Chapter 15

Chemical Equilibrium

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

Equilibrium: A Dynamic Process

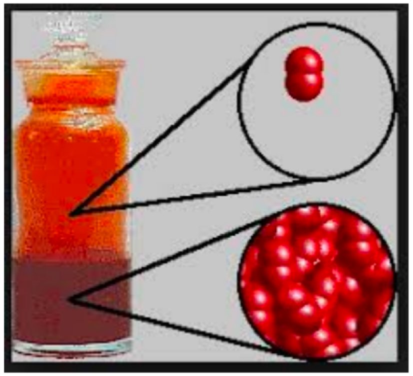
Opposing processes occur at equal rates

- Forward & reverse reactions occur at equal rates
- No outward change is observed
- **Ratio** of reactants to products is constant
- Temperature dependent
- Other factors can also shift equilibrium toward products or reactants
- Represented by double arrows ($\rightleftharpoons$ or $\longleftrightarrow$)

Physical Equilibrium

Ex: Equilibrium between phases

$$Br_2(l) \rightleftharpoons Br_2(g)$$



Chemical Equilibrium

Equilibrium between reactants & products

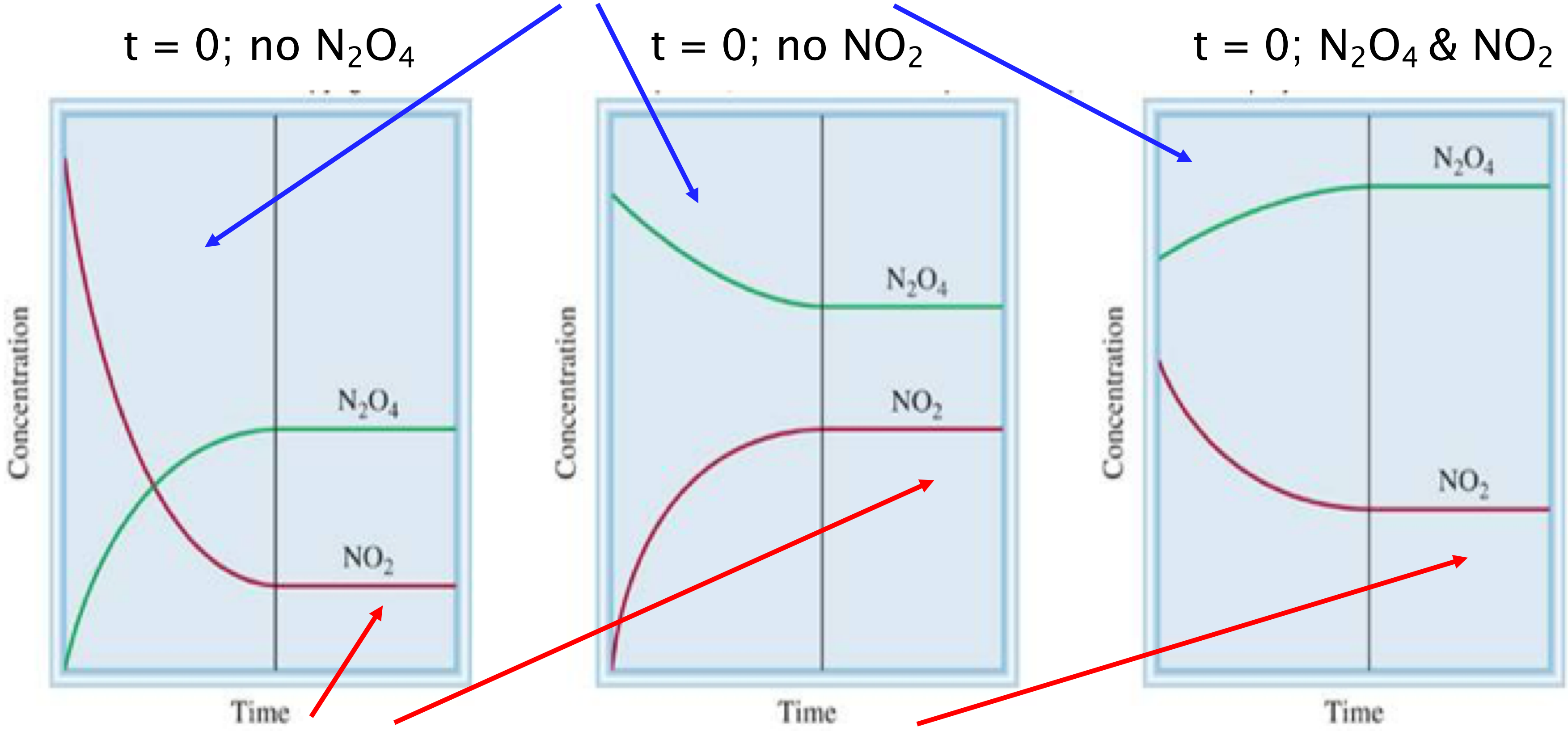
$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Colorless Brown

Initial conditions may vary – concentrations will adjust to establish equilibrium

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

As a system approaches equilibrium, both the forward and reverse reactions are occurring



t = 0; no N_2O_4

t = 0; no NO_2

t = 0; N_2O_4 & NO_2

At equilibrium, the forward and reverse reactions are proceeding at the same rate, so the relative concentrations remain constant.

