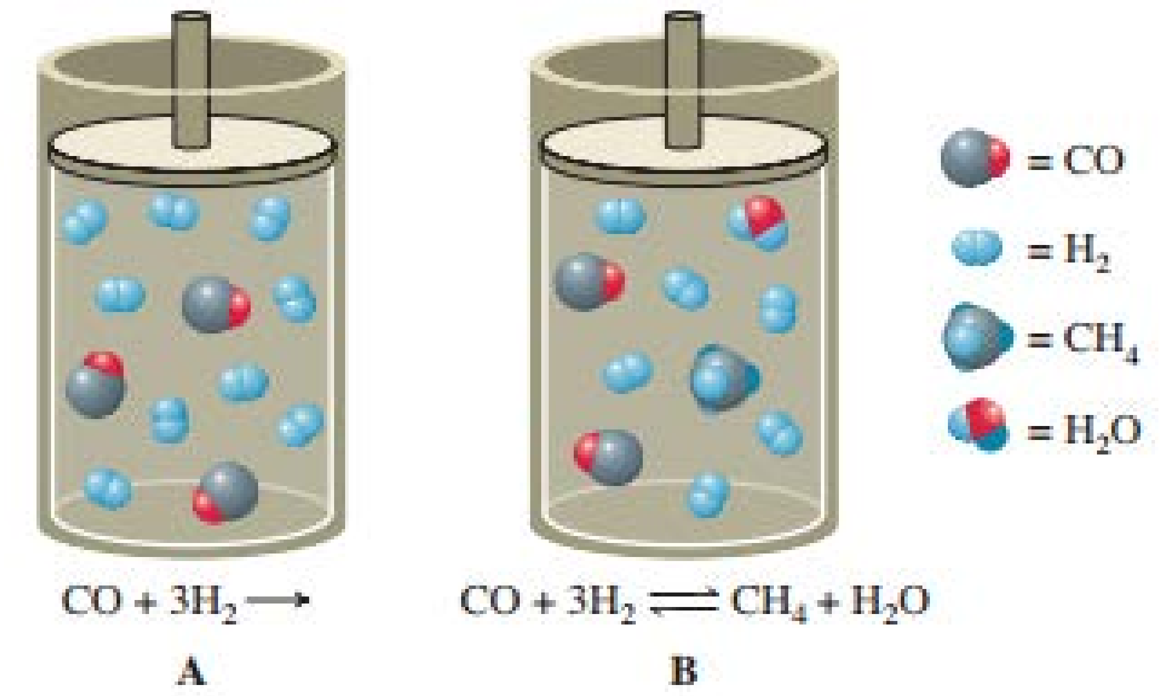
GENERAL CHEMISTRY

CHEMICAL EQUILIBRIUM

Chemical Equilibrium-A Dynamic Equilibrium

Change of rates as reaction proceeds



