Activity and Activity Coefficient

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What is activity?

- Activity is the result of the effects of interactions between ion or molecule and its surroundings.
- Since it is hard to define, it is usually measured with reference to an ideal state.

$$\lim_{\zeta \to \zeta^{\theta}} \frac{a_i}{g(\zeta)} = 1$$

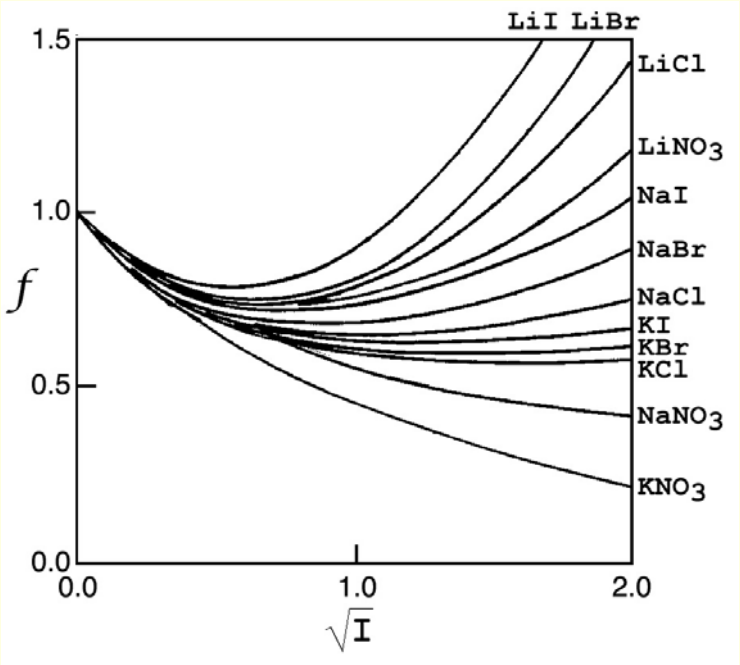
Activity Coefficient

- The activity coefficient measures how much an actual system deviates from a reference system (2).
- Mathematically, the activity coefficient is defined as the limit of the equation derived for activity and has no units.

$$\gamma_i = \frac{a_i}{g(\xi)}$$

Activity Coefficient

- According to the IUPAC, the activity coefficient can be calculated in terms of mole fractions for liquids and solid mixtures, or in terms of molalities for dilute solutions.

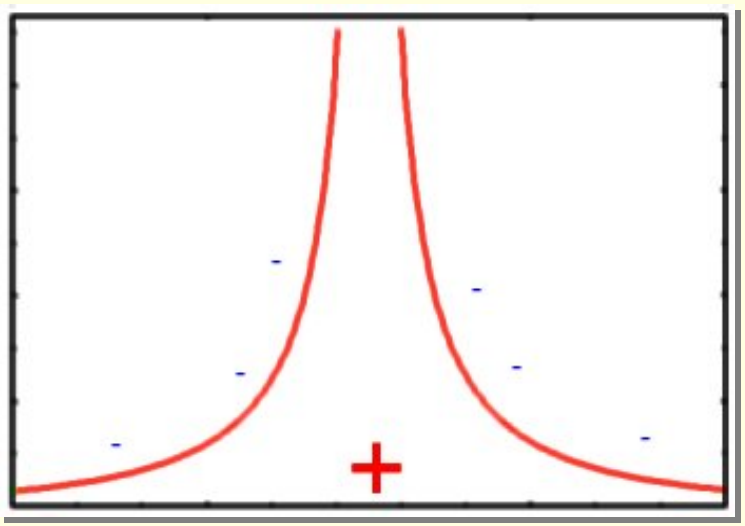


Experimental activity coefficients

Measurement of activity

- The activity of a species can be measured by determining its partial vapor pressure in equilibrium with a number of solutions of different strength.
- There are also electrochemical ways to determine the activity of a species.
- The mean activity coefficient can be measured using the Debye-Huckel theory, the Davies equation or the Pitzer equation.

The Debye-Hückel theory



The shielded potential around a solvated ion

- The Debye-Hückel theory is based on the assumption that in an electrolyte, the effects of the electrical potential on each ion are negligible.

The Debye-Hückel theory

- The ions in an electrolyte have a screening effect on the electric field from individual ions. The screening length is called the Debye length and varies as the inverse square root of the ionic strength.
- Since it is hard to actually calculate activity coefficients, the Debye-Hückel theory can be applied for very low concentrations and depends on the ionic strength.
- The mean ionic activity γ can thus be deduced.

The Davies Equation

- The Davies equation has been used extensively to calculate activity coefficients of electrolytes at fairly low ionic strengths.
- The Davies equation for the activity coefficient of an ion *i* of charge is at 25 degrees celsius is:

$$\log_{10}\gamma_i = -0.5102\, z_i^2 \left(\frac{\sqrt{I_m}}{1+\sqrt{I_m}} - 0.31 m \right)$$

The Pitzer and Brewer equation

$$\log_{10}\gamma_i = \frac{-z_i^2\, 0.5107\sqrt{I_m}}{1+\sqrt{I_m}} + \sum_j B(i,j)\, m_j$$

- The Pitzer and Brewer equation include the summation over *j* term which accounts for all anions for the case that *i* would be a cation.

Reference States

- Thermodynamic variables are always defined in terms of a reference state.
- Since the reference state is one which we can choose, it is often set as an ideal state.
- In the case of measuring activity of a dilute solution or a real gas (in that case, it is fugacity), we can set the activity coefficient to approach 1 as we approach the reference state

Activity and the Chemical Potential

- Since only relative chemical potentials can be measured, any ideal state can be defined as the standard state.
- The deviation of the chemical potential from the reference state can be described mathematically as

$$\mu_i = \mu_i^{\theta} - RT \ln a_i$$

References

- 1) IUPAC Activity coefficient. *http://www.iupac.org/goldbook/A00116.pdf* (accessed December/3, 2006).
- (2) Ulness, D. J. **2006**, *Lecture Notes*, 145-150.
- (3) Wilczek-Vera, G.; Vera, J. H. *Fluid Phase Equilibria* **2005**, *236*, 96-110.