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Chapter 15

Chemical Equilibrium

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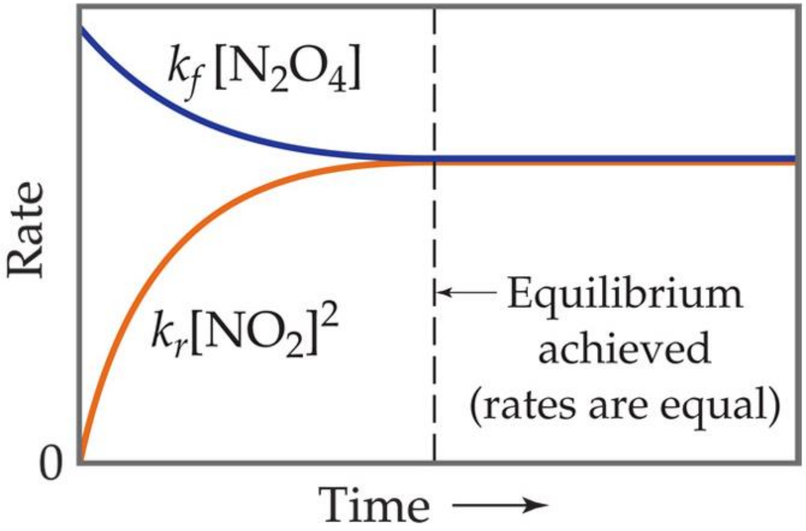
Chemical equilibrium occurs when opposing reactions are proceeding at equal rates: The rate at which the products are formed from the reactants equals the rate at which the reactants are formed from the products.

As a result, concentrations cease to change, making the reaction appear to be stopped. How fast a reaction reaches equilibrium is a matter of kinetics.

15.1
The Concept of Equilibrium

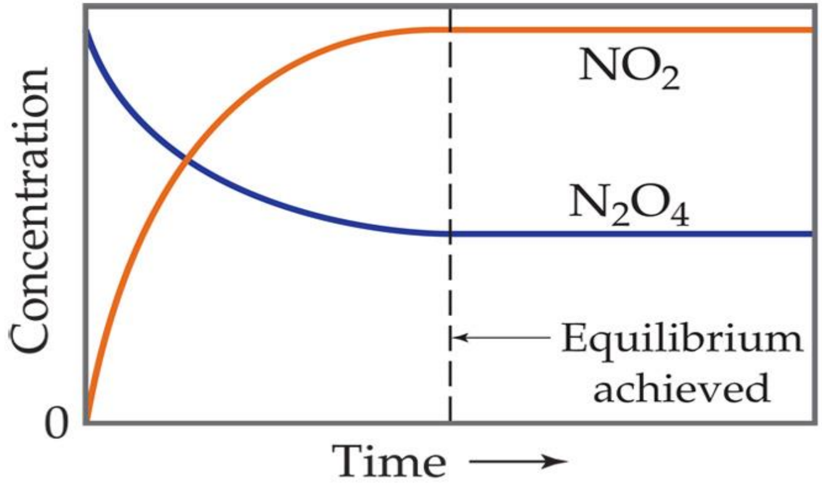
$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$$



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.

Once equilibrium is achieved, the amount of each reactant and product (concentrations) remains constant.



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

$$\underset{\text{Colorless}}{N_2O_4(g)} \rightleftharpoons \underset{\text{Brown}}{2\,NO_2(g)}$$

The equilibrium mixture results because the reaction is **reversible**.

Forward reaction: $N_2O_4(g) \longrightarrow 2\,NO_2(g)$ $\quad \text{Rate}_f = k_f[N_2O_4]$

Reverse reaction: $2\,NO_2(g) \longrightarrow N_2O_4(g)$ $\quad \text{Rate}_r = k_r[NO_2]^2$

Where k_f and k_r are the rate constants for the forward and reverse reactions. At equilibrium, the rate at which products are produced from reactants equals the rate at which reactants are produced from products:

$$\underset{\text{Forward reaction}}{k_f[N_2O_4]} = \underset{\text{Reverse reaction}}{k_r[NO_2]^2}$$

$$\boxed{\frac{[NO_2]^2}{[N_2O_4]} = \frac{k_f}{k_r} = \text{a constant}}$$

At equilibrium the ratio of the concentration terms involving N_2O_4 and NO_2 equals a constant (called equilibrium constant).

- At equilibrium, the concentrations of reactants and products no longer change with time.

- For equilibrium to occur, neither reactants nor products can escape from the system.

- At equilibrium a particular ratio of concentration terms equals a constant.

15.2

The Equilibrium Constant

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

Forward reaction: $N_2O_4(g) \longrightarrow 2\,NO_2(g)$ $\quad \text{Rate}_f = k_f[N_2O_4]$

Reverse reaction: $2\,NO_2(g) \longrightarrow N_2O_4(g)$ $\quad \text{Rate}_r = k_r[NO_2]^2$

- Therefore, at equilibrium
- $\text{Rate}_f = \text{Rate}_r$
- $k_f\,[N_2O_4] = k_r\,[NO_2]^2$
- Rewriting this, it becomes

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

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

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

Consider the generalized reaction

$$a\,\mathrm{A} + b\,\mathrm{B} \rightleftharpoons d\,\mathrm{D} + e\,\mathrm{E}$$

Note that once we know the **balanced chemical equation** for an equilibrium, we can write the equilibrium-constant expression even if we do not know the reaction mechanism.

The **equilibrium-constant expression (or equilibrium expression)** for this reaction would be

$$K_c = \frac{[\mathrm{D}]^d[\mathrm{E}]^e}{[\mathrm{A}]^a[\mathrm{B}]^b}$$

$$\boxed{K_c = \frac{[\mathrm{D}]^d[\mathrm{E}]^e}{[\mathrm{A}]^a[\mathrm{B}]^b} \quad \begin{array}{l} \longleftarrow \text{products} \\ \longleftarrow \text{reactants} \end{array}}$$

The value of the equilibrium constant at any given temperature does not depend on the initial amounts of reactants and products. The value of the equilibrium constant depends only on the particular reaction and on the temperature.

When the reactants and products in a chemical reaction are **gases**, we can formulate the equilibrium-constant expression in terms of partial pressures instead of molar concentrations since pressure is proportional to concentration for gases in a closed system.

We can denote the equilibrium constant as $\boldsymbol{K_p}$ (where the subscript p stands for pressure).

$$K_{\mathrm{p}} = \frac{(P_{\mathrm{D}}{}^{\mathrm{d}})\,(P_{\mathrm{E}}{}^{\mathrm{e}})}{(P_{\mathrm{A}}{}^{\mathrm{a}})\,(P_{\mathrm{B}}{}^{\mathrm{b}})}$$

Sample Exercise 15.1 Writing Equilibrium-Constant Expressions

Write the equilibrium expression for K_c for the following reactions:

(a) $2\,O_3(g) \rightleftharpoons 3\,O_2(g)$

(b) $2\,NO(g) + Cl_2(g) \rightleftharpoons 2\,NOCl(g)$

(c) $Ag^+(aq) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2{}^+(aq)$

Solution

Solve: (a) $K_c = \dfrac{[O_2]^3}{[O_3]^2}$, (b) $K_c = \dfrac{[NOCl]^2}{[NO]^2[Cl_2]}$, (c) $K_c = \dfrac{[Ag(NH_3)_2{}^+]}{[Ag^+][NH_3]^2}$

Relationship Between K_c and K_p

- From the Ideal Gas Law we know that

$$PV = nRT$$

- Rearranging it, we get

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

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

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

where

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

For example, in the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, there are two moles of the product NO_2 (the coefficient in the balanced equation) and one mole of the reactant N_2O_4. Therefore, $\Delta n = 2-1=1$, and $K_p = K_c(RT)$ for this reaction.

From Equation, we see that $K_p = K_c$ only when the same number of moles of gas appears on both sides of the balanced chemical equation, which means that $\Delta n = 0$.

Sample Exercise 15.2 Converting between K_c and K_p

In the synthesis of ammonia from nitrogen and hydrogen,

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

$K_c = 9.60$ at 300 °C. Calculate K_p for this reaction at this temperature.

Solution

There are two moles of gaseous products (2 NH_3) and four moles of gaseous reactants (1 N_2 + 3 H_2). Therefore, $\Delta n = 2 - 4 = -2$. (Remember that Δ functions are always based on products minus reactants.) The temperature, T, is 273 + 300 = 573 K. The value for the ideal-gas constant, R, is 0.0821 L-atm/mol-K. Using $K_c = 9.60$, we therefore have

$$K_p = K_c(RT)^{\Delta n} = (9.60)(0.0821 \times 573)^{-2} = \frac{(9.60)}{(0.0821 \times 573)^2} = 4.34 \times 10^{-3}$$

Equilibrium can be reached from either direction

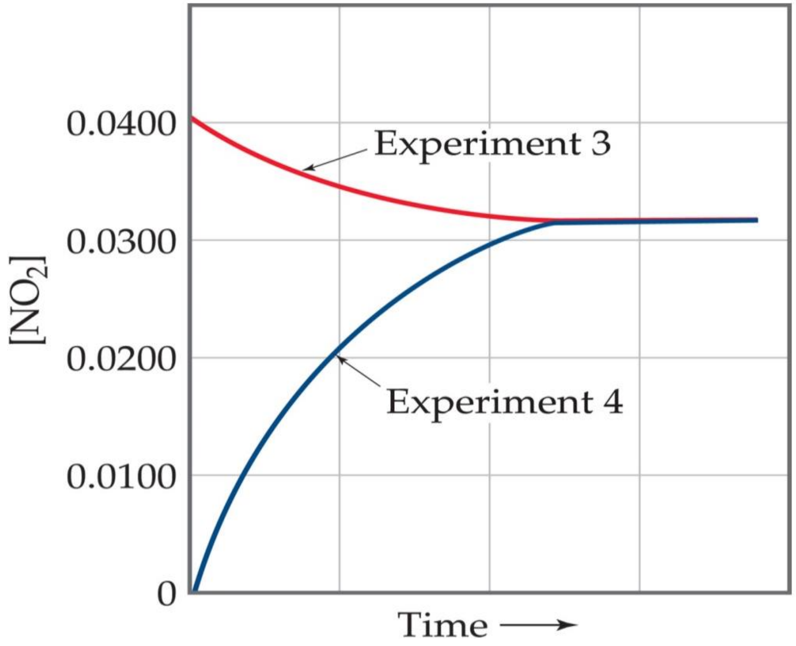
TABLE 15.1 ■ Initial and Equilibrium Concentrations of N_2O_4 and NO_2 in the Gas Phase at 100 °C

