Some Fundamentals of Mineralogy and Geochemistry

Activity and activity coefficients

Activity coefficients $\gamma_i$ are related to the activity $a_i$ of an ion $i$ by the equation

$$ a_i = \gamma_i m_i $$

where $m_i$ is the concentration of ion $i$. The activity coefficient $\gamma_i$ represents the ratio of the activity of ion $i$ to the concentration of ion $i$, and it is used to correct for the effects of ion interaction and non-ideality of a solution on the activity of the ions.

The problem with reality is that we can't see the activity of individual ions, but we can determine the activity coefficient $\gamma_i$. For a given reaction, the activity coefficient $\gamma_i$ for an ion $i$ in a solution suggests that of all the individuals of an ion $i$ or $M^{z+}$ or $Y^{z-}$, some are involved in complexes and thus unavailable to participate in chemical reactions. Thus only some of the individuals of the ion $M^{z+}$ or $Y^{z-}$ are available to participate in chemical reactions.

For example, in the schematic sketch at right, there are twelve individuals of the blue ion $M$. Of those twelve, four are in complexes, and only eight are in the hydrated or aquo-ion condition that we will assume lets them be available for reaction. Thus, rather than using concentration to predict the ion's behavior in a reaction, we use the activity to better estimate the individuals actually available for reaction. This proportionality is

$$ \left( \frac{1}{m} \right) \left( \frac{1}{\gamma} \right) = \frac{1}{a} $$

where $a$ is the activity of the ion. Thus, rather than using concentration, we use the activity coefficient to predict the ion's behavior in a reaction.