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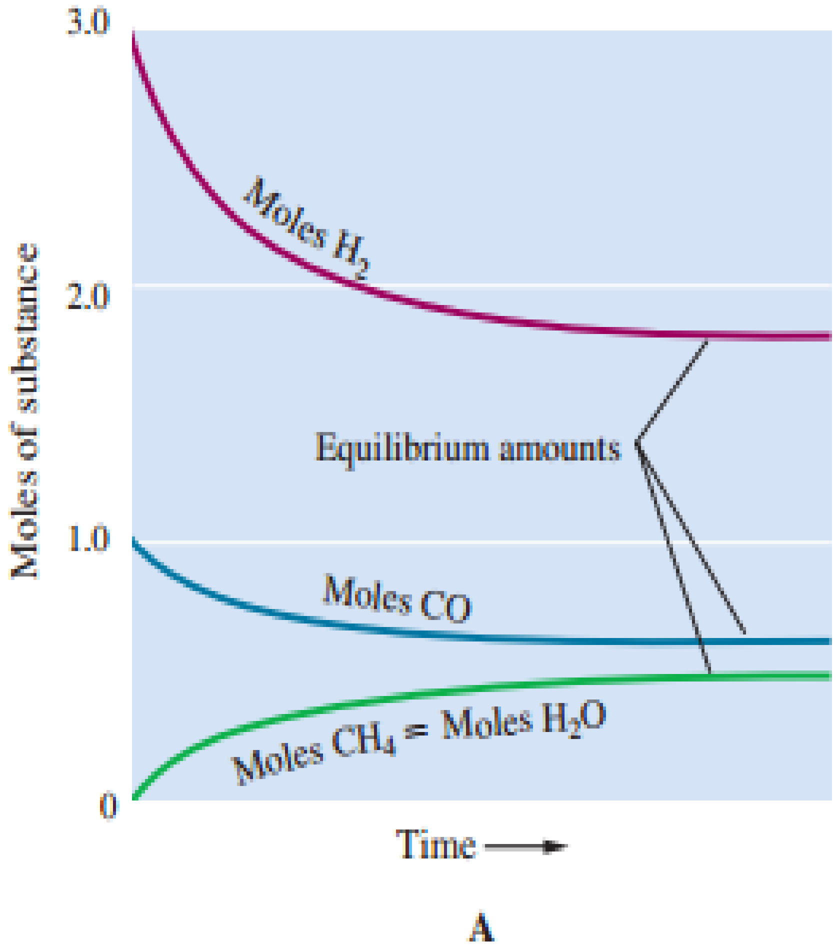
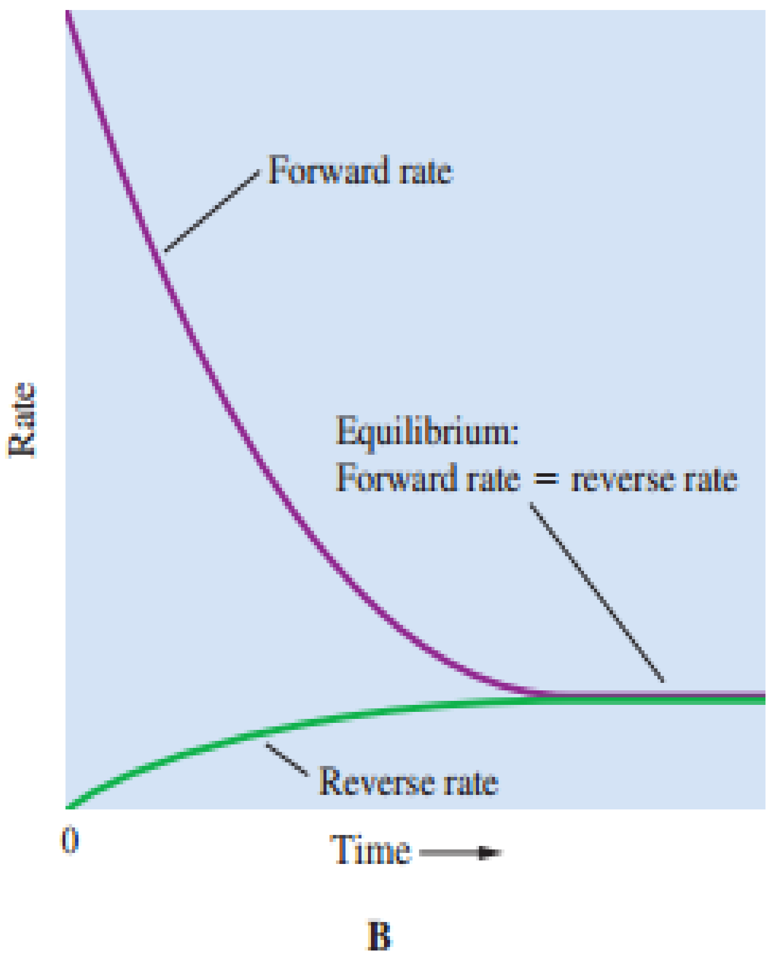
Catalytic methanation reaction approaches equilibrium





