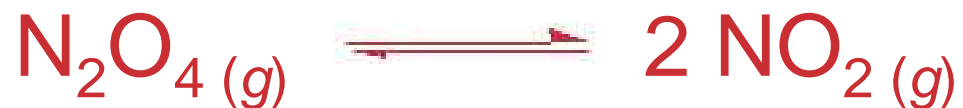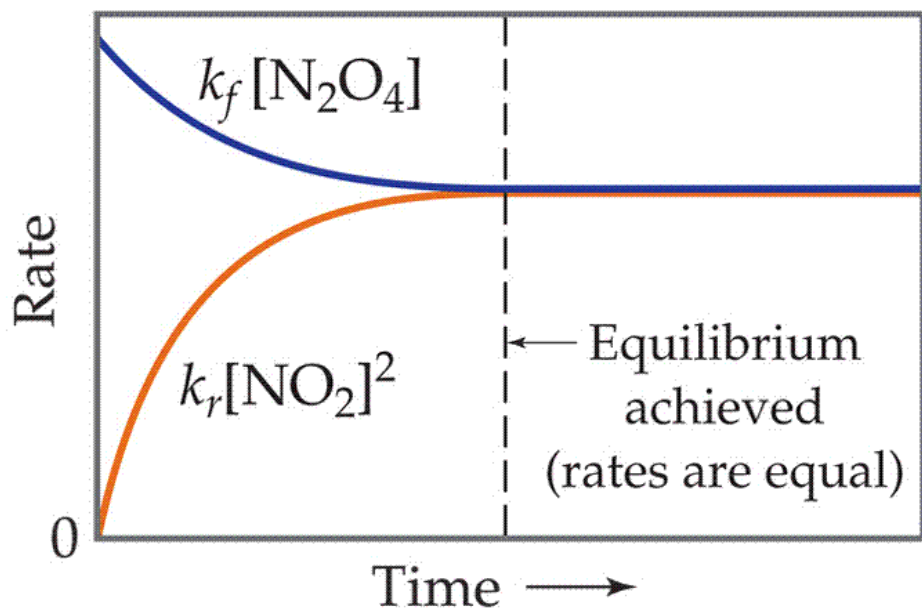

Chemical equilibrium occurs when a reaction and its reverse reaction proceed at the same rate.

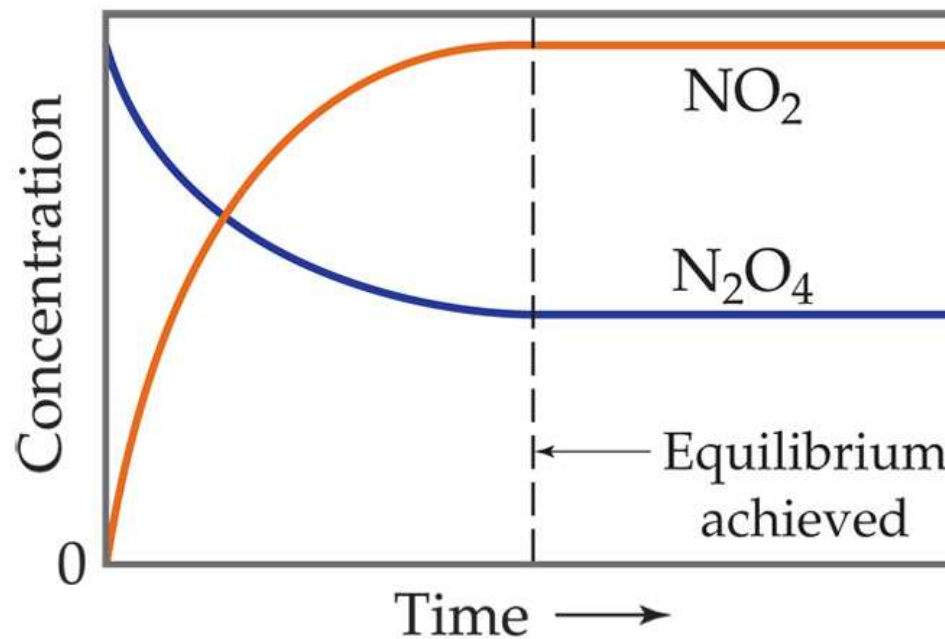Equilibrium

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.

Equilibrium

# A System at Equilibrium

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

Equilibrium

Depicting Equilibrium

In a system at equilibrium, both the forward and reverse reactions are being carried out; as a result, we write its equation with a double arrow

$$N_2O_{4\,(g)} \rightleftharpoons 2\,NO_{2\,(g)}$$

Equilibrium

The Equilibrium Constant

Equilibrium

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$
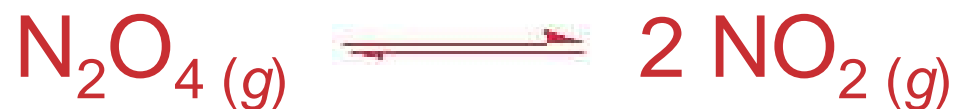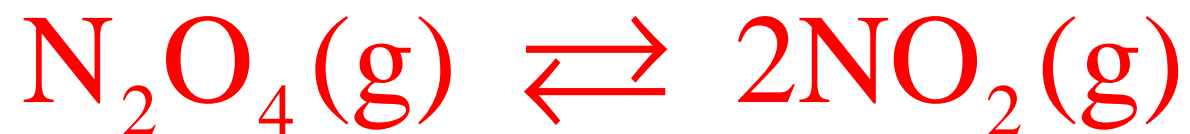
- Remember both forward and reverse reactions are *elementary reactions*

Equilibrium

The Equilibrium Constant

- Forward reaction:

$$N_2O_{4\,(g)} \longrightarrow 2\,NO_{2\,(g)}$$

- Rate law:

$$\text{Rate} = k_f\,[N_2O_4]$$

The Equilibrium Constant

- Reverse reaction:

$$2\ NO_{2\ (g)} \longrightarrow N_2O_{4\ (g)}$$

- Rate law:

Rate = k_r [NO_2]^2

Equilibrium

The Equilibrium Constant

- Therefore, at equilibrium

$$Rate_f = Rate_r$$

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

- Rewriting this, it becomes

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

Equilibrium

The Equilibrium Constant

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

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

Equilibrium

We learn following things from these reactions about equilibrium:

1. When a mixture of reactants and products is formed in which the concentration no longer change with time, it indicates that an equilibrium is reached.

2. For an equilibrium to occur neither reactant or product can escape.

3. At equilibrium the ratio of concentrations remains constant.

Equilibrium

The *Equilibrium Constant*

- To generalize this expression, consider the elementary reaction

$$aA + bB \rightleftharpoons cC + dD$$

- The **law** of **mass action** states that if the system is at equilibrium at a given temperature, then the following ratio is a constant

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

The ***equilibrium constant*** for this reaction would be Kc i.e. the constant when molarity of the solution is considered. This relationship is called equilibrium-constant expression.

Equilibrium

- The Law of Mass Action expresses the relationship between the concentrations of the reactants and products present at equilibrium.

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

Equilibrium

The **equilibrium constant** expression depends only on the stoichiometry of the reaction, not on its mechanism.
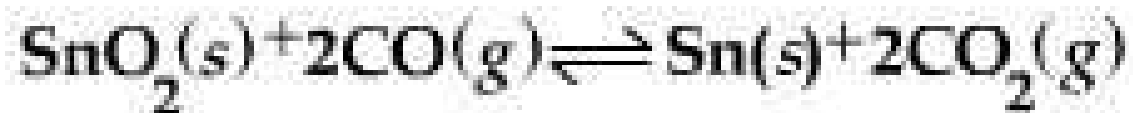
- And remember that the reactants go into the denominator.
- K_c is independent of the initial concentration of the reactants and products, but on the concentrations at the equilibrium.

Equilibrium

- The equilibrium constant is written without a unit.

Equilibrium

What Are the Equilibrium Expressions for These Equilibria?

$$SnO_2(s) + 2CO(g) \rightleftharpoons Sn(s) + 2CO_2(g)$$

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

$$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Cu(s) + Zn^{2+}(aq)$$

Equilibrium

K$_c$ is independent of the initial concentration of the reactants:

Experiment	Initial N$_2$O$_4$ Concentration (M)	Initial NO$_2$ Concentration (M)	Equilibrium N$_2$O$_4$ 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

N$_2$O$_{4\ (g)}$ $\longrightarrow$ 2 NO$_{2\ (g)}$

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

Calculate the Kc for yourself.