Equilibrium Constant (K_c)

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

At equilibrium, $[N_2O_4]$ & $[NO_2]$ are constant

- NOT EQUAL
- Not static – both forward & reverse reactions continue
- Actual amounts depend on system

Rate (forward) = Rate (reverse): $k_1[N_2O_4] = k_{-1}[NO_2]^2$

$$\frac{k_1}{k_{-1}} = \frac{[NO_2]^2}{[N_2O_4]} = K_c$$

[conc]
not equal

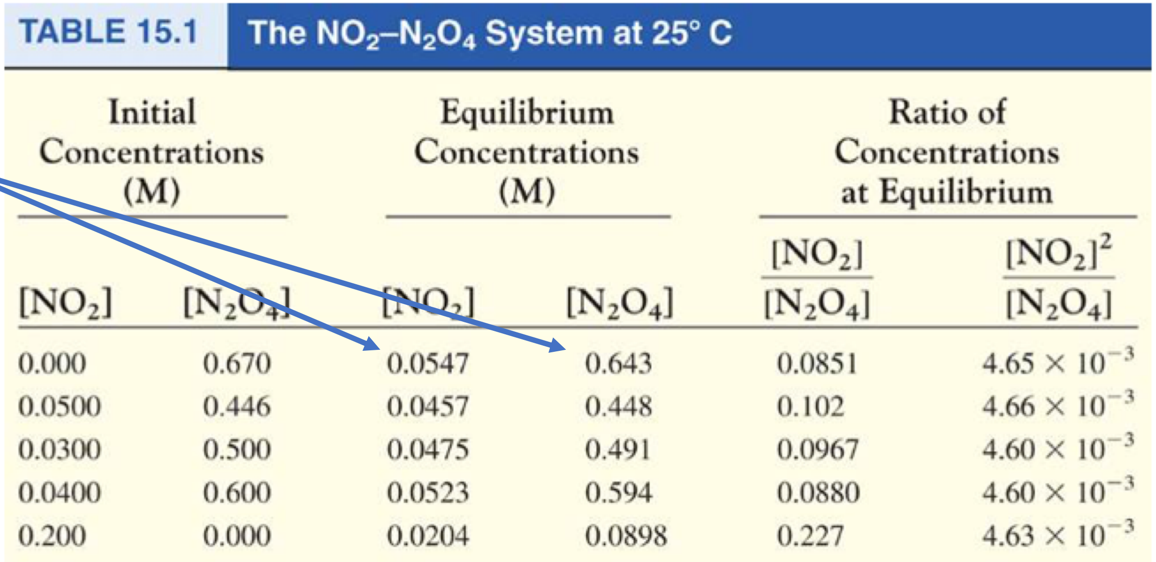


TABLE 15.1 The NO_2–N_2O_4 System at 25° C

Initial Concentrations (M)		Equilibrium Concentrations (M)		Ratio of Concentrations at Equilibrium	
$[NO_2]$	$[N_2O_4]$	$[NO_2]$	$[N_2O_4]$	$\frac{[NO_2]}{[N_2O_4]}$	$\frac{[NO_2]^2}{[N_2O_4]}$
0.000	0.670	0.0547	0.643	0.0851	4.65×10^{-3}
0.0500	0.446	0.0457	0.448	0.102	4.66×10^{-3}
0.0300	0.500	0.0475	0.491	0.0967	4.60×10^{-3}
0.0400	0.600	0.0523	0.594	0.0880	4.60×10^{-3}
0.200	0.000	0.0204	0.0898	0.227	4.63×10^{-3}

Ratio
is equal

Equilibrium Expression

For the reaction: $aA + bB + ... \rightleftharpoons cC + dD + ...$

The Equilibrium Expression is: $K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

For an Equilibrium Expression:

- Concentrations of products are in numerator
- Concentrations of reactants are in denominator
- They are the <u>concentrations at equilibrium</u>
- Exponents ARE coefficients from balanced equation
- Units generally not included
- Also known as a Mass Action Expression

Note difference from rate equation – equilibrium expression IS BASED ON BALANCED EQUATION

Impact of How an Equation is Balanced

Reaction A

$SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$

$$K_c = \frac{[SO_3]}{[SO_2][O_2]^{1/2}}$$

Reaction B

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

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

Equilibrium constants change if the reaction is balanced differently

Numerical values for K_c are related, but different

K_c (reaction B) = $[K_c \text{ (reaction A)}]^2$

It is essential to know how the reaction was balanced

Manipulating Chemical Equations & K_c

When reversing a chemical equation, invert K_c

$$cC + dD \rightleftharpoons aA + bB \qquad K_c = \frac{[A]^a[B]^b}{[C]^c[D]^d} = \frac{1}{K_c}$$

