Chemical Equilibrium

Forward Reaction: $A(g) \rightarrow B(g)$ $\quad Rate = k_f[A]$

Reverse Reaction: $B(g) \rightarrow A(g)$ $\quad Rate = k_r[B]$

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

$$[B] = \frac{n_B}{V} = \frac{P_B}{RT}$$

Forward Reaction: $Rate = k_f \frac{P_A}{RT}$

Reverse Reaction: $Rate = k_r \frac{P_B}{RT}$

Equilibrium is established when
the rate of the forward reaction
equals
the rate of the reverse reaction

$$k_f \frac{P_A}{RT} = k_r \frac{P_B}{RT}$$

$$\frac{P_A}{P_B} = \frac{k_f}{k_r} = K$$

$$\frac{P_B}{P_A} = \frac{k_r}{k_f} = K' = \frac{1}{K}$$

K is called the equilibrium constant

Equilibrium reaction is written as

$$A \rightleftharpoons B$$

Law of Mass Action

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

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

Q is called the reaction quotient

When the concentrations are those at equilibrium Q becomes the equilibrium constant K

$$Q(eq) = K_{eq} = \frac{[C_{eq}] \quad D_{eq}}{[A_{eq}]^a [B_{eq}]^b}$$

$$K_{eq} = \frac{Products}{Reactants}$$

Gaseous Equilibria

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

$$K_{eq} = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

$$P_i \equiv P_i / P_{ref}$$

$$P_{ref} = 1atm$$

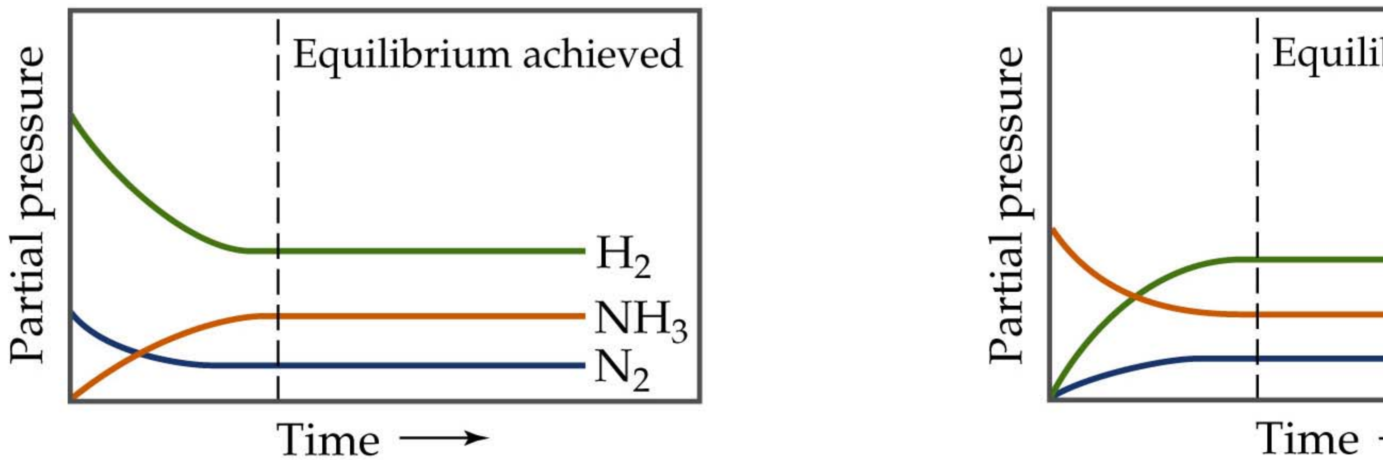
$$\boxed{K_{eq} \text{ is dimensionless}}$$