Equilibrium

The Equilibrium Constant

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

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

Equilibrium

- The numerical value of K_c is different than the numerical value of K_p. We must indicate the subscript c or p

Equilibrium

Relationship between K_c and K_p

- From the ideal gas law we know that

$$PV = nRT$$

- Rearranging it, we get

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

Equilibrium

$\dfrac{n}{V}$ is nothing but molarity (moles / liter)

So for substance A we can write

$$P = \dfrac{n_A}{V} RT$$

$$P = [A] \, RT$$

or $[A] = \dfrac{P}{RT}$

Relationship between K_c and K_p

$$aA + bB \rightleftharpoons cC + dD$$

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

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

$$K_c = \frac{\left(\dfrac{P_C}{RT}\right)^c \left(\dfrac{P_D}{RT}\right)^d}{\left(\dfrac{P_A}{RT}\right)^a \left(\dfrac{P_B}{RT}\right)^b} = \frac{P_C^c P_D^d \left(\dfrac{1}{RT}\right)^{c+d}}{P_A^a P_B^b \left(\dfrac{1}{RT}\right)^{a+b}} = \frac{P_C^c P_D^d}{P_A^a P_B^b}\left(\dfrac{1}{RT}\right)^{c+d-(a+b)}$$

$$= K_p\left(\frac{1}{RT}\right)^{c+d-(a+b)}$$

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

$$K_p = K_c(RT)^{c+d-(a+b)}$$

$$\Delta n = c + d - (a + b)$$

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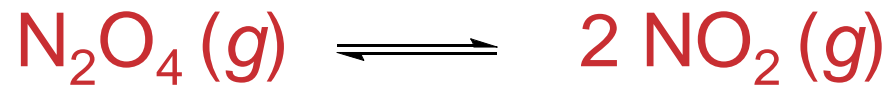
Equilibrium

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

$\Delta n =$ (moles of gaseous product) − (moles of gaseous reactant)

Equilibrium

$$N_2O_4\ (g) \rightleftharpoons 2\ NO_2\ (g)$$

Δn = (moles of gaseous product) − (moles of gaseous reactant)

$\quad$ = 2-1

$\quad$ = 1

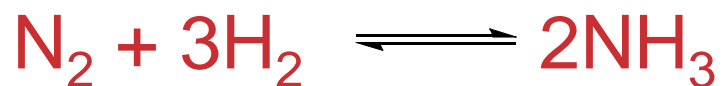$\qquad K_p = K_c\ (RT)^{\Delta n}$

So $\quad K_p = K_c\ (RT)$

If $\Delta n = 0$ i.e. same number of moles of gas appear in the reactant and the product then

$\qquad K_p = K_c$

As anything raised to 0 is 1

Equilibrium

In the synthesis of ammonia from nitrogen and hydrogen,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

$K_c = 9.60$ at 300° C. Calculate K_p

$\Delta n = 2-4 = -2$

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

$= 9.60 (.0821 \times 573)^{-2}$

$= \dfrac{9.60}{(0.0821 \times 573)^2} = 4.34 \times 10^{-3}$

Equilibrium

For the equilibrium

$$2SO_3 \ (g) \rightleftharpoons 2SO_2(g) \ + O_2(g)$$

$K_c = 4.08 \times 10^{-3}$ at 1000K. Calculate K_p

$$Kp = Kc \ (RT)^{\Delta n}$$

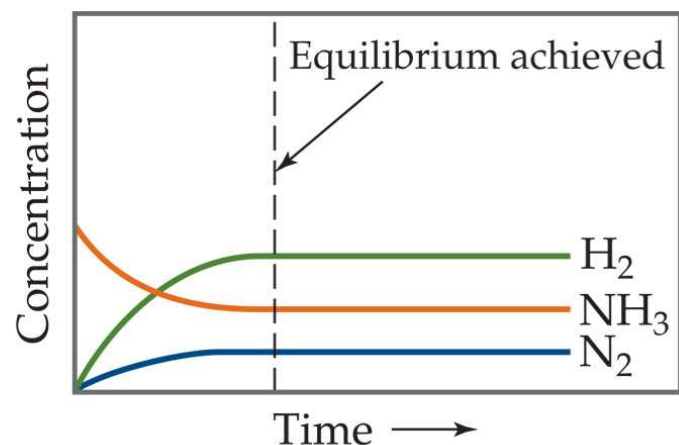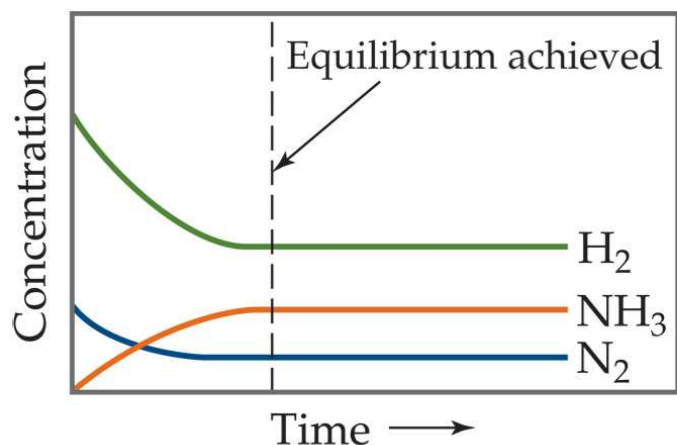Δn = (moles of gaseous product) − (moles of gaseous reactant)

= 3 − 2 = 1

$$Kp = 4.08 \times 10^{-3} \ (\ 0.0821 \times 1000)$$

$$= 0.33496 = 0.3$$

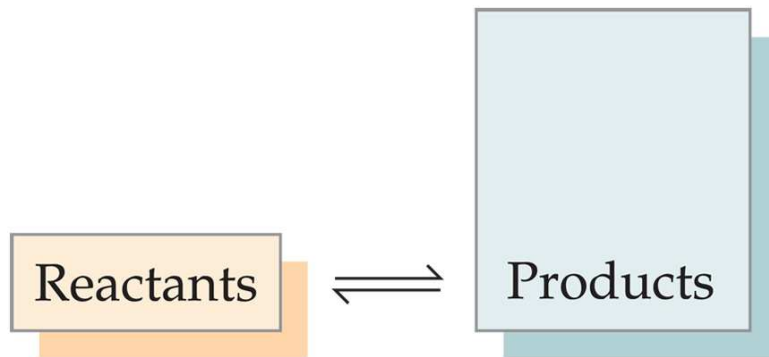Equilibrium

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.
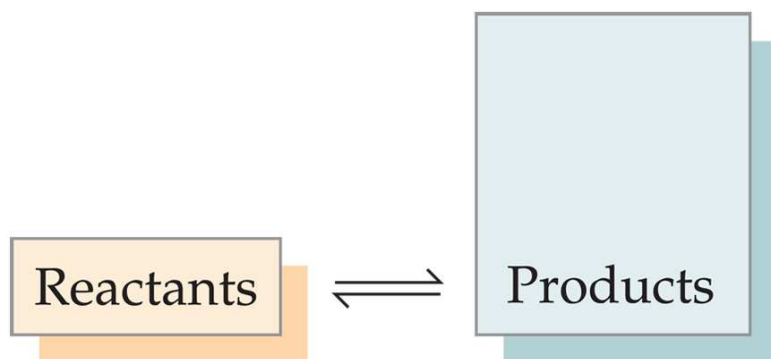
Equilibrium

What Does the Value of *K* Mean?

Reactants $\rightleftharpoons$ Products

(a) $K \gg 1$

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

Equilibrium

What Does the Value of *K* Mean?

Reactants $\rightleftharpoons$ Products

(a) $K \gg 1$

Reactants $\rightleftharpoons$ Products

(b) $K \ll 1$

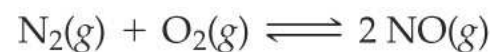- If $K \gg 1$, the reaction is *product-favored*; product predominates at equilibrium.
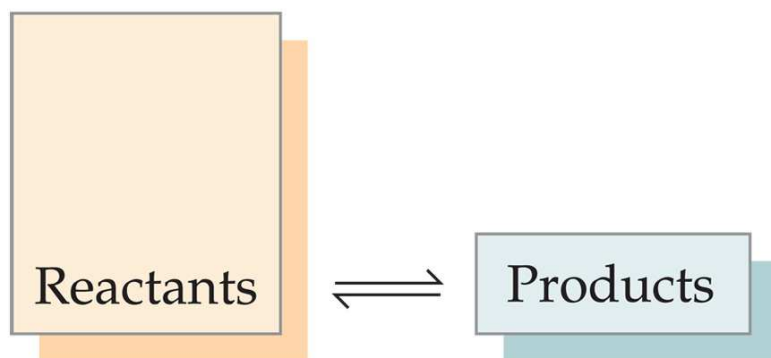
- If K << 1, the reaction is *reactant-favored*; reactant predominates at equilibrium.

Equilibrium

SAMPLE EXERCISE 15.3 Interpreting the Magnitude of an Equilibrium Constant

The reaction of N_2 with O_2 to form NO might be considered a means of "fixing" nitrogen:

$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$$

The value for the equilibrium constant for this reaction at 25°C is $K_c = 1 \times 10^{-30}$. Describe the feasibility of fixing nitrogen by forming NO at 25°C.

Equilibrium

SAMPLE EXERCISE 15.3 Interpreting the Magnitude of an Equilibrium Constant

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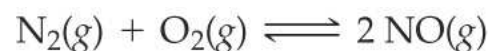
$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$$

The value for the equilibrium constant for this reaction at 25°C is $K_c = 1 \times 10^{-30}$. Describe the feasibility of fixing nitrogen by forming NO at 25°C.

Because *Kc* is so small, very little NO will form at 25°C. The equilibrium lies to the left, **favoring the reactants.** Consequently, this reaction is an extremely poor choice for nitrogen fixation, at least at 25°C.

Equilibrium

PRACTICE EXERCISE

For the reaction $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$, $K_p = 794$ at 298 K and $K_p = 54$ at 700 K. Is the formation of HI favored more at the higher or lower temperature?

