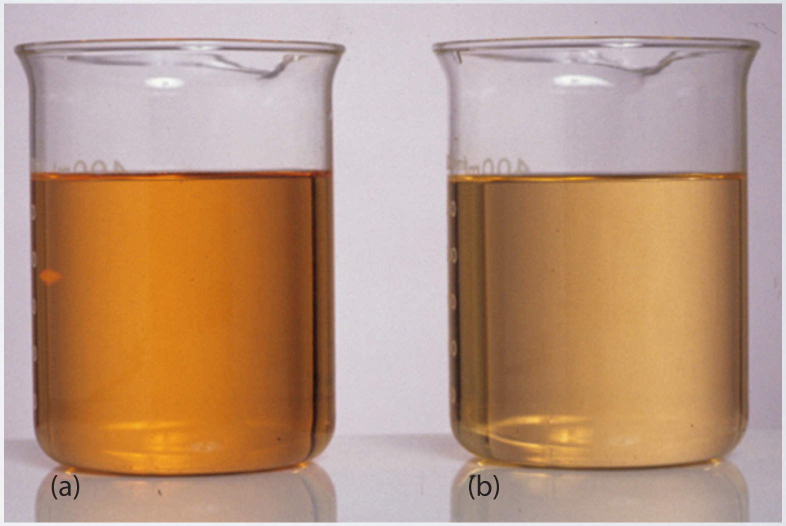
ACTIVITY & ACTIVITY COEFFICIENTS

CHEM 251 SDSU

SHIFTING EQUILIBRIA

$$Fe^{3+}_{(aq)} + SCN^{-}_{(aq)} \rightleftharpoons Fe(SCN)^{2+}_{(aq)}$$

- The metal-ligand complex $Fe(SCN)^{2+}$ is soluble in water and has an orange color.
- Higher concentrations of $Fe(SCN)^{2+}$ produce darker solutions.
- The addition of an inert salt (e.g. KNO_3) is able to reduce the color of the solution without reacting with any of the other ions in solution.



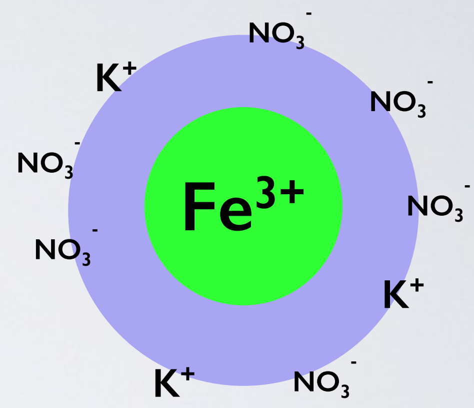
(a) Contains 1 mM $FeCl_3$ and 1.5 mM KSCN.
(b) The same as (a) but with 10 g of KNO_3.

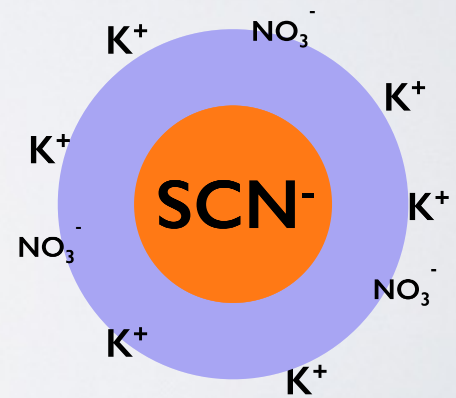
ION ATMOSPHERE

- Though the KNO_3 does not directly interact with either the Fe^{3+}, SCN^-, or $Fe(SCN)^{2+}$ ions, the K^+ and $NO3^-$ do alter the environment around those ions.

- Every ion in solution has an "atmosphere" of other ions surrounding it.

- The surrounding ions impact how the central ion can interact with other ions in solution.