When multiplying coefficients by n, raise K_c to nth power

$$n(cC + dD \rightleftharpoons aA + bB) \qquad K_c = \frac{[A]^{na}[B]^{nb}}{[C]^{nc}[D]^{nd}} = K_c^n$$

When adding equations, multiply the K_c values

$$\begin{array}{rcl} eE & \rightleftharpoons & fF \\ aA + bB & \rightleftharpoons & cC + dD \\ \hline eE + aA + bB & \rightleftharpoons & + fF + cC + dD \end{array}$$

$$K_c = \frac{[C]^c[D]^d[F]^f}{[A]^a[B]^b[E]^e} = K_1 \times K_2$$

K_p The Pressure Version of K_c

Remember the Gas Laws – Chapter 5!

- In a closed system, pressure $\propto$ concentration
  - The equilibrium expression can also be written in terms of pressure
- Very useful since gas phase reactions are often monitored via pressure

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

$\propto$ = proportional to

Writing Equilibrium Expressions

Write the equilibrium constant expression K_p and K_c for:

(a) $3\ NO(g) \rightleftharpoons N_2O(g) + NO_2(g)$

(b) $CH_4(g) + 2\ H_2S(g) \rightleftharpoons CS_2(g) + 4\ H_2(g)$

Manipulating K values

1. For the formation of NH_3 from N_2 and H_2

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

$K_p = 4.34\text{x}10^{-3}$ at 300˚C. What is the value of K_p for the reverse reaction?

A: $2.30\text{x}10^{2}$

2. How does the magnitude of the equilibrium constant K_p for the reaction

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

change if the equilibrium is written as

$$6\ HI(g) \rightleftharpoons 3\ H_2(g) + 3\ I_2(g)$$

A: K_p is cubed

3. Given that, at 700 K, K_p = 54.0 for the reaction:

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

and $K_p = 1.04\times10^{-4}$ for the reaction:

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

determine the value of K_p for the following reaction at 700K:

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

A: 1.51×10^9

What Equilibrium Constants Can Tell Us

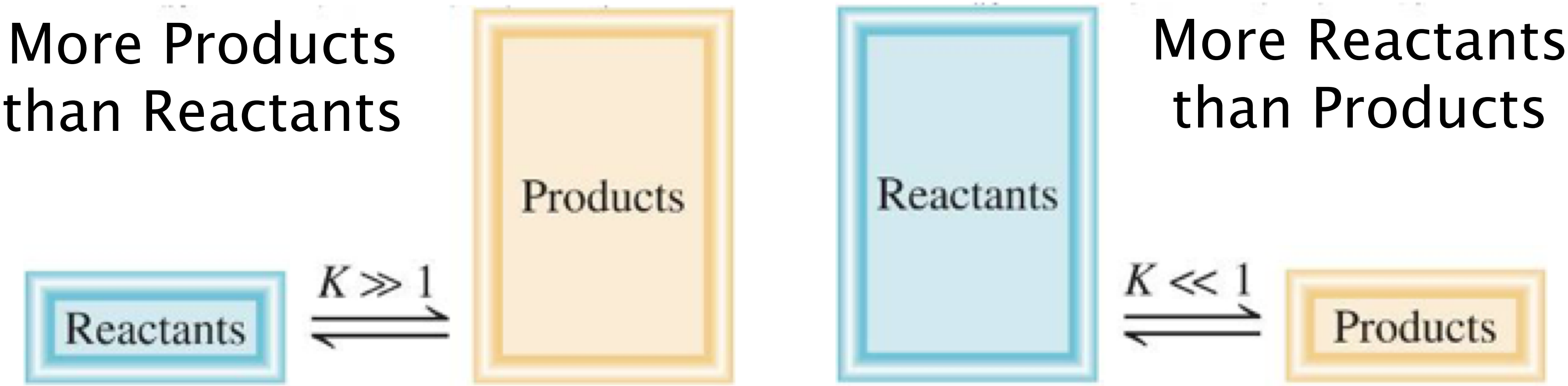
$$aA + bB \rightleftharpoons cC + dD$$

At Equilibrium:

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

K>1
More Products
than Reactants

K<1
More Reactants
than Products



As K goes to infinity, reaction goes to completion.
As K goes to zero, no reaction occurs.

Analyzing K_p/K_c Values

For the reaction: $H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$

K_p = 794 at 298K and K_p = 54 at 700K

Is the formation of HI more favored at the higher or lower temperature?