Equilibrium

PRACTICE EXERCISE

For the reaction $H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$, $K_p = 794$ at 298 K and $K_p = 54$ at 700 K. Is the formation of HI favored more at the higher or lower temperature?
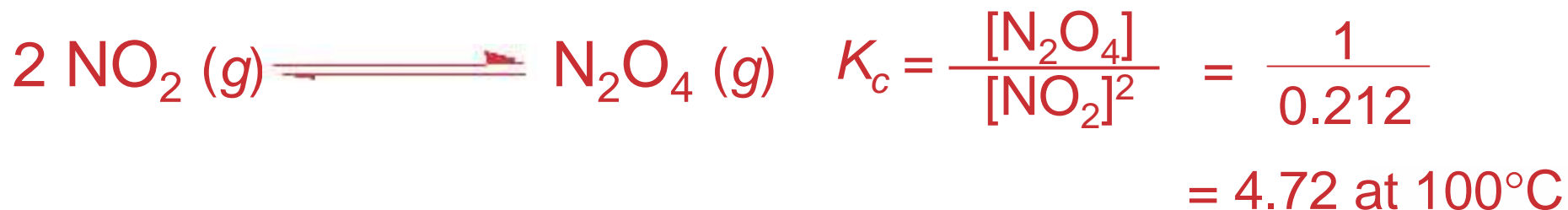
Answer: The formation of product, HI, is favored at the lower temperature because *Kp* is larger at the lower temperature.

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.

$N_2O_4 \ (g) \rightleftharpoons 2 \ NO_2 \ (g)$ $\quad K_c = \dfrac{[NO_2]^2}{[N_2O_4]} = 0.212$ at $100°C$

$2 \ NO_2 \ (g) \rightleftharpoons N_2O_4 \ (g)$ $\quad K_c = \dfrac{[N_2O_4]}{[NO_2]^2} = \dfrac{1}{0.212}$

$= 4.72$ at $100°C$

Equilibrium

- With this information the direction of the reaction needs to be specified when the equilibrium constant is given.

- Also the temperature too needs to be given as the constant depends at the temperature.

Equilibrium

SAMPLE EXERCISE 15.4 Evaluating an Equilibrium Constant When an Equation Is Reversed

(a) Write the equilibrium-constant expression for K_c for the following reaction: $2\ NO(g) \rightleftharpoons N_2(g) + O_2(g)$

(b) Using information in exercise 15.3, determine the value of this equilibrium constant at 25°C.
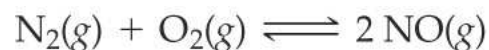
Equilibrium

SAMPLE EXERCISE 15.4 Evaluating an Equilibrium Constant When an Equation Is Reversed

(a) Write the equilibrium-constant expression for K_c for the following reaction: $2 \, NO(g) \rightleftharpoons N_2(g) + O_2(g)$

(b) With the information given in sample exercise 15.3, determine the value of this equilibrium constant at 25°C.

SAMPLE EXERCISE 15.3 Interpreting the Magnitude of an Equilibrium Constant

The reaction of N_2 with O_2 to form NO might be considered a means of "fixing" nitrogen:

$$N_2(g) + O_2(g) \rightleftharpoons 2 \, NO(g)$$

The value for the equilibrium constant for this reaction at 25°C is $K_c = 1 \times 10^{-30}$. Describe the feasibility of fixing nitrogen by forming NO at 25°C.

a. Writing products over reactants, we have

$$K_c = \frac{[N_2][O_2]}{[NO]^2}$$

b.

$$K_c = \frac{[N_2][O_2]}{[NO]^2} = \frac{1}{1 \times 10^{-30}} = 1 \times 10^{30}$$

Equilibrium

PRACTICE EXERCISE

For the formation of NH_3 from N_2 and H_2, $N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)$, $K_p = 4.34 \times 10^{-3}$ at 300°C. What is the value of K_p for the reverse reaction?

- **Answer:** 2.30×10^2

Equilibrium

Manipulating Equilibrium Constants

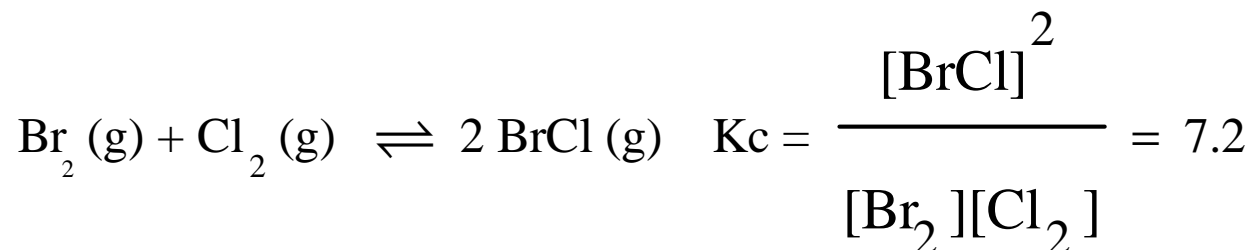The equilibrium constant of a reaction that has been multiplied by a number is the equilibrium constant raised to a power that is equal to that number.

$$N_2O_4\ (g) \rightleftharpoons 2\ NO_2\ (g) \quad K_c = \frac{[NO_2]^2}{[N_2O_4]} = 0.212 \text{ at } 100°C$$

$$2\ N_2O_4\ (g) \rightleftharpoons 4\ NO_2\ (g) \quad K_c = \frac{[NO_2]^4}{[N_2O_4]^2} = (0.212)^2 \text{ at } 100°C$$
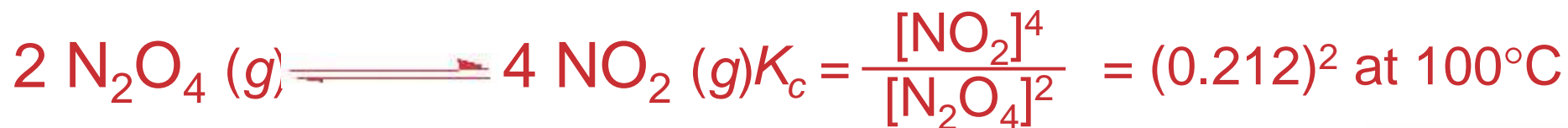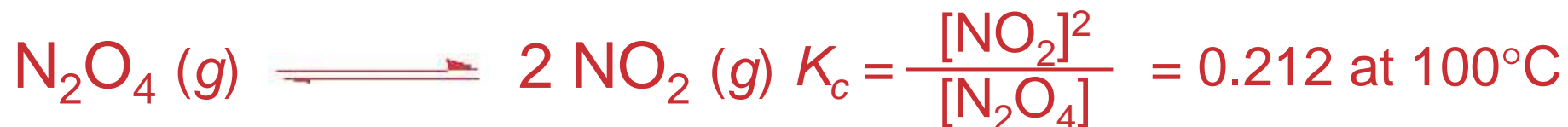
Equilibrium

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.

Equilibrium

$$2NOBr(g) \rightleftharpoons 2NO + Br_2 (g) \qquad K_c = \frac{[NO]^2 [Br_2]}{[NOBr]^2} = 0.014$$

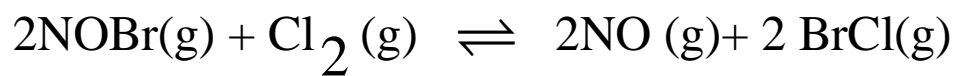$$Br_2 (g) + Cl_2 (g) \rightleftharpoons 2 BrCl (g) \qquad K_c = \frac{[BrCl]^2}{[Br_2][Cl_2]} = 7.2$$
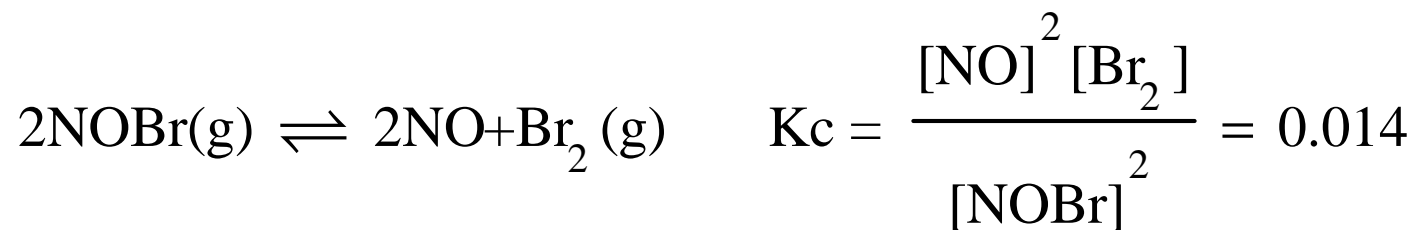
The net sum of these two reactions is

$$2NOBr(g) + Cl_2 (g) \rightleftharpoons 2NO (g) + 2 BrCl(g)$$

$$K_c = \frac{[NO]^2 [BrCl]^2}{[NOBr]^2 [Cl_2]} = \frac{[NO]^2 [Br_2]}{[NOBr]^2} X \frac{[BrCl]^2}{[Br_2][Cl_2]}$$
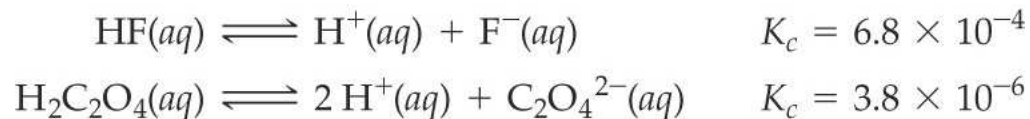
$$= 0.014 \text{ x } 7.2 = 0.10$$

Equilibrium

- What is the difference between this and what happens to ΔH ?
- For ΔH the values are added, here they are multiplied.