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

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

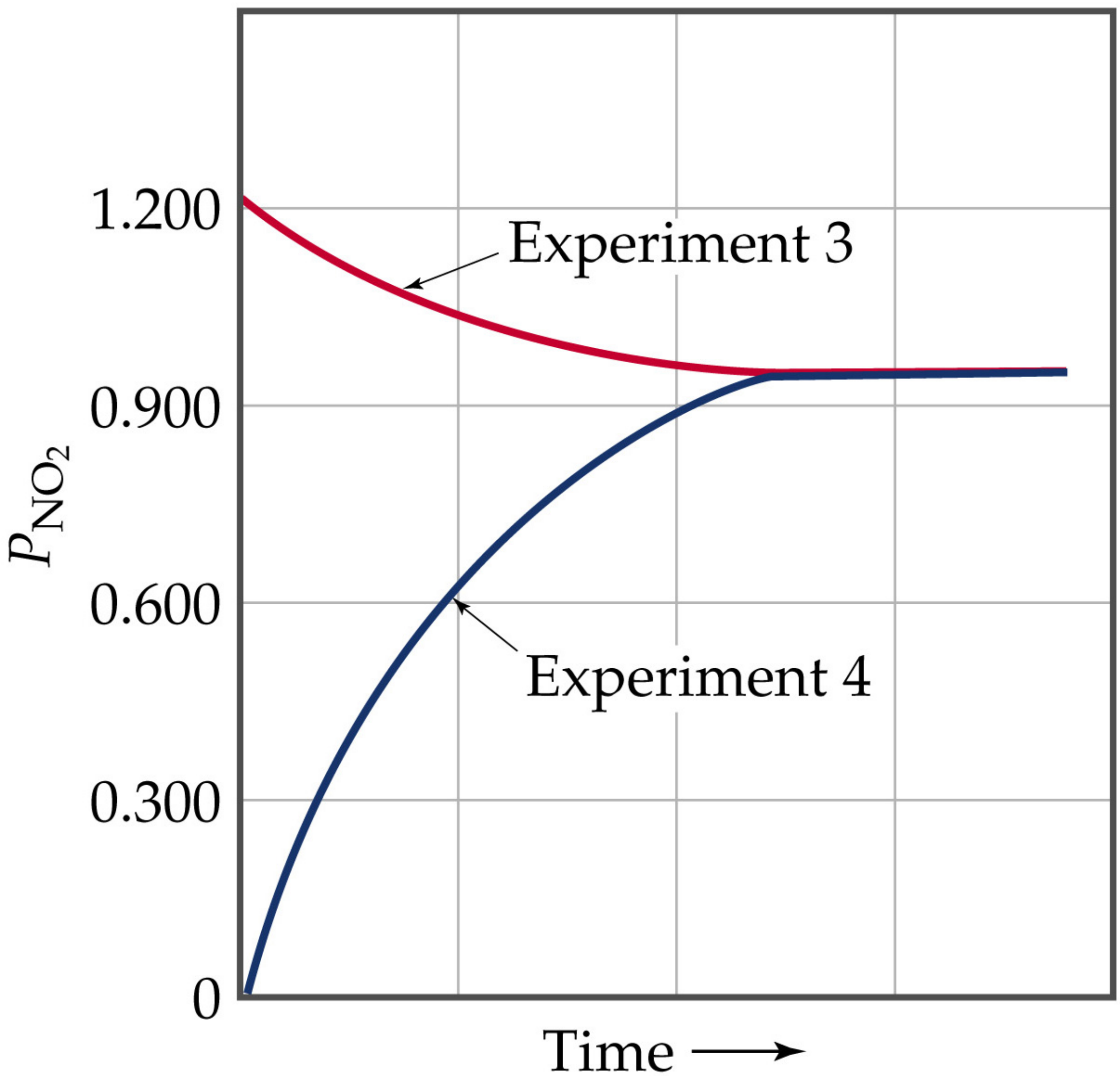
Haber Process

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



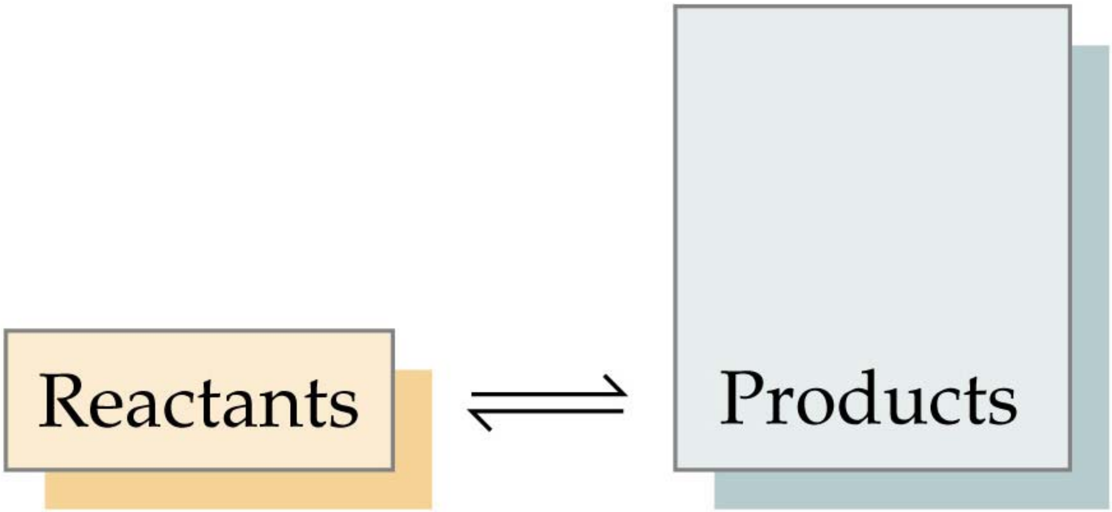
(a)

(b)

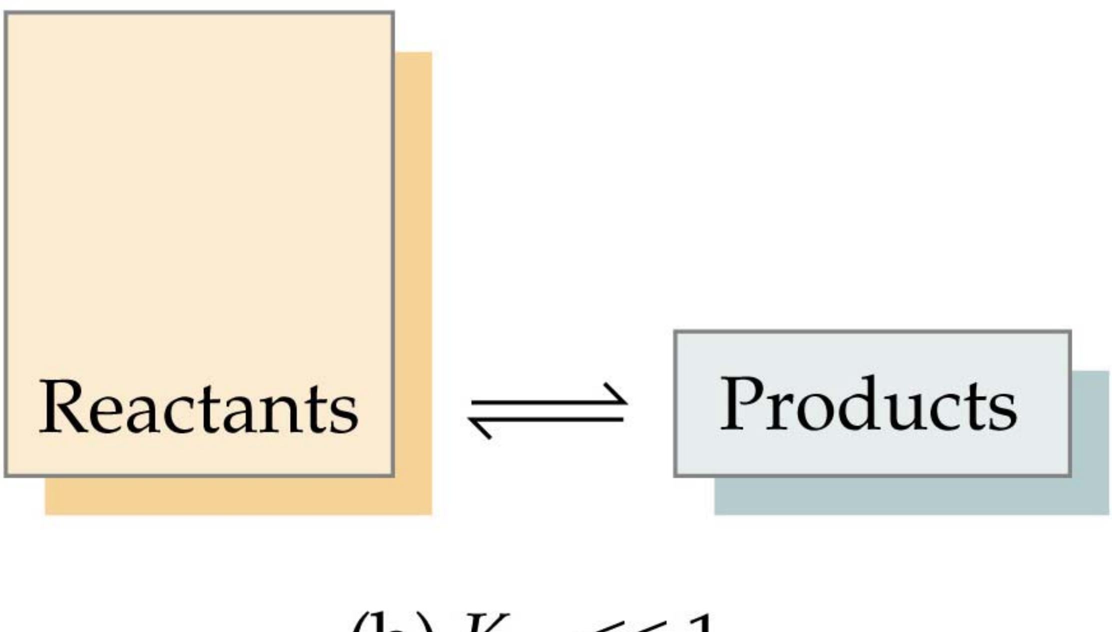


1.200
0.900
0.600
0.300
0
P_{NO_2}
Experiment 3
Experiment 4
Time

Magnitude of K_{eq}



(a) $K_{eq} \gg 1$



(b) $K_{eq} \ll 1$

Characteristics of Equilibrium Constants

1. The equilibrium constant for a reaction written in the reverse direction is the inverse of the equilibrium constant written in the forward direction.

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

3. The equilibrium constant for a net reaction made up of two or more steps is the product of the constants for the individual steps.

