Chapter 15: Principles of Chemical Equilibrium

Dynamic Equilibrium

- So far we have considered reactions that go in one direction
- Equilibrium – two opposing processes taking place at equal rates – NO NET REACTION

$$H_2O(l) \rightleftarrows H_2O(g)$$

$$NaCl(s) \overset{H_2O}{\rightleftarrows} NaCl(aq)$$

$$I_2(H_2O) \rightleftarrows I_2(CCl_4)$$

$$CO(g) + 2\,H_2(g) \rightleftarrows CH_3OH(g)$$

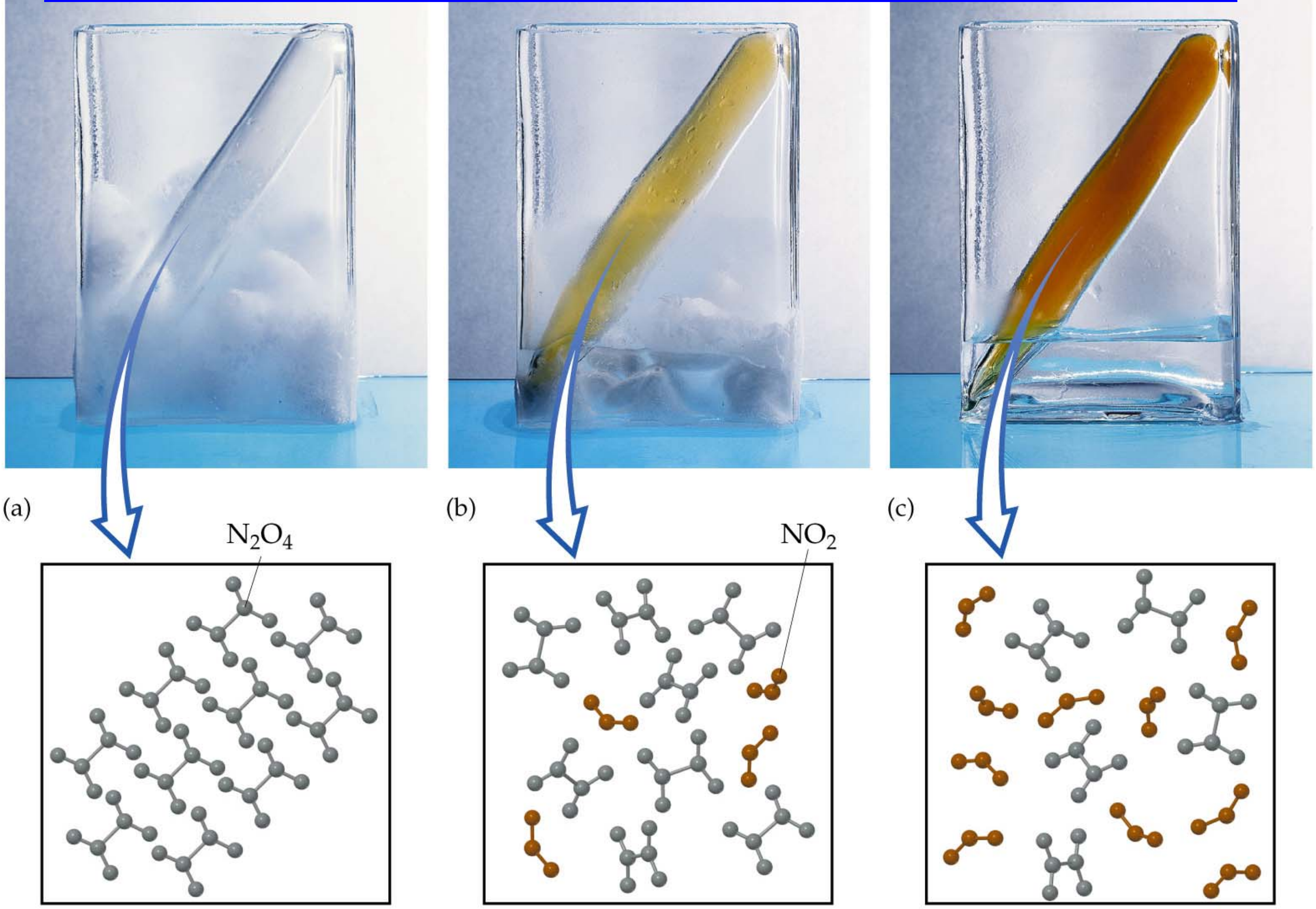
Dynamic Equilibrium

- By definition, dynamic systems are in constant motion.

Other features:

- They are reversible
- They can be approached in either direction
- After a period of time, the concentrations of reactants and products are constant
- The forward and reverse reactions continue after equilibrium is established

The Concept of Equilibrium
NO_2 and N_2O_4



$N_2O_4(s)$

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

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

The Concept of Equilibrium

- Consider colorless frozen N_2O_4. At room temperature, it forms brown NO_2:

$$N_2O_4(g) \rightarrow 2NO_2(g).$$

- Initially we have only $N_2O_4(g)$ some of which reacts to form NO_2(brown)
- At some time, the color stops changing and we have a mixture of N_2O_4 and NO_2.
- Chemical equilibrium is the point at which the concentrations of all species are constant.

The Concept of Equilibrium

- The point at which the rate of decomposition:

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

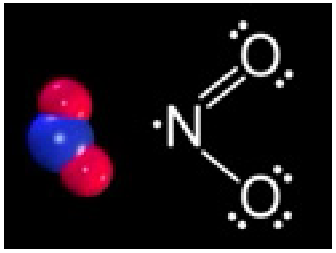
  equals the rate of dimerization:

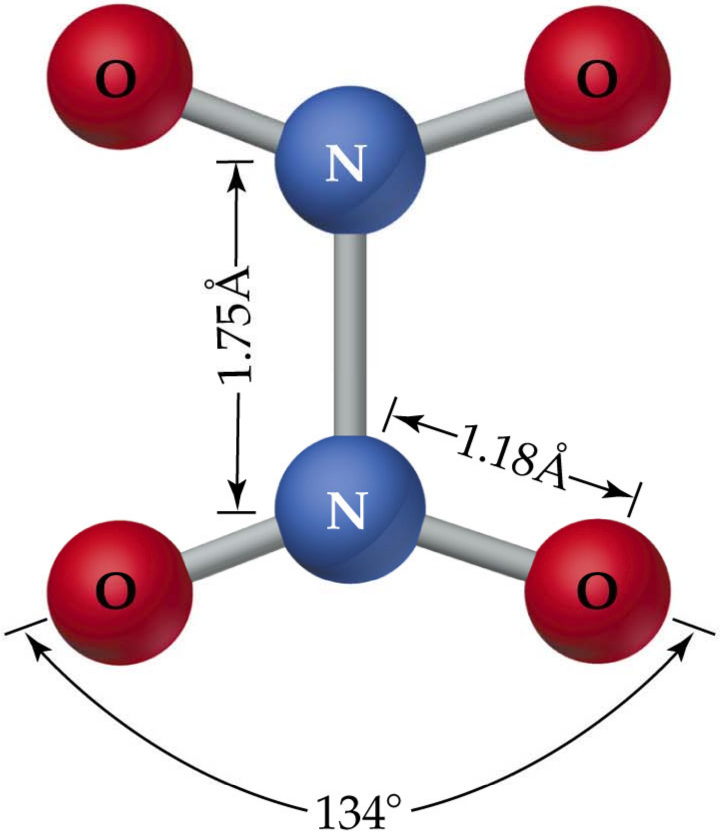
  $$2NO_2(g) \rightarrow N_2O_4(g).$$

  is dynamic equilibrium.
- The equilibrium is dynamic because the reaction has not stopped: the opposing rates are equal.