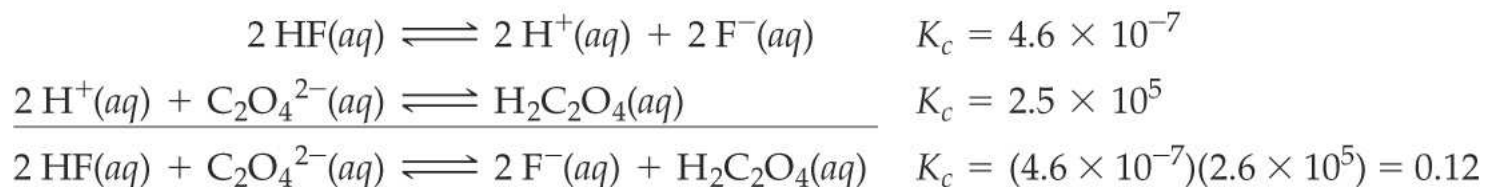Equilibrium

SAMPLE EXERCISE 15.5 Combining Equilibrium Expressions

Given the following information,

$$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq) \qquad\qquad K_c = 6.8 \times 10^{-4}$$

$$H_2C_2O_4(aq) \rightleftharpoons 2\,H^+(aq) + C_2O_4{}^{2-}(aq) \qquad K_c = 3.8 \times 10^{-6}$$

determine the value of K_c for the reaction

$$2\,HF(aq) + C_2O_4{}^{2-}(aq) \rightleftharpoons 2\,F^-(aq) + H_2C_2O_4(aq)$$

Now we have two equations that sum to give the net equation, and we can multiply the individual K_c values to get the desired equilibrium constant.

$$2\,HF(aq) \rightleftharpoons 2\,H^+(aq) + 2\,F^-(aq) \qquad\qquad K_c = 4.6 \times 10^{-7}$$

$$2\,H^+(aq) + C_2O_4{}^{2-}(aq) \rightleftharpoons H_2C_2O_4(aq) \qquad\qquad K_c = 2.5 \times 10^5$$

$$\overline{2\,HF(aq) + C_2O_4{}^{2-}(aq) \rightleftharpoons 2\,F^-(aq) + H_2C_2O_4(aq)} \quad K_c = (4.6 \times 10^{-7})(2.6 \times 10^5) = 0.12$$

Equilibrium

PRACTICE EXERCISE

Given that, at 700 K, $K_p = 54.0$ for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$ and $K_p = 1.04 \times 10^{-4}$ for the reaction $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$, determine the value of K_p for the reaction $2\,NH_3(g) + 3\,I_2(g) \rightleftharpoons 6\,HI(g) + N_2(g)$ at 700 K.

Answer: $\dfrac{(54.0)^3}{1.04 \times 10^{-4}} = 1.51 \times 10^9$

Equilibrium

Heterogeneous Equilibrium

- The example of N_2 and H_2 to give NH_3 is a homogeneous equilibria.
- There can also be heterogeneous equilibria when the substances in the equilibrium are in different phases.

an example is the equilibrium that gets established when a substance is dissolves in water to give a saturated solution.

Example:

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-$$

When a solid or liquids is encountered in a reaction its concentration is not mentioned as the concentrations of solids and liquids are essentially constant

Can you understand why?

The concentration of a solid and liquids can be derived in terms of moles per unit volume but it is not required in equilibrium constant expressions.

Remember we are referring to liquids *not* dissolved substances.

Equilibrium

The Concentrations of Solids and Liquids Are Essentially Constant

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

$$PbCl_2 \ (s) \ \rightleftharpoons \ Pb^{2+} \ (aq) + 2 \ Cl^-(aq)$$

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

Equilibrium

$$CaCO_3\ (s) \rightleftharpoons CO_2\ (g) + CaO\ (s)$$

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

The equilibrium expression for the reaction is

$$K_p = P_{CO_2}$$

and

$$K_c = [CO_2]$$

- When a solvent is involved in a equilibrium as a reactant or a product its concentration is also excluded from the equilibrium constant expression.

- But the concentration of the reactant and product has to be very low.

$$H_2O(l) + CO_3^{2-} \rightleftharpoons OH^-(aq) + HCO^{3-}(aq)$$

- The equilibrium expression will be:

$$Kc = \frac{[OH^-][HCO_3^-]}{[CO_3^{2-}]}$$

Equilibrium

- When added to Fe3O4(*s*) in a closed container, which one of the following substances—$H_2(g)$, $H_2O(g)$, $O_2(g)$ —will allow equilibrium to be established in the reaction in the reaction

$$3Fe(s)+4H_2O(g) \rightleftharpoons Fe_3O_4(s)+4H_2$$

SAMPLE EXERCISE 15.6 **Writing Equilibrium-Constant Expressions**

(a) $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(l)$
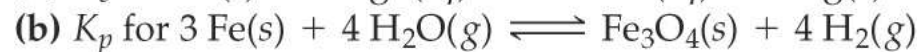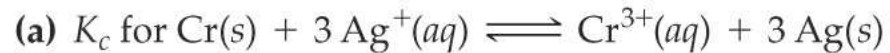(b) $SnO_2(s) + 2\,CO(g) \rightleftharpoons Sn(s) + 2\,CO_2(g)$
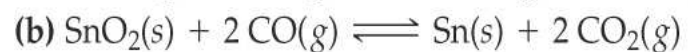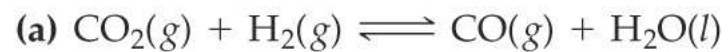
- Write the equilibrium-constant expression for K_c for each of the above

Equilibrium

PRACTICE EXERCISE

Write the following equilibrium-constant expressions:

(a) K_c for $Cr(s) + 3 Ag^+(aq) \rightleftharpoons Cr^{3+}(aq) + 3 Ag(s)$

(b) K_p for $3 Fe(s) + 4 H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4 H_2(g)$

Remember only solids and liquids are not considered. The gases are taken into account.

Answers: **(a)** $K_c = \dfrac{[Cr^{3+}]}{[Ag^+]^3}$, **(b)** $K_p = \dfrac{(P_{H_2})^4}{(P_{H_2O})^4}$
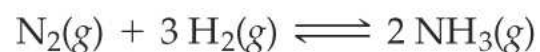
Equilibrium

Equilibrium Calculations

Equilibrium

- ## Direct calculations:

SAMPLE EXERCISE 15.8 **Calculating *K* When All Equilibrium Concentrations Are Known**

A mixture of hydrogen and nitrogen in a reaction vessel is allowed to attain equilibrium at 472°C. The equilibrium mixture of gases was analyzed and found to contain 7.38 atm H_2, 2.46 atm N_2, and 0.166 atm NH_3. From these data, calculate the equilibrium constant K_p for the reaction

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

$$K_p = \frac{(P_{NH_3})^2}{P_{N_2}(P_{H_2})^3} = \frac{(0.166)^2}{(2.46)(7.38)^3} = 2.79 \times 10^{-5}$$

Equilibrium

When the equilibrium concentrations are not known:

- We do not need to know the equilibrium concentration of all the species.
- We can use the stoichiometry of the reaction to deduce the equilibrium concentrations of the unknown ones.

Equilibrium

1. Tabulate all the known initial and equilibriums of all the species.

2. Calculate the change of concentrations for the species for which the initial and equilibrium concentrations are known.

3. Use the stoichiometry of the reaction to calculate the changes in concentration for all other species.

4. Calculate the K_c.

Equilibrium

Equilibrium Calculations

Here is an example

A closed system initially containing
1.000×10^{-3} M H_2 and 2.000×10^{-3} M I_2
At $448°C$ is allowed to reach equilibrium.

Analysis of the equilibrium mixture shows that the
concentration of HI is 1.87×10^{-3} M.
Calculate K_c at $448°C$ for the reaction taking place, which is

$$H_{2\,(g)} + I_{2\,(g)} \rightleftharpoons 2\,HI_{(g)}$$

Equilibrium

What Do We Know?

	$[H_2]$, *M*	$[I_2]$, *M*	$[HI]$, *M*
Initially	1.000×10^{-3}	2.000×10^{-3}	0
Change			
At equilibrium			1.87×10^{-3}

$$H_{2\,(g)} + I_{2\,(g)} \rightleftharpoons 2\,HI_{(g)}$$

Equilibrium

[HI] Increases by 1.87×10^{-3} M

	[H_2], M	[I_2], M	[HI], M
Initially	1.000×10^{-3}	2.000×10^{-3}	0
Change			$+1.87 \times 10^{-3}$
At equilibrium			1.87×10^{-3}

$$H_{2\,(g)} + I_{2\,(g)} \rightleftharpoons 2\,HI_{(g)}$$

Equilibrium

Stoichiometry tells us $[H_2]$ and $[I_2]$ decrease by half as much

	$[H_2]$, M	$[I_2]$, M	$[HI]$, 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}

$$H_{2\,(g)} + I_{2\,(g)} \rightleftharpoons 2\,HI_{(g)}$$

Equilibrium

We can now calculate the equilibrium concentrations of all three compounds…

	$[H_2]$, *M*	$[I_2]$, *M*	$[HI]$, *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}

$$H_{2\,(g)} + I_{2\,(g)} \rightleftharpoons 2\,HI_{(g)}$$

Equilibrium

...and, therefore, the equilibrium constant

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

$$= \frac{(1.87 \times 10^{-3})^2}{(6.5 \times 10^{-5})(1.065 \times 10^{-3})}$$

$$= 51$$

Equilibrium

Applications for Equilibrium Constants

    a. Predict the direction of the reaction

    b. To calculate equilibrium concentrations.

Equilibrium

Suppose we take a mixture of 2.00 mol of H_2, 1.00 mol of N_2 and 2.00 mole of NH_3 in a 1 L container at $472^{\circ}C$.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

The concentration ratio at start of the reaction

$$\frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(2.00M)^2}{(1.00M)(2.00M)^3} = 0.500$$

This ratio is called the reaction quotient Q

when Kc is 0.105

To reach the equilibrium Q, 0.500 will have to decrease to 0.105.