Example

Given

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \quad K_{eq} = 54.0$$

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad K_{eq} = 1.04 \times 10^{-4}$$

what is K_{eq} for

$$2NH_3(g) + 3I_2(g) \rightleftharpoons 6HI(g) + N_2(g)$$

Calculating Equilibrium Constants

1. Given all concentrations

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

$$K_{eq} = \frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3} = \frac{(0.166)^2}{(2.46)(7.38)^3} = 2.79x10^{-5}$$

2. Given the minimal number of concentrations

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

$$P_{SO_3}^0 = 0.500atm \ \ ; \ \ P_{SO_3}^{eq} = 0.200atm$$

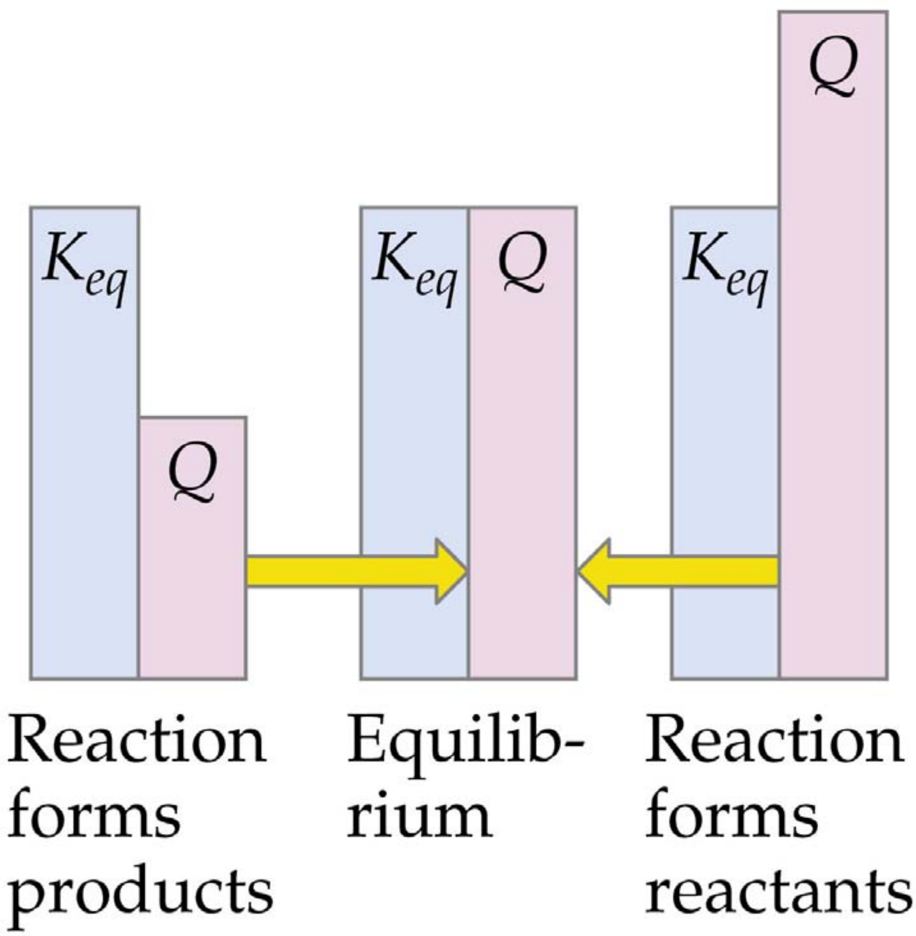
$$K_{eq} = \frac{P_{SO_2}^2 P_{O_2}}{P_{SO_3}^2}$$