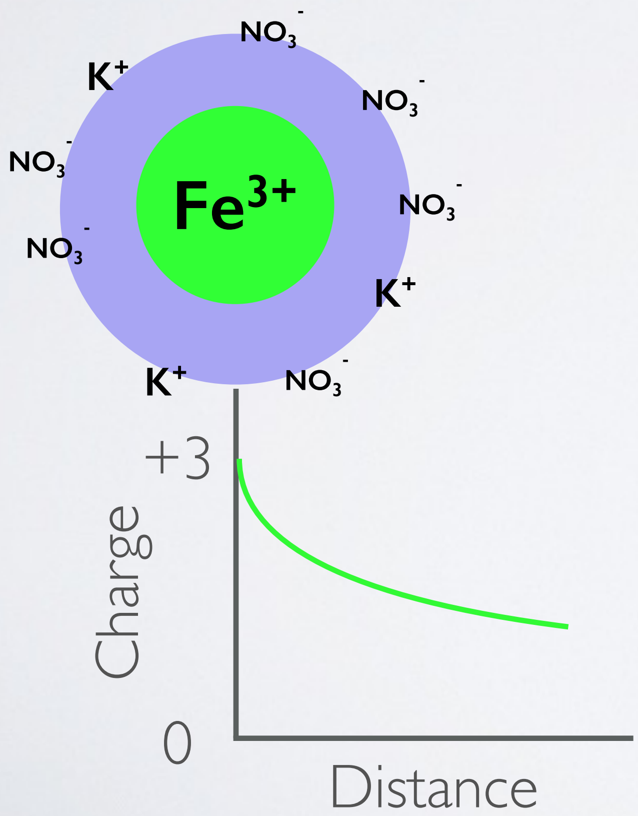


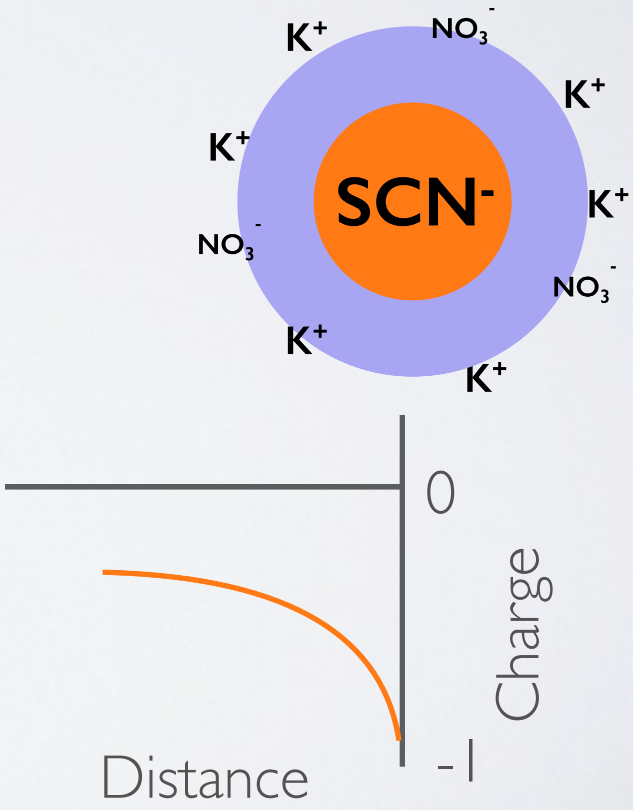


IONIC STRENGTH

The ion atmosphere effectively reduces the charge that is seen by more distant ions

Solution of: Fe^{3+}, SCN^{-}, K^{+} and NO_3^{-}





IONIC STRENGTH

- The higher the number of ions in solution, the greater the influence of the ion atmosphere on all ions.
- Not every ion in solution is equal, the influence of PO_4^{3-} on the atmosphere of a cation will be greater than F^-.
- The ionic strength (μ) of a solution is calculated as a sum of the the products of the ion concentrations and their charges.

Solution Ionic Strength

$$\mu = \frac{1}{2} \sum_i c_i z_i^2$$

c: molar concentration of ion **i**

z: charge of ion **i**

PROBLEM

What is the total ionic strength of an aqueous solution of 10 mM sulfuric acid, 5 mM calcium sulfate, and 3 mM iron(III) chloride?

ION ACTIVITY

$$Fe^{3+}_{(aq)} + SCN^{-}_{(aq)} \rightleftharpoons Fe(SCN)^{2+}_{(aq)}$$

- The influence of the ionic strength is seen in the **activity** (**a**) of ions in solution.

$$K_1 = \frac{[Fe(SCN)^{2+}]}{[Fe^{3+}][SCN^-]}$$

$$a_{Fe^{3+}} = [Fe^{3+}]\gamma_{Fe^{3+}}$$

- The activity is calculated by modifying the molar concentration of the ion by its specific **activity coefficient** (γ) at the given solution ionic strength

$$K_1 = \frac{[Fe(SCN)^{2+}]\gamma_{Fe(SCN)^{2+}}}{[Fe^{3+}]\gamma_{Fe^{3+}}[SCN^-]\gamma_{SCN^-}}$$

DETERMINING THE ACTIVITY COEFFICIENT

- Once the ionic strength of a solution is known the activity coefficient can be calculated with the **extended Debye-Hückle equation.**
- The values of 0.51 and 3.3 are appropriate for aqueous solutions at 25°C and can be altered as needed.
- The ion's effective hydrated radius (α_A) is a tabulated value.
- The equation needs to be modified if the ionic strength of a solution exceeds 0.1M.

Extended Debye-Hückle Equation

$$\log \gamma_A = \frac{-0.51 \times z_A^2 \times \sqrt{\mu}}{1 + 3.3 \times \alpha_A \times \sqrt{\mu}}$$

Table 6.2 Effective Diameters (a) for Selected Ions

Ion	Effective Diameter (nm)
H_3O^+	0.9
Li^+	0.6
Na^+, IO_3^-, HSO_3^-, HCO_3^-, $H_2PO_4^-$	0.45
OH^-, F^-, SCN^-, HS^-, ClO_3^-, ClO_4^-, MnO_4^-	0.35
K^+, Cl^-, Br^-, I^-, CN^-, NO_2^-, NO_3^-	0.3
Cs^+, Tl^+, Ag^+, NH_4^+	0.25
Mg^{2+}, Be^{2+}	0.8
Ca^{2+}, Cu^{2+}, Zn^{2+}, Sn^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}	0.6
Sr^{2+}, Ba^{2+}, Cd^{2+}, Hg^{2+}, S^{2-}	0.5
Pb^{2+}, CO_3^{2-}, SO_3^{2-}	0.45
Hg_2^{2+}, SO_4^{2-}, $S_2O_3^{2-}$, CrO_4^{2-}, HPO_4^{2-}	0.40
Al^{3+}, Fe^{3+}, Cr^{3+}	0.9
PO_4^{3-}, $Fe(CN)_6^{3-}$	0.4
Zr^{4+}, Ce^{4+}, Sn^{4+}	1.1
$Fe(CN)_6^{4-}$	0.5

Source: Kielland, J. *J. Am. Chem. Soc.* **1937**, *59*, 1675–1678.

PROBLEM

What are the activity coefficients for **iron(III)** and **sulfate** in an aqueous solution of 10 mM sulfuric acid, 5 mM calcium sulfate, and 3 mM iron(III) chloride?