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The Equilibrium Constant

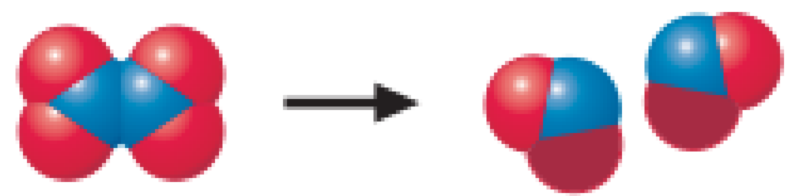
Consider the reaction

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

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

Equilibrium: A Kinetics Argument

Temperature effect on NO_2–N_2O_4 equilibrium



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

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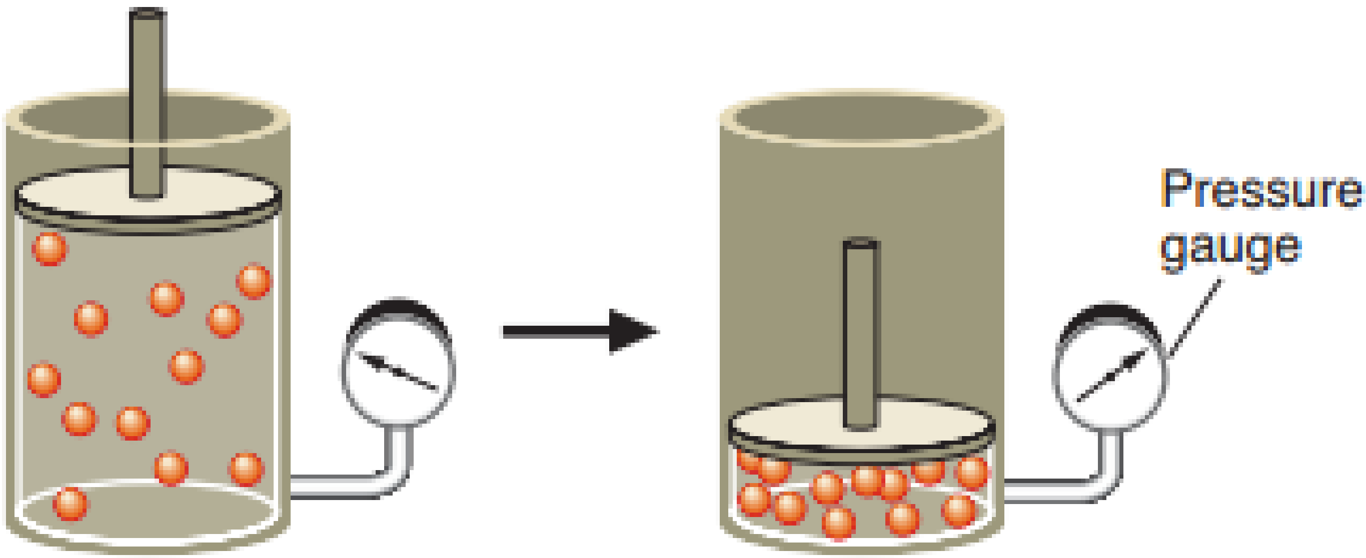
The Equilibrium Constant Kp



The concentration of a gas at a given temperature is proportional to the pressure

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When you express an equilibrium constant for a gaseous reaction in terms of partial pressures, you call it the **equilibrium constant Kp**. For catalytic methanation,