Reaction Quotient

$Q < K_{eq}$ Reaction goes to the right

$Q = K_{eq}$ Reaction is at equilibrium

$Q > K_{eq}$ Reaction goes to the left



Predicting the Direction of a Reaction

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

$$K_{eq} = 2.79\text{x}10^{-5}$$

$[H_2]^0 = 2.00 mol/L$; $[N_2]^0 = 1.00$ mol/L ; $[NH_3]^0 = 2.00$ mol/

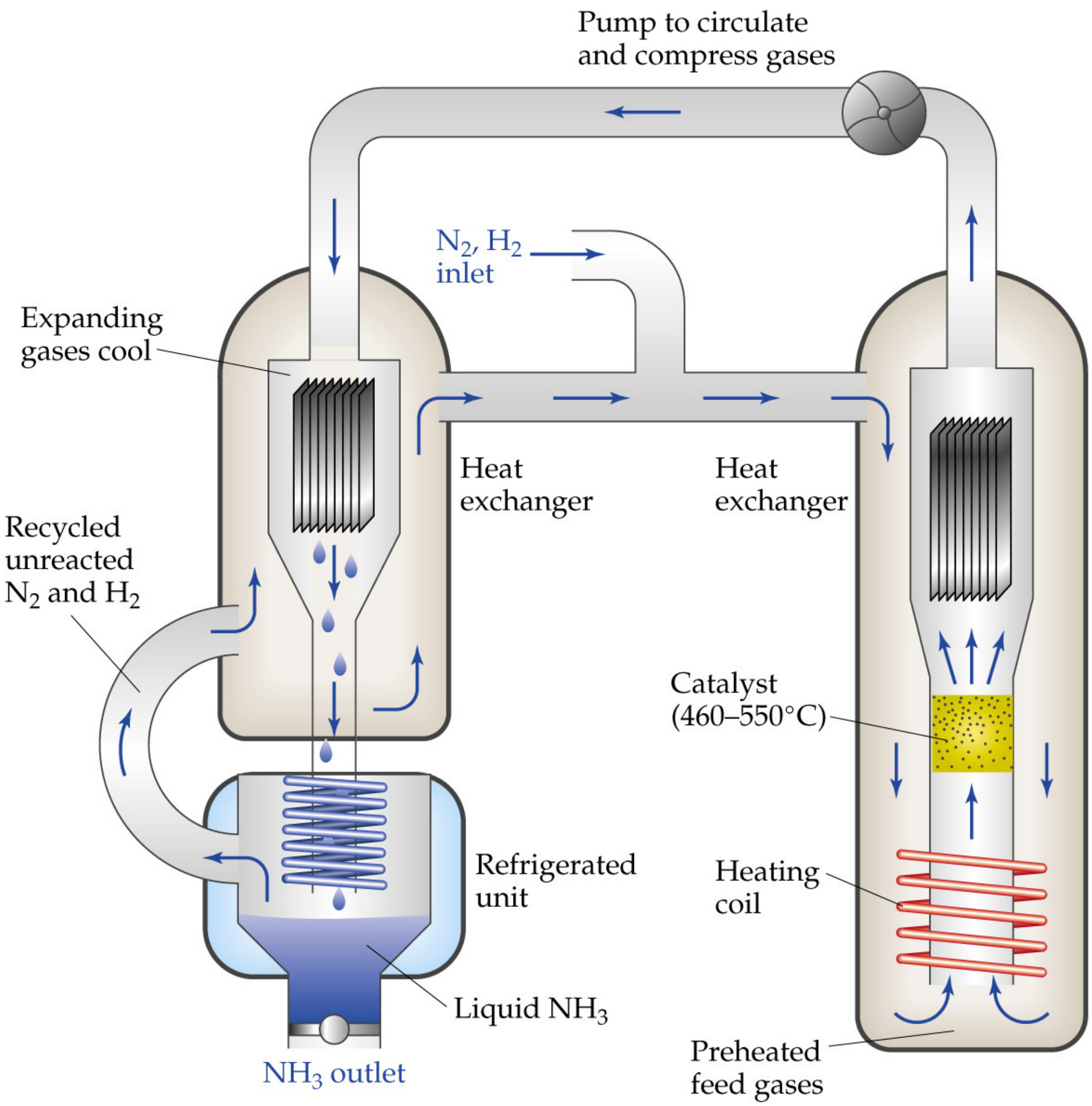
Which way will the reaction proceed?

Calculating Equilibrium Concentrations

Given the equilibrium constant
&
all initial concentrations

A 1.000L flask is filled with 1.000mol of H_2 and 2.000mol of I_2, what are the partial pressures of all species at equilibrium?