Experiment	Initial $[N_2O_4]$ (M)	Initial $[NO_2]$ (M)	Equilibrium $[N_2O_4]$ (M)	Equilibrium $[NO_2]$ (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

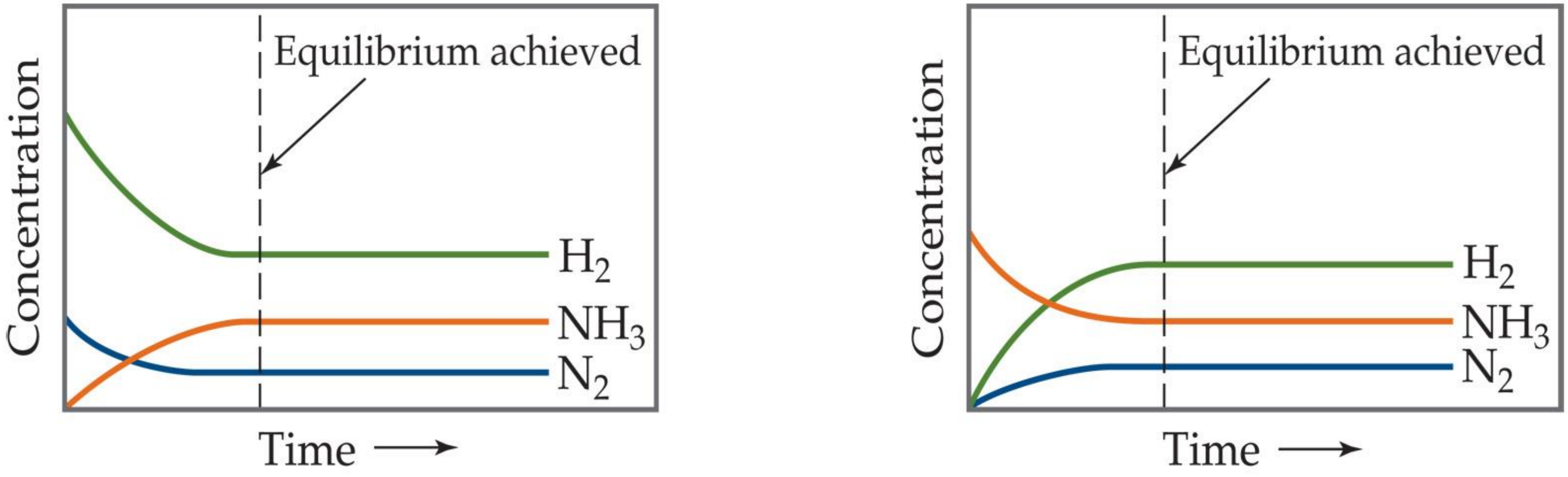
The ratio of $[NO_2]^2$ to $[N_2O_4]$ remains constant at this temperature, no matter what the initial concentrations of NO_2 and N_2O_4 are. This is the data from the last two trials from the table.

Concentration changes approaching equilibrium

The same equilibrium mixture is produced starting with either 0.0400 M NO_2 (Experiment 3) or 0.0200 M N_2O_4 (Experiment 4).



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



Concentration changes approaching equilibrium

(a) Equilibrium for the reaction is approached beginning with H_2 and N_2 present in the ratio 3:1 and no NH_3 present.

(b) Equilibrium for the same reaction is approached beginning with only NH_3 in the reaction vessel.

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.

Notice that an equilibrium mixture is obtained regardless of whether we begin with N_2 and H_2 or only with NH_3. The equilibrium condition can be reached from either direction.

Equilibrium Constants and Units

Equilibrium constants are reported without units. Equilibrium constants derived from thermodynamic measurements are defined in terms of **activities** rather than **concentrations** or **partial pressures**.

The activity of any substance is the ratio of the concentration or pressure of the substance to a reference concentration (1 M) or a reference pressure (1 atm).

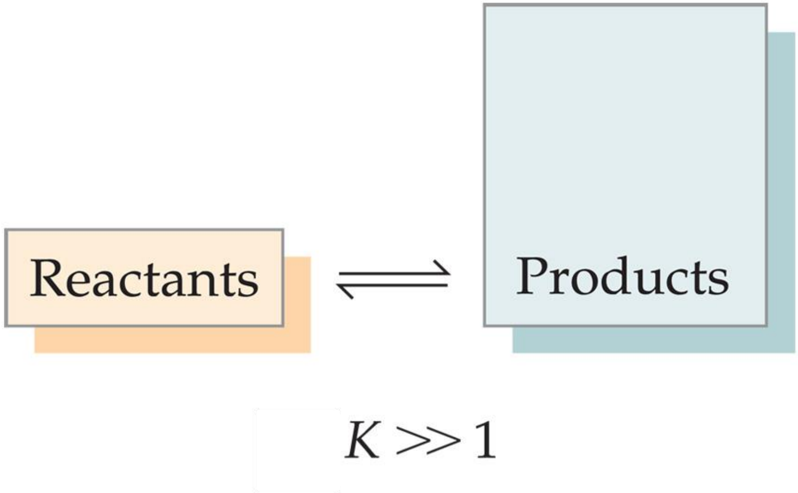
For pure solids and pure liquids, the situation is even simpler because the activities then merely equal 1 (again with no units).

In real systems, activities are also ratios that have no units. As a result, the thermodynamic equilibrium constant derived from them also has no units. Therefore, the equilibrium constants without units as well.

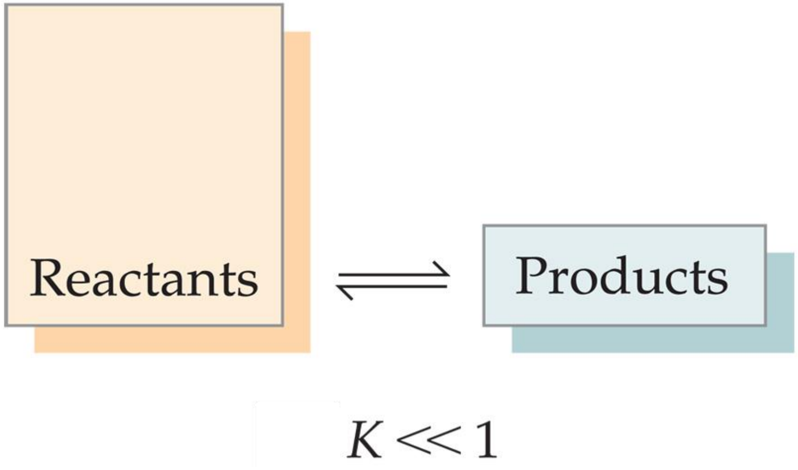
15.3

Interpreting and Working with Equilibrium Constants

What the magnitude of an equilibrium constant can tell us about the relative concentrations of reactants and products in an equilibrium mixture.



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



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

Manipulating Equilibrium Constants

Because an equilibrium can be approached from either direction, the direction in which we write the chemical equation for an equilibrium is arbitrary.

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

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

$$N_2O_{4(g)} \rightleftharpoons 2\,NO_{2(g)} \qquad K_c = \frac{[NO_2]^2}{[N_2O_4]} = 0.212 \text{ (100°C)}$$

$$2\,NO_{2(g)} \rightleftharpoons N_2O_{4(g)} \qquad K_c = \frac{[N_2O_4]}{[NO_2]^2} = 4.72 \text{ (100°C)}$$

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.

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

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = 0.212\ (100°C)$$

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

$$K_c = \frac{[NO_2]^4}{[N_2O_4]^2} = (0.212)^2 = 0.0449\ (100°C)$$

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.

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

$$\mathrm{Br_2}(g) + \mathrm{Cl_2}(g) \rightleftharpoons 2\,\mathrm{BrCl}(g) \qquad K_c = \frac{[\mathrm{BrCl}]^2}{[\mathrm{Br_2}][\mathrm{Cl_2}]} = 7.2$$

The net sum of these two equations is:

$$2\,\mathrm{NOBr}(g) + \mathrm{Cl_2}(g) \rightleftharpoons 2\,\mathrm{NO}(g) + 2\,\mathrm{BrCl}(g)$$

The equilibrium-constant expression for the net equation is the product of the expressions for the individual steps:

$$K_c = \frac{[\mathrm{NO}^2][\mathrm{BrCl}]^2}{[\mathrm{NOBr}]^2[\mathrm{Cl_2}]} = \frac{[\mathrm{NO}]^2[\mathrm{Br_2}]}{[\mathrm{NOBr}]^2} \times \frac{[\mathrm{BrCl}]^2}{[\mathrm{Br_2}][\mathrm{Cl_2}]}$$

Because the equilibrium-constant expression for the net equation is the product of two equilibrium-constant expressions, the equilibrium constant for the net equation is the product of the two individual equilibrium constants:

$$\mathbf{K_c = 0.014 \times 7.2 = 0.10}$$

Sample Exercise 15.4 Evaluating an Equilibrium Constant When an Equation is Reversed

The equilibrium constant for the reaction of N_2 with O_2 to form NO equals $K_c = 1 \times 10^{-30}$ at 25 °C:

$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g) \qquad K_c = 1 \times 10^{-30}$$

Using this information, write the equilibrium constant expression and calculate the equilibrium constant for the following reaction:

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

Solution

Writing products over reactants, we have

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

Both the equilibrium-constant expression and the numerical value of the equilibrium constant are the reciprocals of those for the formation of NO from N_2 and O_2:

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

Sample Exercise 15.5 Combining Equilibrium Expressions

Given the following information,

$$\begin{array}{ll} HF(aq) \rightleftharpoons H^+(aq) + F^-(aq) & K_c = 6.8 \times 10^{-4} \\ H_2C_2O_4(aq) \rightleftharpoons 2\,H^+(aq) + C_2O_4{}^{2-}(aq) & K_c = 3.8 \times 10^{-6} \end{array}$$

determine the value of K_c for the reaction

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

Solution

If we multiply the first equation by 2 and make the corresponding change to its equilibrium constant (raising to the power 2), we get

$$2\,HF(aq) \rightleftharpoons 2\,H^+(aq) + 2\,F^-(aq) \quad K_c = (6.8 \times 10^{-4})^2 = 4.6 \times 10^{-7}$$

Reversing the second equation and again making the corresponding change to its equilibrium constant (taking the reciprocal) gives

$$2\,H^+(aq) + C_2O_4{}^{2-}(aq) \rightleftharpoons H_2C_2O_4(aq) \quad K_c = \frac{1}{3.8 \times 10^{-6}} = 2.6 \times 10^5$$

Now we have two equations that sum to give the net equation,

$$\begin{array}{ll} 2\,HF(aq) \rightleftharpoons 2\,H^+(aq) + 2\,F^-(aq) & K_c = 4.6 \times 10^{-7} \\ 2\,H^+(aq) + C_2O_4{}^{2-}(aq) \rightleftharpoons H_2C_2O_4(aq) & K_c = 2.5 \times 10^5 \\ \hline 2\,HF(aq) + C_2O_4{}^{2-}(aq) \rightleftharpoons 2\,F^-(aq) + H_2C_2O_4(aq) & K_c = (4.6 \times 10^{-7})(2.6 \times 10^5) = 0.12 \end{array}$$

15.4

Heterogeneous Equilibria

Many equilibria, such as the hydrogen-nitrogen-ammonia system, involve substances all in the same phase. Such equilibria are called **homogeneous equilibria**. In other cases the substances in equilibrium are in different phases, giving rise to **heterogeneous equilibria**.

The concentrations of **solids** and **liquids** are essentially **constant**

The concentration of both 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. Therefore, the concentrations of **solids** and **liquids** do not appear in the equilibrium expression.

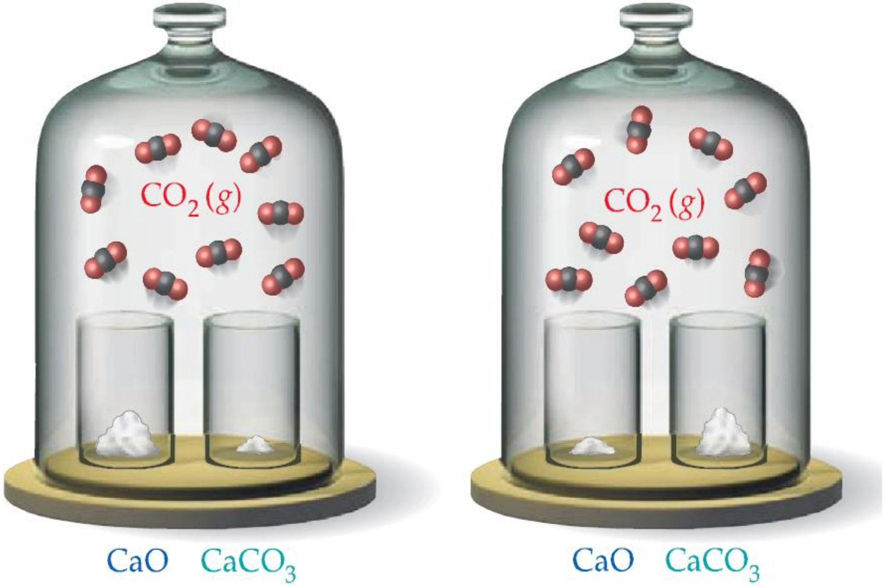
$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,Cl^{-}(aq)$$

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

The omission of pure solids and liquids from equilibrium-constant expressions can be explained by the activity, which is a ratio of the concentration to a reference value. For a pure substance, the reference value is the concentration of the pure substance itself, so that the activity of any pure solid or liquid is always simply 1.

As a further example of a heterogeneous reaction, consider the decomposition of calcium carbonate:

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



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-constant expression for the reaction is

$$K_c = [CO_2] \quad \text{and} \quad K_p = P_{CO_2}$$

The equilibrium involving $CaCO_3$ or CaO and CO_2 is a heterogeneous equilibrium. The equilibrium pressure of CO_2 is the same in the two bell jars as long as the two systems are at the same temperature, even though the relative amounts of pure $CaCO_3$ and CaO differ greatly.

When a solvent is involved as a reactant or product in an equilibrium, its concentration is also excluded from the equilibrium-constant expression, provided the concentrations of reactants and products are low, so that the solvent is essentially a pure substance.

$$H_2O(l) + CO_3^{2-}(aq) \rightleftharpoons OH^-(aq) + HCO_3^-(aq)$$

Gives an equilibrium-constant expression in which [H_2O] is excluded:

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

Sample Exercise 15.6 Writing Equilibrium-Constant Expressions for Heterogeneous Reactions

Write the equilibrium-constant expression for K_c for each of the following reactions:

$$\text{(a)}\ CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(l)$$

$$\text{(b)}\ SnO_2(s) + 2\,CO(g) \rightleftharpoons Sn(s) + 2\,CO_2(g)$$

Solution

(a) The equilibrium-constant expression is

$$K_c = \frac{[CO]}{[CO_2][H_2]}$$

Because H_2O appears in the reaction as a pure liquid, its concentration does not appear in the equilibrium-constant expression.

(b) The equilibrium-constant expression is

$$K_c = \frac{[CO_2]^2}{[CO]^2}$$

Because SnO_2 and Sn are both pure solids, their concentrations do not appear in the equilibrium-constant expression.

15.5

Calculating Equilibrium Constants

A closed system initially containing 1.00 x 10^{-3} *M* H_2 and 2.00 x 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 x 10^{-3} *M*. Calculate K_c at 448 °C for the reaction taking place, which is :

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

What Do We Know?

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

[HI] Increases by 1.87×10^{-3} *M*

	$[H_2]$, *M*	$[I_2]$, *M*	[HI], *M*
Initially	1.00×10^{-3}	2.00×10^{-3}	0
Change			$+1.87 \times 10^{-3}$
At equilibrium			1.87×10^{-3}

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	-0.935×10^{-3}	-0.935×10^{-3}	$+1.87 \times 10^{-3}$
At equilibrium			1.87×10^{-3}

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	-0.935×10^{-3}	-0.935×10^{-3}	$+1.87 \times 10^{-3}$
At equilibrium	0.065×10^{-3}	1.065×10^{-3}	1.87×10^{-3}

and, therefore, the equilibrium constant

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

$$= \frac{(1.87 \times 10^{-3})^2}{(6.5 \times 10^{-5})(1.065 \times 10^{-3})} = 51$$

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

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

Solution

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

15.6

Applications of Equilibrium Constants

We have seen that the magnitude of ***K*** indicates the extent to which a reaction will proceed.

- If ***K*** is very large, the equilibrium mixture will contain mostly substances on the product side of the equation. (That is, the reaction will tend to proceed far to the right).
- If ***K*** is very small (that is, much less than 1), the equilibrium mixture will contain mainly reactants.

The equilibrium constant also allows us to

(1) predict the direction in which a reaction mixture will proceed to achieve equilibrium, and
(2) calculate the concentrations of reactants and products when equilibrium has been reached.

Predicting the Direction of Reaction - Reaction Quotient

The reaction quotient, ***Q***, is a number obtained by substituting reactant and product concentrations or partial pressures at any point during a reaction into an equilibrium-constant expression.

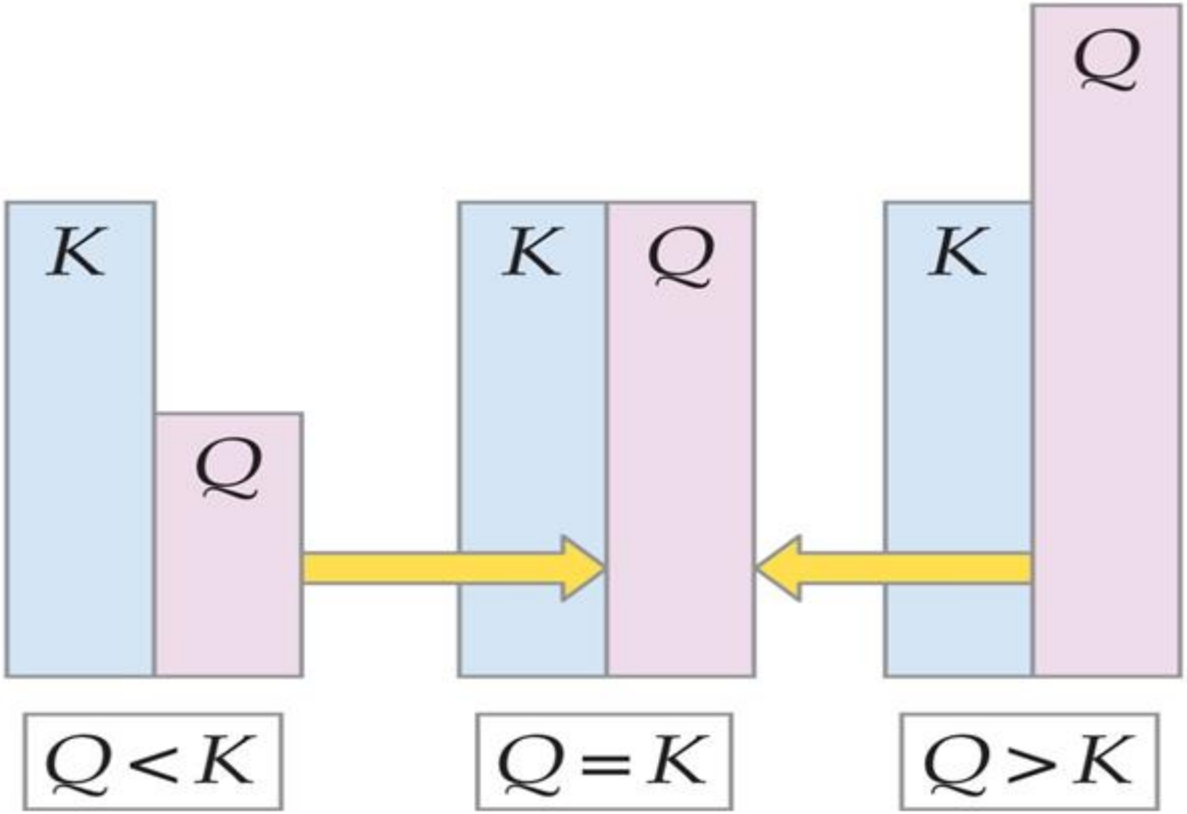
$$a\,\mathrm{A} + b\,\mathrm{B} \rightleftharpoons d\,\mathrm{D} + e\,\mathrm{E}$$

The reaction quotient is defined as:

$$\boxed{Q_c = \frac{[\mathrm{D}]^d[\mathrm{E}]^e}{[\mathrm{A}]^a[\mathrm{B}]^b}}$$

- ***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 (reaction quotient = equilibrium constant).
If $Q > K$, there is too much products, and the equilibrium shifts to the left.
If $Q < K$, there is too much reactants, and the equilibrium shifts to the right.



