Forms of analyte in liquid, gaseous and solid samples and equilibrium between them

Question

- What states of matter do you know?
- What sample types do you know?

Sample types

- Gaseous
- Liquid
- Solid
- Mixed
- What are the differences between gas and liquid?

Mixed samples

- Gas in liquid (oxygen in water)
- Gas in solid (hydrogen sulfide in sulfur)
- Liquid in solid (water in soil)
- Solid in liquid (particulates in water)
- Solid in gas (dust in air)

Forms of analytes

- Molecular
- Atomic
- Ionic (different oxidation state)
- Radical
- Coordination complex

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Key forms of analytes

Liquid sample

Molecular
Ionic
Associate
Complex

Solid sample

Molecular (free in L/G)
Molecular (bound)
Ionic (free in liquid)
Ionic (bound)
Solid crystal

Gaseous sample

Molecular
Radical
Ionic

Importance

- Analyst should understand what is in a sample
- Without understanding, results can be confusing
- Different forms of analyte have different properties

Examples

- Molecular forms of analyte are more volatile
- Ionic forms have greater water solubility
- Cr (VI) is much more toxic than Cr (III)
- Free forms of chemicals in soil are more toxic than bound
- Radicals are more reactive than molecules

Types of analytical methods

- Total concentration of element (all forms)
- Total concentration of a molecule (or corresponding ion)
- Concentration of molecule or ion
- Free (or water soluble) form of molecule/ion
- Concentration of a bound form (e.g., by particles)

Examples

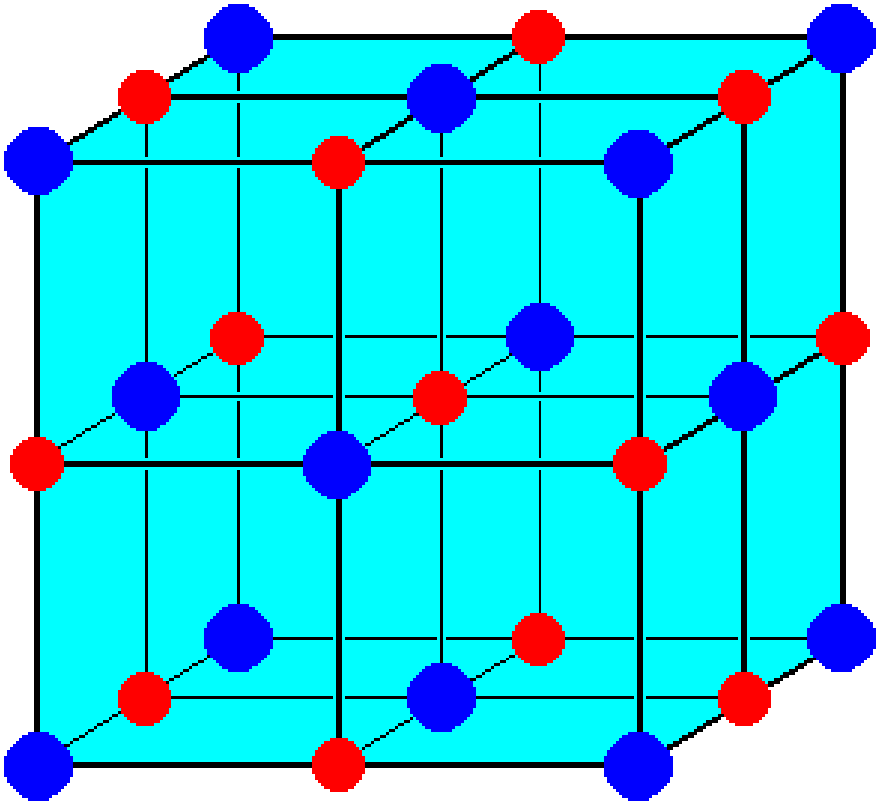
- Water soluble forms of heavy metals in soil
- Total concentration of sorbic acid (or sorbates) in juices
- Concentration of PAHs bound to solid particles
- Concentrations of chloride ions in water
- Concentration of Cr(VI) in drinking water

Question

- What will we have in a 1% water solution of NaCl?

- **Answer:** ions of Na^+ and Cl^-
- NaCl is not present
- Molecules of NaCl are also not present in crystal NaCl

NaCl crystal structure



Cl^-

Na^+

NaCl

Equilibrium

$$A + B \leftrightarrow C + D$$

- How to shift equilibrium to the left?