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

the equilibrium expression in terms of partial pressures becomes

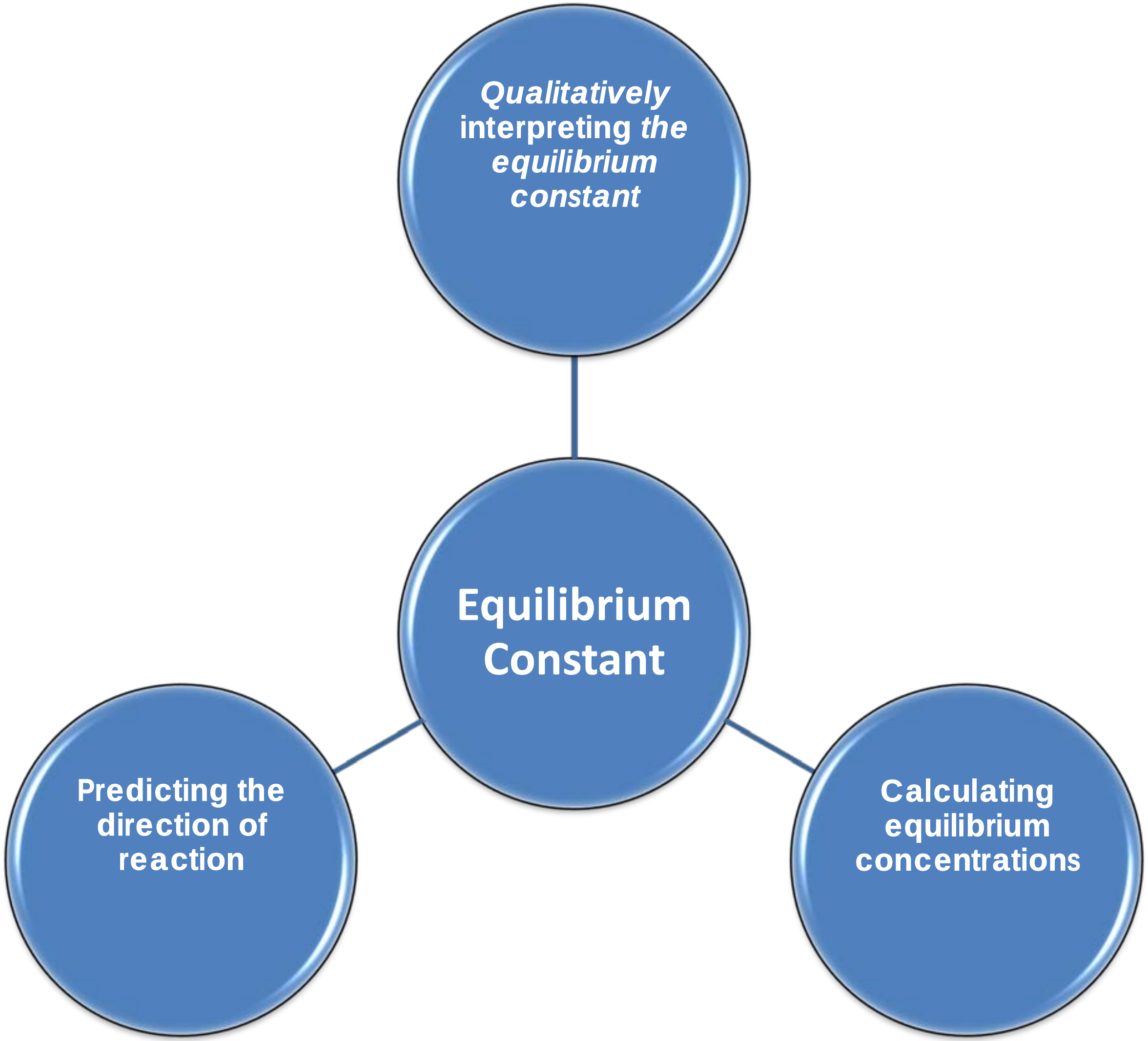
$$K_p = \frac{P_{CH_4} P_{H_2O}}{P_{CO} P_{H_2}{}^3}$$