A: lower

Using the Equilibrium Expression

1. Nitrogen monoxide exists in equilibrium with nitrogen and oxygen gas. At a given temperature, 0.100 moles of NO were added to a 2.00L vessel. At equilibrium, 0.044 moles of NO were remaining. What is the value of K_c?

1. Write the balanced equation & equilibrium constant expression.

2. Find equilibrium <u>molarities</u> of reactants and products.

   We are using concentration, so make sure to convert to Molarity!

3. Calculate K_c

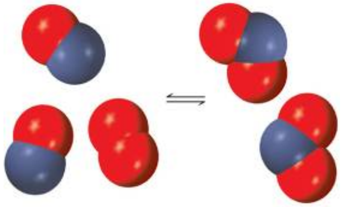
A: $K_c = 0.40$

Types of Equilibria: Homogeneous (K_c & K_p)

All products & reactants are in the same phase

K_c: All chemicals are in units of molarity (mol/L)
Can be either **gas** or **aqueous** solutions

K_p: All chemicals in **gas** phase
Pressure is the partial pressure
– units often atmospheres



$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$

K_c & K_p are related: $\mathbf{K_p = K_c \cdot (RT)^{\Delta n}}$

- Derived from ideal gas law
- R = gas constant (0.0821 L·atm/mol·K)
- T = temperature in Kelvin
- Δn = moles gaseous products – moles gaseous reactants

$K_p = K_c$ if moles product gas = moles reactant gas
If moles product gas ≠ moles reactant gas, there will be a change in pressure

Calculating K_p from K_c

Calculate K_p for the following reactions at 1500˚C.

$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$

$K_c = 12800$

$\Delta n_{gas} = -1$

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

$K_c = 12800$

$\Delta n_{gas} = 0$

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

A: 87.9

A: 12800

Types of Equilibria: Heterogeneous

Are the equilibrium constants for the following two reactions the same?

$SO_3(g) + H_2O(g) \rightleftharpoons H_2SO_4(g)$ & $SO_3(g) + H_2O(l) \rightleftharpoons H_2SO_4(aq)$

$$\text{“}K_1\text{”} = \frac{[H_2SO_4(g)]}{[SO_3(g)]\,[H_2O(g)]} \qquad \text{“}K_2\text{”} = \frac{[H_2SO_4(aq)]}{[SO_3(g)]\,[H_2O(l)]}$$

“K_1” would equal ”K_2” <u>ONLY IF</u> $[H_2SO_4(g)] = [H_2SO_4(aq)]$ <u>AND</u> $[H_2O(g)] = [H_2O(l)]$

$[H_2SO_4(g)]$	dependent on partial pressure	variable
$[H_2SO_4(aq)]$	# moles dissolved in water	variable
$[H_2O(g)]$	dependent on partial pressure	variable
$[H_2O(l)]$	1 g/mL = 1000 g/L for 1L: 1000g(1mol/18g) = 56 mol	56M

The two equilibrium constants are NOT the same!

THE PHASE MATTERS!

Equilibria Involving Mixed Phases (i.e. Heterogeneous)

The subscript "eq" is for general equilibria

K_c & K_p are specific types of K_{eq}

Equilibrium expressions **only include gaseous & aqueous** materials (solids & liquid are NOT included)

$SO_3(g) + H_2O(l) \rightleftharpoons H_2SO_4(aq)$ $\qquad$ $K_{eq} = \dfrac{[H_2SO_4(aq)]}{[SO_3(g)]}$

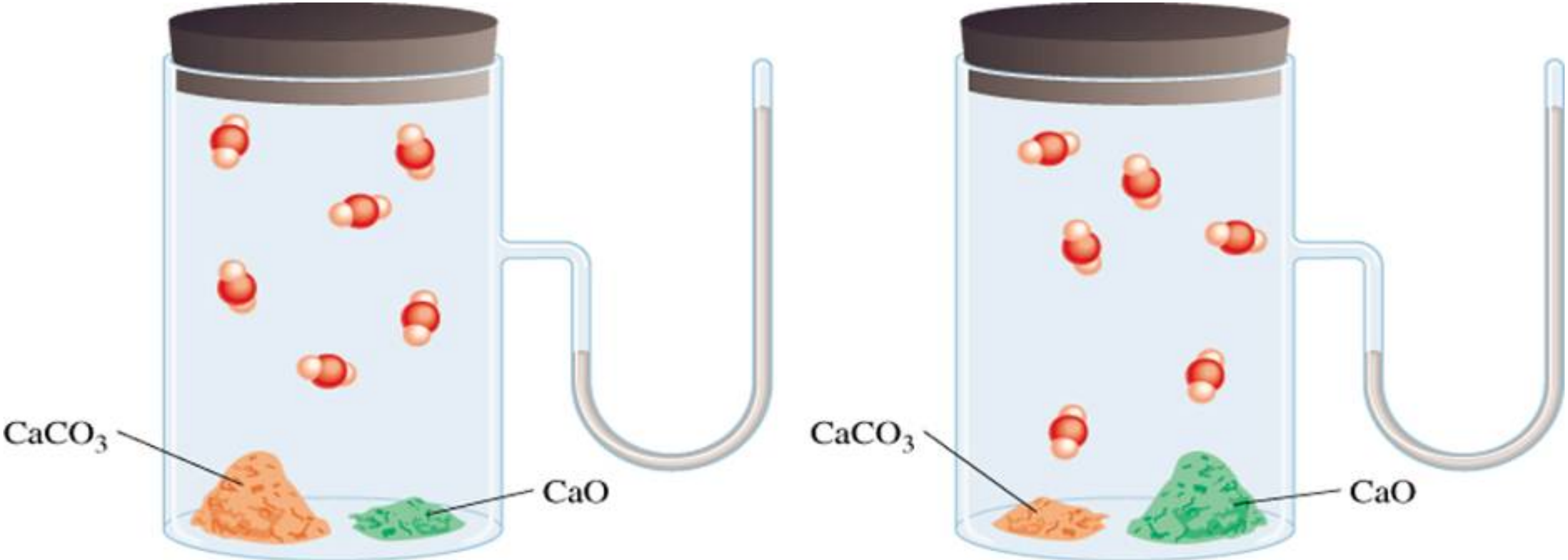
K_p for liquid-vapor equilibrium = vapor pressure of liquid