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \quad K_{eq} = 50.5$$



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
Preheated
feed gases
NH_3 outlet

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, so as to counteract the effect of the disturbance.

Effect of Adding or Removing Reactants or Products

Consider system at equilibrium

$$Reactants \rightleftharpoons Products$$

$$Q = K_{eq} = \frac{(Products)_{eq}}{(Reactants)_{eq}}$$

Add Product

Immediately after addition, $Q > K_{eq}$

System is no longer in equilibrium

System responds by forming more Reactants

An equilibrium mixture of $H_2(g)$, $I_2(g)$, and HI(g) has the composition

$$P_{I_2} = 0.4756 atm \; ; \; P_{H_2} = 0.2056 atm \; ; \; P_{HI} = 3.009 atm$$

Add enough $I_2(g)$ to temporarily increase its pressure to 2.000 *atm*

Do we form more reactants
or
more products?

What are the partial pressures of each gas after equilibrium is re-established?

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \quad K_{eq} = 92.6$$

Effect of Changing the Volume (Pressure)

Decrease volume and increase pressure

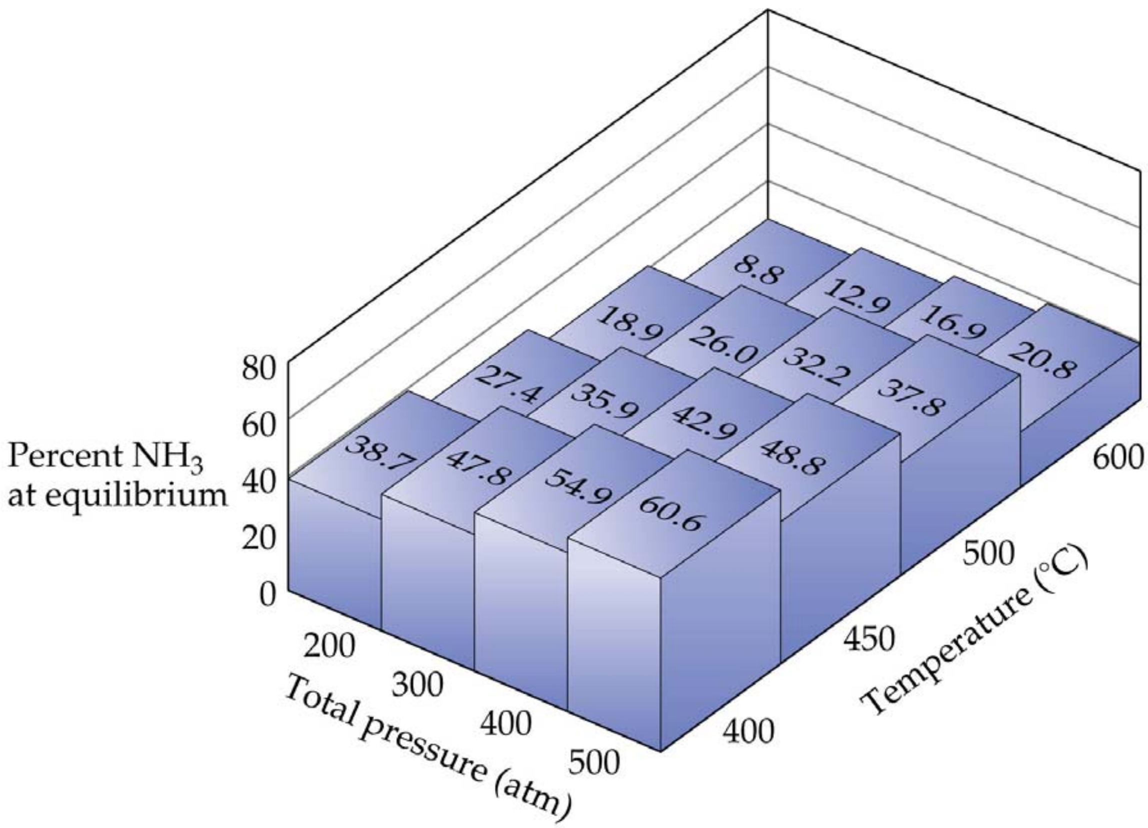
Equilibrium will shift to counter the effect of the decreased volume by shifting in such a way as to decrease the volume occupied by the reactants and products.

$$2P_2(g) \rightleftharpoons P_4(g)$$

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

Consider Haber Process for the synthesis of NH_3

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



Effect of Temperature

Reaction Type	Increase T	Decrease T
exothermic	more reactants	more products
endothermic	more products	more reactants

For each of the following reactions state whether a higher equilibrium yield of products is favored by a higher or lower total volume and a higher or lower temperature.