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

$$K_p = 3.92 \times (0.0821 \times 1200)^{-2} = 4.04 \times 10^{-4}$$

Heterogeneous Equilibria; Solvents in a Homogenous Equilibria

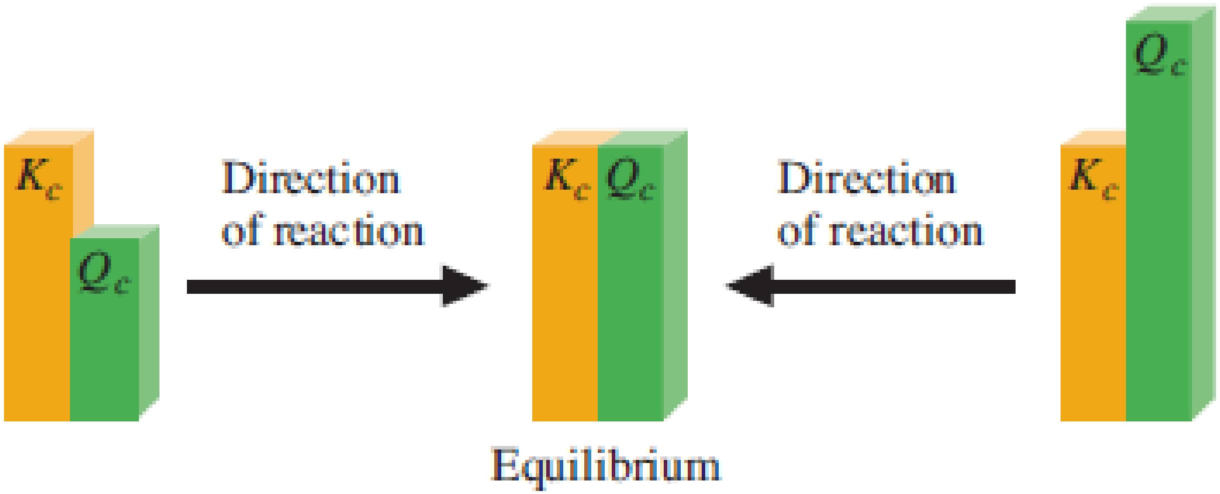
The ways in which an equilibrium constant can be used.



Methane (natural gas) reacts with oxygen

The equilibrium mixture is almost entirely carbon dioxide and water. The equilibrium constant K_c for the reaction $CH_4 + 2O_2 \rightleftharpoons CO_2 + 2H_2O$ is 10^{140} at 25°C.

Direction of reaction



The figure shows the relative sizes of Q_c and K_c. Reaction proceeds in the direction of the arrows. Thus, on the left, $Q_c < K_c$, so the reaction goes to the right, from reactants to products.

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Predicting the Direction of Reaction

Suppose a gaseous mixture from an industrial plant has the following composition at 1200 K: 0.0200 M CO, 0.0200 M H2, 0.00100 M CH4, and 0.00100 M H2O.

If the mixture is passed over a catalyst at 1200 K, would the reaction go toward the right or the left? That is, would the mixture form more CH4 and H2O in going toward equilibrium, or more CO and H2?

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

To answer this question, you substitute the concentrations of substances into the *reaction quotient and compare its value to Kc.*

$$Q_c = \frac{[CH_4]_i[H_2O]_i}{[CO]_i[H_2]_i^3}$$

where the subscript *i indicates concentrations at a particular instant i. When you substitute* the concentrations of the gaseous mixture described earlier, you get

$$Q_c = \frac{(0.00100)(0.00100)}{(0.0200)(0.0200)^3} = 6.25$$

For the general reaction $aA + bB \rightleftharpoons cC + dD$,

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

Then

If $Q_c > K_c$, the reaction will go to the left.
If $Q_c < K_c$, the reaction will go to the right.
If $Q_c = K_c$, the reaction mixture is at equilibrium.

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Using the Reaction Quotient

A 50.0-L reaction vessel contains 1.00 mol N2, 3.00 mol H2, and 0.500 mol NH3. Will more ammonia, NH3, be formed or will it dissociate when the mixture goes to equilibrium at 400C? The equation is

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

K_c is 0.500 at 400°C.