Reaction forms products

Equilibrium

Reaction forms reactants

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.

Solution

The initial concentrations are

$$[HI] = 2.0 \times 10^{-2}\ \text{mol}/2.00\ \text{L} = 1.0 \times 10^{-2}\ M$$

$$[H_2] = 1.0 \times 10^{-2}\ \text{mol}/2.00\ \text{L} = 5.0 \times 10^{-3}\ M$$

$$[I_2] = 3.0 \times 10^{-2}\ \text{mol}/2.00\ \text{L} = 1.5 \times 10^{-2}\ M$$

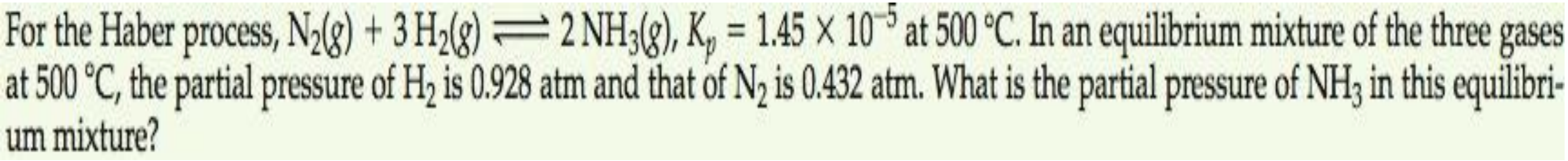
The reaction quotient is therefore

$$Q_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(1.0 \times 10^{-2})^2}{(5.0 \times 10^{-3})(1.5 \times 10^{-2})} = 1.3$$

Because $Q_c < K_c$, the concentration of HI must increase and the concentrations of H_2 and I_2 must decrease to reach equilibrium; the reaction will proceed from left to right as it moves toward equilibrium.

Calculating Equilibrium Concentrations

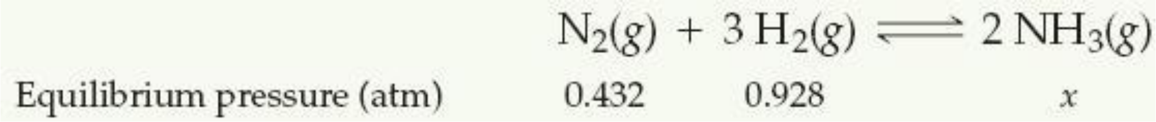
Sample Exercise 15.11 Calculating Equilibrium Concentrations



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?

Solution

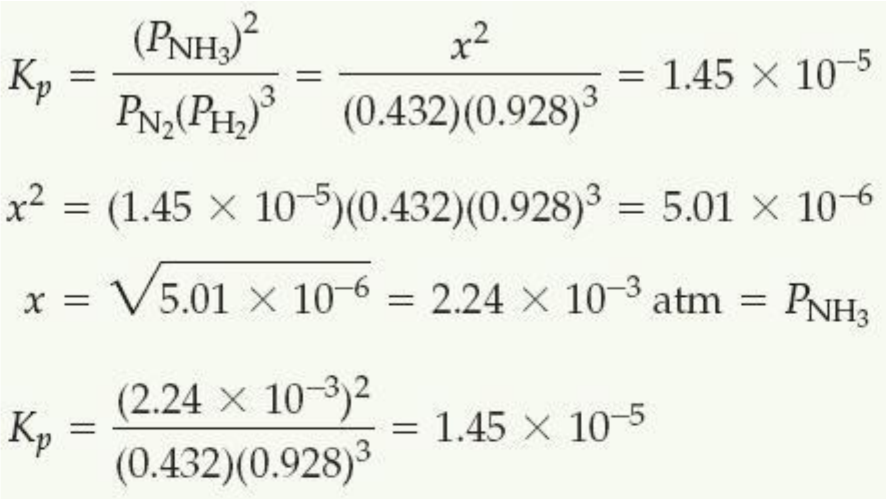
We tabulate the equilibrium pressures as follows:



	$N_2(g)$	$+\ 3\,H_2(g)$	$\rightleftharpoons\ 2\,NH_3(g)$
Equilibrium pressure (atm)	0.432	0.928	x

Because we do not know the equilibrium pressure of NH_3, we represent it with a variable, x. At equilibrium the pressures must satisfy the equilibrium-constant expression:

We now rearrange the equation to solve for x:



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

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

$$x = \sqrt{5.01 \times 10^{-6}} = 2.24 \times 10^{-3}\text{ atm} = P_{NH_3}$$

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

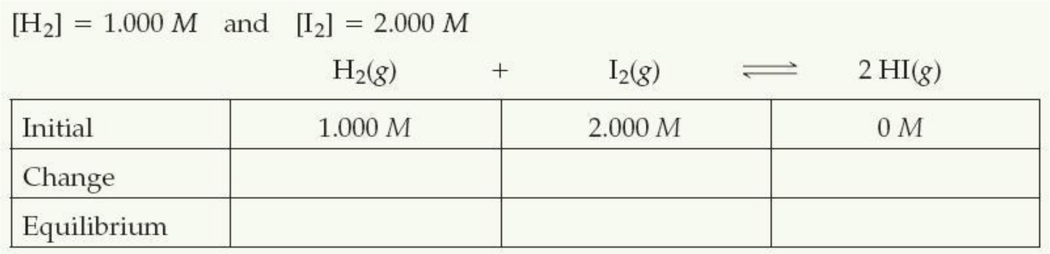
Sample Exercise 15.12 Calculating Equilibrium Concentrations from Initial Concentrations

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

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

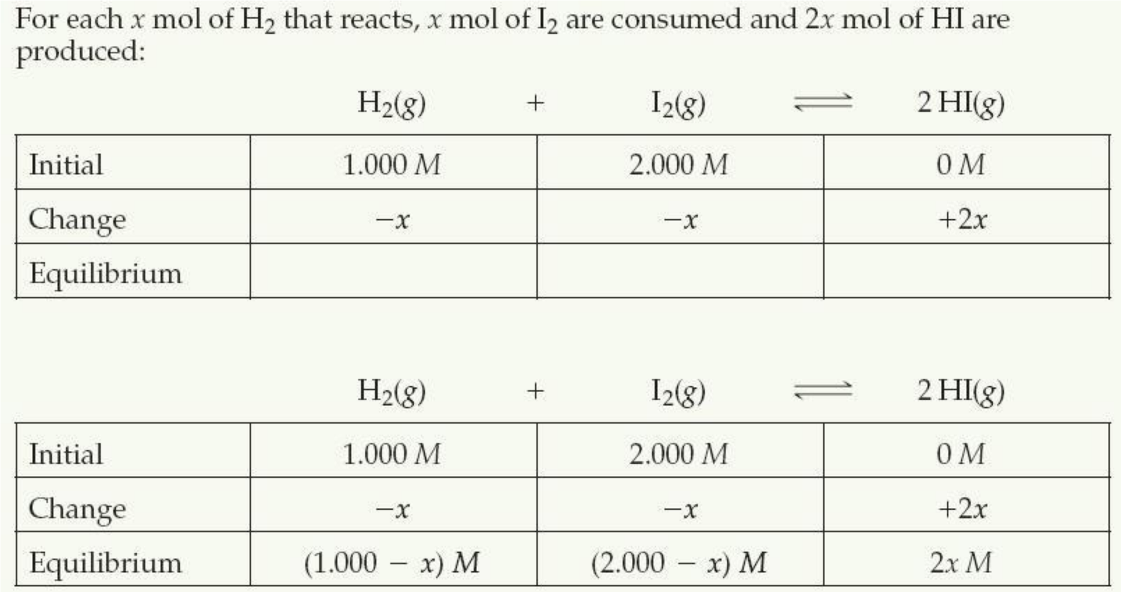
at 448 °C is 50.5. What are the equilibrium concentrations of H_2, I_2, and HI in moles per liter?

