

# Equilibrium

---

## 7.1 Introduction to Equilibrium

When equilibrium is reached, no observable changes occur in the system. Reactants and products are simultaneously present, and the concentration or partial pressures of all species remain constant. The equilibrium state is dynamic, the forward and reverse processes continue to occur at equal rates, resulting in no net observable change.

Graphs of concentration, partial pressure, or rate of reaction versus time for simple chemical reactions can be used to understand the establishment of chemical equilibrium.

## 7.2 Direction of Reversible Reactions

If the rate of the forward reaction is greater than the reverse reaction, then there is a net conversion of reactants to products. If the rate of the reverse reaction is greater than that of the forward reaction, then there is a net conversion of products or reactants. An equilibrium state is reached when these rates are equal.

## 7.3 Reaction Quotient and Equilibrium Constant

The reaction quotient  $Q_c$  describes the relative concentrations of reaction species at any time. For gas phase reactions, the reactant quotient may instead be written in terms of pressures as  $Q_p$ . The reaction quotient tends towards the equilibrium constant such that at equilibrium,  $K_c = Q_c$  and  $K_p = Q_p$ . As examples, for the reaction  $aA + bB \rightleftharpoons cC + dD$  the equilibrium expression for  $(K_c, Q_c)$  is

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

and that for  $(K_p, Q_p)$  is

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

*Will not be assessed on the conversion between  $K_c$  and  $K_p$ .*

*Will not be assessed on equilibrium calculations on systems where a dissolved species is in equilibrium with that species in the gas phase.*

The reaction quotient does not include substances whose concentrations (or partial pressures) are independent of the amount.

*Solids and pure liquids are not included in the reaction quotient.*

## 7.4 Calculating the Equilibrium Constant

Equilibrium constants can be determined from experimental measurements from the concentrations or partial pressures of the reactants and products at equilibrium. Substitute your given values in order to find  $K$ .

## 7.5 Magnitude of the Equilibrium Constant

Products are directly proportional to  $K$ . This means that if products are favored,  $K$  will be larger. As  $K$  approaches  $\infty$ , the reaction will proceed essentially to completion in the forward direction.

Reactants are inversely proportional to  $K$ , meaning that if reactants are favored  $K$  will be smaller. As  $K$  approaches  $\frac{1}{\infty}$ , the reaction barely proceeds at all in the forward direction.

## 7.6 Properties of the Equilibrium Constant

When a reaction is reversed,  $K$  is inverted.

$$K_{forward} = \frac{1}{K_{reverse}}$$

When the stoichiometric coefficients of a reaction are multiplied by a factor  $c$ ,  $K$  is raised to the power  $c$ .

$$\begin{array}{l} A \rightarrow B \\ K_1 = \frac{[B]}{[A]} \end{array}$$

$$\begin{array}{l} xA \rightarrow xB \\ K_2 = \frac{[B]^x}{[A]^x} \end{array}$$

When reactions are added together, the  $K$  of the resulting overall reaction is the product of the  $K$ 's for the reactions that were summed.

$$K_{overall} = K_1 \times K_2 \times K_3 \dots$$

Since the expression for  $K$  and  $Q$  have identical mathematical forms, all valid algebraic manipulations of  $K$  also apply to  $Q$ .

## 7.7 Calculating Equilibrium Concentrations

If  $K = Q$ , the reaction is at equilibrium.

If  $K < Q$ , the reverse reaction is favored.

If  $K > Q$ , the forward reaction is favored.

**|** *If one of the reactants/products is 0, the reaction goes towards that direction.*

## Small x Approximation

### Small $K_c$

- When reaction is strongly reactant forward ( $K \leq 1 \times 10^{-4}$ )
- Can assume that reactants do not change that much

### Large $K_c$

- When reaction is strongly product forward ( $K \geq 1 \times 10^4$ )
- Assume reaction goes 100% to products
- Make ICE table for a reverse reaction

## 7.8 Representations of Equilibrium

Particulate representations can be used to describe the relative numbers of reactant and product particles present prior to and at equilibrium, and the value of the equilibrium constant.

## 7.9 Introduction to Le Châtelier's Principle

Le Châtelier's principle can be used to predict the response of a system to stress such as addition or removal of a chemical species., change in temperature, change in volume/pressure of a gas-phase system, or dilution of a reaction system.

Le Châtelier's principle can be used to predict the effect that a stress will have on experimentally measurable properties such as pH, temperature, and color of a solution.

### Adding a Reactant or Product

Reaction shifts in the opposite direction of the addition.

### Subtracting a Reactant or Product

Reaction shifts in direction of the subtraction.

