

Appendix 11: Chemistry related issues

A11.1. The mass action law

The term Mass Action law refers to the equilibrium condition for chemical reactions. It states that the product of the concentrations of the reacting molecules or ions divided by the product of the concentrations of the reaction products equals a constant. For a reaction of the form:



where A, B and C are the molecules or ions and a , b and c are the integers needed to match the stoichiometry requirement. The equilibrium condition is then given by:

$$[A]^a + [B]^b = k(T)[C]^c \quad (\text{A11.1.2})$$

where the square brackets denote the concentrations of each molecule or ion.

This equation simply states that the probability of a reaction taking place is proportional to the probability that each of the reacting elements are available which in turn is proportional to the concentration. In the case where more than one molecule of the same type is needed the concentration of that molecule is multiplied with itself as many times as this molecule is needed in the reaction.

Similarly one calculates the probability that a reaction takes place in the reverse direction. In equilibrium the ratio of both probabilities is a constant, named $k(T)$ where the temperature dependence is added explicitly to indicate that this constant depends (rather strongly) on temperature.

A11.2. Example: dissociation of water

Applying the mass action law to the dissociation of water as described by the following chemical reaction:



one obtains:

$$[H^+] + [OH^-] = k_{H_2O}[H_2O] \quad (\text{A11.2.2})$$

Since the concentration of water is almost constant as the concentration of the ions is much smaller than the concentration of water molecules, this equation reduces at room temperature to:

$$[\text{H}^+][\text{OH}^-] = 10^{-14} \text{ (moles/liter)}^2 \quad (\text{A11.2.3})$$

A11.3. pH of aqueous solutions

The pH of an aqueous solution is given by the logarithm of the hydrogen ion concentration in units of moles/liter.

$$\text{pH} = -\log([\text{H}^+]) \quad (\text{A11.3.1})$$

To apply this equation to the dissociation of pure water one first has to find the concentration of the hydrogen ions. Since a water molecule dissociates into one hydroxyl ion and one hydrogen ion the hydroxyl concentration equals the hydrogen concentration so that at room temperature both equal 10^{-7} moles/liter or $6.0 \times 10^{13} \text{ cm}^{-3}$. One mole/liter contains 6.022×10^{23} atoms/liter, which corresponds to a density of $6.0 \times 10^{20} \text{ cm}^{-3}$. The pH of water at room temperature therefore equals 7.

A11.4. Resistivity of pure water

The conductivity of pure water is due to the motion of the hydroxyl and hydrogen ions, while the neutral water molecules do not contribute. At room temperature (25°C) the conductivity is $1/(18.3 \text{ M}\Omega\text{cm})$. Assuming that the hydrogen ions have a much higher mobility (due to their smaller size) one finds their mobility to be $5.7 \times 10^{-3} \text{ cm}^2/\text{V}\cdot\text{s}$.

A11.5. Analogy between semiconductors and aqueous solution

Based on the review above one finds that electrons and holes in semiconductors have a lot in common with hydroxyl and hydrogen ions in aqueous solutions: just like electron-hole pairs are generated in intrinsic semiconductors, hydroxyl and hydrogen ions are created in equal quantities in pure water. Adding a base increases the hydroxyl concentration which then forces the hydrogen concentration to go down to satisfy the equilibrium condition. The pH increases logarithmically with the hydroxyl density. This is analogous to adding donors to an intrinsic semiconductor, which adds electrons and reduces the hole density. The Fermi energy increases with the logarithm of the electron density. Adding an acid to an aqueous solution is analogous to adding acceptors to a semiconductor. This explains why the term mass-action law is used to describe the relation between the electron and hole densities in thermal equilibrium.