

Ch 14: Chemical Equilibrium

Reading: 601-632, (section 18.6, 803-807)

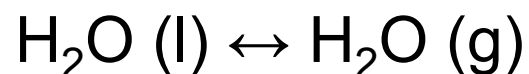
Learning Goals

What is equilibrium?

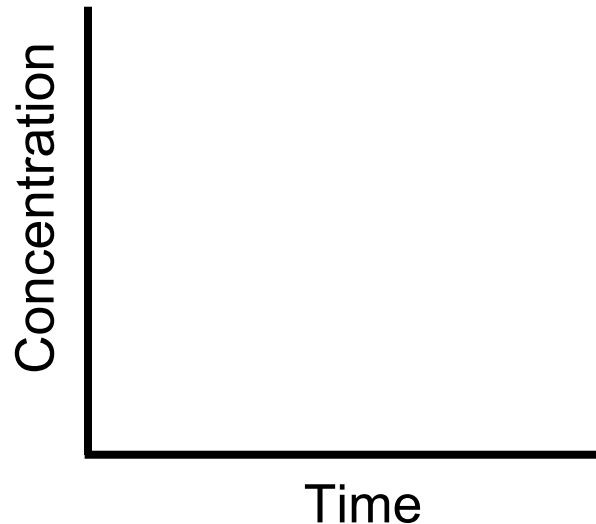
- balance between two or more processes
- NOT a static situation

The concept of equilibrium and the equilibrium constant

Most chemical reactions or physical processes are reversible



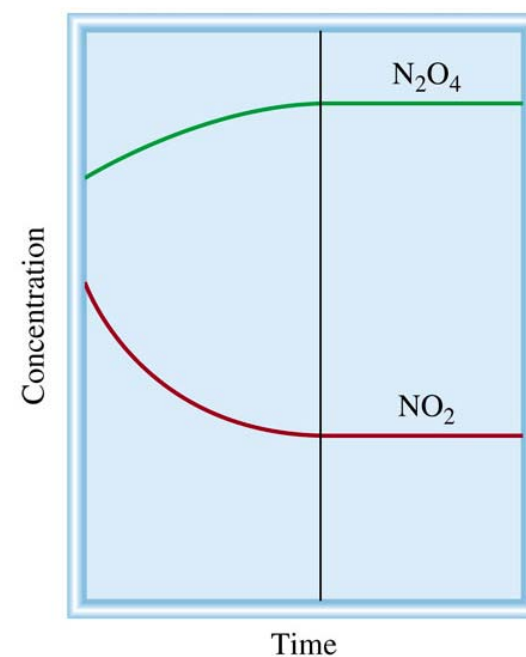
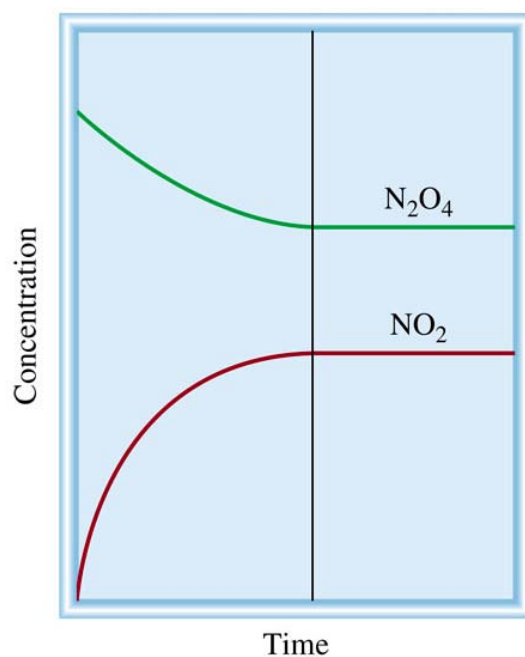
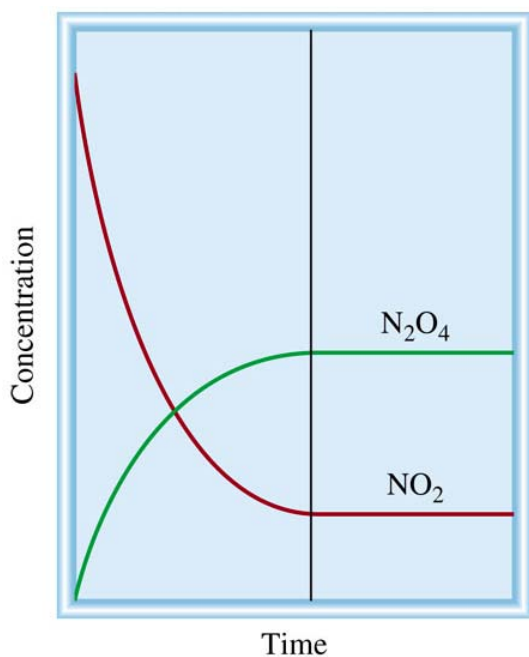
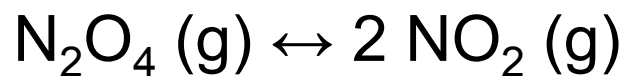
How do the concentrations change if we start with liquid water?