Solution



$[H_2] = 1.000\ M$ and $[I_2] = 2.000\ M$

	$H_2(g)$ +	$I_2(g)$ $\rightleftharpoons$	$2\ HI(g)$
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 2*x* 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			

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

Solution (continued)

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

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

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

$$x = \frac{-(-151.5) \pm \sqrt{1(-151.5)^2 - 4(46.5)(101.0)}}{2(46.5)} = 2.323 \text{ or } 0.935$$

$$[H_2] = 1.000 - x = 0.065\ M$$
$$[I_2] = 2.000 - x = 1.065\ M$$
$$[HI] = 2x = 1.87\ M$$

15.7

Le Chatelier's Principle

The Haber Process

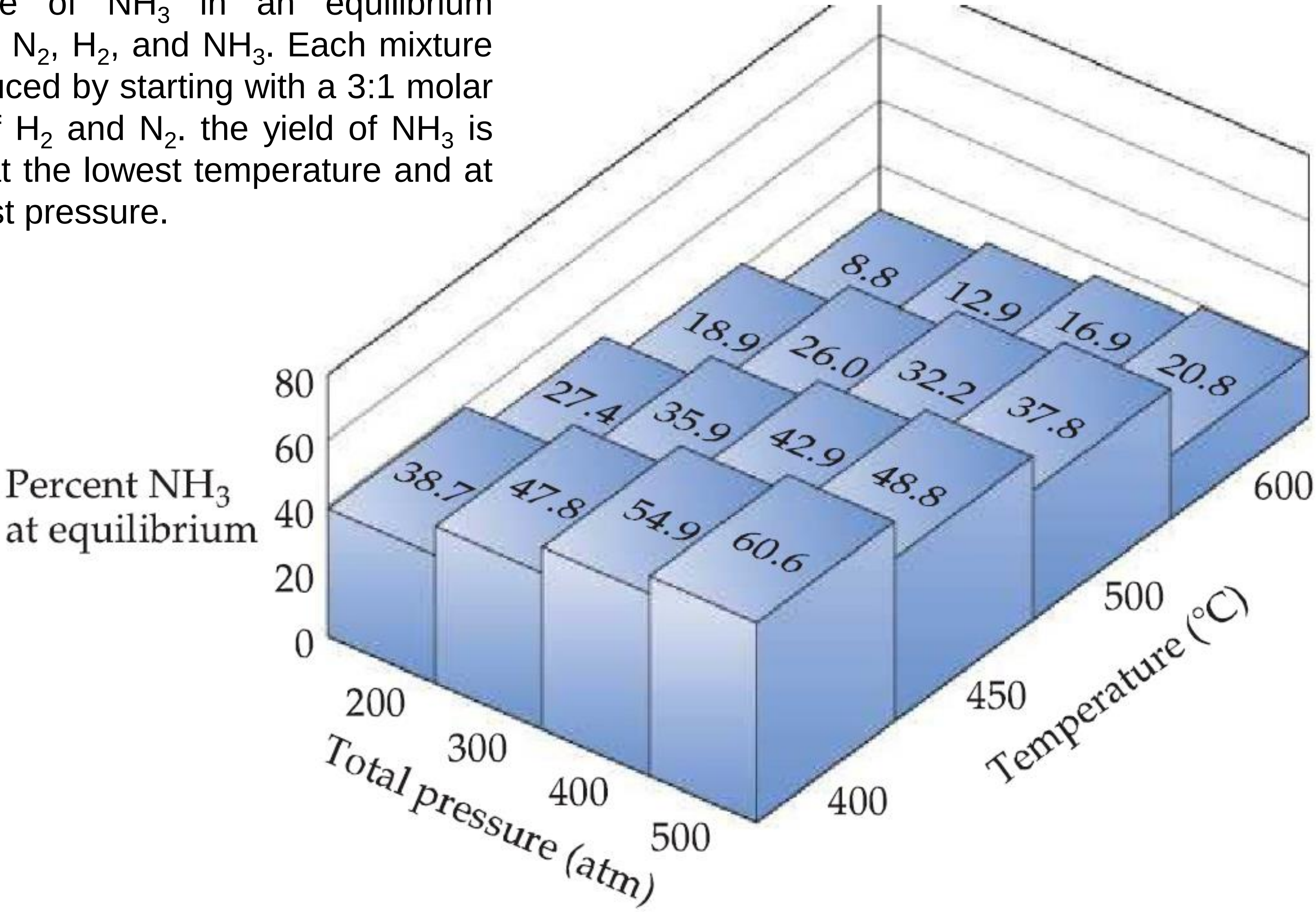
The transformation of nitrogen and hydrogen into ammonia (NH_3) is of tremendous significance in agriculture, where ammonia-based fertilizers are of utmost importance.

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

When Haber developed his process for making ammonia from N_2 and H_2, he sought the factors that might be varied to increase the yield of NH_3. Using the values of the equilibrium constant at various temperatures, he calculated the equilibrium amounts of NH_3 formed under a variety of conditions.

Notice that the percent of NH_3 present at equilibrium **decreases** with **increasing temperature** and **increases** with **increasing pressure**. We can understand these effects in terms of a principle first put forward by Henri-Louis Le Chatelier.

Effect of temperature and pressure on the percentage of NH_3 in an equilibrium mixture of N_2, H_2, and NH_3. Each mixture was produced by starting with a 3:1 molar mixture of H_2 and N_2. the yield of NH_3 is greatest at the lowest temperature and at the highest pressure.



Le Chatelier’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”.

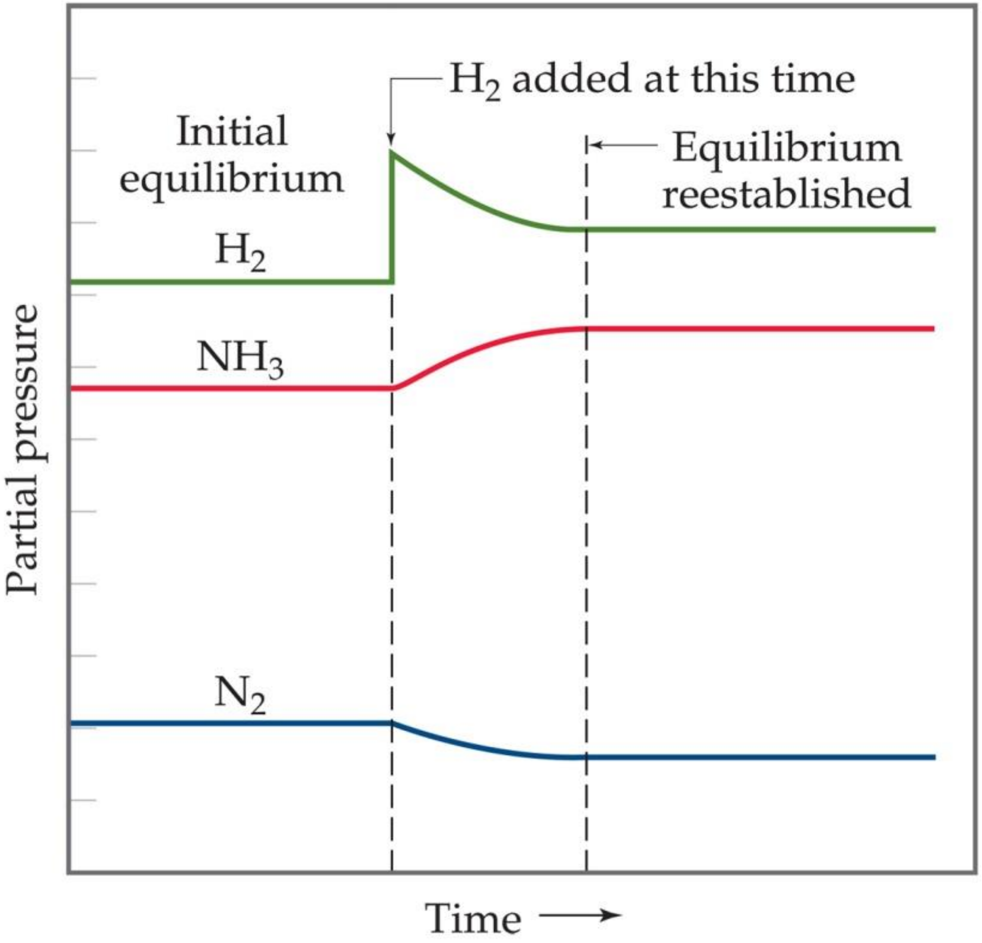
We will consider three ways that a chemical equilibrium can be disturbed:

(1) Adding or removing a reactant or product.
(2) Changing the pressure by changing the volume.
(3) Changing the temperature.

Change in Reactant or Product Concentrations

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

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



If a chemical system is at equilibrium and we increase or decrease the concentration of a substance (either a reactant or a product), the system reacts to consume or produce some of the substance to re-establish the equilibrium.

Some of the added ammonia would decompose to form N_2 and H_2. In the Haber reaction, therefore, removing NH_3 from an equilibrium mixture of N_2, H_2, and NH_3 causes the reaction to shift from left to right to form more NH_3.

