Introduction to Kinetics and Equilibrium

Kinetics and equilibrium are two of the most important areas in chemistry. Entire books and courses at the undergraduate and graduate level are devoted to them.

Chemical kinetics – the study of the rates of chemical processes

Equilibrium - the condition of a system in which competing influences are balanced

Chemical equilibrium – the state in which the concentrations of the reactants and products have ***no net change over time***

↑

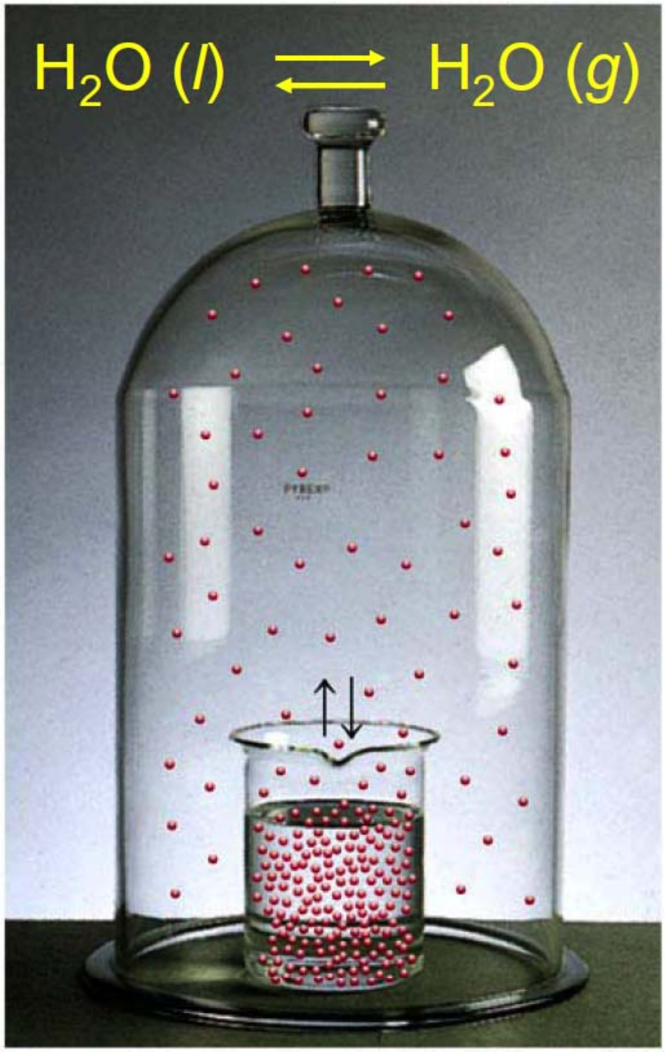
concentrations at equilibrium are determined by thermodynamics ($\Delta_r G°$)