Equilibrium is reached after a certain point in time when the rate of the forward reaction equals the rate of the reverse reaction.

- the concentrations of the $\text{H}_2\text{O (l)}$ and $\text{H}_2\text{O (g)}$ remain constant
- this does NOT imply that their concentrations are equal
- equilibrium is a dynamic process

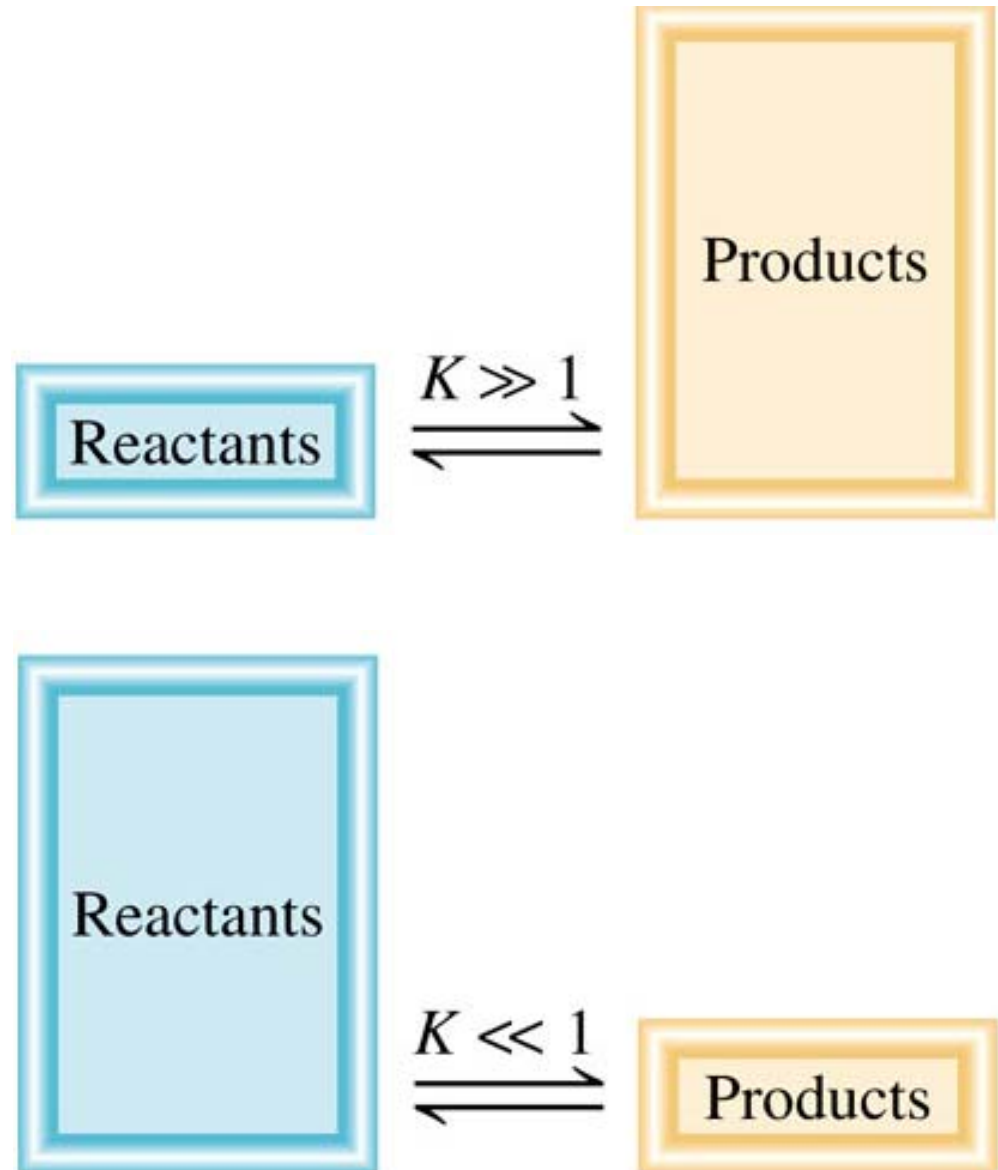
Chemical Equilibrium: The rates of the forward and reverse reactions are equal and the concentrations of the reactants and products are constant (but NOT equal).