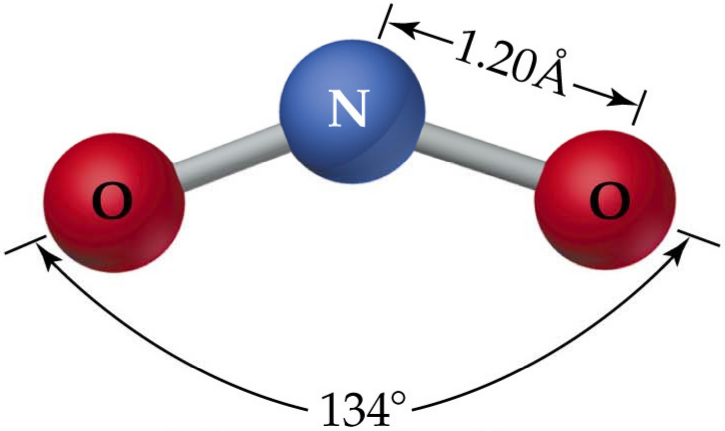
The Concept of Equilibrium

The equilibrium between NO_2 and N_2O_4 is a good example.





Dinitrogen tetroxide



Nitrogen dioxide

The Concept of Equilibrium

- For an equilibrium we write $A \rightleftharpoons B$
- If we start with pure A, as the reaction progresses
  - [A] decreases to a constant,
  - [B] increases from zero to a constant.
  - When [A] and [B] are constant, equilibrium is achieved.

The Equilibrium Constant

- For a general reaction

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

the equilibrium constant expression for everything in an ***ideal*** solution can be represented as

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

where K_{eq} is the equilibrium constant.

The Equilibrium Constant

- K_{eq} is based on the activities of reactants and products (see pg. 659 and 844 for more details)
- Activities are dimensionless quantities and give dimensionless K_{eq}.

In ***ideal*** conditions:

- For solutions the activity is the numerical value of the molarity – M.
- For gases it is the pressure - P.
- For pure substance as a solid or liquid the activity is 1.

Properties of Equilibrium Constants

1. K_{eq} is related to the stoichiometry of the balanced net reaction.

2. K_{eq} applies only at equilibrium.

3. K_{eq} is independent of initial conditions.

Determining K_{eq}

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

Place 2.00 mol of NOCl is a 1.00 L flask. At equilibrium you find 0.66 mol/L of NO. Calculate K.

Solution:

Set up a table of concentrations

	[NOCl]	[NO]	$[Cl_2]$
Initial	2.00	0	0
Change			
Equilibrium		0.66	

Determining K_{eq}

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

Place 2.00 mol of NOCl is a 1.00 L flask. At equilibrium you find 0.66 mol/L of NO. Calculate K.

Solution:

Set up a table of concentrations

	[NOCl]	[NO]	$[Cl_2]$
Initial	2.00	0	0
Change	-0.66	+0.66	+0.33
Equilibrium	1.34	0.66	0.33

Determining K_{eq}

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

	[NOCl]	[NO]	$[Cl_2]$
Initial	2.00	0	0
Change	-0.66	+0.66	+0.33
Equilibrium	1.34	0.66	0.33

$$\mathbf{K = \frac{[NO]^2[Cl_2]}{[NOCl]^2}}$$

$$\mathbf{= \frac{(0.66)^2(0.33)}{(1.34)^2} = 0.080}$$

Manipulating Equilibrium Constant Expressions

$$2\ \mathrm{NOCl(g)} \rightleftarrows 2\ \mathrm{NO(g)} + \mathrm{Cl_2(g)}$$

$$K = \frac{[\mathrm{NO}]^2[\mathrm{Cl_2}]}{[\mathrm{NOCl}]^2}$$

- Reversing an equation we invert *K*.

$$2\ \mathrm{NO(g)} + \mathrm{Cl_2(g)} \rightleftarrows 2\ \mathrm{NOCl(g)}$$

$$K' = 1/K = \frac{[\mathrm{NOCl}]^2}{[\mathrm{NO}]^2[\mathrm{Cl_2}]}$$

Manipulating Equilibrium Constant Expressions

- If two chemical equations are added, their equilibrium constants are multiplied:

Eqn 1: $2\ NOCl(g) \rightleftarrows 2\ NO(g) + Cl_2(g)$

$$K_1 = \frac{[NO]^2[Cl_2]}{[NOCl]^2}$$

Eqn 2: $2\ NO(g) + O_2(g) \rightleftarrows 2\ NO_2(g)$

$$K_2 = \frac{[NO_2]^2}{[NO]^2[O_2]}$$

Manipulating Equilibrium Constant Expressions

- If two chemical equations are added, their equilibrium constants are multiplied:

$$2\ NOCl(g) \rightleftarrows 2\ NO(g) + Cl_2(g)$$

$$2\ NO(g) + O_2(g) \rightleftarrows 2\ NO_2(g)$$

$$\text{Eqn 3: } 2\ NOCl(g) + O_2(g) \rightleftarrows Cl_2(g) + 2\ NO_2(g)$$

$$K_3 = K_1 \times K_2 = \frac{\cancel{[NO]^2}[Cl_2]}{[NOCl]^2} \times \frac{[NO_2]^2}{\cancel{[NO]^2}[O_2]}$$

$$K_3 = \frac{[NO_2]^2[Cl_2]}{[NOCl]^2[O_2]}$$

Gases: The Equilibrium Constant, K_{eq}

- Mixtures of gases are solutions just like liquids.
- K can be written with gas concentrations.
- However, activity of a gas is defined in terms of P.
- K_{eq} is based upon *partial pressures* of gases (the activity of a gas).

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

$$\frac{[SO_3]^2}{[SO_2]^2\,[O_2]} = K \quad \neq \quad K_{eq} = \frac{P_{SO_3}^{\,2}}{P_{SO_2}^{\,2}\,P_{O_2}}$$

Can be interconverted!