Physical Equilibrium

Balance of competing physical processes

- Evaporation vs condensation
- Freezing vs melting

$H_2O\ (l) \rightleftharpoons H_2O\ (s)$



Chemical Equilibrium

Balance of two or more chemical reactions

Forward reaction:
Decomposition

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

Colorless gas

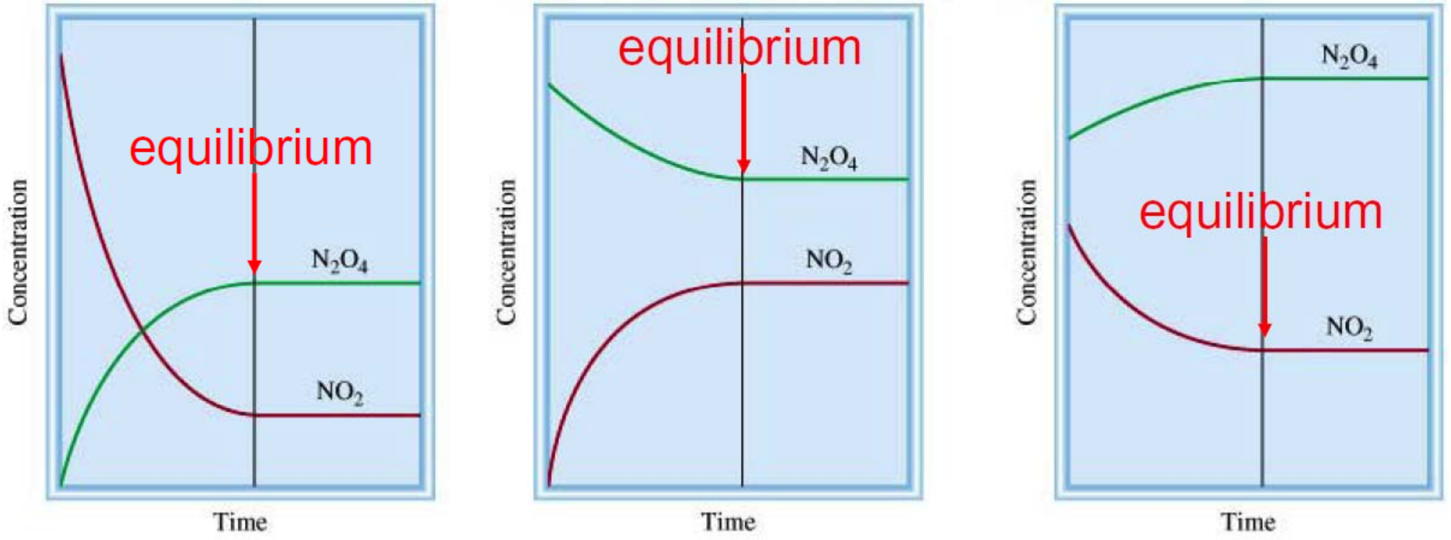
Reverse reaction:
Dimerization

Yucky-brown

Decomposition is exactly balanced by dimerization at equilibrium

Concentrations of NO_2 and N_2O_4 do not change with time

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



Start with NO_2 Start with N_2O_4 Start with NO_2 & N_2O_4

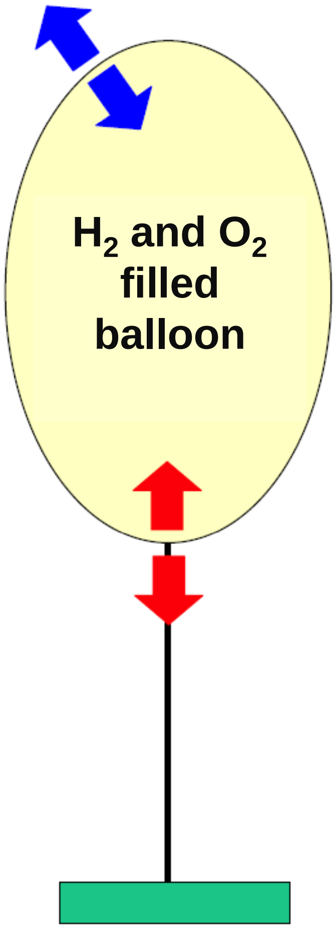
- *Equilibrium is not achieved instantaneously*
- *Concentrations stop changing at equilibrium but reactions do not stop*

Is Equilibrium Common?

- *Equilibrium systems are often localized and/or constrained within larger systems that are NOT at equilibrium*

- *Equilibrium may disappear when such constraints are removed*

Demo



We have physical equilibrium:

- Equilibrium 1: H_2 pressure balanced by balloon wall surface tension
- Equilibrium 2: Balloon buoyancy balanced by the string tension

Do we have chemical equilibrium?? NO!

$$2\ H_2\ (g) + O_2\ (g) \rightarrow 2\ H_2O\ (g) \qquad \Delta_r G^\circ = -457.2\ \text{kJ/mol}$$

- Combustion to make water is favored, but extremely slow at PSCB 100 temp.
- Removing constraints: heating with candle destroys equilibria 1&2 and (nearly) achieves chemical equilibrium simultaneously

Limiting Reagents

Was all the H_2 and O_2 in the balloon converted to water?

It depends on the initial amounts of the two gases. Suppose:

$$2\,H_2\,(g) + O_2\,(g) \rightarrow 2\,H_2O\,(g)$$

Before candle:	0.75 atm	0.75 atm	0.0 atm
Change:	- 2x	- x	+ 2x
After candle:	0.0 atm	0.38 atm	0.75 atm

Limiting reagent:
molecule that is used up, causing the reaction to stop

Reagent in excess

80's Australian rock band?

Reactions That Don't Go to Completion

Reactions either:

- go to completion (all limiting reactants are consumed)

$$\boxed{\text{reactants} \rightarrow \text{products}}$$

- e. g. combustion reactions (like the balloon demo)

- or establish a chemical ***equilibrium*** (some reactants, some products)

$$\boxed{\text{reactants} \rightleftarrows \text{products}}$$

- these are the reactions introduced in this part of the course

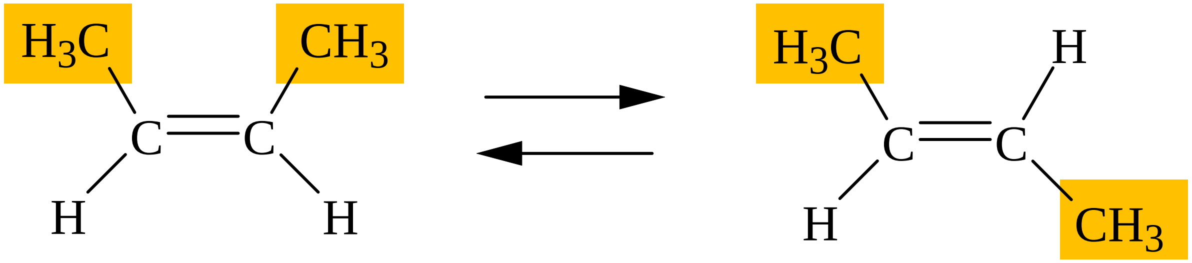
Reactions That Don't Go to Completion

- When an equilibrium is established, each reactant (and product) has a nonzero concentration and these concentrations are constant with respect to time.
- When an equilibrium is established, the limiting reagent has a nonzero concentration.
- The reactions do not stop at equilibrium. The rates of the forward and reverse reactions are balanced, so there is ***no net change in concentrations***.

concentration is specified as Moles per Liter
and written as **[reactant]** or **[product],**
or
as partial pressures for gas phase reactions

A Gas Phase Equilibrium

Consider a simple gas phase reaction, the conversion of *cis*-2-butene to *trans*-2-butene, an example of ***isomerization***:

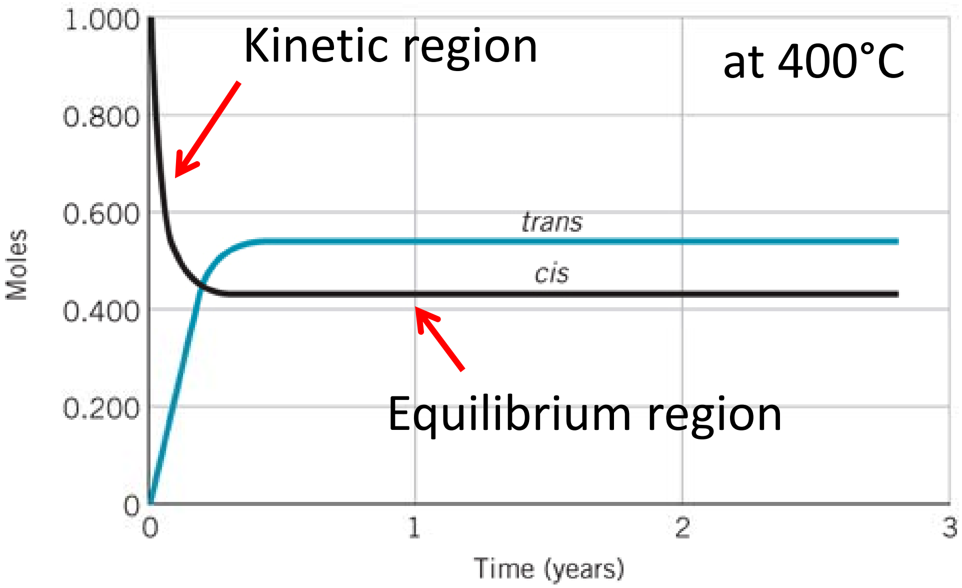


cis-2-butene *trans*-2-butene

- The ⇄ is used to indicate an equilibrium.
- Here, both species are gases.
- The total number of moles of gas remains constant.
- This reaction does not go to completion.
  - An equilibrium is established.

A Gas Phase Equilibrium

cis ⇄ trans



Equilibrium Constant

- In the equilibrium region, the concentrations of products and reactants are related in an equation called the ***equilibrium constant expression***
- In the 2-butene case,

$$\text{cis} \rightleftarrows \text{trans}$$

$$K_c = \frac{[products]}{[reactants]} = \frac{[trans - 2 - butene]}{[cis - 2 - \text{butene}]} = 1.27 \qquad \text{(at 400 °C)}$$

  - K_c is called the ***equilibrium constant***.
  - For K_c, species are expressed as M (Moles L^{-1})
  - Products in numerator, reactants in denominator.
  - Concentrations raised to their stoichiometric coefficients in the balanced reaction (1 in this case).

Sample Question

A quantity of cis-2-butene is added to a 2 Liter flask and heated to 400°C for 2 years. The concentration of trans-2-butene was then determined to be 0.50 *M*. What is the concentration of cis-2-butene in the flask?

$$K_c = \frac{[trans-2-butene]}{[cis-2-\mathrm{butene}]} = 1.27$$

$$\frac{[0.5\ M]}{[cis-2-\mathrm{butene}]} = 1.27$$

$$[cis-2-\mathrm{butene}] = \frac{0.5}{1.27} = \boxed{0.39\ M}$$

Generic Equilibrium Constant

$$a\,A + b\,B \rightleftarrows c\,C + d\,D$$

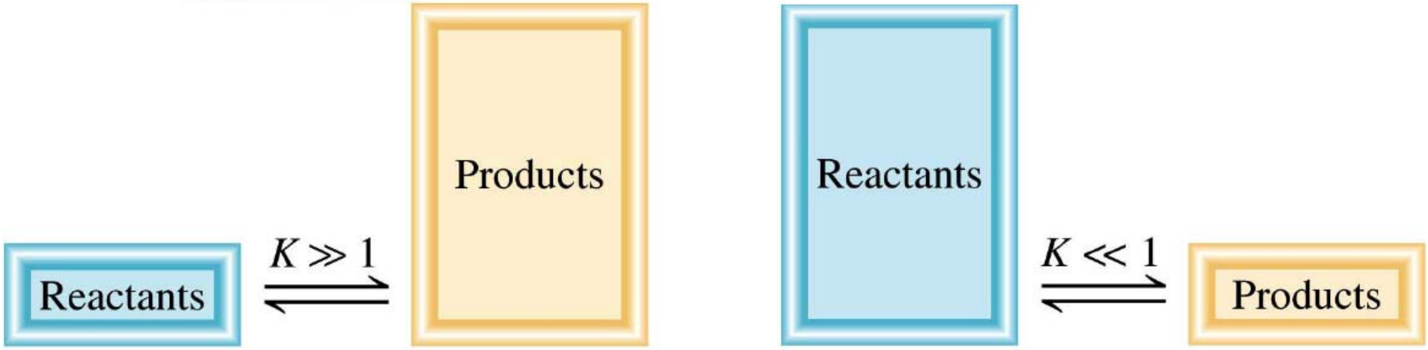
$$K_c = \frac{[C]_{eq}^{c}[D]_{eq}^{d}}{[A]_{eq}^{a}[B]_{eq}^{b}}$$

Constant for a given temperature

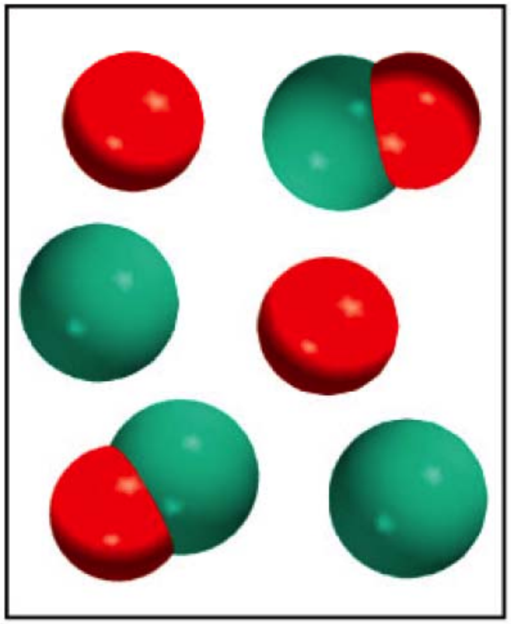
- Ratio of equilibrium concentrations of products over reactants
- Concentrations raised to the stoichiometric coefficients in the balanced reaction equation

$$aA + bB \rightleftarrows cC + dD \qquad K_C = \frac{[C]_{eq}^{c}[D]_{eq}^{d}}{[A]_{eq}^{a}[B]_{eq}^{b}}$$