This can happen only if the concentration of NH_3 decreases and the concentration d H_2 and N_2 increases.

So the reaction is going to proceed from right to left.

Equilibrium

The Reaction Quotient (Q)

- To calculate Q, one substitutes the initial concentrations on reactants and products into the equilibrium expression.

- Q gives the same ratio the equilibrium expression gives, but for a system that is *not* at equilibrium.
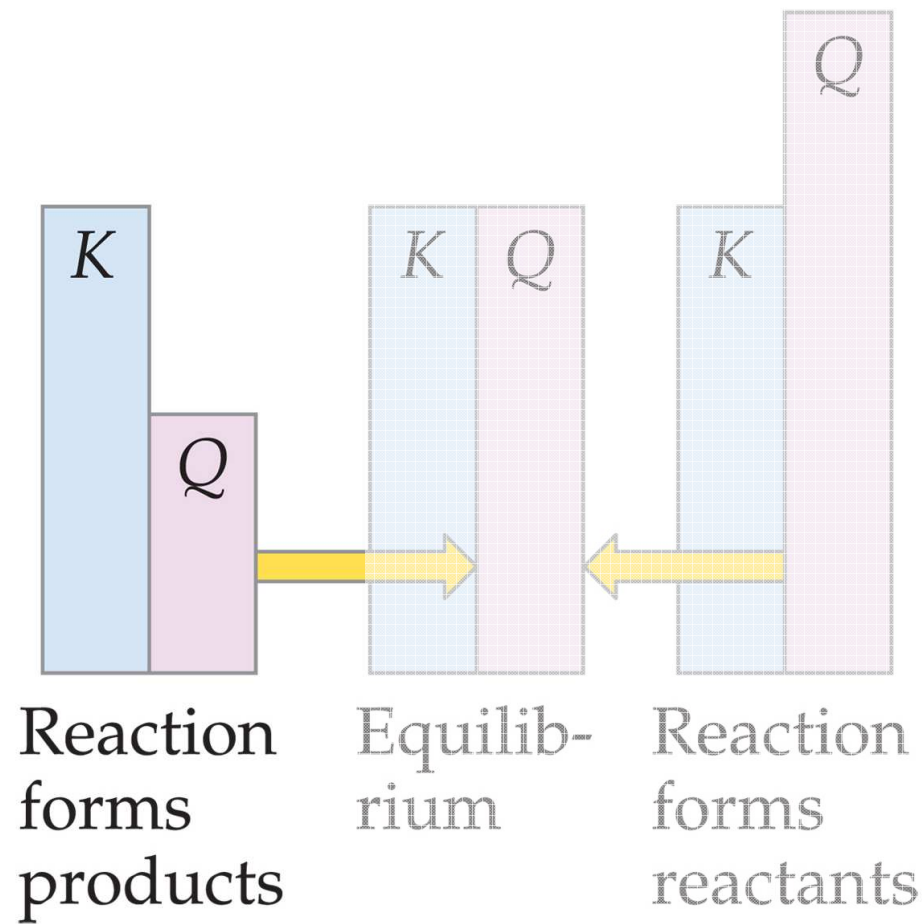
Equilibrium

If *Q* = *K*,

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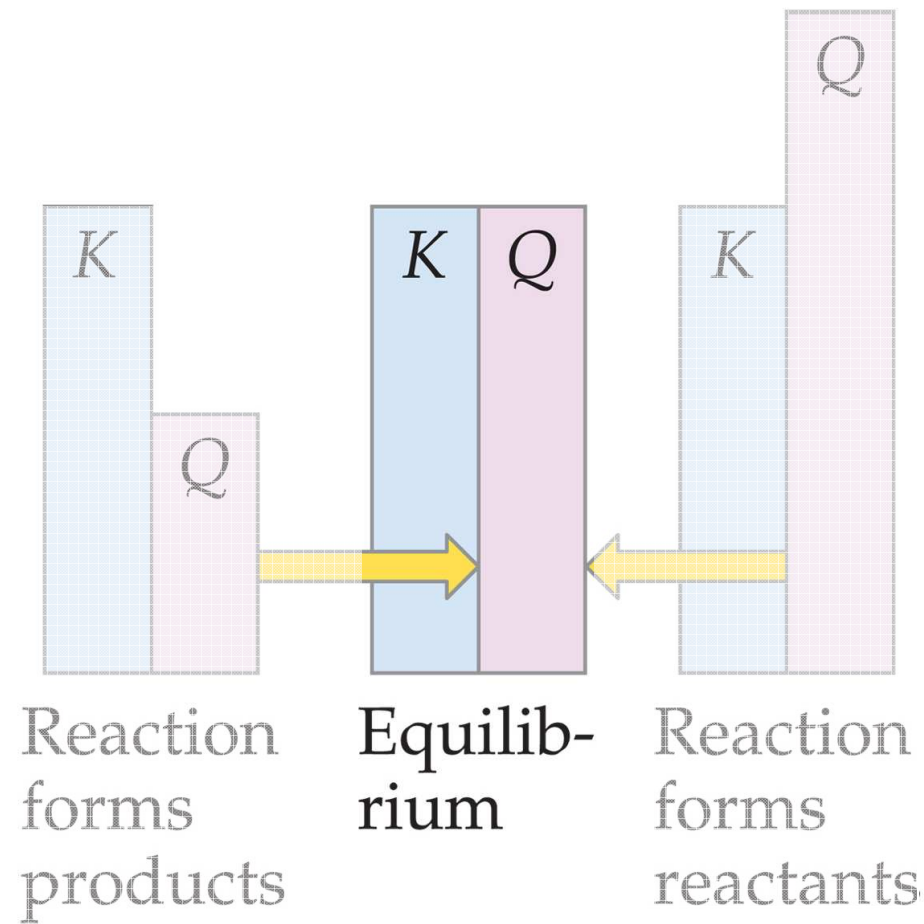
If $Q > K$,
there is too much product and the equilibrium shifts to the left.

Reaction forms products

Equilib-rium

Reaction forms reactants
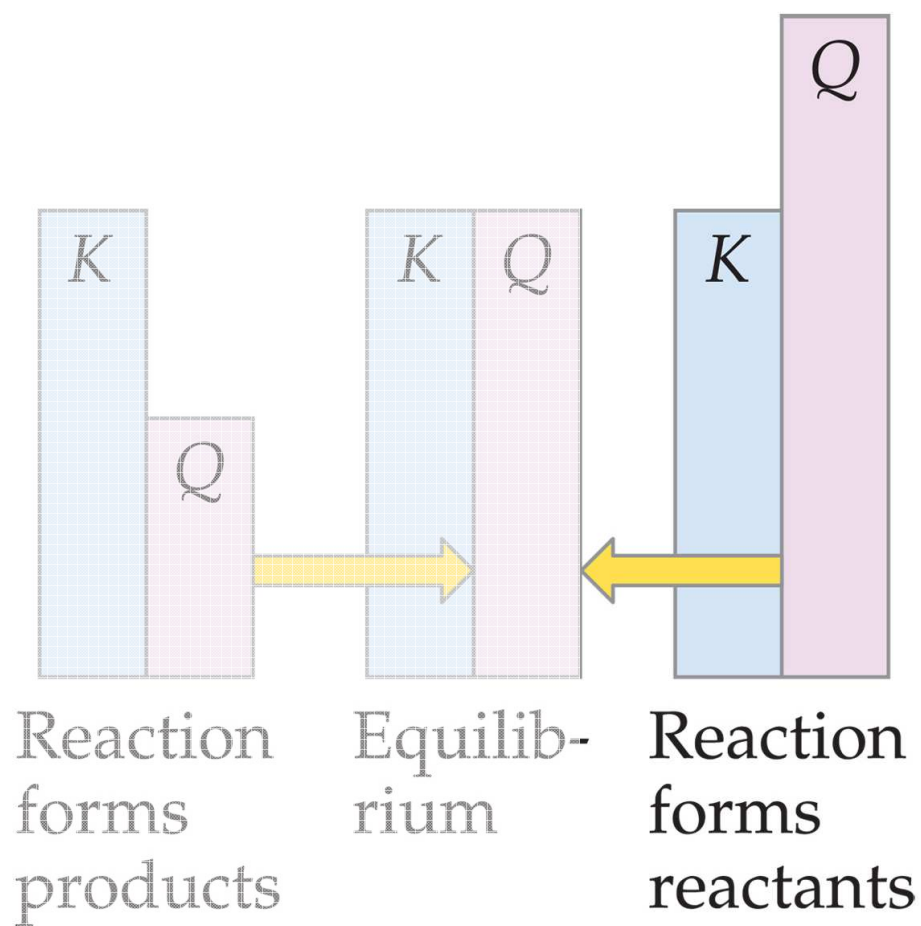
Equilibrium

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

Reaction forms products

Equilib-rium

Reaction forms reactants

Equilibrium

SAMPLE EXERCISE 15.10 Predicting the Direction of Approach to Equilibrium

At 448°C the equilibrium constant K_c for the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2\, HI(g)$$
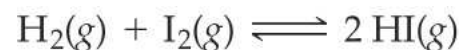
is 50.5. Predict in which direction the reaction will proceed to reach equilibrium at 448°C if we start with 2.0×10^{-2} mol of HI, 1.0×10^{-2} mol of H_2, and 3.0×10^{-2} mol of I_2 in a 2.00-L container.

First calculate the concentration or Molarity as the moles are given and the volume is given.
Then calculate the reaction quotient.