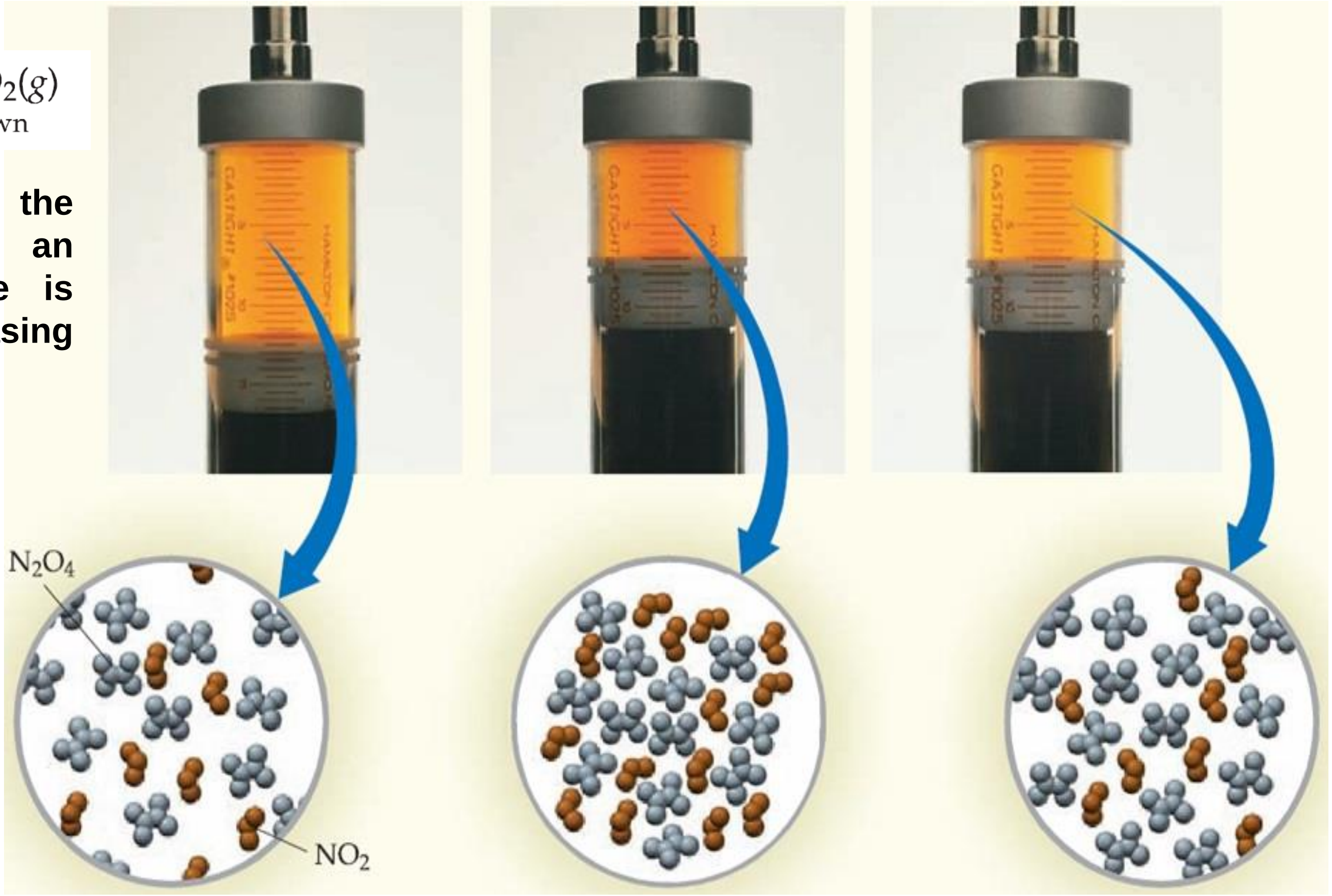
Effects of Volume and Pressure Changes

If a system is at equilibrium and its volume is decreases thereby increasing its total pressure, Le Chatelier’s principle indicates that the system will respond by shifting its equilibrium position to reduce the pressure.

A system can reduce its pressure by reducing the total number of gas molecules. Thus, at constant temperature, reducing the volume of a gaseous equilibrium mixture causes the system to shift in the direction that reduces the number of moles of gas.

$$\underset{\text{Colorless}}{N_2O_4(g)} \rightleftharpoons \underset{\text{Brown}}{2\,NO_2(g)}$$

What happens if the total pressure of an equilibrium mixture is increased by decreasing the volume ?



According to Le Chateliers principle, we expect the equilibrium to shift to the side that reduces the total number of moles of gas, which is the reactant side in this case. We therefore expect the equilibrium to shift to the left, so that NO_2 is converted into N_2O_4 as equilibrium is reestablished.

Examples:

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

Four molecules of reactant are consumed for every two molecules of product produced. Consequently, an increase in pressure (decrease in volume) causes a shift toward the side with fewer gas molecules, which leads to the formation of more NH_3.

In the case of the reaction $H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$, the number of molecules of gaseous products (two) equals the number of molecules of gaseous reactants; therefore, changing the pressure will not influence the position of the equilibrium.

Note: changes in concentrations or partial pressures cause shifts in equilibrium without changing the value of the equilibrium constant.

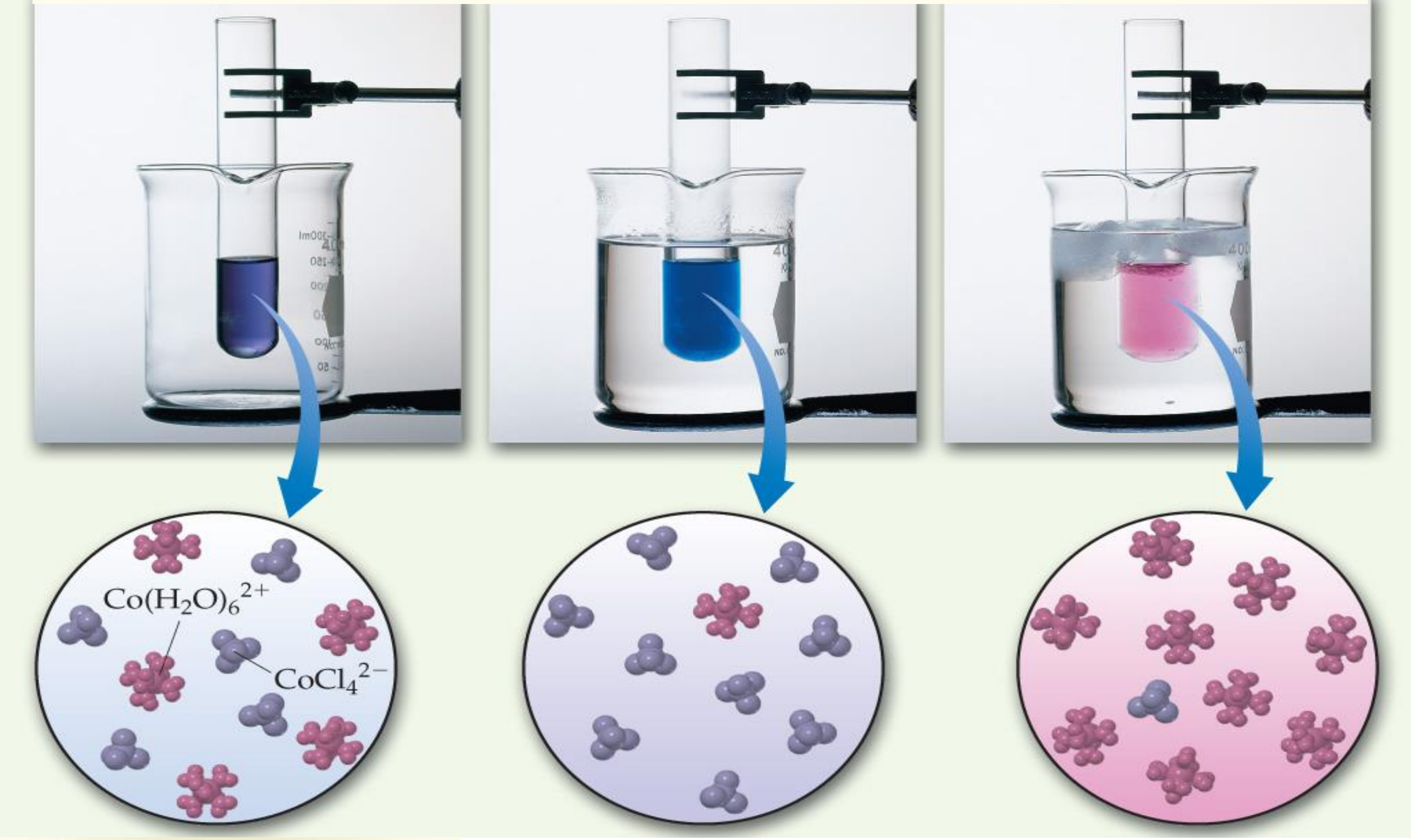
Effect of Temperature Changes

Changes in concentrations or partial pressures cause shifts in equilibrium without changing the value of the equilibrium constant. In contrast, almost every equilibrium constant changes in value as the temperature changes.

In an endothermic reaction, heat is absorbed as reactants are converted to products. Increasing the temperature causes the equilibrium to shift to the right and ***K*** to increase. Lowering the temperature shifts the equilibrium in the direction that produces heat, to the left, decreasing ***K***.

Endothermic reaction

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



At room temperature both the pink $Co(H_2O)_6^{2+}$ and blue $CoCl_4^{2-}$ ions are present in significant amounts, giving a violet color to the solution.

Heating the solution shifts the equilibrium to the right, forming more blue $CoCl_4^{2-}$.

Cooling the solution shifts the equilibrium to the left, toward pink $Co(H_2O)_6^{2+}$.

A simple way to do this is to treat heat as if it were a chemical reagent.

In an endothermic (heat-absorbing) reaction we can consider heat as a reactant, whereas in an exothermic (heat-releasing) reaction we can consider heat as a product.

Endothermic: $\text{Reactants} + \textit{heat} \rightleftharpoons \text{products}$

Exothermic: $\text{Reactants} \rightleftharpoons \text{products} + \textit{heat}$

- Endothermic: Increasing T results in an increase in K.
- Exothermic: Increasing T result in a decrease in K.

Sample Exercise 15.13 Using Le Châtelier's Principal to Predict shifts in Equilibrium

Consider the equilibrium

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

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?

Solution

(a) The system will adjust to decrease the concentration of the added N_2O_4, so the equilibrium shifts to the right, in the direction of products.

(b) The system will adjust to the removal of NO_2 by shifting to the side that produces more NO_2; thus, the equilibrium shifts to the right.

(c) Adding N_2 will increase the total pressure of the system, but N_2 is not involved in the reaction. The partial pressures of NO_2 and N_2O_4 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 N_2O_4. Note that only this last change also affects the value of the equilibrium constant, K.

Sample Exercise 15.14 Predicting the Effect of Temperature on *K*

(a) Using the standard heat of formation data in Appendix C, determine the standard enthalpy change for the reaction

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

(b) Determine how the equilibrium constant for this reaction should change with temperature.