Once a reaction or process reaches equilibrium, the reactant and product concentrations are constant.

We can use this fact to uncover details about the reaction or process.

What does the equilibrium constant (K) tell us?

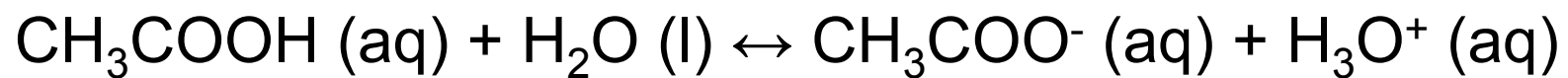


Writing equilibrium constant expressions for various types of reactions.

Homogeneous Equilibrium: all species in same phase

For reactions that are in the gaseous state, we can use partial pressure as a measure of concentration and write:

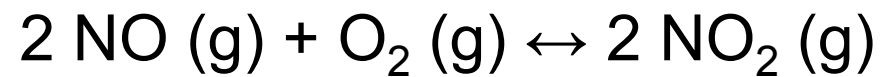
Write the equilibrium constant expression for the ionization of acetic acid:



K_c' , includes [solvent]

K_c , excludes [solvent]

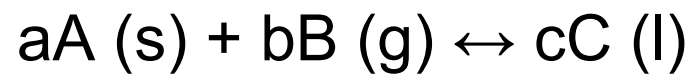
Write K_c and K_p expressions for the following reaction:



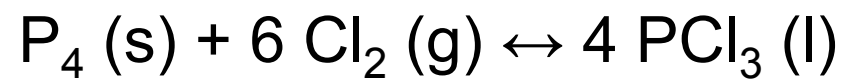
Heterogeneous Equilibria: species in different phases



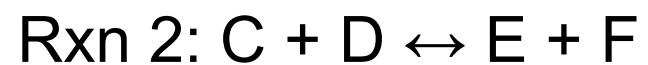
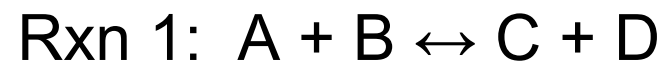
Expressions with pure liquids:



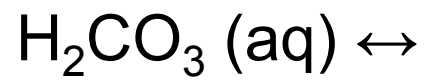
Write K_c and K_p for:



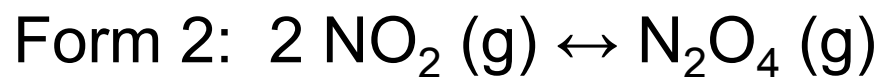
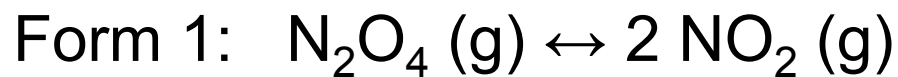
What if a reaction takes place in multiple steps?