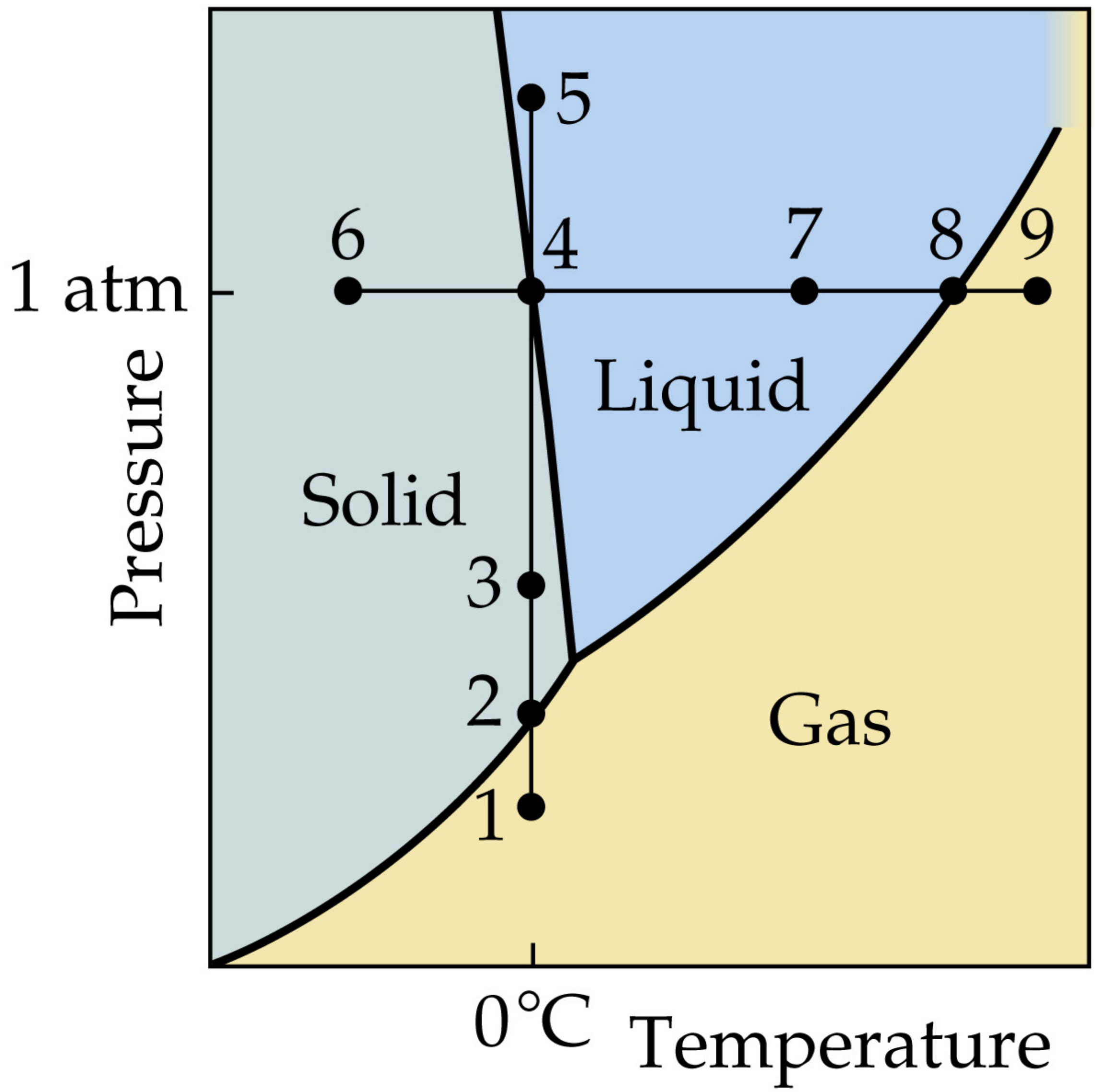
$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g) \;\; ; exothermic$$