$H_2O(l) \rightleftharpoons H_2O(g)$ $\qquad$ $K_p = P_{(H2O)}$ liquid not included

To write an appropriate equilibrium expression from a balanced equation, the equation MUST show the phase of each reactant & product.

Equilibria Involving Pure Solids & Liquids

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



$$K_p = P_{CO2}$$

P_{CO2} does not depend on the amount of $CaCO_3$ or CaO

As long as there is <u>some</u> $CaCO_3$ & CaO in the system, the amount of CO_2 above the solid will remain the same

Equilibria Involving Solids & Liquids

A mixture of H_2, S, and H_2S is held in a 1.0L vessel at 90˚C and reacts according to the equation:

$$H_2(g) + S(s) \rightleftharpoons H_2S(g)$$

An equilibrium mixture contains 0.46g H_2S & 0.40g H_2.

(a) Write the equilibrium constant expression for this reaction.

(b) What is the value of K_c for the reaction at this temp.?

A: 0.068

(c) Why can we ignore the amount of S when doing the calculation in part b?

Predicting the Direction of a Reaction

$$aA + bB + \ldots\ldots \rightleftharpoons cC + dD + \ldots\ldots \qquad K_{eq} = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

If the value of K_{eq} is very large

- [C] & [D] very large or [A] & [B] very small
- Reaction will go to completion
- Equilibrium favors products

If the value of K_{eq} is very small

- [C] & [D] very small or [A] & [B] very large
- Reaction proceeds very slowly or no reaction (NR) at all
- Equilibrium favors reactants

Note that K_{eq} has its origins in thermodynamics, but kinetics are also important. The value of K_{eq} does not guarantee that a reaction will occur in either direction.

The Reaction Quotient (Q_c or Q_p)

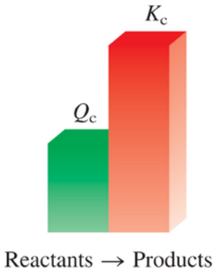
$$aA + bB + \ldots\ldots \rightleftharpoons cC + dD + \ldots\ldots \qquad Q_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

Essentially K_{eq} but at non-equilibrium conditions

- Indicates direction of reaction to get to equilibrium

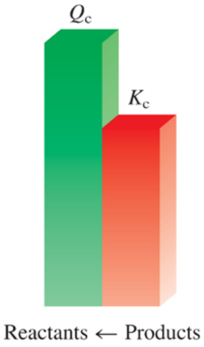
Q < K

- [Products] < equilibrium concentration
- Higher rate in forward direction



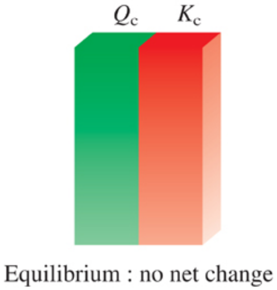
Q > K

- [Products] > equilibrium concentration
- Higher rate in reverse direction



Q = K

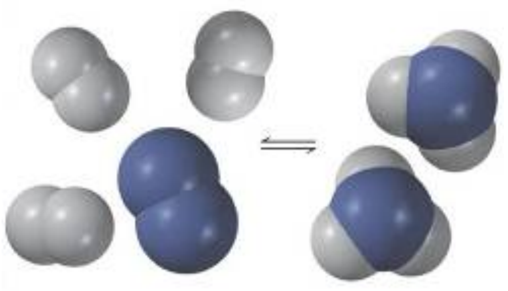
- [Products] = equilibrium concentration
- Forward rate = Reverse rate
- No macroscopic changes observed



Reaction Quotient

1. For the reaction of hydrogen with nitrogen to form ammonia at 25˚C, $K_c = 4.0\text{x}10^8$. The equilibrium concentrations were found to be $1.0\text{x}10^{-3}$M in both hydrogen & nitrogen and 0.020M in ammonia. If you add 0.010M nitrogen, in which direction does the reaction shift?

