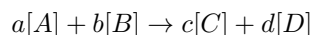


1 Equilibrium

Last time when we discussed reaction rates, we focused on the rate at which the *forward* reaction progresses—the rate at which reactants become products. Of course, reactions can progress in both the forward and reverse direction, and it is frequently thermodynamically favorable for this to happen. A reaction reaches a dynamic equilibrium when both the forward and reverse reaction are proceeding at the same rate.

The *equilibrium constant*, K_{eq} , is a ratio between the reverse reaction and the forward reaction in equilibrium. For a reaction



the equilibrium constant is

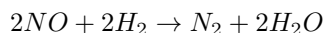
$$K_{eq} = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (\text{use when system is in equilibrium})$$

Each reaction has an equilibrium constant, and here, the superscripts are the stoichiometric coefficients (unlike the rate constant!). When the system is not in equilibrium, such as when the system is perturbed or the reactants are first mixed, the ratio of the rate constants is usually represented by a Q .

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (\text{use when system is not in equilibrium})$$

By comparing Q and K_{eq} , the progress of the reaction can be determined. The reaction has reached equilibrium when $Q=K_{eq}$. If $Q < K_{eq}$, the reaction proceeds to produce more products. If $Q > K_{eq}$, the reaction proceeds to produce more reactants.

Example: Write an expression for the equilibrium constant for the following reaction:



We can read off the expression for the equilibrium constant from the balanced equation.

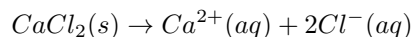
$$K_{eq} = \frac{[N_2][H_2O]^2}{[NO]^2[H_2]^2}$$

2 Solubility product

The *solubility product* is the equilibrium constant for the dissolution of a solid in a solution. The solid that is dissolving is called the *solute*, and the liquid that is doing the dissolving is called the *solvent*. For a solubility product, the solid isn't included: you can think of the concentration of the solid as being constant throughout the reaction.

Example: Find the solubility product of calcium chloride dissolving in water.

The equation governing the dissolution of calcium chloride is just the splitting of the compound into constituent ions:



To write the solubility product, we will ignore the solid part and focus only on the ions in solution, noted (aq) for aqueous. Therefore, the solubility product can be expressed as

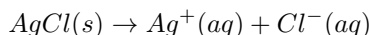
$$K_{sp} = [Ca^{2+}][Cl^-]^2$$

3 Common ion effect

The presence of additional ions in solution can have an impact on the solubility of a solid. In particular, if two solids that share an ion are both dissolved in solution, the equilibrium solubility shifts. The solubility of a salt is usually lower in the presence of another soluble salt which shares a common ion.

Example: What happens if we add silver chloride to an 0.2 M solution of calcium chloride? The solubility product if silver chloride is 1.77×10^{-10} .

First, we need to write a balanced equation for the dissolution of AgCl:



Correspondingly, the expression for the solubility product is

$$K_{sp} = [Ag^+][Cl^-]$$

We want to solve for the concentration of AgCl in solution which already contains calcium ions: one handy tool for this process is an ICE table, which stands for initial, change, equilibrium. When setting up an ICE table, we consider the species that is actively dissolving, not the species that already exists in solution.

The initial concentration of ions in solution is determined by the calcium chloride solution: we know it's an 0.2M solution. Let's call the amount of AgCl that dissolves x . From our balanced equation above, we know that there are the same number of moles of Ag and Cl ions in solution. We can set up the ICE table for AgCl as follows:

	[AgCl] _s	[Ag ⁺](aq)	[Cl ⁻](aq)
Initial	solid	0 M	0.2 M
Change	-	+ x M	+ x M
Final	-	x M	0.2 + x M

At every point as the reaction is proceeding, the equation governing the solubility product must be satisfied. Therefore we can solve for the final concentration of AgCl in solution as follows:

$$K_{sp} = [Ag^+][Cl^-] = x(0.2 + x) = 1.77 \times 10^{-10}$$

$$x^2 + 0.2x - 1.77 \times 10^{-10} = 0$$

Here, we can either directly solve the quadratic equation and keep only the physical solutions (positive concentration), or we can linearize and solve (since x is small). Either way, we come up with

$$x = 8.85 \times 10^{-10} M$$

Therefore, the concentration of of AgCl that will dissolve in 0.2 M CaCl₂ is 8.85×10^{-10} M.

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