	Equilibrium Will	
$K_C >> 1$	Lie to the right	Favor products
$K_C << 1$	Lie to the left	Favor reactants

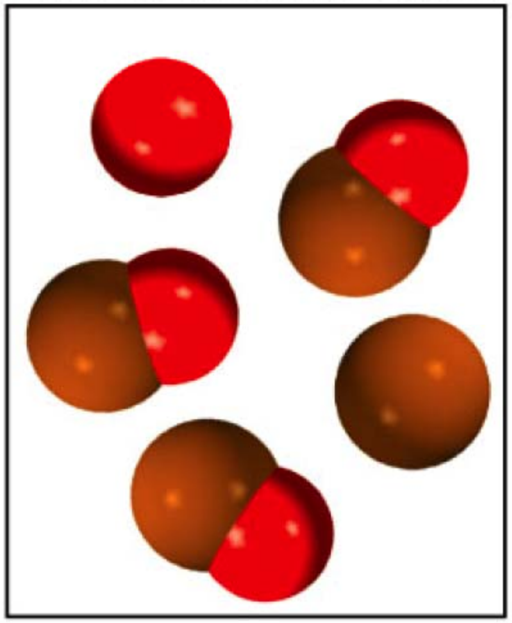


Equilibrium Constant



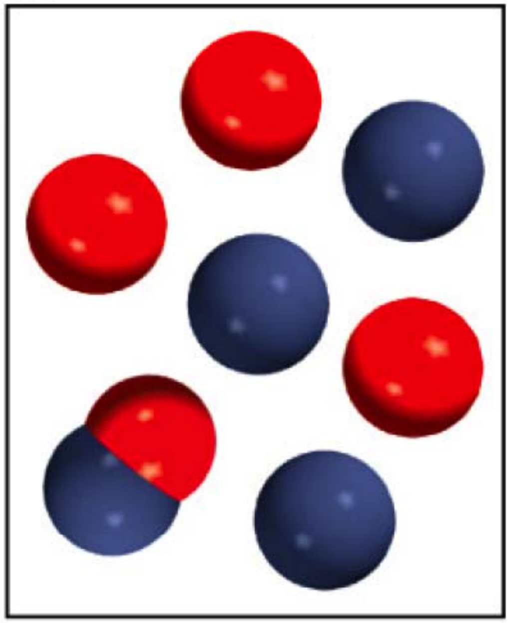
$\mathrm{A + B \rightleftharpoons AB}$

$$K = \frac{[AB]}{[A][B]} = \frac{2}{2\times 2} = \frac{1}{2}$$



$\mathrm{A + C \rightleftharpoons AC}$

$$K = \frac{[AC]}{[A][C]} = \frac{3}{1\times 1} = 3$$



$\mathrm{A + D \rightleftharpoons AD}$

$$K = \frac{[AD]}{[A][D]} = \frac{1}{3\times 3} = \frac{1}{9}$$

Origin of Equilibrium Constant

Equilibrium occurs when the ***rates*** of the forward and reverse reactions are exactly equal

$$\text{rate}_{\text{forward}} = \text{rate}_{\text{reverse}}$$

Reaction rate is the number (mol) of molecules produced or consumed in a chemical reaction per reaction volume (L) per time (s)

Reaction rate is usually measured in mol L^{-1} s^{-1}

$$A \longrightarrow B$$

Reaction rate is the number of mol/L of **A** that are converted into **B** every second

$$\text{rate}_{\text{forward}} = -\frac{\Delta[A]}{\Delta t}$$

$\Delta[A]$ = change in concentration of A over time period Δt

$$\text{rate}_{\text{forward}} = \frac{\Delta[B]}{\Delta t}$$

$\Delta[B]$ = change in concentration of B over time period Δt

Because [A] decreases with time, $\Delta[A]$ is negative.

Origin of Equilibrium Constant

For simple reactions (like this one), reaction rate is proportional to the concentrations of the reactants raised to their stoichiometric coefficients

$$A \longrightarrow B \qquad\qquad B \longrightarrow A$$

Rate definition: $\text{rate}_{\text{forward}} = -\dfrac{\Delta[A]}{\Delta t}$ $\qquad$ $\text{rate}_{\text{reverse}} = -\dfrac{\Delta[B]}{\Delta t}$

***Rate law*:** $\text{rate}_{\text{forward}} = k_f \times [A]$ $\qquad$ $\text{rate}_{\text{reverse}} = k_r \times [B]$

rate constants

At equilibrium: $k_f \times [A] = k_r \times [B]$ ➡ $\boxed{K_c = \dfrac{k_f}{k_r} = \dfrac{[B]}{[A]}}$

Example

The reaction of CO with Cl_2 to form $COCl_2$ is another single-step reaction. A vessel is filled with only CO and Cl_2. Describe how equilibrium is achieved and the connection between the reaction rates and the equilibrium constant.