$$CH_3OH(g) \rightleftharpoons CO(g) + 2H_2(g) \;\; ; exothermic$$

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \;\; ; endothermic$$

Heterogeneous Equilibria

Gas – Solid
Gas – Liquid
Liquid - Solid



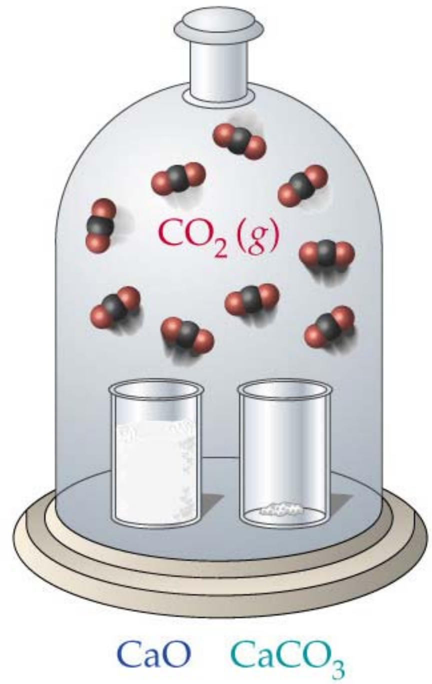
Gas – Solid

$$CO_2(s) \rightleftharpoons CO_2(g)$$

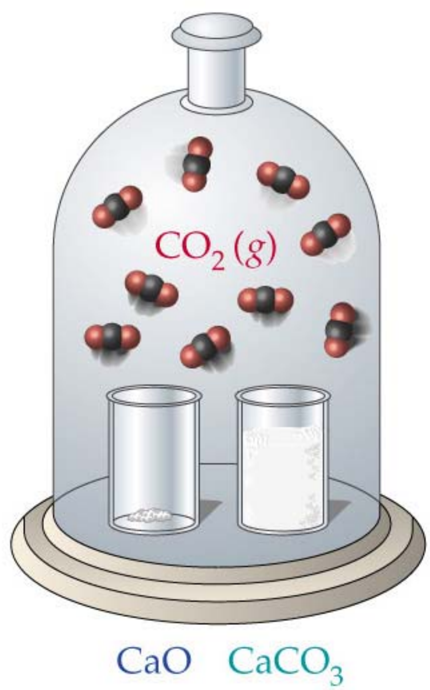
$$K_{eq} = \frac{P_{CO_2}}{[CO_2(s)]} \equiv P_{CO_2}$$

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

$$K_{eq} = \frac{[CaO(s)]P_{CO_2}}{[CaCO_3(s)]} \equiv P_{CO_2}$$



(a)



(b)

Generalize to any form of heterogeneous equilibrium

1. Partial pressures of gases are substituted into the equilibrium expression

2. Pure solids, pure liquids, and solvents are not included in the equilibrium expression

3. Molar concentrations of dissolved species are substituted in the equilibrium expression

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

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

$$Sn(s) + 2H^+(aq) \rightleftharpoons Sn^{+2}(aq) + H_2(g)$$

Consider the "water gas" reaction

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

$$K_{eq}=14.1 \text{ at } T=800\ ^0C$$

Start with *C(s)*

&

0.100 mol of H_2O in a 1.00L vessel

a. What are the partial pressures of $H_2O(g)$, $H_2(g)$, and $CO(g)$ at equilibrium?

b. What is the minimum amount of Carbon required to achieve equilibrium?

c. What is the total pressure in the vessel at equilibrium?

d. At 25^0C K_{eq} for this reaction is $1.7x10^{-21}$. Is the reaction exothermic or endothermic?

f. Should we increase or decrease the pressure to increase the amount of product?