Pure Liquids and Solids

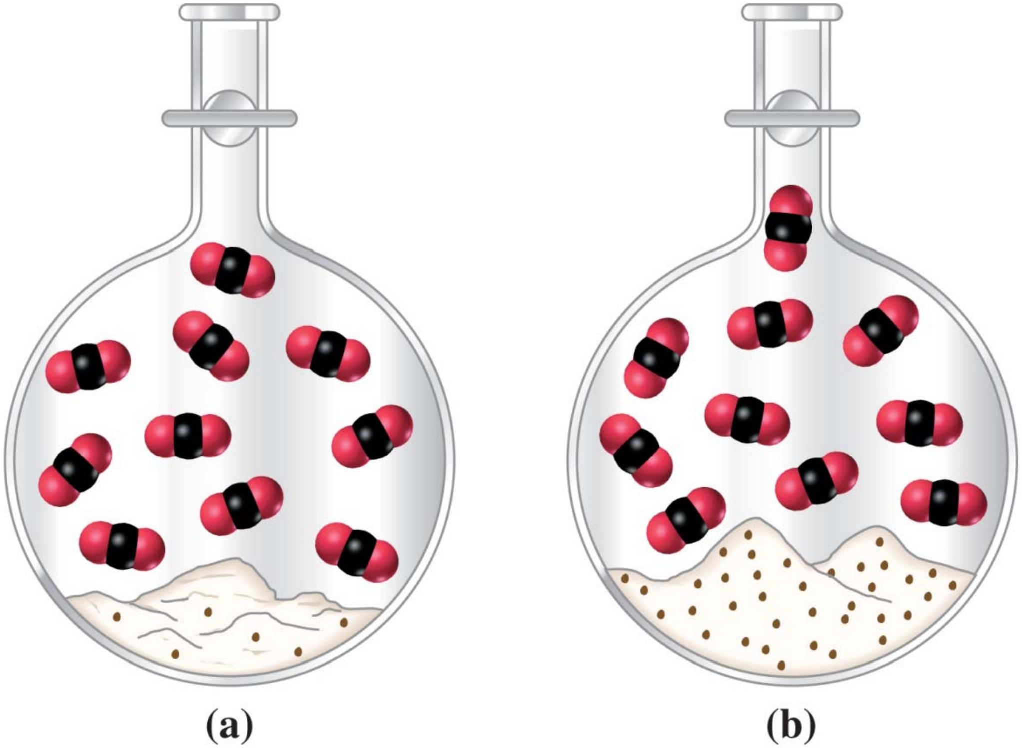
- Equilibrium constant expressions do not contain concentration terms for solid or liquid phases of a single component (that is, pure solids or liquids).
- This is because we defined the activity as unity.

$$C(s) + H_2O(g) \rightleftarrows CO(g) + H_2(g)$$

$$K_{eq} = \frac{P_{CO}P_{H_2}}{P_{H_2O}}$$

K_{eq} with Pure Liquids and Solids

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

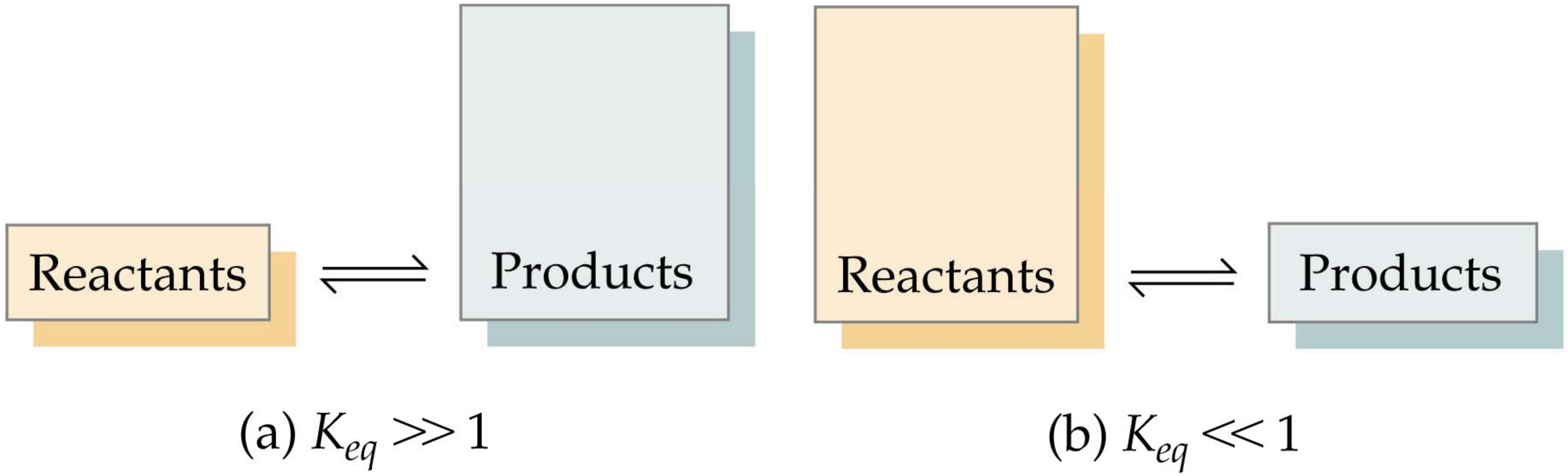


$$K = P(CO_2)$$

Independent of the amount of either solid!

The Equilibrium Constant

- The equilibrium constant, *K*, is the ratio of products to reactants. Two limiting conditions



(a) $K_{eq} >> 1$ (b) $K_{eq} << 1$

- *K* >> 1, then products dominate at equilibrium = equilibrium lies to the right.
- If *K* << 1, then reactants dominate at equilibrium = equilibrium lies to the left.
- ***The same equilibrium is established not matter how the reaction begins.***

Magnitude of the Equilibrium Constant.

Some typical values:

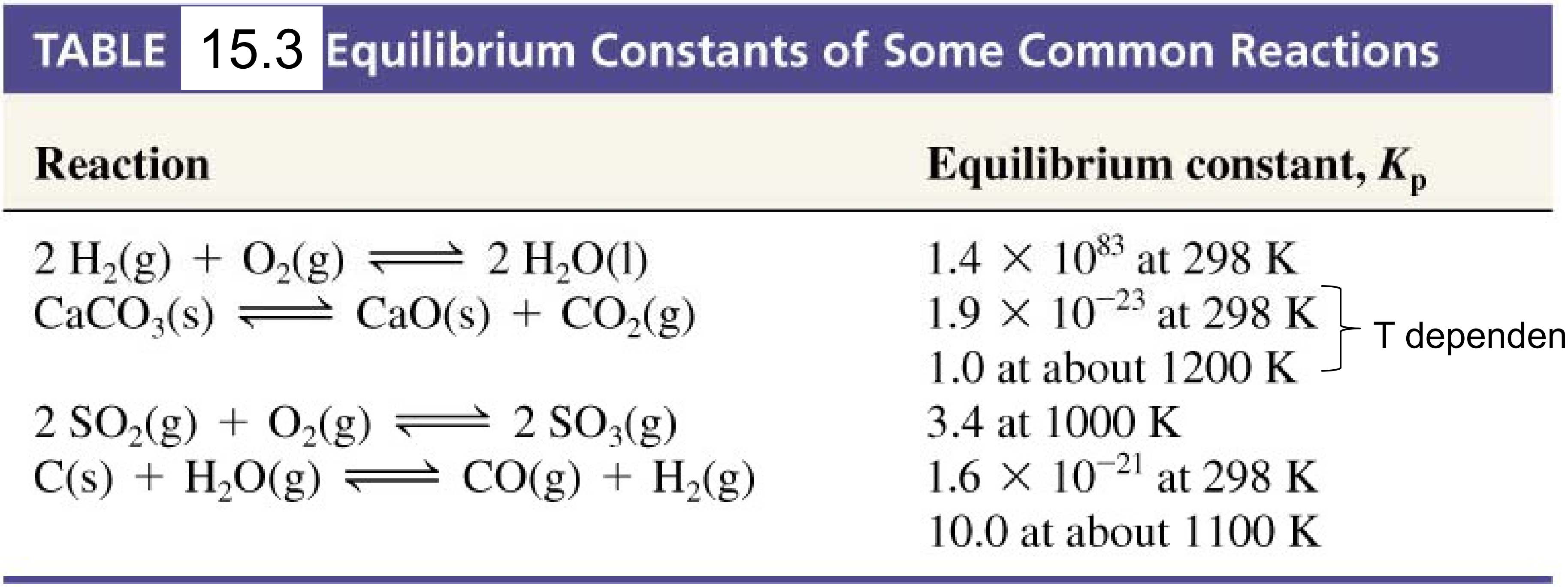


TABLE 15.3 Equilibrium Constants of Some Common Reactions

Reaction	**Equilibrium constant, K_p**
$2\,H_2(g) + O_2(g) \rightleftharpoons 2\,H_2O(l)$	1.4×10^{83} at 298 K
$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$	1.9×10^{-23} at 298 K
	1.0 at about 1200 K
$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$	3.4 at 1000 K
$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$	1.6×10^{-21} at 298 K
	10.0 at about 1100 K

T dependent

But, what if the reaction is not at equilibrium?

The Reaction Quotient, *Q*: Predicting the Direction of Net Change.

Consider the reaction:

$$CO(g) + 2\,H_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} CH_3OH(g)$$

- How will we know the direction of change of this reaction with various starting conditions?
- Equilibrium can be approached various ways.
- We need to develop a qualitative determination of change of initial conditions as equilibrium is approached.

The Reaction Quotient, *Q*: Predicting the Direction of Net Change.

- We define *Q*, the reaction quotient, for a general reaction

  $$a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D}$$

  as

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

- *Q* = *K* only at equilibrium!

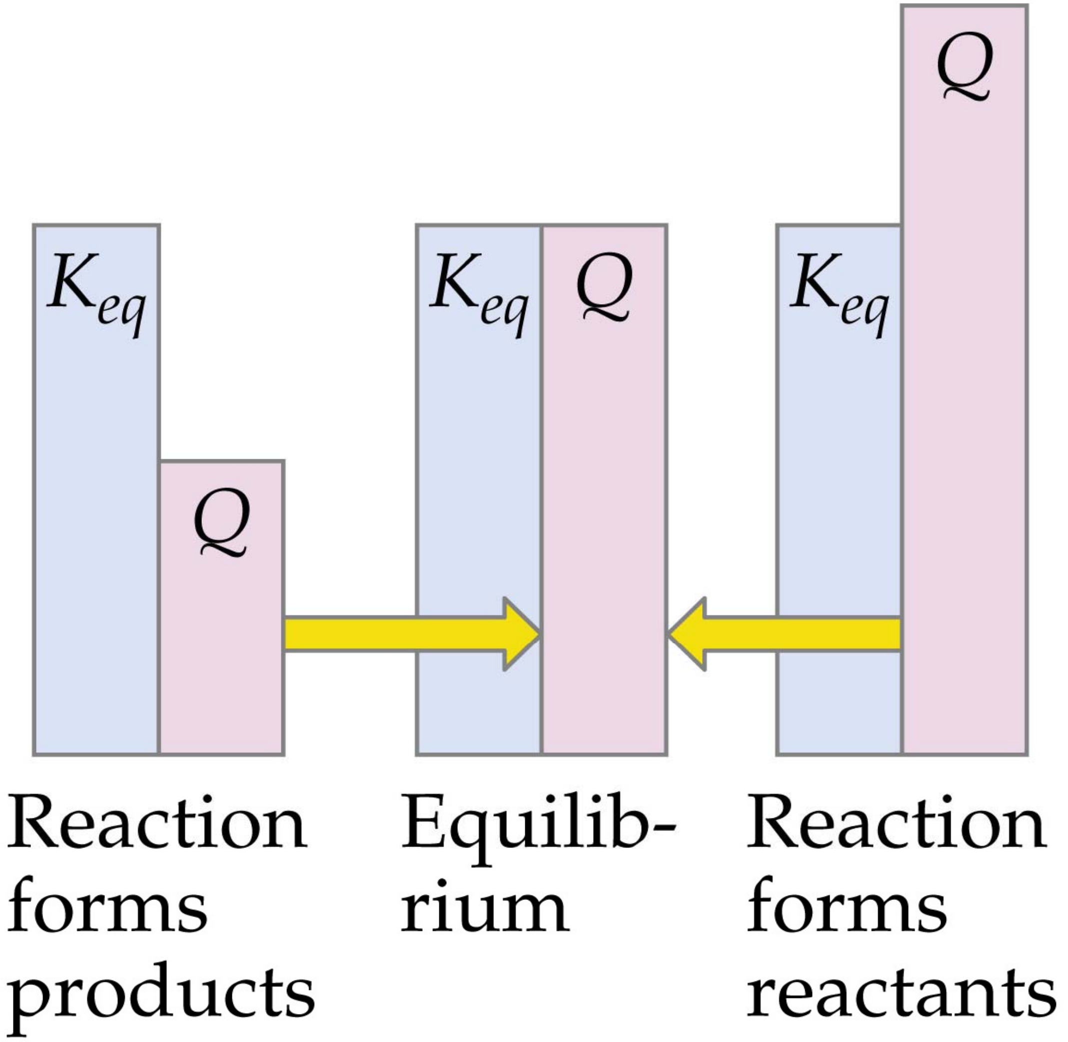
The Reaction Quotient, *Q*.

Predicting the Direction of Reaction

- We can now use the relationship of *Q* with K_{eq}
- If *Q* > *K* - ***there are too many products to be at equilibrium.*** The reverse reaction must occur to reach equilibrium - products are consumed, reactants are formed. The numerator in *Q* decreases until it equals *K*.
- If *Q* < *K* - ***there are too few products to be at equilibrium.*** The forward reaction must occur to reach equilibrium.
- If *Q* = *K* then the reaction is at equilibrium and there is no net change.

The Reaction Quotient, *Q*: Predicting the Direction of Net Change.

A graphical view of the relationship of *Q* to K_{eq}



Equilibrium Conditions:
Le Châtelier's Principle

- Our approach with *Q* suggests a treatment for equilibrium systems that undergo a perturbation –

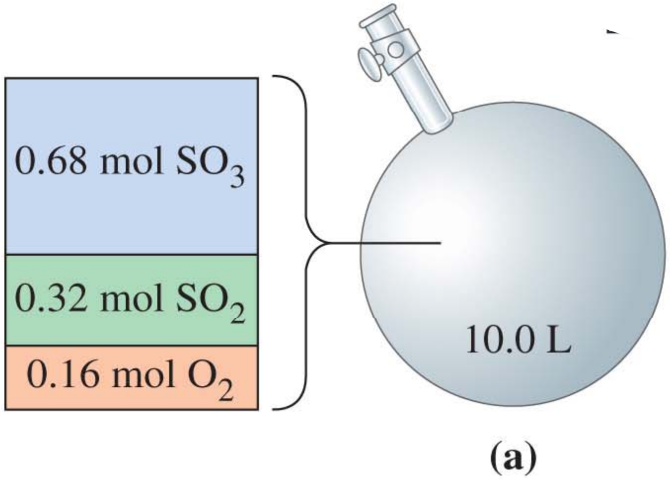
Le Châtelier's Principle

- Le Châtelier's Principle: When a system at equilibrium system is subjected to a change in temperature, pressure, or concentration of a reacting species, the system responds by attaining a new equilibrium that *partially* offsets the impact of the change.