Equilibrium

PRACTICE EXERCISE

At 1000 K the value of K_p for the reaction $2\,SO_3(g) \rightleftharpoons 2\,SO_2(g) + O_2(g)$ is 0.338. Calculate the value for Q_p, and predict the direction in which the reaction will proceed toward equilibrium if the initial partial pressures are $P_{SO_3} = 0.16$ atm; $P_{SO_2} = 0.41$ atm; $P_{O_2} = 2.5$ atm.

Equilibrium

Answer: $Q_p = 16$; $Q_p > K_p$, and so the reaction will proceed from right to left, forming more SO_3.

Calculating equilibrium concentrations

We earlier learnt to calculate the equilibrium constant when the initial concentrations of the reactants as given.

Now we will learn to calculate the equilibrium concentrations of the various components.

Equilibrium

Calculating equilibrium concentrations.

For the Haber process, $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$, $K_p = 1.45 \times 10^{-5}$ at 500°C. In an equilibrium mixture of the three gases at 500°C, the partial pressure of H_2 is 0.928 atm and that of N_2 is 0.432 atm. What is the partial pressure of NH_3 in this equilibrium mixture?

Calculating equilibrium concentrations.

For the Haber process, $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$, $K_p = 1.45 \times 10^{-5}$ at 500°C. In an equilibrium mixture of the three gases at 500°C, the partial pressure of H_2 is 0.928 atm and that of N_2 is 0.432 atm. What is the partial pressure of NH_3 in this equilibrium mixture?

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

| Equilibrium pressure (atm) | 0.432 | 0.928 | x |
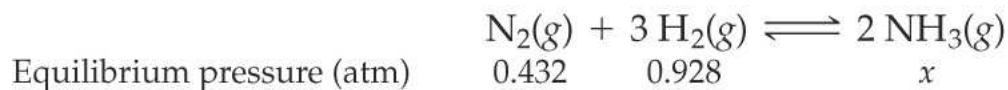
$$K_p = \frac{(P_{NH_3})^2}{P_{N_2}(P_{H_2})^3} = \frac{x^2}{(0.432)(0.928)^3} = 1.45 \times 10^{-5}$$

We now rearrange the equation to solve for x:

$$x^2 = (1.45 \times 10^{-5})(0.432)(0.928)^3 = 5.01 \times 10^{-6}$$

$$x = \sqrt{5.01 \times 10^{-6}} = 2.24 \times 10^{-3}\ \text{atm} = P_{NH_3}$$
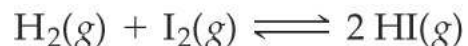
Comment: We can always check our answer by using it to recalculate the value of the equilibrium constant:

$$K_p = \frac{(2.24 \times 10^{-3})^2}{(0.432)(0.928)^3} = 1.45 \times 10^{-5}$$

Equilibrium

SAMPLE EXERCISE 15.12 Calculating Equilibrium Concentrations
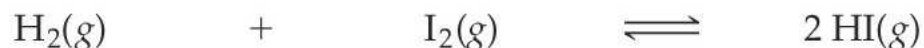
A 1.000-L flask is filled with 1.000 mol of H_2 and 2.000 mol of I_2 at 448°C. The value of the equilibrium constant K_c for the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$$

at 448°C is 50.5. What are the equilibrium concentrations of H_2, I_2, and HI in moles per liter?

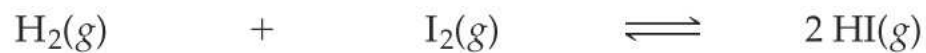$$[H_2] = 1.000\ M \text{ and } [I_2] = 2.000\ M$$

SAMPLE EXERCISE 15.12

	$H_2(g)$	$+$	$I_2(g)$	$\rightleftharpoons$	$2\,HI(g)$
Initial	1.000 M		2.000 M		0 M
Change					
Equilibrium					

For each x mol of H_2 that reacts, x mol of I_2 are consumed and $2x$ mol of HI are produced:
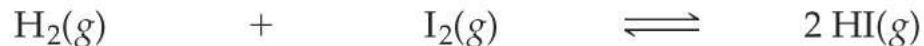
	$H_2(g)$	$+$	$I_2(g)$	$\rightleftharpoons$	$2\,HI(g)$
Initial	1.000 M		2.000 M		0 M
Change	$-x$		$-x$		$+2x$
Equilibrium					

Equilibrium

	$H_2(g)$	+	$I_2(g)$	$\rightleftharpoons$	$2\,HI(g)$
Initial	1.000 M		2.000 M		0 M
Change	$-x$		$-x$		$+2x$
Equilibrium	$(1.000 - x)\,M$		$(2.000 - x)\,M$		$2x\,M$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2x)^2}{(1.000 - x)(2.000 - x)} = 50.5$$

$$(1.000 - x)(2.000 - x)$$

$$= 2.000 - 1.000x - 2.000x + x^2$$
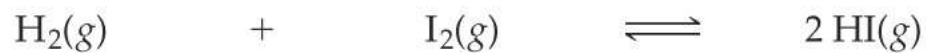
$$= 2.000 - 3.000x + x^2$$

$$(2.000 - 3.000x + x^2)50.5$$

$$= 101 - 151.5x + 50.5x^2$$

$$4x^2 = 101 - 151.5x + 50.5x^2$$

$$0 = 101 - 151.5x + 50.5x^2 - 4x^2$$

$$0 = 101 - 151.5x + 46.5x^2$$

$$0 = 46.5x^2 - 151.5x + 101$$

Equilibrium

	$H_2(g)$	+	$I_2(g)$	$\rightleftharpoons$	$2\,HI(g)$
Initial	1.000 M		2.000 M		0 M
Change	$-x$		$-x$		$+2x$
Equilibrium	$(1.000 - x)\,M$		$(2.000 - x)\,M$		$2x\,M$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2x)^2}{(1.000 - x)(2.000 - x)} = 50.5$$

$$4x^2 = 50.5(x^2 - 3.000x + 2.000)$$
$$46.5x^2 - 151.5x + 101.0 = 0$$

Quadratic Equations:

$$ax^2 + bx + c = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

	$H_2(g)$	$+$	$I_2(g)$	$\rightleftharpoons$	$2\,HI(g)$
Initial	1.000 M		2.000 M		0 M
Change	$-x$		$-x$		$+2x$
Equilibrium	$(1.000 - x)\,M$		$(2.000 - x)\,M$		$2x\,M$

Quadratic Equations:

$$ax^2 + bx + c = 0 \qquad K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2x)^2}{(1.000 - x)(2.000 - x)} = 50.5$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$4x^2 = 50.5(x^2 - 3.000x + 2.000)$$

$$46.5x^2 - 151.5x + 101.0 = 0$$

Solving the quadratic equation (Appendix A.3) leads to two solutions for x:

$$x = \frac{-(-151.5) \pm \sqrt{(-151.5)^2 - 4(46.5)(101.0)}}{2(46.5)} = 2.323 \text{ or } 0.935$$

$$[H_2] = 1.000 - x = 0.065\,M$$
$$[I_2] = 2.000 - x = 1.065\,M$$
$$[HI] = 2x = 1.870\,M$$

Check: We can check our solution by putting these numbers into the equilibrium-constant expression:

Equilibrium

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(1.870)^2}{(0.065)(1.065)} = 51$$

Le Châtelier's Principle

Equilibrium

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."
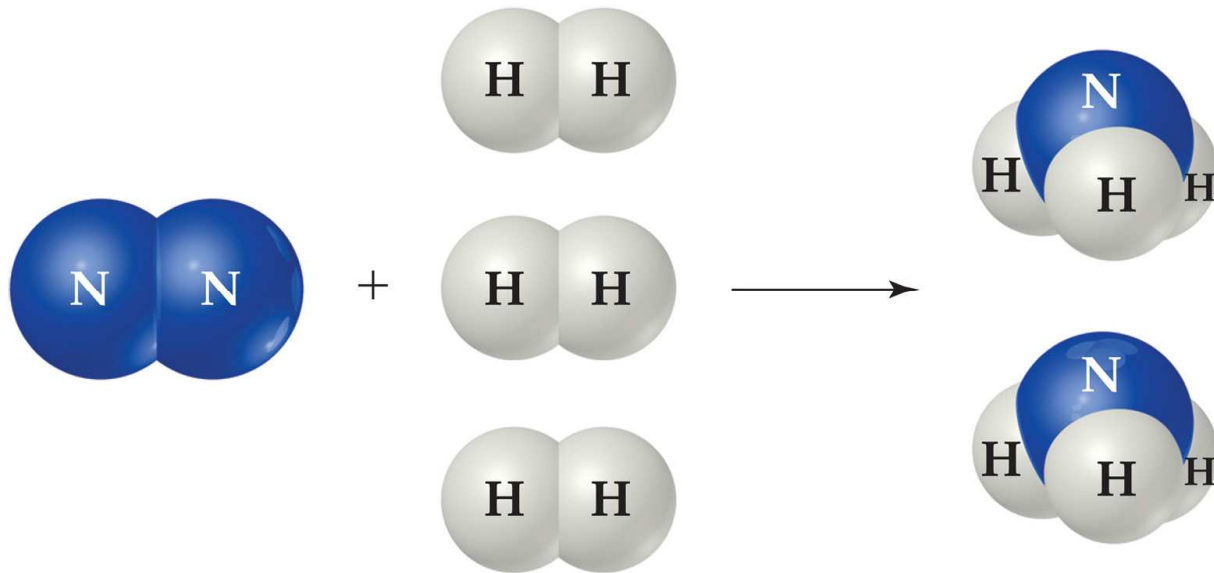
Equilibrium

Change in the Reactant or Product Concentration

- If a chemical system is in equilibrium and we add one of the substances, either a reactant or the product, the reaction will shift as to reestablish the equilibrium in a manner that the change is nullified.

