

## Mass and Charge Balances

Sometimes when performing a calculation concerning a process at chemical equilibrium there are no simplifying assumptions that can be made. If the system is a relatively simple one, like the dissolution of a weak acid or base in water, the problem can be answered by solving a quadratic formula. At other times, the problem can be considerably more complex with many more species found in the solution. In such an instance the problem usually must be answered by writing and solving a set of simultaneous equations. To determine the number of equations needed, one must first determine the number of unknowns in the solution. As an example, consider the first problem that we solved in this course, a solution of ammonia in water. It turns out that in this case, there are four unknowns in the solution.



Did we use four equations to solve this? We used the  $K_b$  for ammonia and the  $K_w$  for water (remember, using the  $K_b$ , we ended up calculating the pOH, which we then converted to pH using  $K_w$ ). A third equation we used (probably without you realizing it) is what is known as a **mass balance**. In this case, if we were told that the initial concentration of ammonia was 0.10 M, we wrote an expression for the final concentration as  $(0.10 - x)$ . Another way of saying this is:

$$[\text{NH}_3]_{\text{Final}} + [\text{NH}_4^+]_{\text{Final}} = [\text{NH}_3]_{\text{Initial}} = 0.10 \text{ M.} \quad (5)$$

Before going on, convince yourself that the equation above is correct.

The fourth equation we used to solve the problem was to say that the concentration of ammonium ion in the final solution equaled the concentration of hydroxide ion (remember, we assumed that the initial amount of hydroxide ion was small compared to what was produced by the reaction of the ammonia).

$$[\text{NH}_4^+]_{\text{Final}} = [\text{OH}^-]_{\text{Final}} \quad (6)$$

This equation is known as a **charge balance**. It is important to realize that all solutions must be electrically neutral; that is, for every substance of positive charge there must be an equivalent amount of negative charge to balance it out. If something dissolves in water and produces positive ions, then there must be negative ions around to balance them out.

It is also worth pointing out that the equation shown above is not really the entire charge balance for that solution, (we ignored some original hydroxide and hydronium ion in solution). The exact form would actually be:

$$[\text{NH}_4^+]_{\text{Final}} + [\text{H}_3\text{O}^+]_{\text{Final}} = [\text{OH}^-]_{\text{Final}} \quad (7)$$

When faced with a problem requiring a set of simultaneous equations, in addition to all of the relevant equilibrium constant expressions, the mass and charge balances are usually needed to come up with as many equations as there are unknowns.

Consider another example, that of dissolving sodium acetate in water to make up a 0.10 M solution. We can write two mass balance expressions.

$$[\text{Na}^+] = 0.10 \text{ M}$$

Remember that the sodium acetate will dissociate into its component ions. The sodium ion does not undergo any reaction with water, but acetate does to produce acetic acid. The concentration of acetic acid in the final solution will drop below 0.10 M, but the total of the two species must equal 0.10 M, the initial amount that was put into solution.

$$[\text{Acetic acid}] + [\text{acetate}] = 0.10 \text{ M}$$

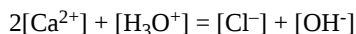
The charge balance must account for all positively charged (sodium and hydronium ions) and negatively charged (acetate and hydroxide ions) species in solution. We can only write one complete charge balance for a solution.

$$[\text{Na}^+] + [\text{H}_3\text{O}^+] = [\text{acetate}] + [\text{OH}^-]$$

Charge balances get interesting when one of the ions has a charge greater than one. If you consider calcium(II)chloride ( $\text{CaCl}_2$ ), note that two chloride ions result for each calcium ion.



The charge balance for a solution of calcium chloride in water is written as follows (assuming that neither calcium nor chloride ions undergo any reactions with water, hydronium, or hydroxide).



**You must convince yourself that the above equation is correct, especially that the concentration of calcium ion should be multiplied by two.** Many people are initially troubled that the (2+) ion gets multiplied by two, since that seems counter-intuitive. What you must realize is that the equation actually equates concentrations of species in solution. Leave out the hydronium and hydroxide ions from the equation, and notice again in the reaction written above, that for every one calcium ion there are two chloride ions produced. If you plug in a 1 for calcium in the charge balance equation, you will see that the concentration of chloride calculates to be 2. Once you appreciate that the coefficient is in the right place, you may also appreciate that this can be generalized. The concentration of an ion with a charge of (3-) will be multiplied by 3, the concentration of an ion with a charge of (4+) will be multiplied by 4, etc. Knowing how to write mass and charge balances correctly is a critical skill to have when solving equilibrium problems.

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