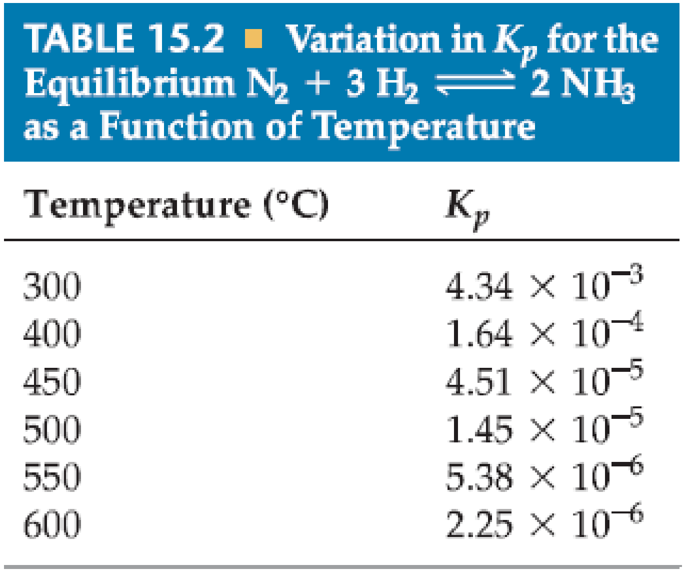


TABLE 15.2 ■ **Variation in K_p for the Equilibrium $N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3$ as a Function of Temperature**

Temperature (°C)	K_p
300	4.34×10^{-3}
400	1.64×10^{-4}
450	4.51×10^{-5}
500	1.45×10^{-5}
550	5.38×10^{-6}
600	2.25×10^{-6}

Solution

(a) At 25 °C, ΔH^o_f for $NH_3(g)$ is –46.19 kJ/mol. The ΔH^o_f values for $H_2(g)$ and $N_2(g)$ are zero by definition because the enthalpies of formation of the elements in their normal states at 25 °C are defined as zero. Because 2 mol of NH_3 is formed, the total enthalpy change is

$$(2\text{ mol})(-46.19\text{ kJ/mol}) - 0 = -92.38\text{ kJ}$$

(b) Because the reaction in the forward direction is exothermic, we can consider heat a product of the reaction. An increase in temperature causes the reaction to shift in the direction of less NH_3 and more N_2 and H_2. This effect is seen in the values for K_p presented in **Table 15.2**. Notice that K_p changes markedly with changes in temperature and that it is larger at lower temperatures.

Q & A

When a reaction is at a state of equilibrium, the rate of the forward reaction ______________ the rate of the reverse reaction.

a. is equal to
b. is slower than
c. is faster than
d. is the reverse of

At equilibrium, the equilibrium constant is equal to:

a. [reactants] / [products]
b. [products] / [reactants]
c. [reactants] x [products]
d. [reactants] + [products]

A large value of the equilibrium constant indicates that when the reaction reaches equilibrium, mostly _______ will be present.

a. reactants
b. products
c. catalysts
d. shrapnel

When equilibrium is achieved:

a. $Q > K$

b. $Q < K$

c. $Q = K$

d. $Q^2 = K$

$CO_2 + H_2 \leftarrow\rightarrow CO + H_2O$

If all species are gases and H_2 is added, the amount of CO present at equilibrium will:

a. increase
b. decrease
c. remain unchanged
d. disappear

For the reaction:

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

The equilibrium constant 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 K_p is larger at the lower temperature

$CO_2 + H_2 \leftrightarrow CO + H_2O$

If all species are gases and H_2O is added, the amount of CO present at equilibrium will:

a. increase
b. decrease
c. remain unchanged
d. disappear

$CO_2 + H_2 \leftrightarrow CO + H_2O$

If all species are gases and CO_2 is removed, the amount of CO present at equilibrium will:

a. increase
b. decrease
c. remain unchanged
d. disappear

$CO_2 + H_2 \leftrightarrow CO + H_2O$

If the reaction is endothermic and the temperature is raised, the amount of CO present will:

a. increase
b. decrease
c. remain unchanged
d. disappear

$CO_2 + H_2 \leftrightarrow CO + H_2O$

If all species are gases and the container is compressed, the amount of CO present will:

a. increase
b. decrease
c. remain unchanged
d. disappear

$CO_2 + H_2 \leftrightarrow CO + H_2O$

If a catalyst is added to the equilibrium, the amount of CO present will:

a. increase
b. decrease
c. remain unchanged
d. disappear

What is K_p in terms of K_c for the following reaction ?

$$2\ \mathrm{NO}(g) \quad + \quad \mathrm{O_2}(g) \longrightarrow 2\ \mathrm{NO_2}(g)$$

- $K_p = K_c RT$
- $K_p = K_c/RT$
- $K_p = K_c R/T$
- $K_p = K_c$
- $K_p = K_c/(RT)^2$

What is the correct equilibrium constant expression for the reaction:

$$P_4(s) \quad + \quad 6\,Cl_2(g) \longrightarrow 4\,PCl_3(l)$$

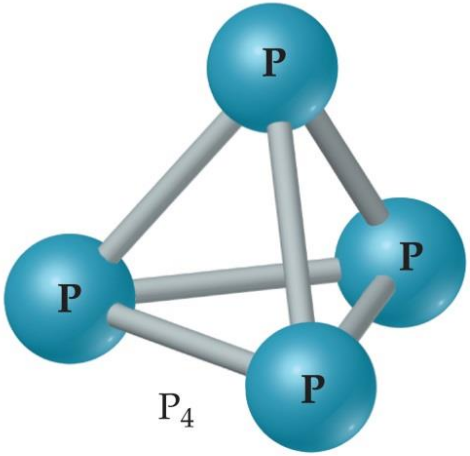
1. $\frac{[PCl_3]^4}{[P_4][Cl_2]^6}$

2. $\frac{[PCl_3]^4}{[Cl_2]^6}$

3. $\boxed{\frac{1}{[Cl_2]^6}}$

4. $\frac{[Cl_2]^6}{[PCl_3]^4}$

5. $\frac{[4\,PCl_3]^4}{[P_4][6\,Cl_2]^6}$



Which accurately reflects the changes in concentration that will occur if O_2 is added to disturb the equilibrium?

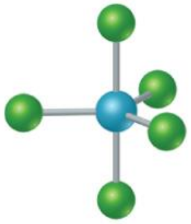
$$2\,NO(g) + O_2(g) \rightleftharpoons 2\,NO_2(g)$$

	[NO]	$[O_2]$	[NO]
1.	Increase	Increase	Increase
2.	Increase	Increase	Decrease
3.	Decrease	Decrease	Decrease
4.	Decrease	Decrease	Increase
5.	Decrease	Increase	Increase

Which of the following will result in an equilibrium shift to the right?

$$\mathbf{PCl_3(\mathit{g}) + Cl_2(\mathit{g}) \longrightarrow PCl_5(\mathit{g})} \quad \Delta H^\circ = -87.9\ \mathrm{kJ/mol}$$

- Increase temperature/increase volume
- Increase temperature/decrease volume
- Decrease temperature/increase volume
- Decrease temperature/decrease volume
- None of the above



PCl_5

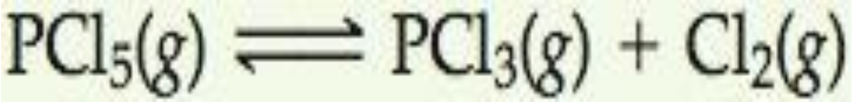
What is the value of K_c for the reaction?

$2\,CO(g) + O_2(g) \longrightarrow 2\,CO_2(g)$ $K_c = 5.0 \times 10^{18}$ at 25 °C

$CO_2(g) \longrightarrow CO(g) + 1/2\,O_2(g)$ $K_c = ??$ at 25 °C

- $K_c = 1/(5.0 \times 10^{18})^{1/2}$
- $K_c = 1/(2.5 \times 10^{18})$
- $K_c = -(5.0 \times 10^{18})/2$
- $K_c = -(5.0 \times 10^{18})^{1/2}$
- $K_c = 2/(5.0 \times 10^{18})^{1/2}$

At 500 K the reaction



$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

has K_p = 0.497. In an equilibrium mixture at 500 K, the partial pressure of PCl_5 is 0.860 atm and that of PCl_3 is 0.350 atm. What is the partial pressure of Cl_2 in the equilibrium mixture?

Answer: 1.22 atm

For the reaction:

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

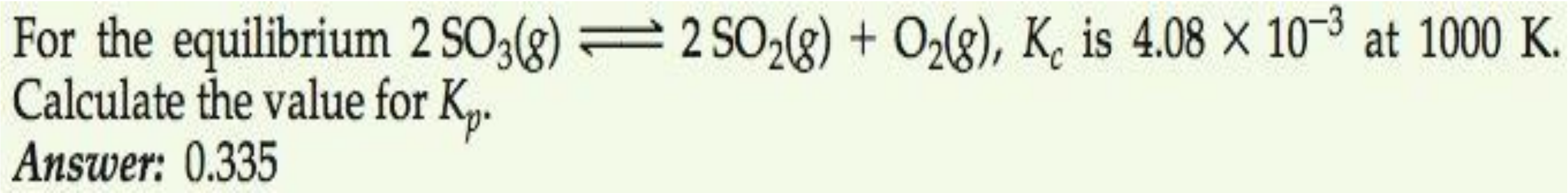
The equilibrium constant K_p has the value 0.497 at 500 K. A gas cylinder at 500 K is changed with PCl_5(g) at an initial pressure of 1.66 atm. What are the equilibrium pressures of PCl_5, PCl_3, and Cl_2 at this temperature?