The composition of the gas has been given in terms of moles. You convert these to molar concentrations by dividing by the volume (50.0 L). This gives 0.0200 M N2, 0.0600 M H2, and 0.0100 M NH3.

Substituting these concentrations into the reaction quotient gives

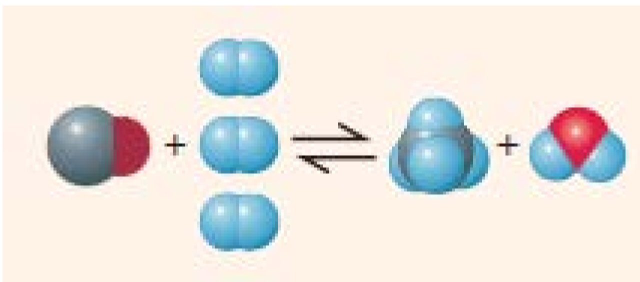
$$Q_c = \frac{[NH_3]_i^2}{[N_2]_i[H_2]_i^3} = \frac{(0.0100)^2}{(0.0200)(0.0600)^3} = 23.1$$

Because Qc 23.1 is greater than Kc 0.500, the reaction will go to the left as it approaches equilibrium. Therefore, **ammonia will dissociate.**

Obtaining One Equilibrium Concentration Given the Others

A gaseous mixture contains 0.30 mol CO, 0.10 mol H2, and 0.020 mol H2O, plus an unknown amount of CH4, in each liter. This mixture is at equilibrium at 1200 K.

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$



What is the concentration of CH4 in this mixture? The equilibrium constant Kc equals 3.92.

Solution

The equilibrium-constant equation is

$$K_c = \frac{[CH_4][H_2O]}{[CO][H_2]^3}$$

Substituting the known concentrations and the value of *Kc gives*

$$3.92 = \frac{[CH_4](0.020)}{(0.30)(0.10)^3}$$

You can now solve for [CH4]

$$[CH_4] = \frac{(3.92)(0.30)(0.10)^3}{(0.020)} = 0.059$$

The concentration of CH4 in the mixture is **0.059 mol/L.**

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Solving an Equilibrium Problem (Involving a Linear Equation in *x*)

The reaction

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

is used to increase the ratio of hydrogen in synthesis gas (mixtures of CO and H2). Suppose you start with 1.00 mol each of carbon monoxide and water in a 50.0-L vessel. How many moles of each substance are in the equilibrium mixture at 1000C? The equilibrium constant Kc at this temperature is 0.58.

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Solution

Step 1: The starting concentrations of CO and H2O are

$$[CO] = [H_2O] = \frac{1.00 \text{ mol}}{50.0 \text{ L}} = 0.0200 \text{ mol/L}$$

Concentration (M)	$CO(g)$	+	$H_2O(g)$	$\rightleftharpoons$	$CO_2(g)$	+	$H_2(g)$
Starting	0.0200		0.0200		0		0
Change	$-x$		$-x$		$+x$		$+x$
Equilibrium	$0.0200 - x$		$0.0200 - x$		x		x

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Step 2: You then substitute the values for the equilibrium concentrations into the equilibrium-constant equation,

$$K_c = \frac{[CO_2][H_2]}{[CO][H_2O]}$$

and you get

$$0.58 = \frac{(x)(x)}{(0.0200 - x)(0.0200 - x)}$$

or

$$0.58 = \frac{x^2}{(0.0200 - x)^2}$$

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Step 3: You now solve this equilibrium equation for the value of x. Note that the right hand side is a perfect square. If you take the square root of both sides, you get

$$\pm 0.76 = \frac{x}{0.0200 - x}$$

We have written +,- to indicate that you should consider both positive and negative values, because both are mathematically possible. Rearranging the equation gives

$$x = \frac{0.0200 \times 0.76}{1.76} = 0.0086 \quad \text{and} \quad x = \frac{-0.0200 \times 0.76}{0.24} = -0.063$$

$$0.0114 \text{ mol/L} \times 50.0 \text{ L} = 0.570 \text{ mol}$$

The equilibrium composition of the reaction mixture is **0.570 mol CO, 0.570 mol H_2O, 0.43 mol CO_2, and 0.43 mol H_2.**