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



A: Reaction shifts toward products

2. At 1000K, the value of K_p for the following reaction is 0.338.

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

Given the following pressures:

$P_{SO3} = 0.16$ atm; $P_{SO2} = 0.41$ atm; $P_{02} = 2.5$ atm

(a) Is the system at equilibrium? A: No

(b) If not, predict the direction in which the reaction will shift to reach equilibrium. A: toward reactants

Using K_{eq} to Find Equilibrium Concentrations

1. Write the properly balanced chemical equation.
   - Need the stoichiometry & species involved in the reaction.
2. Set up a table of concentrations for all components.
   - Use coefficients from balanced equation to express all unknown concentrations in terms of a single reactant or product, x.
3. Write out the equilibrium constant expression for the reaction (i.e. the equation for K).
4. Substitute the values from step 2 into the K_{eq} equation.
5. Solve the equation for x.
6. Substitute the value you calculated for x into the expressions for the other equilibrium concentrations.

"Ice Tables" will be used in most of the remaining chapters!

Using K_{eq} to Find Equilibrium Concentrations

1. The decomposition of BrCl to bromine & chlorine has a K_c of 0.14 at 350K. If the initial concentration of BrCl is 0.062M, what are the equilibrium concentrations of all components?

1. Balanced Equation:
2. ICE Table

3. K_{eq} Expression

6. Use x to determine conc.

4 & 5. Substitute values from table & Solve for x

2. Carbon monoxide reacts with water at 1000˚C to give carbon dioxide and hydrogen with $K_c = 0.58$. A reaction was started with the following composition: CO_2 0.20M; H_2 1.20M; H_2O 0.50M; CO 1.00M. What are the equilibrium concentrations of all components?

1. Balanced Equation:
2. ICE Table

3. K_{eq} Expression

4. Substitute values from table

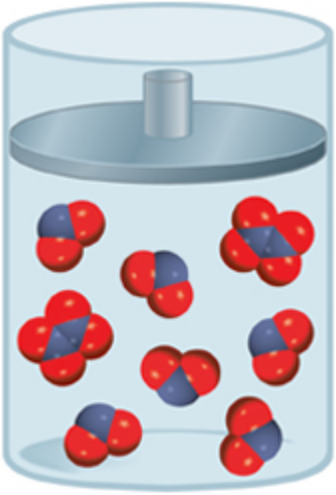
Need quadratic equation!

5. Solve for x using quadratic equation: $\frac{-b \pm \sqrt{b^2-4ac}}{2a}$

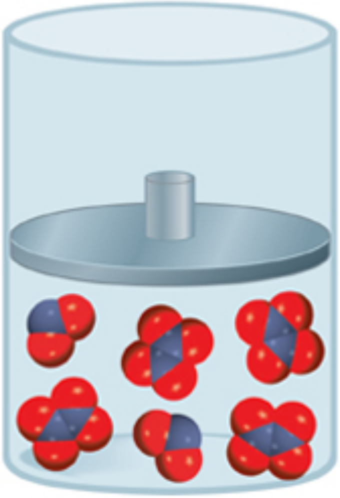
6. Use x to determine concentrations

Factors that Affect Chemical Equilibrium: Le Châtelier's Principle

When stress is applied to a system at equilibrium, the system will shift to reduce the applied stress and re-establish equilibrium



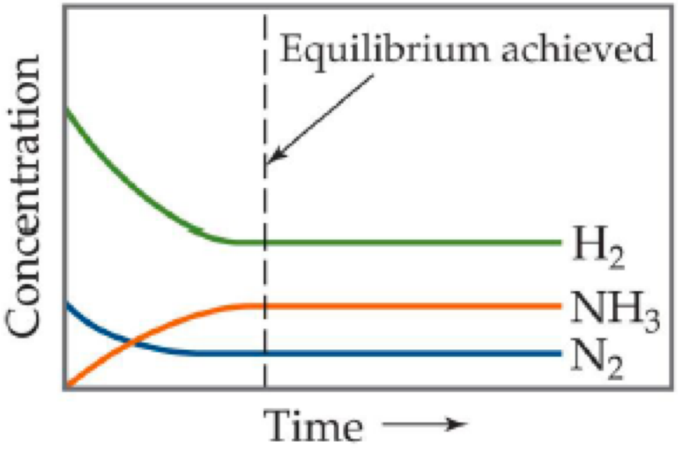
$$2NO_2(g) \rightleftharpoons 1N_2O_{4(g)}$$