### Increase Volume/Decrease Pressure

Reaction shifts in direction with the most moles of gas.

### Decrease volume/Increase Pressure

Reaction shifts in direction with the least moles of gas.

### Concentration

Reaction will shift to side with the least number of aqueous species.

### Dilution

Reaction will shift to side with the greatest number of aqueous species.

### Adding Heat

Reaction favors the endothermic direction.  $K$  is changed. For endothermic reactions,  $K_{new} > K_{old}$ , and for exothermic reactions,  $K_{new} < K_{old}$ .

## Removing Heat

Reaction favors the exothermic direction.  $K$  is changed.

## 7.10 Reaction Quotient and Le Châtelier's Principle

A disturbance to a system at equilibrium causes  $Q$  to differ from  $K$ , thereby taking the system out of equilibrium. The system responds to bringing  $Q$  back into agreement with  $K$ , thereby establishing a new equilibrium state.

Some stresses, such as changes in concentration, cause a change in  $Q$  only. A change in temperature causes a change in  $K$ . In either case, the concentrations or partial pressures of species redistribute to bring  $Q$  and  $K$  back into equality.

If products increase or reactants decrease,  $Q > K$ . There is too much product relative to reactant, and the reaction will shift to consume product and form reactant.

If products decrease or reactants increase,  $Q < K$ . There is not enough product relative to reactant, and the reaction will shift left to form product and consume reactant.

## 7.11 Introduction to Solubility Equilibria

Solubility ( $S$ ): amount of a salt that will dissolve to form a saturated solution at a given temperature

Note: sodium salts are assumed to be 100% soluble

The dissolution of a salt is a reversible process whose extent can be described by  $K_{sp}$ , the solubility-product constant. The solubility of a substance can be calculated from the  $K_{sp}$  for the dissolution process. This relationship can also be used to predict the relative solubility of different substances. The solubility rules can be quantitatively related to  $K_{sp}$ , in which  $K_{sp}$  values  $> 1$  correspond to soluble salts.

ION RATIO	$K_{sp}$ IN TERMS OF MOLAR SOLUBILITY “ $S$ ”
1:1	$K_{sp} = S \times S = S^2$
1:2	$K_{sp} = S \times (2S)^2 = 4S^3$
1:3	$K_{sp} = S \times (3S)^3 = 27S^4$
2:3	$K_{sp} = (2S)^2 \times (3S)^3 = 108S^5$

## Will a Precipitate Form?

If  $Q_{sp} < K_{sp}$ , there is not enough ions (solutions unsaturated) and no precipitate forms.

If  $Q_{sp} > K_{sp}$ , there are too many ions and the reaction shifts to form precipitate.

## Comparing Solubility

It is best compare solubility (S), not  $K_{sp}$  values. You can only compare  $K_{sp}$  values if the salts contain the same number of ions.

## 7.12 Common-Ion Effect

The solubility of a salt is reduced when it is dissolved in a solution that already contains one of the ions present in the salt. The impact of this “common-ion effect” on solubility can be understood qualitatively using Le Châtelier’s principle or called from the  $K_{sp}$  for the dissolution process.

When solving using an ICE table, you can neglect the  $x$  that is subtracted from the initial concentration.

## 7.13 pH and Solubility

The solubility of a salt is pH sensitive when one of the constituent ions is a weak acid or base. These effects can be understood qualitatively using Le Châtelier’s principle.

*Will not be assessed on computations of solubility of a function of pH.*

## 7.14 Free Energy of Dissolution

Entropy is a measure of the dispersal of energy and matter. As the number of attractive forces decreases, molecules tend to separate, and entropy increases. An increase in entropy means there are more ways to arrange a system (more microstates).

$+\Delta S^\circ$  is favorable.  $-\Delta S^\circ$  is unfavorable.

The free energy change ( $\Delta G^\circ$ ) for a dissolution of a substance reflects a number of factors:

- The breaking of the intermolecular interactions that hold the solid together
- The reorganization of the solvent around the dissolved species

- The interaction of the dissolved species with the solvent

It is possible to estimate the sign and relative magnitude of the enthalpic and entropic contributions to each of these factors. However, making predictions for the total change in free energy of dissolution can be challenging due to the cancellations among the free energies associated with the three factors cited.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

## Summary

Free energy combines both enthalpy and entropy.

- $-\Delta H^\circ_{dissolution}$  is favorable
- $+\Delta S^\circ_{dissolution}$  is favorable
- If  $\Delta G^\circ_{dissolution}$  is positive, the salt will be slightly soluble and is thermodynamically unfavorable
- If  $\Delta G^\circ_{dissolution}$  is negative, the salt will be soluble and is thermodynamically favorable