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Solving an Equilibrium Problem (Involving a Quadratic Equation in *x*)

Hydrogen and iodine react according to the equation

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

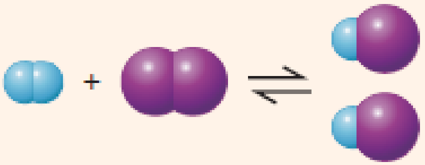
Suppose 1.00 mol H2 and 2.00 mol I2 are placed in a 1.00-L vessel. How many moles of substances are in the gaseous mixture when it comes to equilibrium at 458C? The equilibrium constant Kc at this temperature is 49.7.

Solution

Step 1: The concentrations of substances are as follows:

Step 1: The concentrations of substances are as follows:

Concentration (M)	$H_2(g)$	+	$I_2(g)$	$\rightleftharpoons$	$2HI(g)$
Starting	1.00		2.00		0
Change	$-x$		$-x$		$2x$
Equilibrium	$1.00 - x$		$2.00 - x$		$2x$



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Step 2: Substituting into the equilibrium-constant equation,

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

you get

$$49.7 = \frac{(2x)^2}{(1.00 - x)(2.00 - x)}$$

Step 3: Because the right-hand side is not a perfect square, you must use the quadratic formula to solve for x. *The equation rearranges to give*

$$(1.00 - x)(2.00 - x) = (2x)^2/49.7 = 0.0805x^2$$

or

$$0.920x^2 - 3.00x + 2.00 = 0$$

Hence,

$$x = \frac{3.00 \pm \sqrt{9.00 - 7.36}}{1.84} = 1.63 \pm 0.70$$

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A quadratic equation has two mathematical solutions. You obtain one solution by taking the upper (positive) sign in and the other by taking the lower (negative) sign. You get

$$x = 2.33 \qquad \text{and} \qquad x = 0.93$$

However, *x=2.33 gives a negative value to 1.00-x (the equilibrium concentration* of H2), which is physically impossible. Only *x=0.93 remains. You substitute* this value of *x into the last line of the table in Step 1 to get the equilibrium* concentrations and then multiply these by the volume of the vessel (1.00 L) to get the amounts of substances. The last line of the table is rewritten

Concentration (M)	$H_2(g)$	+	$I_2(g)$	$\rightleftharpoons$	$2HI(g)$
Equilibrium	$1.00 - x = 0.07$		$2.00 - x = 1.07$		$2x = 1.86$

The equilibrium composition is **0.07 mol H_2, 1.07 mol I_2, and 1.86 mol HI.**

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Removing Products or Adding Reactants

One way to increase the yield of a desired product is to change concentrations in a reaction mixture by removing a product or adding a reactant. Consider the methanation reaction,

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

If you place 1.000 mol CO and 3.000 mol H2 in a 10.00-L reaction vessel, the equilibrium composition at 1200 K is 0.613 mol CO, 1.839 mol H2, 0.387 mol CH4, and 0.387 mol H2O. Can you alter this composition by removing or adding one of the substances to improve the yield of methane?

To answer this question, you can apply **Le Châtelier's principle.**

$$CO(g) + 3H_2(g) \longrightarrow CH_4(g) + H_2O(g)$$

Removing Products or Adding Reactants

Stage of Process	Mol CO	Mol H_2	Mol CH_4	Mol H_2O
Original reaction mixure	0.613	1.839	0.387	0.387
After removing water (before equilibrium)	0.613	1.839	0.387	0
When equilibrium is reestablished	0.491	1.473	0.509	0.122

Effect of Removing Water Vapor from a Methanation Mixture
(in a 10.00-L Vessel)

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Consider the ammonia synthesis