Le Châtelier's Principle
Changing the amount of a substance

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

- $K_c = 2.8 \times 10^2$ at 1000K



$$Q = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = K_c$$

New conc. to make $Q = K_c$

Le Châtelier’s Principle

- Consider the production of ammonia – the Haber Process

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

- As the pressure increases, the amount of ammonia present at equilibrium increases.
- As the temperature decreases, the amount of ammonia at equilibrium increases.
- Can this be predicted?

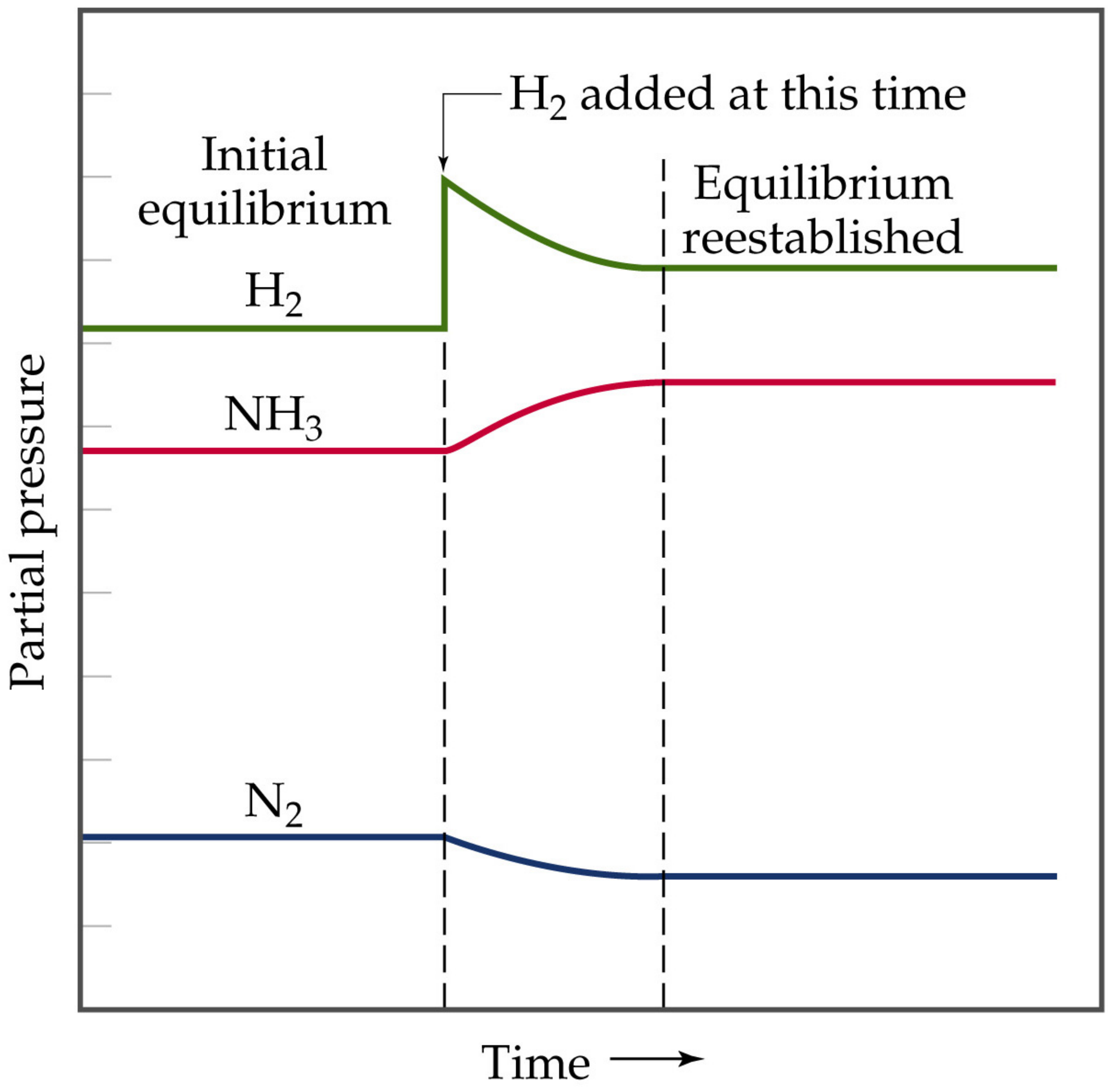
Le Châtelier's Principle

Change in Reactant or Product Concentrations

- Consider the Haber process

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

- If H_2 is added while the system is at equilibrium, the system must respond to counteract the added H_2 (by Le Châtelier).
- The system must consume the H_2 and produce products until a new equilibrium is established.
- So, $[H_2]$ and $[N_2]$ will decrease and $[NH_3]$ increases.