Equilibrium

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.
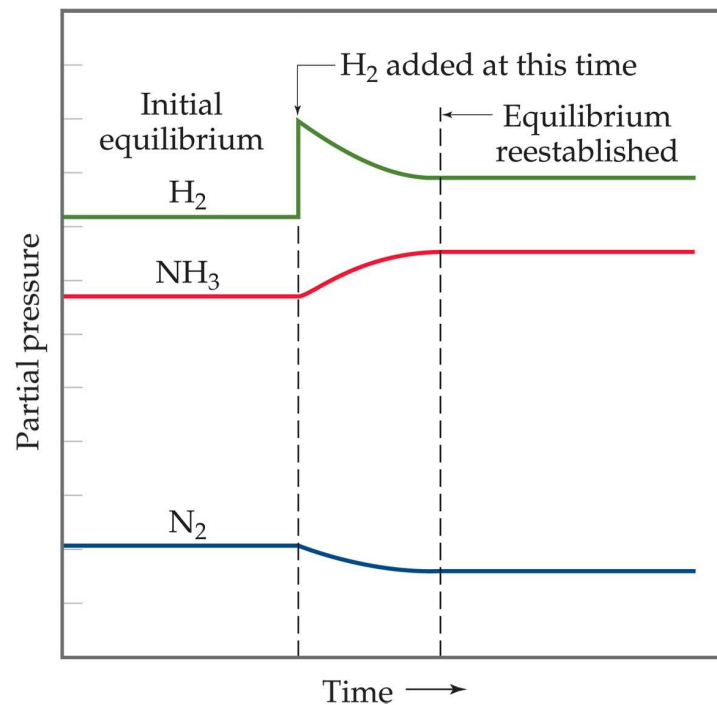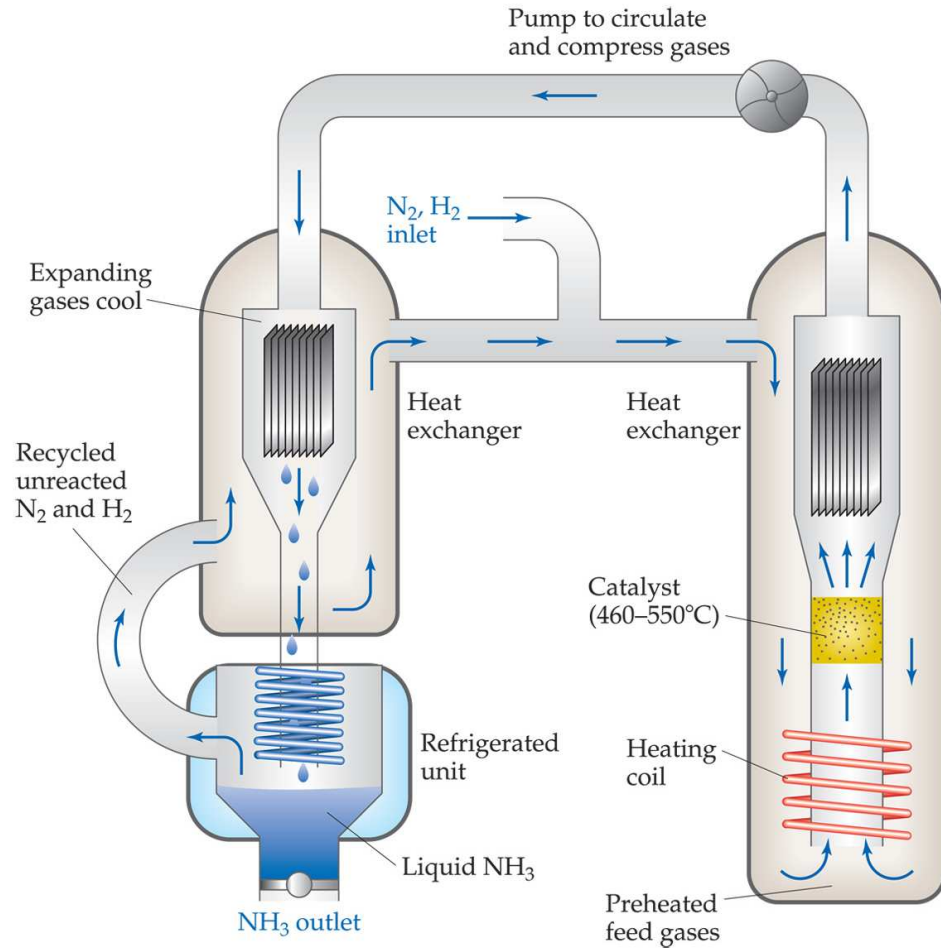

Equilibrium

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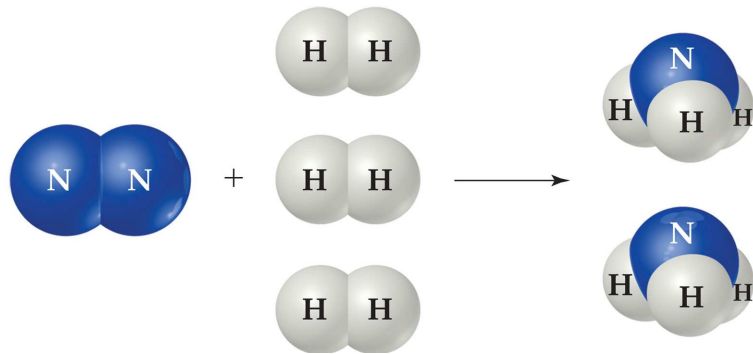
If H_2 is added to the system, N_2 will be consumed and the two reagents will form more NH_3.

Equilibrium

The Haber Process

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

Effect of Volume and Pressure on Equilibrium

- Reducing the volume of the reaction, hence increasing the pressure causes the equilibrium to move in a direction that reduces the number of moles of gas.
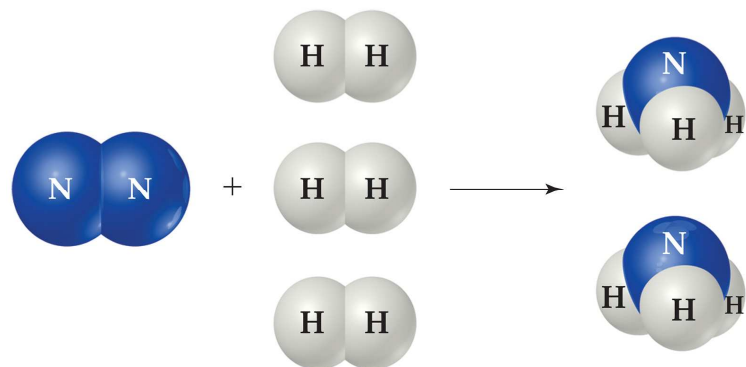
- More product will be formed

Equilibrium

What will be effect of increasing the pressure on the following reaction;

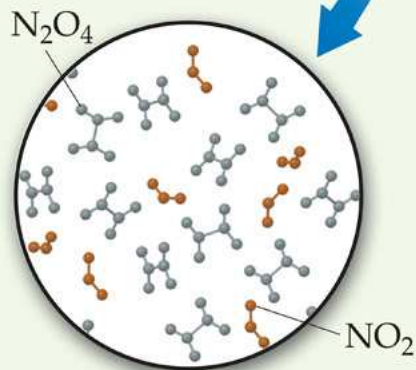$$N_2O_{4\,(g)} \rightleftharpoons 2\,NO_{2\,(g)}$$

The equilibrium will have more reactant.

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.

N_2O_4

NO_2

An equilibrium mixture of brown $NO_2(g)$ (red) and colorless $N_2O_4(g)$ (gray) held in a gas-tight syringe.
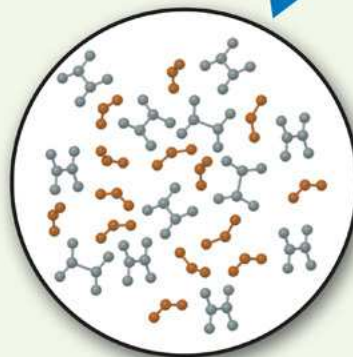
The volume and hence the pressure are changed by moving the plunger. Compression of the mixture temporarily increases the concentration of NO_2.
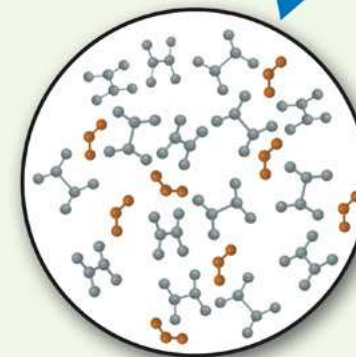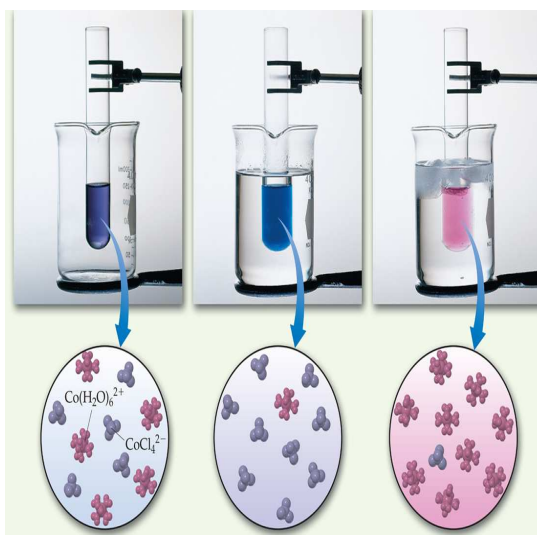
When the mixture reestablishes equilibrium, the color is as light as that at the beginning because the formation of $N_2O_4(g)$ is favored by the pressure increase.