- Almost no reaction has 100% degree
- Everything in the environment is at the equilibrium

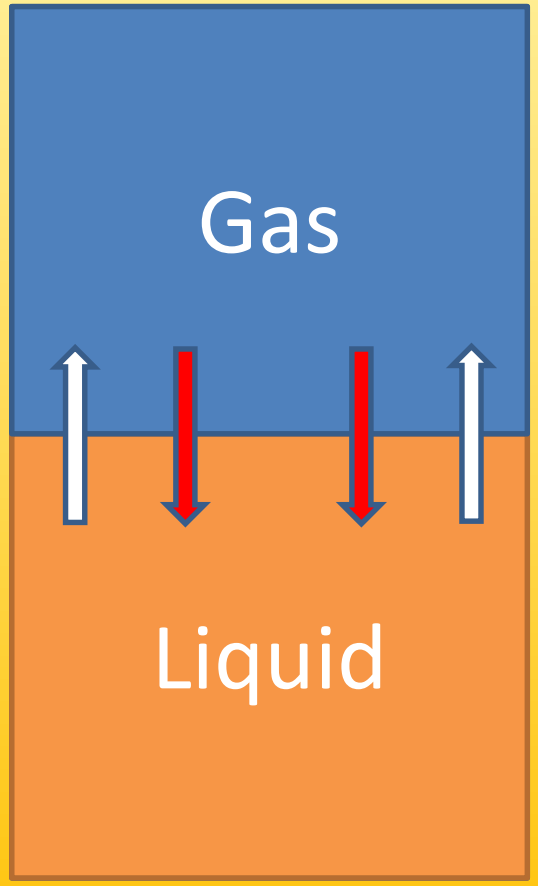
How do you understand equilibrium?

- Concentrations of reagents do not change
- Rates of forward and reverse reactions are equal (=)

Life example

Capital does not change with time (at equilibrium)

Heterogeneous equilibrium



Equilibrium

Rate of evaporation
=
Rate of condensation

Acid-base equilibrium

For acids:

$$HA \leftrightarrow H^+ + A^-$$

For bases:

$$BOH \leftrightarrow B^+ + OH^-$$

Acids and bases

$$HA \leftrightarrow H^+ + A^-$$

$$A + OH^- \leftrightarrow AOH^-$$

$$BOH \leftrightarrow B^+ + OH^-$$

$$B + H_2O \leftrightarrow BH^+ + OH^-$$

Equilibrium constant (K)

- General form:

$$K = k\frac{[A]_1}{[A]_2}$$

- $[A]_1$ – equilibrium analyte concentration in form 1
- $[A]_2$ – equilibrium analyte concentration in form 2
- k – coefficient depending on concentrations of other compounds

Chemical equilibrium constant

$$K = \frac{Concentrations\ of\ products}{Concentrations\ of\ reagents}$$

Acidity constant

- For the reaction

$$HAc \leftrightarrow H^+ + Ac^-$$

$$K_a = \frac{[Ac^-]\,[H^+]}{[HAc]}$$

Basicity constant

- For the reaction:

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$$

$$K_b = \frac{[NH_4^+]\,[OH^-]}{[NH_3]}$$

- https://www.youtube.com/watch?v=l5fk7HPmo5g

Question

- What will be present in a solution of acetic acid in water.

$$HAc \leftrightarrow H^+ + Ac^-$$

$$HAc + H_2O \leftrightarrow H_3O^+ + Ac^-$$

- What will be concentrations of HAc and Ac^- if 0.15 g of pure (100%) HAc was dissolved in 250 mL of water (C = 0.1 mol/L)

Solution

$$\mathrm{K_a} = \frac{[Ac^-]\,[H^+]}{[HAc]} = 1.75 \times 10^{-5}$$

- Concentrations of all species (Ac^-, H^+, HAc) are unknown
- We only know initial concentration (C_0) of HAc, which should decrease due to a partial dissociation
- $[Ac^-] = [H^+]$ because dissociation of 1 HAc molecule leads to a formation of one Ac^- ion and one H^+ ion

Solution (continued)

- If one Ac^- ion was formed, number of HAc molecules decreased by one
- $C_0 = [HAc] + [Ac^-]$
- Let's express $[Ac^-]$ as x

$$K_a = \frac{x \times x}{C_0 - x} = 1.75 \times 10^{-5}$$

$$x^2 + 1.75 \cdot 10^{-5}\, x - 1.75 \cdot 10^{-6} = 0$$

Solution (continued)

- $D = b^2 - 4ac = 3.06 \cdot 10^{-10} + 4 \cdot 1.75 \cdot 10^{-6} = 7 \cdot 10^{-6}$

$$x_1 = \frac{-b + \sqrt{D}}{2a} = \frac{1.75 \times 10^{-5} + 0.002646}{2} = 0.00133$$

- $[Ac^-] = 0.00133$ mol/L
- $[H^+] = 0.00133$ mol/L
- [HAc] = 0.1-0.00133 = 0.0987 mol/L

Question

- What will be present in a solution of sodium acetate in water.

$$Na^+ + Ac^- + H_2O \leftrightarrow Na^+ + HAc + OH^-$$

$$Ac^- + H_2O \leftrightarrow HAc + OH^-$$

- What will be concentrations of the ions?

Task

- Water sample (V=100 mL) containing benzene at C = 10 µg/L was extracted by 10 mL hexane.

- What are equilibrium concentrations of benzene in water and hexane if distribution constant between hexane and water is 100?