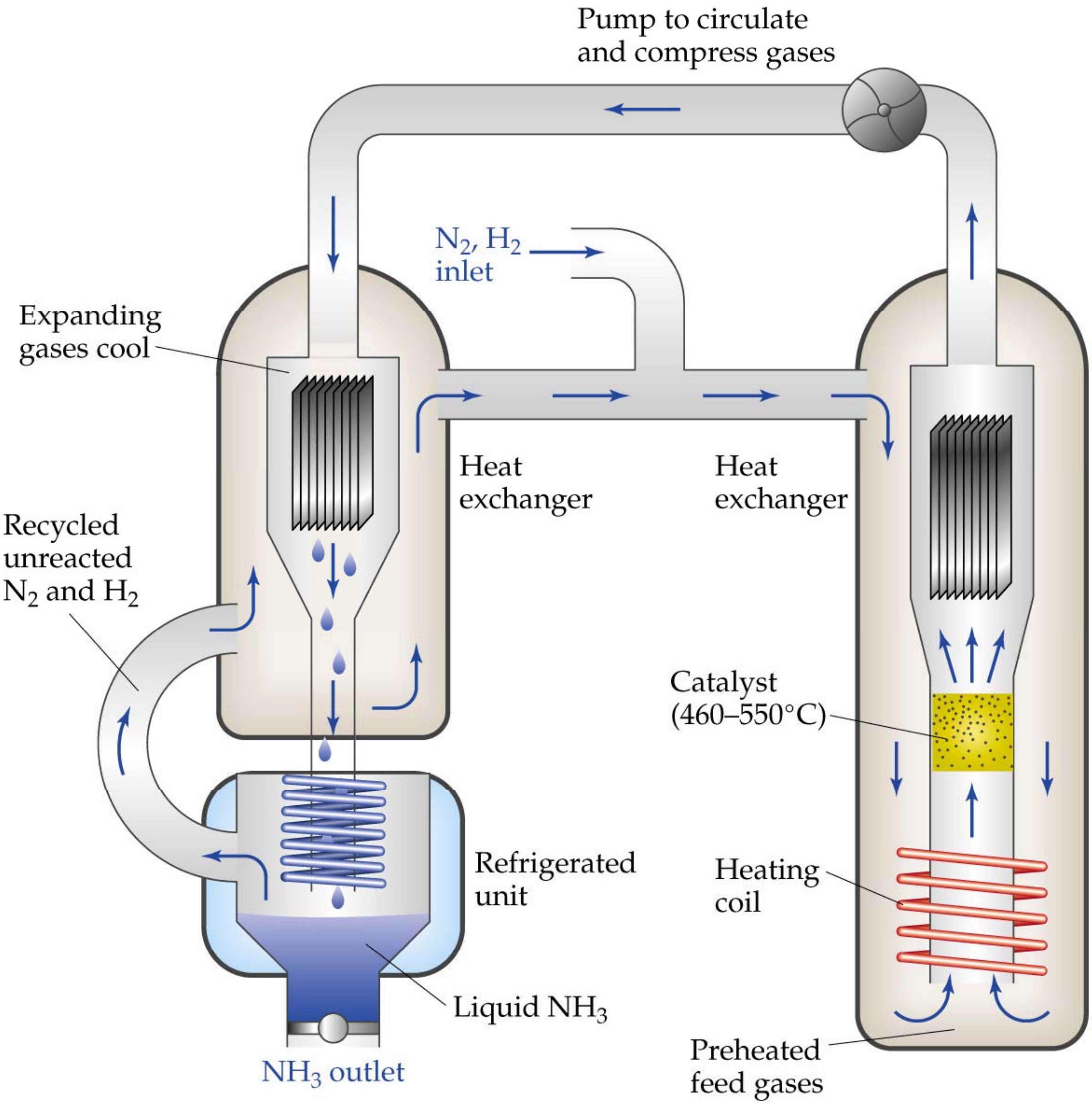


H_2 added at this time
Initial equilibrium
Equilibrium reestablished
H_2
NH_3
N_2
Partial pressure
Time →

Le Châtelier’s Principle

Change in Reactant or Product Concentrations

- Adding a reactant or product shifts the equilibrium away from the increase.
- Removing a reactant or product shifts the equilibrium towards the decrease.
- To optimize the amount of product at equilibrium, we need to flood the reaction vessel with reactant and continuously remove product (Le Châtelier).
- We illustrate the concept with the industrial preparation of ammonia.

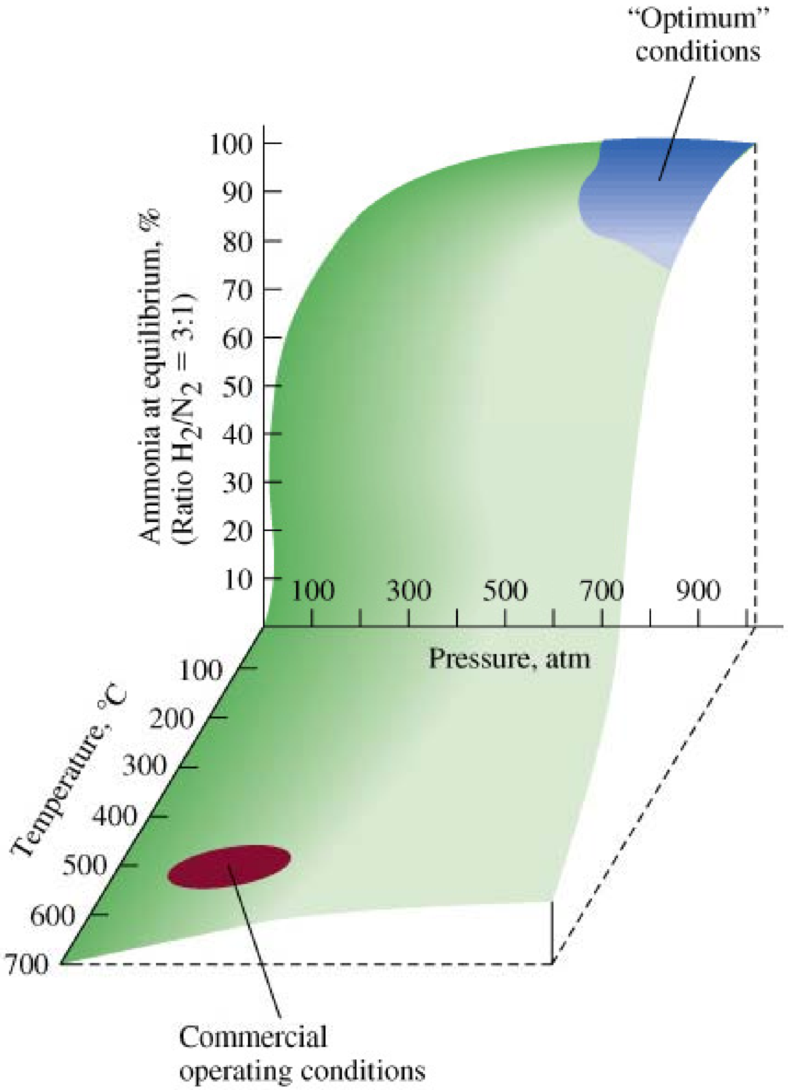

Pump to circulate and compress gases
N_2, H_2 inlet
Expanding gases cool
Heat exchanger
Heat exchanger
Recycled unreacted N_2 and H_2
Catalyst (460–550°C)
Refrigerated unit
Heating coil
Liquid NH_3
NH_3 outlet
Preheated feed gases

Le Châtelier’s Principle

Change in Reactant or Product Concentrations

- N_2 and H_2 are pumped into a chamber.
- The pre-heated gases are passed through a heating coil to the catalyst bed.
- The catalyst bed is kept at 460 - 550 °C under high pressure.
- The product gas stream (containing N_2, H_2 and NH_3) is passed over a cooler to a refrigeration unit.
- In the refrigeration unit, ammonia liquefies not N_2 or H_2.
- The equilibrium amount of ammonia is optimized because the product (NH_3) is continually removed and the reactants (N_2 and H_2) are continually being added.

Synthesis of Ammonia



The optimum conditions are only for the equilibrium position and do not take into account the *rate* at which equilibrium is attained.

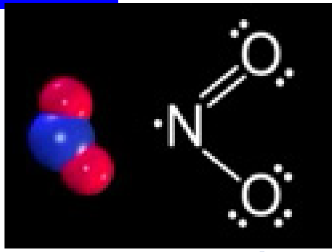
Le Châtelier’s Principle

Effects of Volume and Pressure Changes

- As volume is decreased pressure increases.
- Le Châtelier’s Principle: if pressure is increased the system will shift to counteract the increase.
  i.e. the system shifts to remove gases and decrease pressure.
- An increase in pressure favors the direction that has fewer moles of gas.
- In a reaction with the same number of product and reactant moles of gas, pressure has no effect.

Le Châtelier’s Principle

Effects of Volume and Pressure Changes



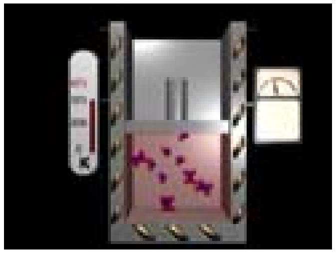
$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

- An increase in pressure (by decreasing the volume) favors the formation of colorless N_2O_4.
- The instant the pressure increases, the system is not at equilibrium and the concentration of both gases has increased.
- The system moves to reduce the number moles of gas (i.e. the reverse reaction is favored).
- A new equilibrium is established in which the mixture is lighter because colorless N_2O_4 is favored

Le Châtelier's Principle

Effect of Temperature Changes

- The equilibrium constant is temperature dependent.
- For an endothermic reaction, $\Delta H > 0$ and heat can be considered as a reactant.
- For an exothermic reaction, $\Delta H < 0$ and heat can be considered as a product.