Diprotic Acid Example:



Equilibrium constant equation depends on how you write and balance the chemical equation.

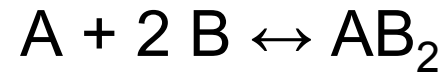


Guidelines for writing equilibrium constant expressions (pg 615)

- 1) liquid phase concentration expressed in mol/L, K_c
gas phase concentration expressed in atm, K_p
- 2) pure solids, pure liquids, and solvents do not appear in the equilibrium constant expressions
- 3) the constants themselves (K_c or K_p) are unitless
- 4) must specify BOTH the equilibrium constant (K_c or K_p) along with the balanced chemical equation
- 5) the overall equilibrium constant for multi-step reactions is the product of the constants for the individual steps

Connecting Kinetics to Equilibrium

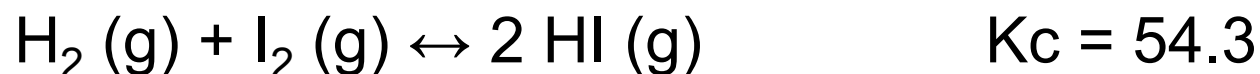
-consider this reversible elementary reaction



At equilibrium, how are the rates related?

Using the equilibrium constant to give us information about a reaction.

Predicting the direction of a reaction:



What happens if we place the following in container?

0.243 mol H_2

0.146 mol I_2

1.98 mol HI

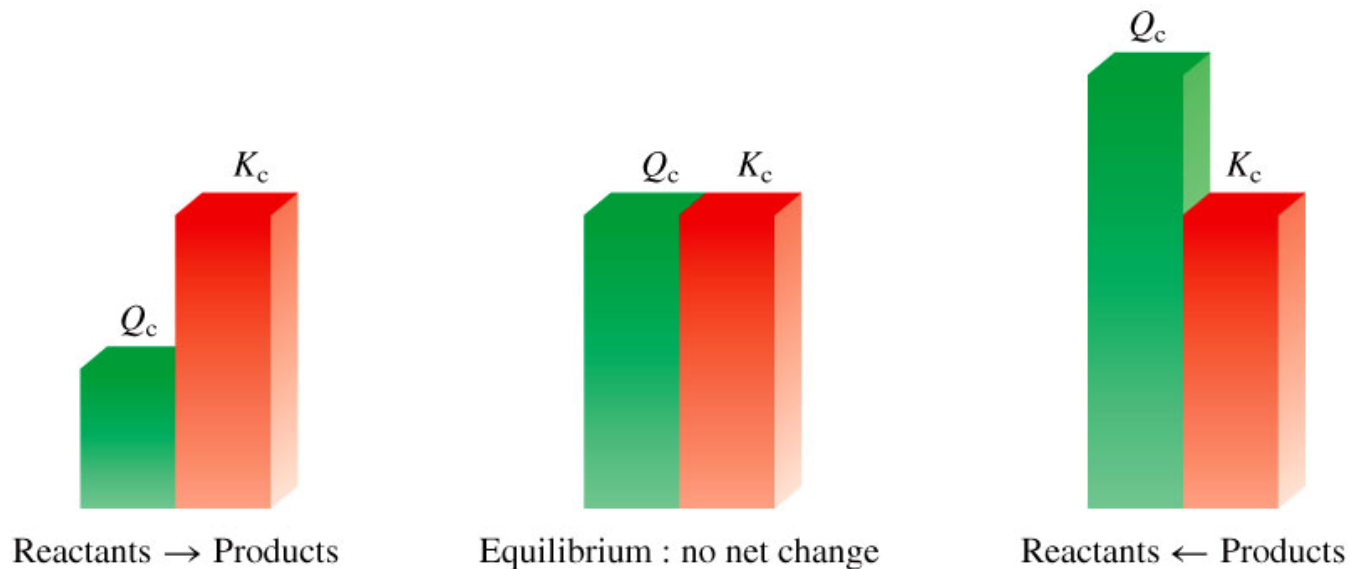
To figure out what happens, set up a ratio using the initial concentrations of the products and reactants.

