

Activity and Activity Co-efficients

Chemical reactivity refers to the overall tendency of a species to react. It depends on a number of familiar factors such as concentration, temperature, pressure and a factor that is often omitted in introductory treatments, the concentration of other *non-reacting species* in the system. We will define the chemical reactivity as the *Activity* of a species, {A} or a . Any description of chemical reactivity must be based on a comparison to a species activity in some standard state, which can be arbitrarily assigned a value of unity (1.00...). If a species in a given system is less reactive than it is in this arbitrary system (set of conditions), then its *Activity* < 1.

The complete set of conditions describing the standard comparison system is called the standard state.

{std state} = {std conc} + {reference conditions}

for solutes, {std conc} = 1.0 mol/L

reference conditions include; std pressure of 1 atm
std temperature of 25°C
std composition of 'infinite dilution'

Activities are dimensionless because they are defined as ratios of actual reactivity to reactivity in a std state. Environmental conditions will always differ from reference conditions (i.e., 'infinite dilution').

The activity co-efficient (γ) can be defined as the ratio

$$\gamma = \frac{\text{reactivity per mole in a real system}}{\text{reactivity per mole in reference system}} = \frac{\frac{\{A\}_{\text{real}}}{[C]_{\text{real}}}}{\frac{\{A\}_{\text{reference}}}{[C]_{\text{reference}}}}$$

Since the *Activity* in the reference system is 1 and the concentration in the reference system is 1 M, we can see that the activity co-efficient is a unitless quantity that is numerically equal to $\{A\}_{\text{real}}/[C]_{\text{real}}$

In other words, $\{A\}_{\text{real}} = \gamma \times [C]_{\text{real}}$

Thus, activity co-efficients are a proportionality constant that convert molar concentrations (an analytical determined quantity) to chemical *Activity* (a thermodynamic quantity). The activity co-efficient for a given species may vary widely over a range of solution compositions. When the actual and the reference states (infinite dilution) are very close, then $\gamma \rightarrow 1$ (i.e., $\{A\} \sim [C]$). This is generally true for most species in freshwater. To the extent that the actual conditions differ from the reference state, $\{A\} \neq [C]$. This is generally the case for species in brines, seawater and many wastewaters.

To summarize, the chemical *Activity* of a substance incorporates factors related to the substances molar concentration, its' physical environment and the chemical composition of its surroundings into a single variable. It is a measure of the tendency of a species to participate in a reaction under a particular set of conditions. Clearly, there is more to the reactivity of a species than its molar concentration alone predicts.

Predicting activity co-efficients from solution composition

The activity co-efficient varies with:

- ionic strength of the solution (I)
- charge of the ion (z)
- size of the ion (a_o)
- temperature

The ionic strength of a solution is related to solution composition by the following expression:

$$I = 0.5 \sum c_i z_i^2$$

where c_i is the molar concentration of each ion and z_i is the ionic charge on each ion.

There are several approaches to predicting activity co-efficients summarized below;

1. For dilute solutions ($I < 0.005$ M), use the **Debye-Huckel equation:**

$$\log \gamma_{DH} = -A z^2 \sqrt{I}$$

or for somewhat more concentrated solutions ($I < 0.1$ M)

$$\log \gamma_{DH} = \frac{-A z^2 \sqrt{I}}{1 + B a_o \sqrt{I}}$$

where A and B are constants, z is the ionic charge and a_o is the hydrated ion radius. At 20°C, $A = 0.505$ and $B = 0.328 \times 10^8$

2. For more concentrated solutions ($I < 0.5$ M) use the **Davies equation:**

$$\log \gamma_{Davies} = -A z^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3 I \right)$$

3. More elaborate models allow for the prediction of activity co-efficients in more concentrated solutions such as seawater, $I > 0.1$ M. For example the **extended Debye-Huckel treatment, which requires the use of several ion specific parameters (a_o and b, see below) is given by:**

$$\log \gamma = \frac{-A z^2 \sqrt{I}}{1 + B a_o \sqrt{I}} + bI$$

a_o is the hydrated ion radius (see accompanying table)

b is a calculated value available for major ions only (see accompanying table)

Ion parameters for use in the extended Debye-Huckel equation

Ion	Hydrated Ion Radius $a_0 \times 10^{-8}$	b
Ca ²⁺	6	0.165
Mg ²⁺	8	0.20
Na ⁺	4	0.075
K ⁺	3	0.015
Al ³⁺	9	
Fe ³⁺	9	
H ⁺	9	
Mn ²⁺	6	
Fe ²⁺	6	
Li ⁺	6	
Sr ²⁺	5	
Ba ²⁺	5	
NH ₄ ⁺	3	
Cl ⁻	3	0.015
SO ₄ ²⁻	4	-0.04
HCO ₃ ⁻	4	0
CO ₃ ²⁻	5	0
S ²⁻	5	
PO ₄ ³⁻	4	
OH ⁻	3	
F ⁻	3	
Br ⁻	3	
NO ₃ ⁻	3	