Le Châtelier's Principle

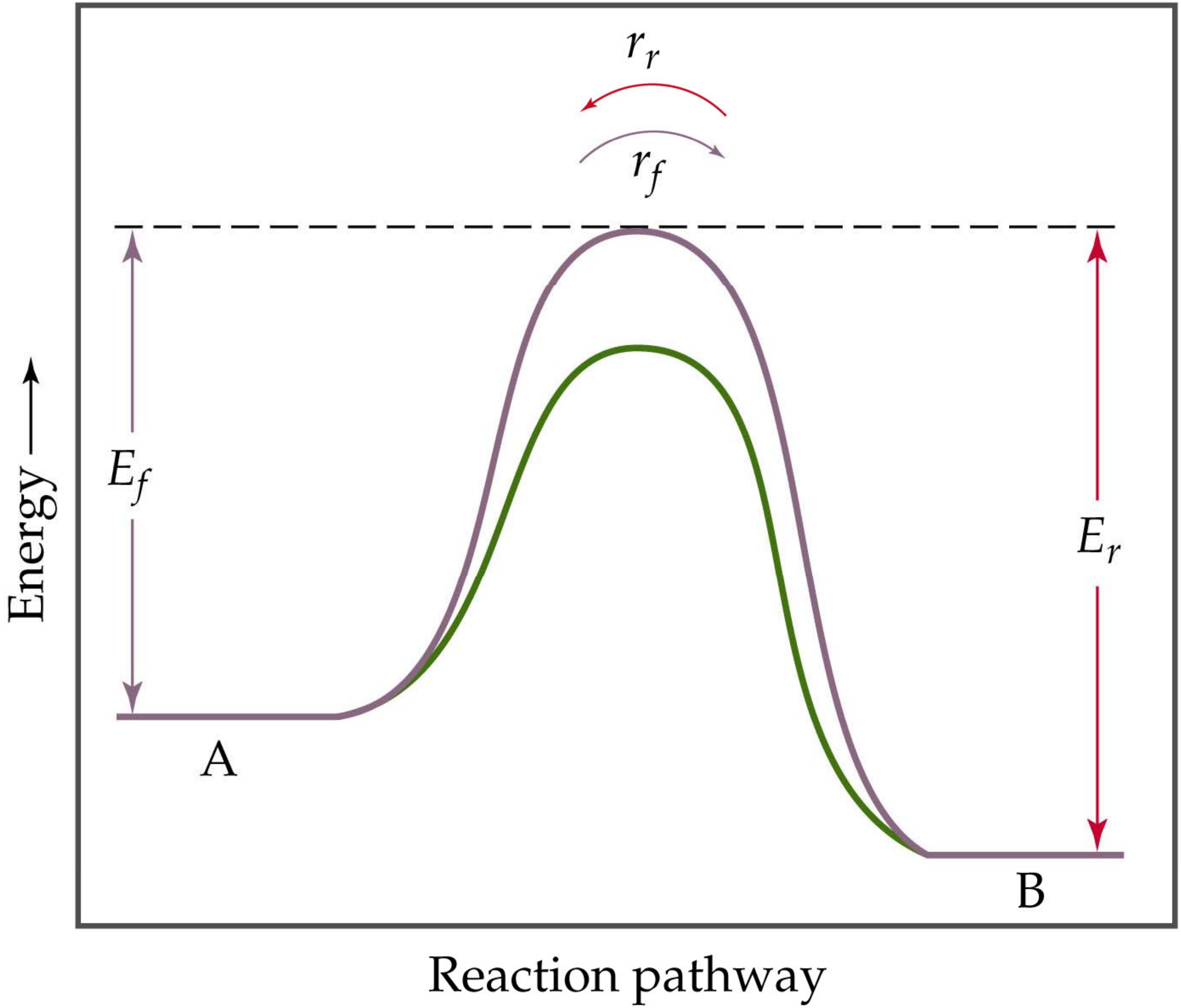
Effect of Temperature Changes

- Adding heat (i.e. heating the vessel):
  - – if $\Delta H > 0$, adding heat favors the forward reaction,
  - – if $\Delta H < 0$, adding heat favors the reverse reaction.
- Removing heat (i.e. cooling the vessel:
  - – if $\Delta H > 0$, cooling favors the reverse reaction,
  - – if $\Delta H < 0$, cooling favors the forward reaction.

Le Châtelier’s Principle

The Effect of Catalysis

- A catalyst lowers the activation energy barrier for the reaction.
- Therefore, a catalyst will decrease the time taken to reach equilibrium.
- A catalyst does not effect the composition of the equilibrium mixture.


r_r
r_f
E_f
E_r
Energy
A
B
Reaction pathway

An Example

In a 25.0°C laboratory, 5.00 mL of H_2 and 7.00 mL of F_2 are injected by syringe into an evacuated 100. mL flask. These components are made to react to produce HF. If K_p is 5.10, what is the partial pressures of all of the components?

$$H_{2(g)} + F_{2(g)} \rightleftharpoons 2HF_{(g)}$$

Data

T = 25.0 °C

V = 100. mL

$$K_p = 5.10 = \frac{P_{HF}^2}{P_{H2}P_{F2}}$$

So, all of the components are gaseous and reported in pressure units

K > 1, so the reaction is slightly product-favored

Amount of the Added Gases

…5.00 mL of H_2 and 7.00 mL of F_2 are injected by syringe…

The syringe pressure are 1 atm:

$$\mathrm{n\ H_2} = \frac{\mathrm{PV}}{\mathrm{RT}} = \frac{\mathrm{(1atm)(0.00500\ L)}}{\mathrm{(0.08206\ atm\ L/mol\ K)(298.15\ K)}} = 2.04\mathrm{x}10^{-4}\ \mathrm{mol}$$

$$\mathrm{n\ F_2} = \frac{\mathrm{PV}}{\mathrm{RT}} = \frac{\mathrm{(1atm)(0.00700\ L)}}{\mathrm{(0.08206\ atm\ L/mol\ K)(298.15\ K)}} = 2.86\mathrm{x}10^{-4}\ \mathrm{mol}$$

Initial Pressures of Gases in the Flask

Since we have added these two components to a 100. mL flask, we have to calculate their new pressures:

$$P\,(H_2) = \frac{nRT}{V} = \frac{(2.04\text{x}10^{-4}\,\text{mol})(0.08206\,\text{atm L/mol K})(298.15\,\text{K})}{0.100\,\text{L}} = 0.0500\,\text{atm}$$

$$P(F_2) = \frac{nRT}{V} = \frac{(2.86\text{x}10^{-4}\,\text{mol})(0.08206\,\text{atm L/mol K})(298.15\,\text{K})}{0.100\,\text{L}} = 0.0700\,\text{atm}$$