Balanced Reaction: $CO\,(g) + Cl_2\,(g) \rightleftarrows COCl_2\,(g)$

Initially, we have only reactants: $CO_{(g)} + Cl_{2(g)} \rightarrow COCl_{2(g)}$

$$\text{rate}_{\text{forward}} = k_f \times [CO][Cl_2]$$

$$\boxed{\text{Initially:}\quad \text{rate}_{\text{forward}} \gg \text{rate}_{\text{reverse}}}$$

As products form, the rate of the reverse reaction increases:

$$CO_{(g)} + Cl_{2(g)} \leftarrow COCl_{2(g)}$$

$$\text{rate}_{\text{reverse}} = k_r \times [COCl_2]$$

When the forward and reverse rates become equal, the system has achieved chemical equilibrium.

$$\text{rate}_{\text{forward}} = \text{rate}_{\text{reverse}}$$

$$k_f[\mathrm{CO}][\mathrm{Cl_2}] = k_r[\mathrm{COCl_2}]$$

Equilibrium constant expression

Equilibrium constant

$$\boxed{K_c = \frac{k_f}{k_r} = \frac{[\mathrm{COCl_2}]}{[\mathrm{CO}][\mathrm{Cl_2}]} = \text{constant}}$$

Law of Mass Action

- Products in numerator, reactants in denominator.
- By convention, the units of K_c (if any) are ignored
- Concentrations raised to the stoichiometric coefficients (1 in this case).

Equilibrium Expressed in Partial Pressures

$$a\,A + b\,B \rightleftarrows c\,C + d\,D$$

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

Since PV = nRT, we can write for gas phase reactions:

$$P \propto \frac{n}{V} \quad \Rightarrow \quad K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

K_p expresses equilibrium in terms of the ***partial pressures***

Equilibrium Expressed in Partial Pressures

In general $K_c \neq K_p$, but they are related:

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

$$P = \left[\frac{n}{V}\right] \times RT = [\text{gas}] \times RT$$

$$K_p = \frac{([C]RT)^c\ ([D]RT)^d}{([A]RT)^a\ ([B]RT)^b} = K_c \times (RT)^{c+d-a-b}$$

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

Δn = moles of gaseous products – moles of gaseous reactants

= $(c + d) - (a + b)$

Sample Problem

The equilibrium concentrations for the reaction between carbon monoxide and molecular chlorine to form $COCl_2$ (*g*) at 74^0C are [CO] = 0.012 *M*, $[Cl_2]$ = 0.054 *M*, and $[COCl_2]$ = 0.14 *M*. Calculate the equilibrium constants K_c and K_p (R = *0.082 L atm K^{-1} mol^{-1}*)

$$CO\,(g) + Cl_2\,(g) \rightleftharpoons COCl_2\,(g)$$

$$K_c = \frac{[COCl_2]}{[CO][Cl_2]} = \frac{0.14}{0.012 \times 0.054} = 220$$

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

$\Delta n = 1 - 2 = -1$ $\quad$ $R = 0.0821$ $\quad$ $T = 273 + 74 = 347$ K

$$K_p = 220 \times (0.0821 \times 347)^{-1} = 7.7$$

Homogeneous Equilibria

Refers to reactions in which all reactants and products are in the *same phase*.

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

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} \qquad K_p = \frac{P^2_{NO_2}}{P_{N_2O_4}}$$

Heterogeneous Equilibria

In ***heterogeneous equilibria***, reactants and products are in different phases

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

$$K = \frac{[CaO][CO_2]}{[CaCO_3]}$$

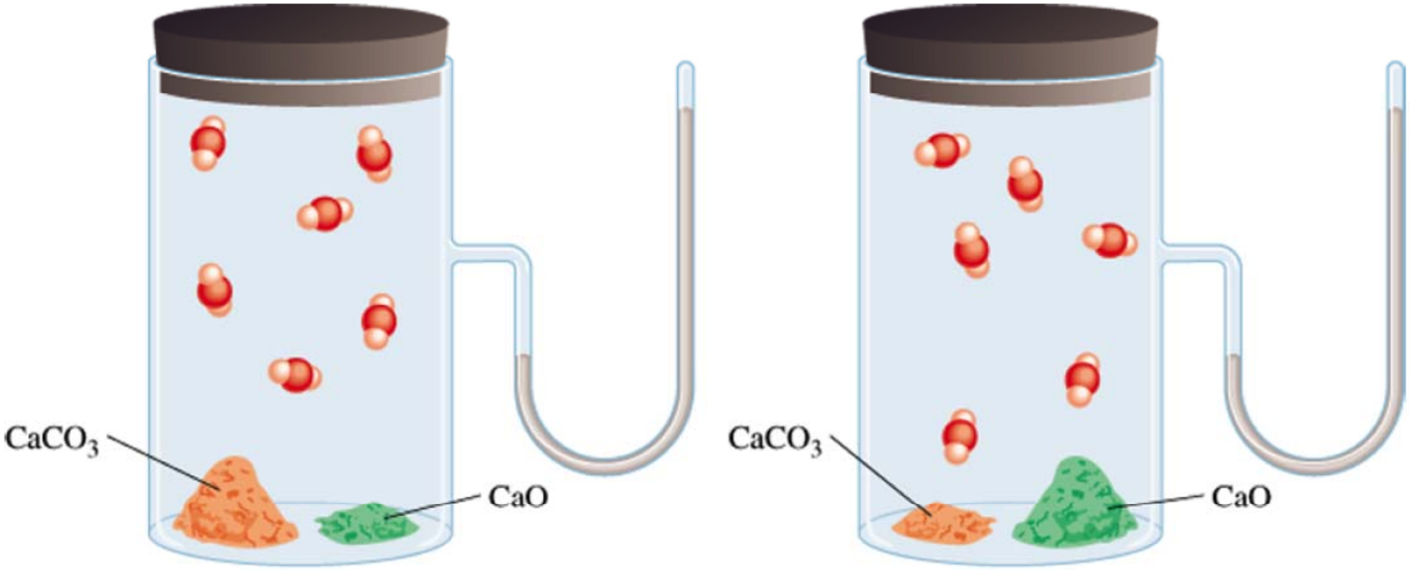
$[CaCO_3]$ = constant
$[CaO]$ = constant

$$K_c = K \times \frac{[CaCO_3]}{[CaO]} = [CO_2]$$

$$K_p = P_{CO_2}$$

The concentrations of pure solids and pure liquids are constant and are not included in the expression for the equilibrium constant