- The volume and pressure do not change the value of K as long as the temperature remains constant.

Equilibrium

The Effect of Changes in Temperature

$$Co(H_2O)_6^{2+}{}_{(aq)} + 4\ Cl^-{}_{(aq)} \rightleftharpoons CoCl_4{}^{2-}{}_{(aq)} + 6\ H_2O{}_{(l)}$$

- This is an endothermic reaction and heat is absorbed when the product is formed.

Equilibrium

We can treat heat as one of the reactants

In an endothermic reaction

Reactant + heat → Product

In an Exothermic reaction

Reactant → Product + heat

When the temperature of a reaction is increased the reaction moves in the direction that consumes heat.

And vice versa

Equilibrium

Endothermic reactions

Reactants + heat $\rightleftharpoons$ Product

Increasing T
Results in more product $\quad K = \dfrac{[\text{Products}]}{[\text{Reactants}]} \quad$ increases K

Exothermic reactions

Reactant $\rightleftharpoons$ Product + heat

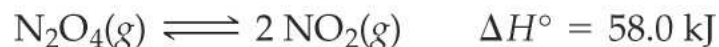Incresing T
results in less
product $\qquad K = \dfrac{[\text{Products}]}{[\text{Reactants}]} \qquad$ reduces K

Equilibrium

SAMPLE EXERCISE 15.13 Using Le Châtelier's Principle to Predict Shifts in Equilibrium

Consider the equilibrium

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g) \qquad \Delta H^\circ = 58.0\ kJ$$

In which direction will the equilibrium shift when (a) N_2O_4 is added, (b) NO_2 is removed, (c) the total pressure is increased by addition of $N_2(g)$, (d) the volume is increased, (e) the temperature is decreased?

(a) The system will adjust to decrease the concentration of the added N2O4, so the equilibrium shifts to the right, in the direction of products.

(b) The system will adjust to the removal of NO2 by shifting to the side that produces more NO2; thus, the equilibrium shifts to the right.

(c) Adding N2 will increase the total pressure of the system, but N2 is not involved in the reaction.The partial pressures of NO2 and N2O4 are therefore unchanged, and there is no shift in the position of the equilibrium.

(d) If the volume is increased, the system will shift in the direction that occupies a larger volume (more gas molecules); thus, the equilibrium shifts to the right.

(e) The reaction is endothermic, so we can imagine heat as a reagent on the reactant side of the equation. Decreasing the temperature will shift the equilibrium in the direction that produces heat, so the equilibrium shifts to the left, toward the formation of more N2O4. Note that only this last change also affects the value of the equilibrium constant, *K*.
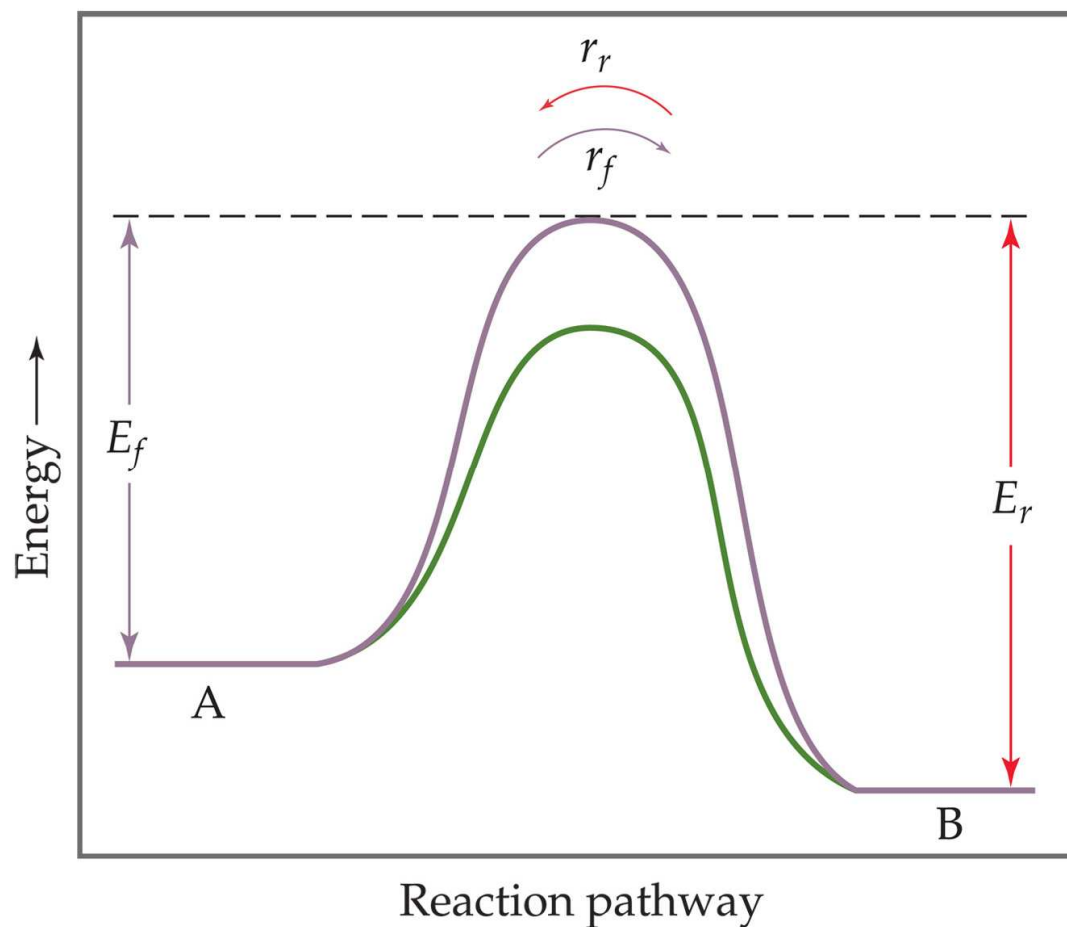
Equilibrium

Catalysts increase the rate of both the forward *and* reverse reactions as the activation energy of the forward and reverse reaction is lowered to the same extent .

Reaction pathway
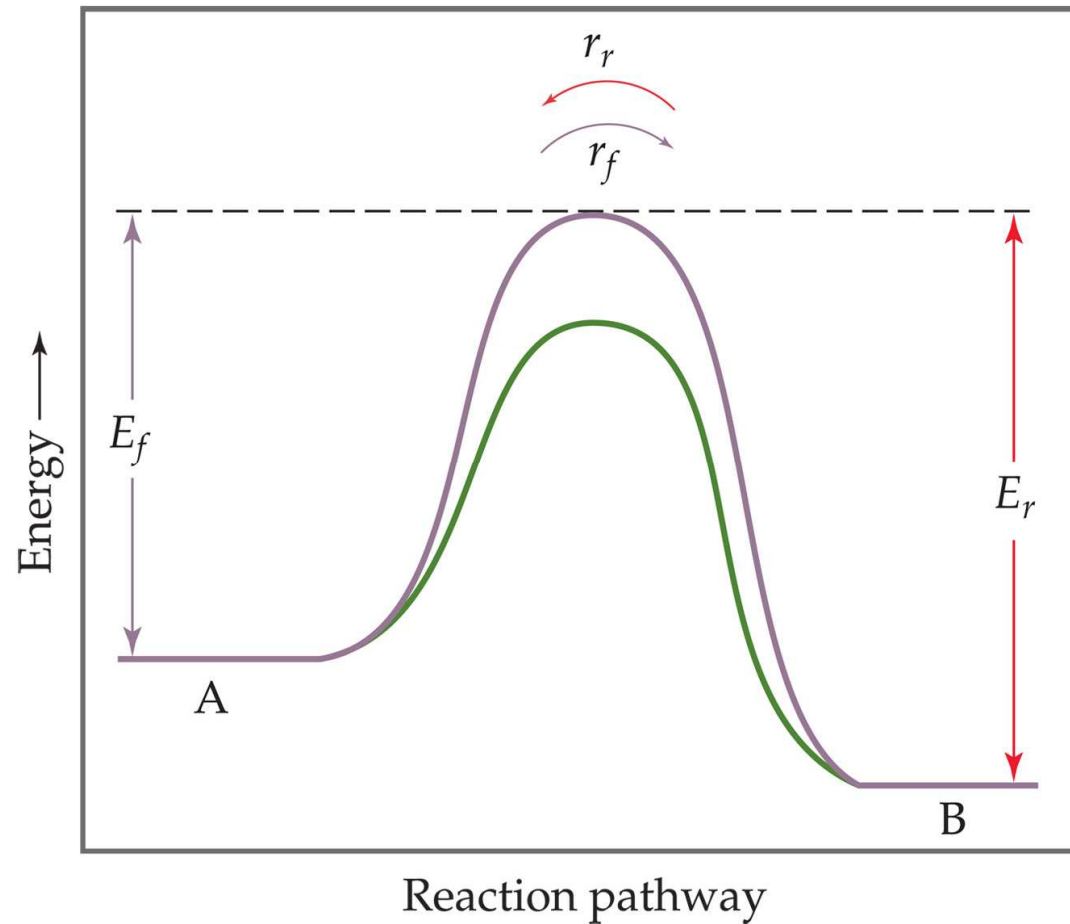
Equilibrium

Equilibrium is achieved faster, but the equilibrium composition remains unaltered.

Homework question:

- Sample integrative exercise page 657

Equilibrium