Expressing Solute Concentrations

- Concentrations Expressed As an Equivalent Amount of a Different Species or Other Item
  - Often used to express concentrations of chemical composites
  - Species used for "equivalency" is usually logical, but sometimes obscure (based on a historical convention that is no longer relevant; e.g., hardness *as CaCO₃*)
  - Basis of the equivalency is usually implicit and therefore potentially ambiguous (10 pennies are equivalent to one dime in terms of purchasing power, but not in size, mass, etc.)

- Examples
  - Charge (one mole of Ca^{2+} is two equivalents of charge)
  - Acquisition/release of H^+ in acid/base reactions: $H_2CO_3 \leftrightarrow 2H^+ + CO_3^{2-}$; one mole H_2CO_3 is two "acid equivalents"

- 10 μg/L Bromoform ($CHBr_3$, MW 250)

$$\frac{10 \ \mu g/L \ CHBr_3}{1 \ \mu mol/250 \ \mu g \ CHBr_3} = 0.04 \frac{\mu mol}{L}$$

$$0.04 \frac{\mu mol \ CHBr_3}{L}\left(\frac{3 \ \mu mol \ X}{\mu mol \ CHBr_3}\right) = 0.12 \frac{\mu mol \ TOX}{L}$$

$$0.04 \frac{\mu mol \ CHBr_3}{L}\left(\frac{[3x79.9] \ \mu g \ Br}{\mu mol \ CHBr_3}\right) = 9.48 \frac{\mu g \ Br}{L}$$

$$0.12 \frac{\mu mol \ TOX}{L}\left(\frac{35.5 \ \mu g \ Cl}{\mu mol \ X}\right) = 4.26 \frac{\mu g \ TOX}{L} \ as \ Cl$$

Ionic Strength

- I or μ: A composite, calculated (not measurable) property of the solution (not of individual species)

$$I \equiv \frac{1}{2} \sum_{all \ ions} c_i z_i^2$$

  - Always calculated using c values in mol/L, but commonly reported without dimensions
  - Includes contributions from all ions, but not neutral species
  - Indicator of the ability of the solution to neutralize the electrical field surrounding an ion (by attraction of like-charged and repulsion of oppositely-charged ions)
  - High ionic strength reduces an ion's "sphere of influence" and shields it from interactions with the rest of solution

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Composite Parameters for Overall Solute Concentrations

- Conductivity, Specific Conductance (κ; microSiemens, μS)
  - Measurable indicator of overall ionic content of a solution
  - Includes contributions from all ions, weighted by their charge and mobility

- Total Dissolved Solids (TDS; mg/L)
  - Non-specific indicator of overall mineral content
  - Includes contributions from all solutes that do not easily volatilize (evaporate)

Conceptual Models for Chemical Reactivity

- Chemical species can undergo many potential changes that reduce their concentration. The (chemical) **activity** of a species is an indicator of the species' tendency to undergo change via a *chemical* process; *i.e.*, it quantifies the 'desire' of the species to undergo a chemical change

  - Directly related to chemical potential energy of the species: higher potential energy → higher activity → greater tendency to undergo change that reduces concentration

  - Includes components related to both concentration and environment: higher concentration always means greater activity; environment (T, P, other species in the system) can enhance or reduce activity

Quantifying Chemical Activity

- Goal: Define a scale of chemical activity that avoids the need to specify all details of concentration and environmental conditions

- Approach

  - Define a **standard state** in which the activity of a species is assigned a value of 1.0; the standard state must specify both a standard concentration and a standard environment

  - Compare tendency for the species to undergo a change that reduces its concentration in various systems to that in the standard state. Define activity based on these comparisons (i.e., one-half as likely to undergo change → activity equals 0.5)

  - Relate experimental observations of activities in various systems to concentration, quantifiable environmental parameters, and the energy needed to convert a system from the standard state to the system of interest

Chemical Activity: An Analogy

- Define a standard "consumption activity" (i.e., an activity of 1.0) based on the rate at which food is consumed by 100 people at a banquet with excess food available, and with each person eating at the rate that would apply if they were the only person in the room.

- Application

  - In a real banquet, we expect the rate of food consumption to be proportional to the number of people present, so the actual "concentration" of consumers can be different from the standard value (100)

  - When the "environmental" conditions change (e.g., time of day, ratio of genders present, physical arrangement of the food), the consumption activity changes, even if the consumer concentration remains constant.

  - Note that the consumer concentration is also part of the environment; e.g., increasing crowdedness probably decreases activity.

  - Note also that it is unlikely that the conditions in the standard state can ever be met exactly: if 100 people are present, they probably won't eat as though each was present alone. Nevertheless, the definition is unambiguous and therefore acceptable.

Defining the Standard State

- Common choices for the **concentration** in the standard state:

  - For **gaseous** species: The concentration that corresponds to a partial pressure of 1.0 atm for an ideal gas at a standard temperature (20° or 25°C)

$$c_{G,i}\big|_{std.state} = \frac{n_i}{V_G}\bigg|_{std.state} = \frac{P_i}{RT}\bigg|_{std.state} = \frac{1.0\ \text{atm}}{RT}$$

  - For **solutes** in aqueous solutions: A concentration of 1.0 mol/L

  - For **water** in aqueous solutions (or the bulk component of any liquid phase): The concentration of the component when present as a pure phase, conventionally in units of mole fraction ($x_i = 1.0$)

  - For components of **solids**: The concentration of the component in the solid phase, conventionally in units of mole fraction ($x_i = 1.0$)