Answer: $P_{PCL5} = 0.967$ atm

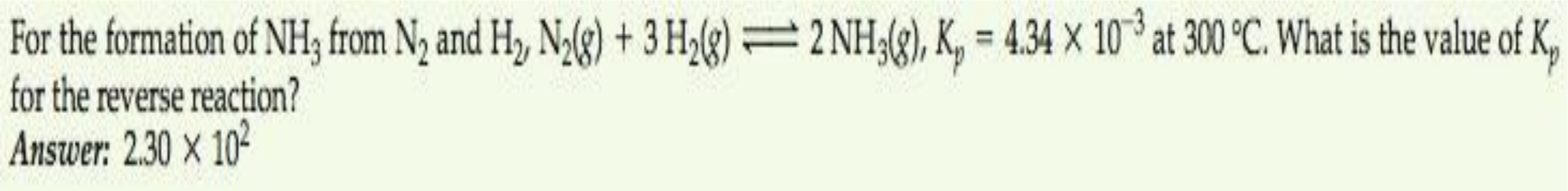
$P_{PCl3} = P_{Cl2} = 0.693$ atm

Write the equilibrium-constant expression K_c, for **(a)** $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$, **(b)** $Cd^{2+}(aq) + 4\,Br^{-}(aq) \rightleftharpoons CdBr_4{}^{2-}(aq)$

Answers: **(a)** $K_c = \dfrac{[HI]^2}{[H_2][I_2]}$; **(b)** $K_c = \dfrac{[CdBr_4{}^{2-}]}{[Cd^{2+}][Br^{-}]^4}$

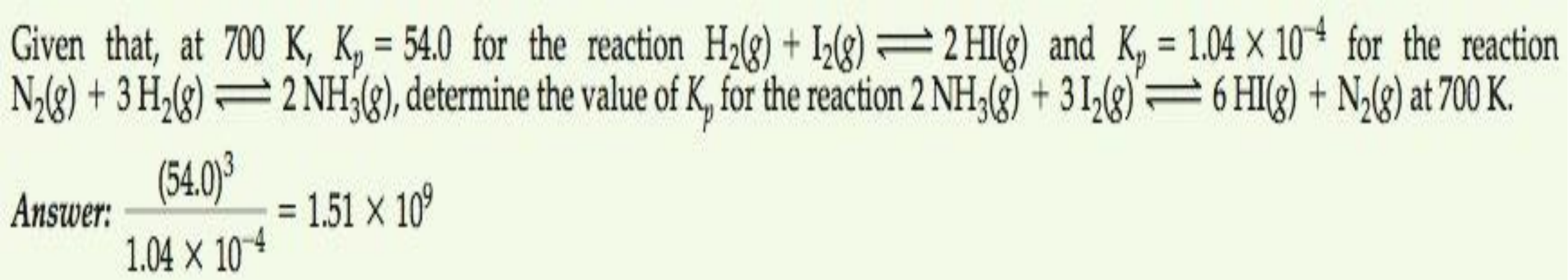


For the equilibrium $2\,SO_3(g) \rightleftharpoons 2\,SO_2(g) + O_2(g)$, K_c is 4.08×10^{-3} at 1000 K. Calculate the value for K_p.
Answer: 0.335



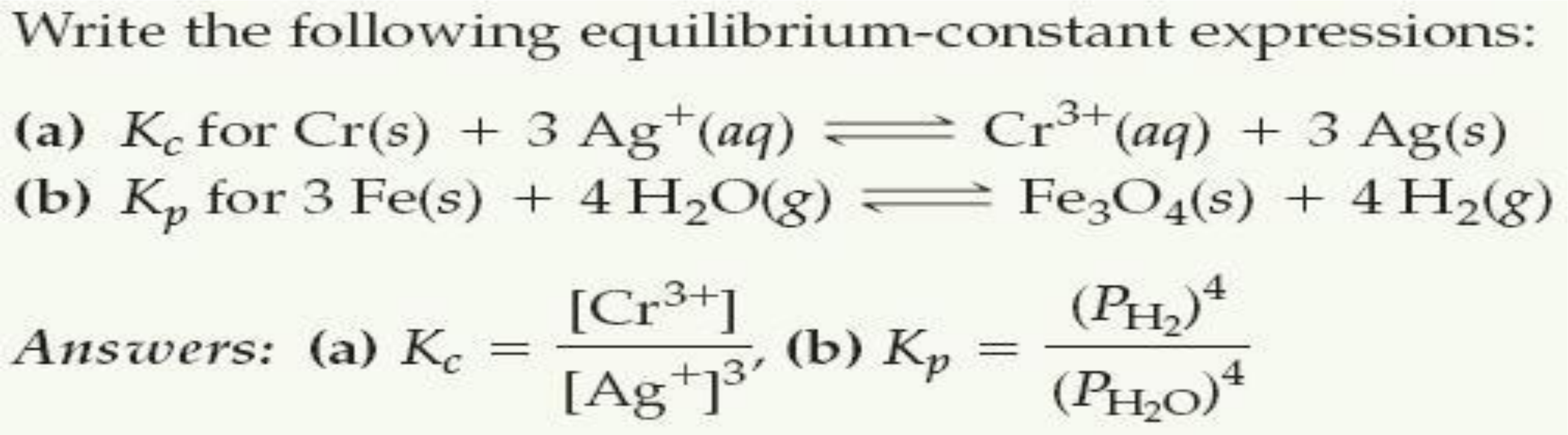
For the formation of NH_3 from N_2 and H_2, $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$, $K_p = 4.34 \times 10^{-3}$ at 300 °C. What is the value of K_p for the reverse reaction?

Answer: 2.30×10^2



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



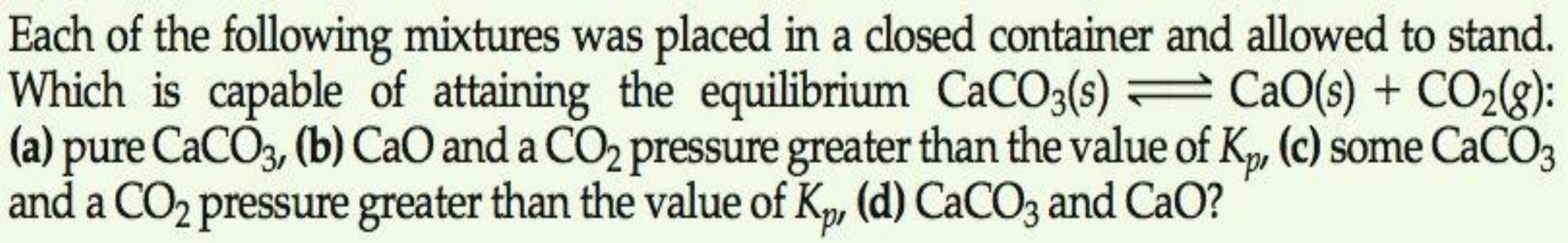
Write the following equilibrium-constant expressions:

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

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

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

Sample Exercise Analyzing a Heterogeneous Equilibrium



Each of the following mixtures was placed in a closed container and allowed to stand. Which is capable of attaining the equilibrium $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$: **(a)** pure $CaCO_3$, **(b)** CaO and a CO_2 pressure greater than the value of K_p, **(c)** some $CaCO_3$ and a CO_2 pressure greater than the value of K_p, **(d)** $CaCO_3$ and CaO?

Solution

Equilibrium can be reached in all cases except (c) as long as sufficient quantities of solids are present. **(a)** $CaCO_3$ simply decomposes, forming $CaO(s)$ and $CO_2(g)$ until the equilibrium pressure of CO_2 is attained. There must be enough $CaCO_3$, however, to allow the CO_2 pressure to reach equilibrium. **(b)** CO_2 continues to combine with CaO until the partial pressure of the CO_2 decreases to the equilibrium value. **(c)** There is no CaO present, so equilibrium cannot be attained because there is no way the CO_2 pressure can decrease to its equilibrium value (which would require some of the CO_2 to react with CaO). **(d)** The situation is essentially the same as in (a): $CaCO_3$ decomposes until equilibrium is attained. The presence of CaO initially makes no difference.

When added to $Fe_3O_4(s)$ 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 $3\,Fe(s) + 4\,H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4\,H_2(g)$?

Answer: only $H_2(g)$

An aqueous solution of acetic acid is found to have the following equilibrium concentrations at 25 °C: $[HC_2H_3O_2] = 1.65 \times 10^{-2}\ M$; $[H^+] = 5.44 \times 10^{-4}\ M$; and $[C_2H_3O_2^-] = 5.44 \times 10^{-4}\ M$. Calculate the equilibrium constant K_c for the ionization of acetic acid at 25 °C. The reaction is

$$HC_2H_3O_2(aq) \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq)$$

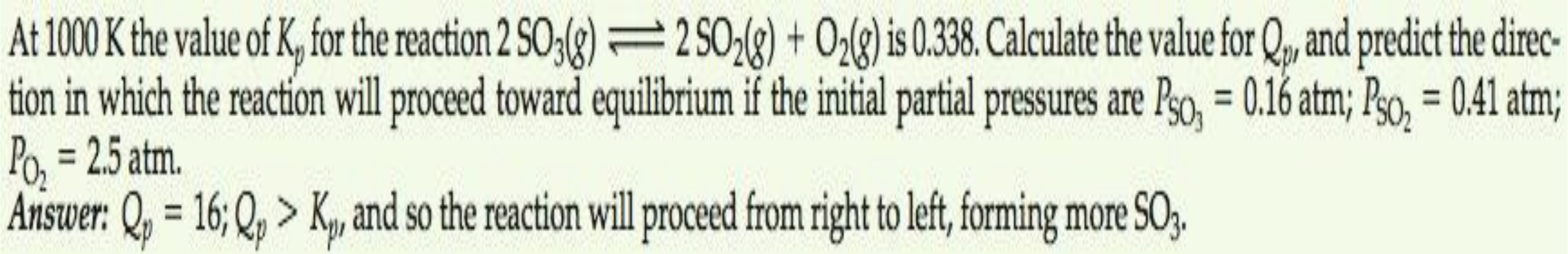
Answer: 1.79×10^{-5}

Sulfur trioxide decomposes at high temperature in a sealed container:

Initially, the vessel is charged at 1000 K with $SO_3(g)$ at a partial pressure of 0.500 atm. At equilibrium the SO_3 partial pressure is 0.200 atm. Calculate the value of K_p at 1000 K.

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

Answer: 0.338



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.

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

For the reaction

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \qquad \Delta H^\circ = 87.9\ \text{kJ}$$

in which direction will the equilibrium shift when **(a)** $Cl_2(g)$ is removed, **(b)** the temperature is decreased, **(c)** the volume of the reaction system is increased, **(d)** $PCl_3(g)$ is added?

Answer: **(a)** right, **(b)** left, **(c)** right, **(d)** left

Using the thermodynamic data in Appendix C, determine the enthalpy change for the reaction

$$2\,POCl_3(g) \rightleftharpoons 2\,PCl_3(g) + O_2(g)$$

Use this result to determine how the equilibrium constant for the reaction should change with temperature.

Answer: $\Delta H^o = 508.3$ kJ; the equilibrium constant will increase with increasing temperature


Thank You!