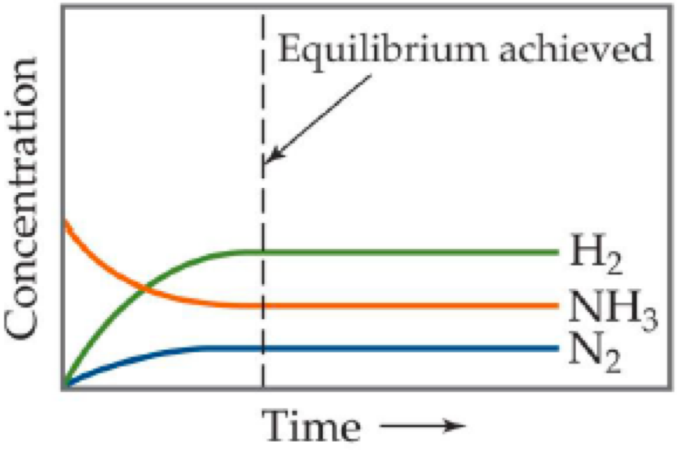


Addition of pressure causes the reaction to shift towards products – fewer moles of gas decreases the pressure (i.e. the stress)

Remember: Equilibrium Can Be Reached From Either Direction

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





It doesn’t matter whether you start with N_2 and H_2 or with NH_3 – you will have the same proportions of all three substances at equilibrium

Many different types of stress can affect equilibrium, such as:

Change in components

Change in concentrations

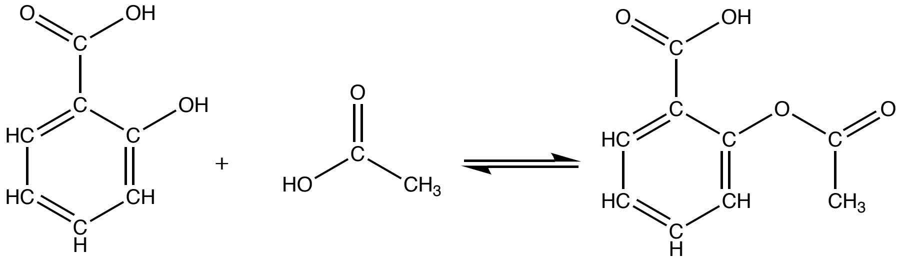
Change in partial pressure

Change in external pressure

Change in total volume

Change in temperature

Changing Components, Concentration, or Partial Pressure



$$K_{eq} = \frac{[\text{Asp.}]}{[\text{AA}][\text{SA}]}$$

Synthesis of Aspirin from Salicylic Acid & Acetic Acid is an equilibrium process. We want to make as much aspirin as possible.

Addition of a component: Add Acetic Acid

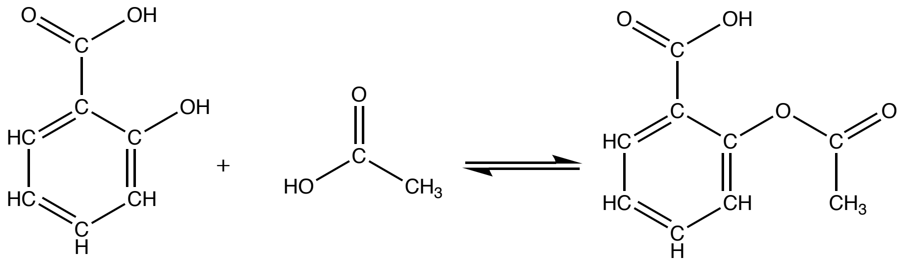
K_{eq} must remain constant

$$K_{eq} = \frac{[\text{Asp.}]}{[\text{AA}][\text{SA}]}$$

To keep K_{eq} constant, we need to increase the numerator – reaction will shift toward the products (make more aspirin).

If we add more AA, the denominator gets larger

Changing Components, Concentration, or Partial Pressure



$$K_{eq} = \frac{[\text{Asp.}]}{[\text{AA}][\text{SA}]}$$

Synthesis of Aspirin from Salicylic Acid & Acetic Acid is an equilibrium process. We want to make as much aspirin as possible.

Decrease in conc. of a component: Remove Aspirin

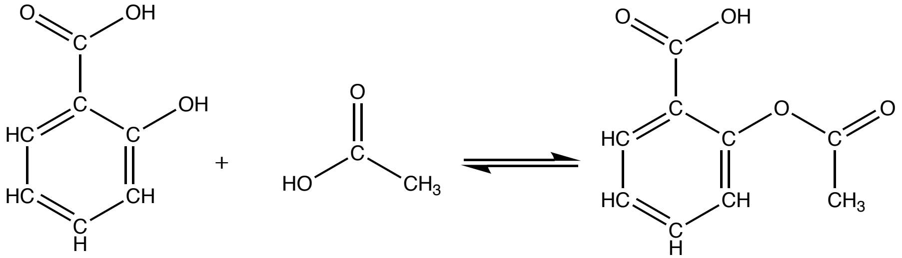
K_{eq} must remain constant →

$$K_{eq} = \frac{[\text{Asp.}]}{[\text{AA}][\text{SA}]}$$

To keep K_{eq} constant, we need to decrease the denominator – reaction will shift toward the products (use up AA & SA, & make more aspirin).