Note: we could have used Boyle’s Law

$$P_1V_1 = P_2V_2$$

Solution

T = 25.0 °C, V = 100. mL, $P_{initial}(H_2)$ = 0.0500 atm, $P_{initial}(F_2)$ =0.0700 atm. Now we have to define an equation and an equilibrium table.

$$H_{2(g)} + F_{2(g)} \rightleftharpoons 2HF_{(g)}$$

	H_2	**F_2**	**HF**
Initial	0.0500	0.0700	0
Change	-x	-x	2x
Equil.	0.0500-x	0.0700-x	2x

$$K = \frac{P_{HF}^{2}}{P_{H_2}P_{F_2}} = \frac{(2x)^2}{(0.0500-x)(0.0700-x)} = 5.10$$

Solving a Quadratic Equation

$$\frac{(2x)^2}{(0.0500 - x)(0.0700 - x)} = \frac{4x^2}{0.00350 - 0.120x + x^2} = 5.10$$

$$4x^2 = 0.0178 - 0.612x + 5.10x^2$$

$$1.10x^2 - 0.612x + 0.0178 = 0$$

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

x = 0.636 or **0.0373**

Calculating the Pressures

Equation	H_2	F_2	HF
Initial P	0.0500	0.0700	0
Change	-x	-x	2x
	x =0.0373		
Equilibrium	0.0500- 0.0373	0.0700- 0.0373	2(0.0373)
	0.0127	0.0327	0.0746

$P_{H_2} = 0.0127$

$P_{F_2} = 0.0327$

$P_{HF} = 0.0746$

An Example Using the Reaction Quotient Q

In a 25.0°C laboratory, 6.00 mL HF, 5.00 mL of H_2 and 7.00 mL of F_2 are injected by syringe into an evacuated 100. mL flask. These components are allowed to reach equilibrium. If K_p is 5.1, what is the partial pressures of all of the components?

Data

T = 25.0 °C
V = 100. mL

$P_{\text{initial}}\ H_2 = 0.0500$ atm

$P_{\text{initial}}\ F_2 = 0.0700$ atm

Calculating the Pressure of HF

$$P_1V_1 = P_2V_2$$

$$P_{HF} = P_1V_1 / V_2$$

$$= (1\ \text{atm})(6.00\ \text{mL}) / (100.\ \text{mL})$$

$$= 0.0600\ \text{atm}$$

$$H_{2(g)} + F_{2(g)} \rightleftharpoons 2\,HF_{(g)}$$

Equation	**H_2**	**F_2**	**HF**
Initial	0.0500	0.0700	0.0600

Which direction will this reaction go?

Calculate Q

$$Q = \frac{P_{HF}{}^{2}}{P_{H2}P_{F2}} = \frac{0.0600^{2}}{0.0500(0.0700)} = 1.02$$

1.02 < 5.10

Q < K

Therefore the reaction is overloaded from the reactant side, and will equilibrate by forming product.

REACTION WILL GO TO THE RIGHT

Solution

$$H_{2(g)} + F_{2(g)} \rightleftharpoons 2\,HF_{(g)}$$

Equation	**H_2**	**F_2**	**HF**
Initial	0.0500	0.0700	0.0600
Change	-x	-x	2x
Equilibrium	0.0500-x	0.0700-x	0.0600 + 2x

$$K = \frac{P_{HF}{}^{2}}{P_{H2}P_{F2}} = \frac{(0.0600 + 2x)^2}{(0.0500 - x)(0.0700 - x)} = 5.10$$

Solving the Quadratic Equation

$$\frac{0.00360 + 0.120x + 4x^2}{0.00350 - 0.120x + x^2} = 5.10$$

$0.00360 + 0.120\mathbf{x} + 4\mathbf{x}^2 = 0.0178 – 0.612\mathbf{x} + 5.10\mathbf{x}^2$

$1.10\mathbf{x}^2 – 0.732\mathbf{x} + 0.0216 = 0$

$x = 0.768$ or $\mathbf{0.0374}$

Calculating the Pressures

Equation	**H_2**	**F_2**	**HF**
Initial P	0.0500	0.0700	0.0600
Change	-x	-x	2x
		x =0.0374	
Equilibrium	0.0500- 0.0374	0.0700- 0.0374	0.0600 + 2(0.0374)
	0.0126	0.0326	0.135

$P_{H_2} = 0.0126$

$P_{F_2} = 0.0326$

$P_{HF} = 0.135$

Calculating Equilibrium

$CO(g) + H_2O \rightleftharpoons HCHO_2$ $K_c = 3.4 \times 10^{-5}$ at 400 °C and 1 atm

If we start with [CO] = **0.20 M** and $[H_2O]$ = **0.30 M**, what are the equilibrium concentrations?

	$[H_2O]$ +	[CO]	$[HCHO_2]$
Initial	0.30	0.20	
Change	-x	-x	+x
Equilibrium	0.30-x	0.20-x	x

$$K_c = \frac{[HCHO_2]}{[H_2O][CO]} = \frac{(x)}{(0.20-x)(0.30-x)} = 3.4 \times 10^{-5}$$

Calculating Equilibrium

$CO(g) + H_2O \rightleftarrows HCHO_2$ $K_c = 3.4 \times 10^{-5}$ at 400 °C and 1 atm

$$K_c = \frac{[HCHO_2]}{[H_2O][CO]} = \frac{(x)}{(0.20-x)(0.30-x)} = 3.4 \times 10^{-5}$$

$3.4\text{x}10^{-5}\,\mathbf{x}^2 - \mathbf{x} + 2.0\text{x}10^{-6} = 0$ a = **$3.4\text{x}10^{-5}$** , b = -1, c = **$2.0\text{x}10^{-6}$**

Therefore, x = 29411 or **$2.0\text{x}10^{-6}$**

Calculating Equilibrium

$CO(g) + H_2O \rightleftharpoons HCHO_2$ $K_c = 3.4 \times 10^{-5}$ at 400 °C and 1 atm

	$[H_2O]$	$[CO]$	$[HCHO_2]$
Initial	0.30	0.20	
Change	**$-2.0\text{x}10^{-6}$**	**$-2.0\text{x}10^{-6}$**	**$+2.0\text{x}10^{-6}$**
Equilibrium	0.30	0.20	$2.0\text{x}10^{-6}$

Notice that $[H_2O]$ and $[CO]$ don't change within their significant figures!

We can use this to establish an assumption that will save us from having to solve a quadratic.

An Assumption

If K << [reactant], then **x** can be neglected **for the reactants** in the expression:

$$K = \frac{[HCHO_2]}{[H_2O][CO]} = 3.4 \times 10^{-5} = \frac{x}{(0.30\mathbf{-x})(0.20\mathbf{-x})}$$

$$= \frac{x}{(0.30)(0.20)}$$

$x = (0.06)\ 3.4\text{x}10^{-5}$

$x =$ **$2.0\text{x}10^{-6}$** (compare to **$2.0\text{x}10^{-6}$** from the rigorous calculation)

If the [reactant] > 100 x K then this assumption generally works and simplifies the calculations.

Suggested Chapter 15 Problems

10th ed Ch. 15

18, 23, 31, 34, 38, 51, 54, 59, 63, 64, 76, 85, 94

9th ed Ch. 15

16, 19, 27, 30, 34, 45, 48, 53, 57, 58, 64, 73, 82