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



$$K_p = P_{CO_2}$$

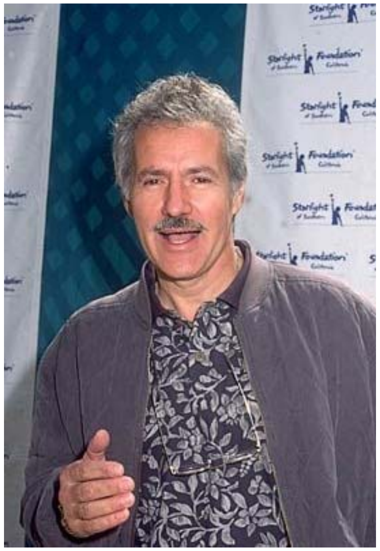
P_{CO_2} does not depend on the amount of $CaCO_3$ or CaO

Example

Consider the following equilibrium at 295 K:

$$NH_4HS\ (s) \rightleftharpoons NH_3\ (g) + H_2S\ (g)$$

The partial pressure of each gas is 0.265 atm. Calculate K_P and K_C for the reaction.



$$K_P = P_{NH_3}P_{H_2S} = 0.265 \text{ x } 0.265 = 0.0702$$

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

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

$$\Delta n = 2 - 0 = 2 \qquad T = 295 \text{ K}$$

$$K_C = 0.0702 \text{ x } (0.0821 \text{ x } 295)^{-2} = 1.20 \text{ x } 10^{-4}$$

Manipulating Equilibrium Constant Expressions

- Each of these proper chemical equations will have a different equilibrium expression and a different numerical value of K_c:

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

$$K_{c1} = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$1/2N_2(g) + 3/2H_2(g) \rightleftarrows NH_3(g)$

$$K_{c2} = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}} = K_{c1}^{1/2}$$

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

$$K_{c3} = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{1}{K_{c1}}$$

Changing the reaction stoichiometry by a factor of *x* raises K_c to the power of *x*

The K_c's of a forward and reverse reaction are reciprocals of each other

K of Forward and Reverse Reactions

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

$$K = \frac{[NO_2]^2}{[N_2O_4]} = 4.63 \times 10^{-3}$$

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

$$K' = \frac{[N_2O_4]}{[NO_2]^2} = \frac{1}{K} = 216$$

When the equation for a reversible reaction is written in the opposite direction, the equilibrium constant becomes the reciprocal of the original equilibrium constant.

Multiple Equilibria

$$A + B \rightleftharpoons \cancel{C} + \cancel{D} \qquad K'_C = \frac{[C][D]}{[A][B]}$$

$$\cancel{C} + \cancel{D} \rightleftharpoons E + F \qquad K''_C = \frac{[E][F]}{[C][D]}$$

$$A + B \rightleftharpoons E + F \qquad K_C = \frac{[E][F]}{[A][B]} = \frac{[E][F]}{\cancel{[C][D]}} \times \frac{\cancel{[C][D]}}{[A][B]} = K'_C K''_C$$

If a reaction can be expressed as the sum of two or more reactions, the equilibrium constant for the overall reaction is given by the product of the equilibrium constants of the individual reactions.

Example

$N_2\,(g) + O_2\,(g) \rightleftarrows 2\,NO\,(g)$ $$K_{c1} = \frac{[NO]^2}{[N_2][O_2]} = 2.3 \times 10^{-19}$$

$+ \quad 2\,NO(g) + O_2(g) \rightleftarrows 2\,NO_2(g)$ $$K_{c2} = \frac{[NO_2]^2}{[NO]^2[O_2]} = 3 \times 10^{6}$$

$N_2\,(g) + 2\,O_2\,(g) \rightleftarrows 2\,NO_2\,(g)$

$$K_c = \frac{[NO]^2}{[N_2][O_2]} \times \frac{[NO_2]^2}{[NO]^2[O_2]} = \frac{[NO_2]^2}{[N_2][O_2]^2} = 2.3 \times 10^{-19} \times 3 \times 10^{6} = \boxed{7 \times 10^{-13}}$$

K_c is equal to the ***product*** of the equilibrium constants for the individual reactions

Another Example

You know equilibrium constants for the following reactions:

1. $S(s) + O_2(g) \Leftrightarrow SO_2(g)$ $K_1 = 10^{52}$
2. $2S(s) + 3O_2(g) \Leftrightarrow 2SO_3(g)$ $K_2 = 10^{129}$

What is the equilibrium constant for reaction:

3. $2SO_2(g) + O_2(g) \Leftrightarrow 2SO_3(g)$ $K_3 = ???$

Reactions 1, 2 and 3 are related as follows:

2x{Reverse Reaction 1} + {Reaction 2} = {Reaction 3}

So:

$K_1^{-1} \text{ x } K_1^{-1} \text{ x } K_2 = K_3$

Solving for K_3:

$10^{-52} \text{ x } 10^{-52} \text{ x } 10^{129} = 10^{25}$

Reaction Quotients

- We can determine the direction in which a reaction has to shift to reach equilibrium by calculating the ***reaction quotient, Q_c***

$$aA + bB \rightleftarrows cC + dD$$

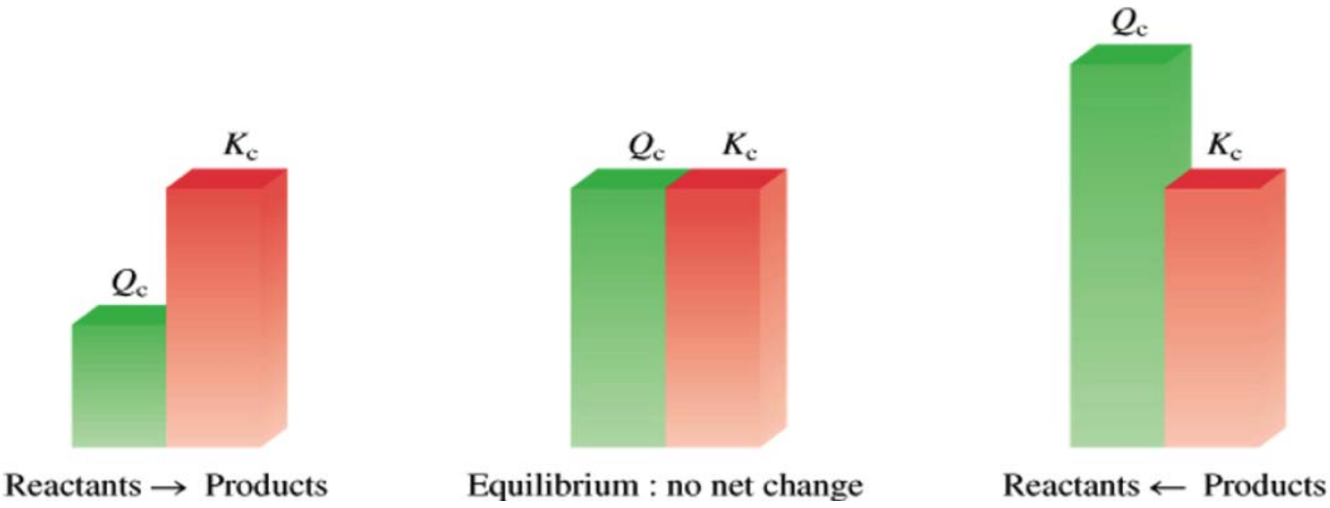
$$K_C = \frac{[C]_{eq}^{c}[D]_{eq}^{d}}{[A]_{eq}^{a}[B]_{eq}^{b}} \qquad Q_C = \frac{[C]_{initial}^{c}[D]_{initial}^{d}}{[A]_{initial}^{a}[B]_{initial}^{b}}$$

- The expression for Q_c is the same as K_c. The difference is that the ***instantaneous concentration values*** are used when calculating Q_c.

- Q_c can vary from zero (no products) to infinity (no reactants)

Three possible situations:

- $Q_c < K_c$
  - Too many reactants. There must be additional net conversion of reactants to products to achieve equilibrium.
- $Q_c = K_c$
  - Equilibrium.
- $Q_c > K_c$
  - Too many products. There must be additional net conversion of products to reactants to achieve equilibrium.



Sample Problem

Assume that the reaction quotient for the following reaction is 1.0×10^{-8}

$2\,NO_2\,(g) \rightleftarrows 2\,NO\,(g) + O_2\,(g)$ $\quad K_c = 7.4 \times 10^{-16}$ (at 25°C)

From this we can conclude:

Q > K

(a) The reaction is at equilibrium.
(b) Equilibrium could be reached by adding enough NO or O_2 to the system.
(c) The reaction must proceed from left to right to reach equilibrium.
→ (d) The reaction must proceed from right to left to reach equilibrium.
(e) The reaction can never reach equilibrium.

Sample Problem

If the equilibrium constant for the following reaction is $K_c = 1 \times 10^2$

$$2\,C_2H_6\,(g) + 7\,O_2\,(g) \rightleftarrows 4\,CO_2\,(g) + 6\,H_2O\,(g)$$

and all the concentrations were initially 0.10 *M*,
we can predict that the reaction:

$$Q_c = \frac{[CO_2]^4[H_2O]^6}{[C_2H_6]^2[O_2]^7} = \frac{(0.1)^{10}}{(0.1)^9} = 0.1$$

(a) is at equilibrium initially.
→ (b) must shift from left to right to reach equilibrium.
(c) must shift from right to left to reach equilibrium.
(d) cannot reach equilibrium.
(e) cannot be determined unless we have the information necessary to calculate Q_c for the reaction.

$Q < K$

Sample Problem

At 1400K, K_C = 4.7 for reaction

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

Which direction will the reaction proceed in a mixture containing 0.035M H_2O, 0.050M CH_4, 0.15M CO and 0.20M H_2?

Reaction quotient for this mixture is:

$$Q = \frac{[CO][H_2]^3}{[H_2O][CH_4]} = \frac{0.15 \times 0.20^3}{0.035 \times 0.050} = 0.69$$

The reaction will proceed to the right (towards the products) because $Q < K_C$

Calculating Equilibrium Concentrations

When $Q_c \neq K_c$, we can calculate exactly how much additional reactant or product will form in order to reach equilibrium.

Consider this equilibrium:

$$PCl_5\,(g) \rightleftarrows PCl_3\,(g) + Cl_2\,(g) \qquad K_c = 0.030$$

A system initially containing only PCl_5 at a concentration of 0.100 *M* has a $Q_c = 0$, which is less than 0.030. What are the equilibrium concentrations of the three gases?