If we remove aspirin, the numerator gets smaller

Changing Components, Concentration, or Partial Pressure



$$K_{eq} = \frac{[\text{Asp.}]}{[\text{AA}][\text{SA}]}$$

Synthesis of Aspirin from Salicylic Acid & Acetic Acid is an equilibrium process. We want to make as much aspirin as possible.

What if we added aspirin?

K_{eq} must remain constant

$$K_{eq} = \frac{[\text{Asp.}]}{[\text{AA}][\text{SA}]}$$

If we add aspirin, the numerator gets larger

To keep K_{eq} constant, we need to increase the denominator – reaction will shift toward the reactants (make more AA & SA).

Changing Components, Concentration, or Partial Pressure

For the following reaction,

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

what happens to the equilibrium if:

(a) O_2 is added to the system?

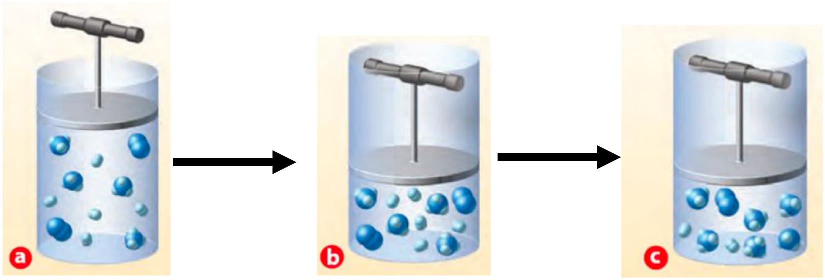
(b) NO is removed?

Changing Volume or External Pressure

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

When pressure is increased:

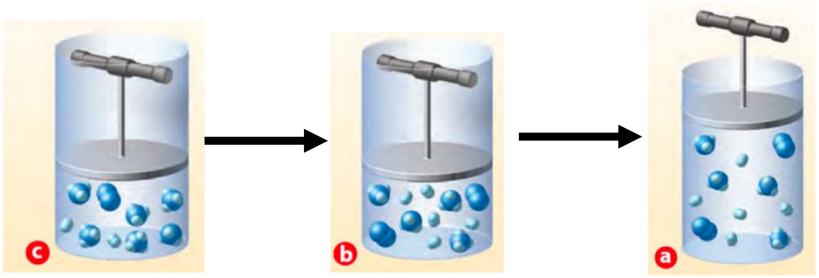
Equilibrium shifts to produce smaller # moles of gas



Toward products – 2 moles < 4 moles

When Pressure is decreased:

Equilibrium shifts to produce larger # moles of gas



Toward reactants – 4 moles > 2 moles

If a reaction has the same number of moles of gas on both sides (e.g. $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$):

Changes in external pressure do not affect equilibrium

Changing Volume or External Pressure

For the following reaction,

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

what happens to the equilibrium if:

(a) The volume of the system is increased?

(b) The external pressure exerted on the system is increased?

Changing Temperature

Exothermic Reaction:

Heat is released

→ heat is a product

Increase T: K decreases

→ favors reactants

Decrease T: K increases

→ favors products

Endothermic Reaction:

Heat is absorbed

→ heat is a reactant

Increase T: K increases

→ favors products

Decrease T: K decreases

→ favors reactants

High T:
More NO_2

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

red — clear

Exothermic Reaction

$\Delta H = -58\text{kJ/mol}$

Low T:
More N_2O_4

Adding a Catalyst or Inhibitor

Catalysts:

- Catalysts lower activation energy.
- Cause a reaction to reach equilibrium faster
- DO NOT AFFECT THE EQUILIBRIUM ITSELF

Inhibitors

- Act to slow the rate of a reaction
- Prevent equilibrium from being reached as quickly
- DO NOT AFFECT THE EQUILIBRIUM ITSELF
- It may seem like the reaction is not occurring at all, but in reality it is just infinitely slow.

Which way does the reaction shift if……

$N_2O_3(g) \rightleftharpoons NO(g) + NO_2(g)$ $\Delta H = +39.7 kJ/mol$

NO is added?

Volume of reaction vessel is reduced?

The total internal pressure is increased by adding He gas?

The temperature is increased?

A catalyst is added?

How does each of the following changes affect the yield of NO at equilibrium?

$$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$$

$$\Delta H = -904.4 \text{ kJ/mol}$$

Increase $[NH_3]$

Increase $[H_2O]$

Decrease $[O_2]$

Decrease the volume of the container

Add a catalyst

Increase temperature