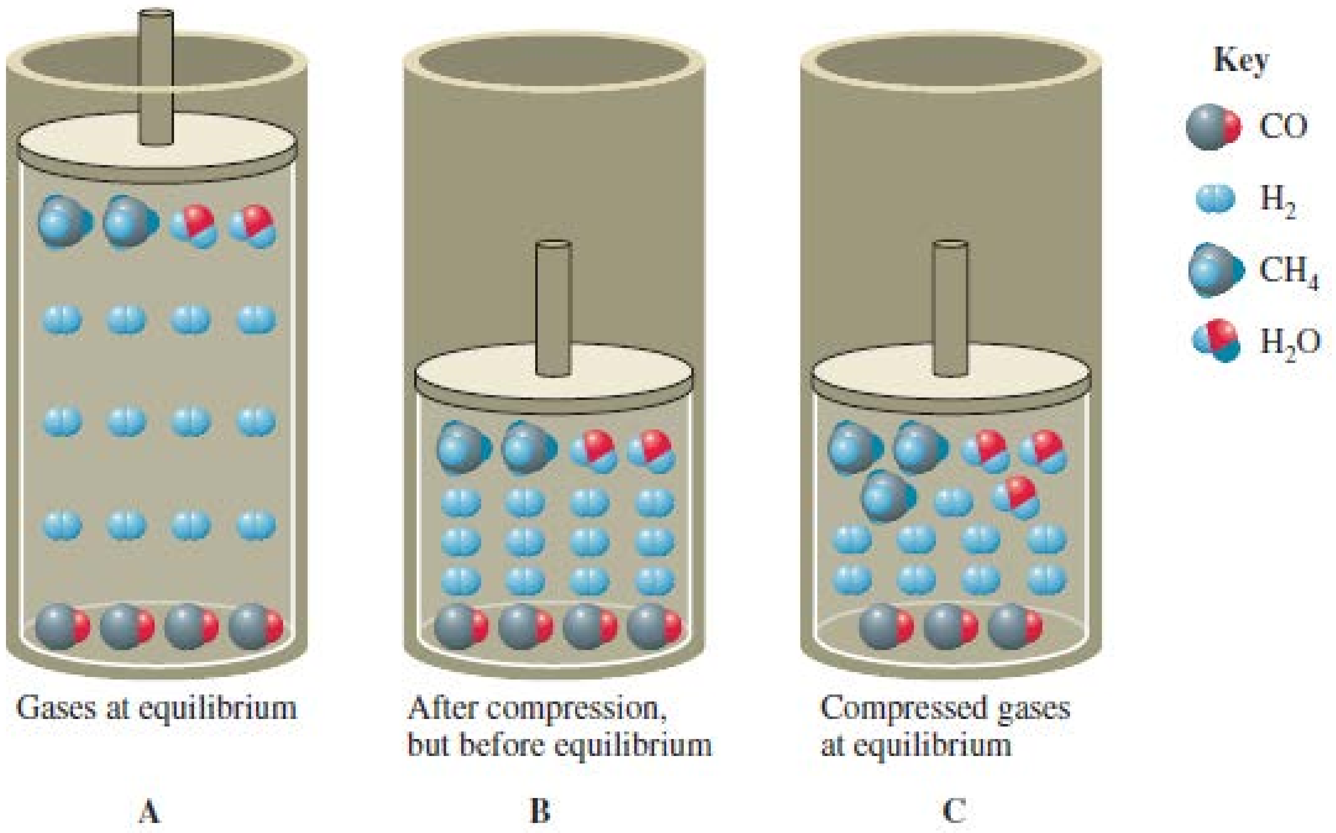
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

According to Le Chatelier’s principle, the reaction will now go in the direction that will use up some of the added nitrogen.

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

$$Q_c = \frac{[CH_4]_i[H_2O]_i}{[CO]_i[H_2]_i^3}$$

Effect on chemical equilibrium of changing the pressure



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azizochka1964@gmail.com