1. Express the equilibrium concentrations of all species in terms of the initial concentrations and a single unknown *x*, which represents the *change in concentration*.
2. Write the equilibrium constant expression in terms of the equilibrium concentrations. Knowing the value of the equilibrium constant, solve for *x*.
3. Having solved for *x*, calculate the equilibrium concentrations of all species.

Set up the problem in the following way:

$$PCl_5\,(g) \rightleftarrows PCl_3\,(g) + Cl_2\,(g) \qquad K_c = 0.030$$

Initial:	0.10	0	0
Change:	-x	+x	+x
Equilibrium:	0.10 – x	x	x

The equation to be solved is: $$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{x^2}{0.10 - x} = 0.030$$

Rearrange to give quadratic equation: $$x^2 + 0.030x - 0.0030 = 0$$

Solve with quadratic formula: $$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Reject negative root!

x= 0.042 *M*

The concentrations at equilibrium are:

PCl_5	PCl_3	Cl_2
0.10 M – 0.042 M = 0.058 M	0.042 M	0.042 M

Check for yourself that this gives K_c!

Sample Problem

The equilibrium constant for the decomposition of solid NH_4Cl is $K_p = 0.01$ atm at a certain high temperature. Calculate the equilibrium vapor pressures of ammonia gas and HCl gas starting from pure NH_4Cl (s).

Let x be the equilibrium NH_3 pressure. HCl pressure will have to be the same based on reaction stoichiometry

$NH_4Cl(s) \rightleftharpoons$	$NH_3(g)$ +	$HCl(g)$
Initial (P)	0.000	0.000
Change (P)	+x	+x
Equilibrium (P)	x	x

$$K_P = 0.01 = P_{NH_3} P_{HCl} = x^2 \quad \Longrightarrow \quad \begin{gathered} x^2 = 0.01 \\ x = 0.1 \end{gathered}$$

Therefore, $P_{NH3} = P_{HCl} = 0.1$ atm at equilibrium

Sample Problem

At 1280^0C the equilibrium constant (K_c) for the reaction

$$Br_2\,(g) \rightleftharpoons 2Br\,(g)$$

Is 1.1×10^{-3}. If the initial concentrations are $[Br_2] = 0.063$ *M* and $[Br] = 0.012$ *M*, calculate the concentrations of these species at equilibrium.

First calculate *Q*, compare with *K:* $Q = (0.012)^2/0.063 = 0.0023$

Q > *K*, reaction goes to reactants!

Let *x* be the change in concentration of Br_2

	$Br_2\,(g) \rightleftharpoons$	$2Br\,(g)$
Initial (*M*)	0.063	0.012
Change (*M*)	+x	-2x
Equilibrium (*M*)	0.063 + x	0.012 – 2x

$$K_c = \frac{[Br]^2}{[Br_2]} \qquad K_c = \frac{(0.012 - 2x)^2}{0.063 + x} = 1.1 \times 10^{-3}$$

Solve for *x*

$$\frac{(0.012 - 2x)^2}{0.063 + x} = 1.1 \times 10^{-3}$$

$$(0.012 - 2x)^2 = 0.0011x + 6.93 \times 10^{-5}$$

$$4x^2 - 0.048x + 0.000144 = 0.0011x + 6.93 \times 10^{-5}$$

$$\boxed{4x^2 - 0.0491x + 0.0000747 = 0}$$

$$ax^2 + bx + c = 0 \qquad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$x = 0.0105$, $x = 0.00178$

	$Br_2\ (g) \rightleftharpoons$	$2Br\ (g)$
Initial (*M*)	0.063	0.012
Change (*M*)	+x	-2x
Equilibrium (*M*)	0.063 + x	0.012 – 2x

x = 0.0105 gives nonsense; reject it

At equilibrium: [Br] = 0.012 – 2(0.00178) = 0.00844 M

$[Br_2]$ = 0.063 + 0.00178 = 0.0648 M

Making Approximations

- We don’t always need to solve the quadratic, or higher, equations that appear in these types of equilibrium problems.

- Suppose we had this equilibrium:

$$2\ SO_3\ (g) \rightleftarrows 2\ SO_2\ (g) + O_2\ (g) \qquad K_c = 1.6 \times 10^{-10}$$

Initial:	0.10	0	0
Change:	-2x	+2x	+x
Eq.:	0.10 – 2x	2x	x

The equation to solve would be: $$\frac{(2x)^2 x}{(0.10 - 2x)^2} = 1.6 \times 10^{-10}$$

This is a cubic equation! Truly frightening.

Making Approximations

$$\frac{(2x)^2 x}{(0.10 - 2x)^2} = 1.6 \times 10^{-10}$$

- Note that the equilibrium constant is very small. When equilibrium is reached, 2*x* will be very small compared to 0.100, so we can ignore it.

- The resulting approximate (but quite accurate) equation to solve is

$$\frac{(2x)^2 x}{(0.10)^2} = 1.6 \times 10^{-10}$$

Which gives: $4x^3 = 1.6 \times 10^{-12}$

$x = 7.4 \times 10^{-5}\ M$

2x is much smaller than 0.10, so 0.10 – 2x ≈ 0.10 and ***our approximation is valid!***

The concentrations at equilibrium are:

SO_3	SO_2	O_2
$0.10\ M - 2(7.4 \times 10^{-5})$	$2(7.4 \times 10^{-5})$	$7.4 \times 10^{-5}\ M$
$\approx 0.10\ M$	$= 1.5 \times 10^{-4}\ M$	

With these numbers, $K_c = 1.7 \times 10^{-10}$, very close to the real value, which again confirms that our approximation is okay.

The 5% Rule: if the change in concentration is less than 5% of the initial concentration, we can safely ignore it.