Comparing the reaction quotient (Q_c) to the equilibrium constant (K_c), to determine reaction direction

$$Q_c > K_c$$

$$Q_c < K_c$$

$$Q_c = K_c$$



Example: Predict the direction of the following reaction which takes place in a 2.0 L flask at 35 °C.



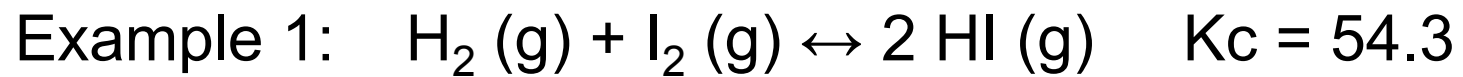
Initial amounts: NO = $(2.0 \times 10^{-2} \text{ mol})$, Cl₂ = $(8.3 \times 10^{-3} \text{ mol})$, NOCl = (6.8 mol)

When performing reactions, we generally start with known amounts (concentrations) of reactants.

How do we use this initial information to determine the concentrations of reactants and products at equilibrium?

ICE method

Write equilibrium constant expression



A mixture of 0.500 mol H_2 and 0.500 mol I_2 are placed in a 1.0 L container, calculate the equilibrium concentrations of all species.

Example 2: $\text{H}_2 (\text{g}) + \text{I}_2 (\text{g}) \leftrightarrow 2 \text{HI} (\text{g}) \quad K_c = 54.3$

A mixture of 0.00623 M H_2 and 0.00414 M I_2 are placed in a container, calculate the equilibrium concentrations of all species.

$$\frac{(2x)^2}{(6.23 \times 10^{-3} - x)(4.14 \times 10^{-3} - x)} = 54.3$$

First...Outside...Inside...Last

The quadratic equation: $ax^2 + bx + c = 0$

Solutions to a quadratic equation: $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

Ch 18.6: Free Energy and Equilibrium

In Ch 18 we learned how to use tabulated data to calculate the change in free energy (ΔG°) for reactants and products in their standard states (25 °C, 1 atm, most stable form).

We can now use the reaction quotient (Q_c) to help us determine a change in free energy for reactants and products that are NOT in their standard state.

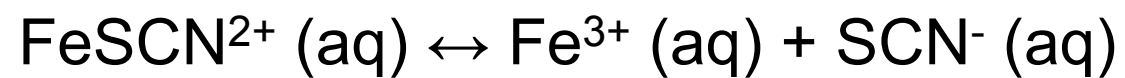
$$\Delta G = \Delta G^\circ + RT \ln Q_c$$

If our reaction is at equilibrium:

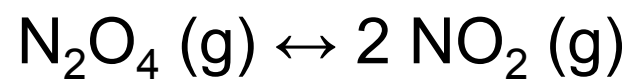
Once a reaction is at equilibrium, what happens if we make a change?

Le Chatlier's Principle: if an external stress is applied to a system at equilibrium, the system will adjust in such a way to partially off-set the stress and reach a new equilibrium position.

Changes in Concentration:



Changes in Volume or Pressure:



Changes in Temperature: When changes in concentration, pressure, or volume are made, the equilibrium position shifts.

However, the value of the equilibrium constant (K_c) does not change.

A change in temperature does change the equilibrium constant (K_c) value.

