TOPIC I ENSC 4734

CHEMISTRY REVIEW

NECESSARY CONCEPTS

- Gram atomic wt (6.02 x 10^{23} atoms)
- Gram molecular wt (6.02 x 10^{23} molecules)
- Above terms replaced by **MOLE**

NECESSARY CONCEPTS

- Mole is the chemists six-pack and is the amount of an element or compound containing Avogadro's number of atoms or molecules
- Moles = grams/atomic or formula weight

NECESSARY CONCEPTS

- Avogadro’s number of C atoms in 12 grams of carbon
- Or Avogadro’s number of water molecules in 18 grams of water

NECESSARY CONCEPTS

- In soil chemistry mole is used to denote Avogadro’s number of fundamental charge units on surfaces or ions.
- Example: 1 mole of Ca^{2+} ions carries 2 $\text{moles}_{(c)}$ charge.

Example

- Calculate the number of grams in one mole of $CaSO_4\cdot 7H_2O$:

Example

- Calculate the number of moles in 5 grams of $NaWO_4$ (FW =293.8 g/mole)

Molarity

- Simply the moles of a substance in 1 liter of solution
- Molarity (M) = Moles/L

Example

- A solution is prepared by dissolving 1.26 g $AgNO_3$ (FW = 169.9 g mole $^{-1}$) in a 250 ml volumetric flask and diluting to volume. Calculate the molarity.

Dimensional Analysis

- How many mmoles of $AgNO_3$ were dissolved?

Dimensional Analysis

- Soil example: Given a soil with 4 $cmol_+$ Al^{3+} kg^{-1}. How many Kg of Al^{3+} in a HFS of soil?

Normality and Equivalents

- Equivalent weight is the formula weight divided by the number of reacting units or equivalents (g/eq)
- For Ca^{2+} reacting unit is charge
  - Hence equivalent weight is 20 g

Normality and Equivalents

- Normalizing (hence normality) to the basic fundamental reacting unit (e.g. proton, charge, etc.)
- In soil chemistry these reacting units are most often *charge*

Normality and Equivalents

- Normality is Equivalents divided by volume (liters)

Example

- What is the equivalent weight of H_2SO_4?
- In this example the proton is the reacting unit
- Eq. wt. = Formula Wt./ # of equivalents

Example

- What is the Normality of a 1M solution of H_2SO_4?

Example

- A 250 ml extract from a 100 grams of soil was found to contain 3 mM of Ca^{+2}. Express this in meq/100 g
- Remember to use dimensional analysis:

Example

- Soil Scientists no longer use meq $100g^{-1}$
- The units $cmol_{(c)}\ kg^{-1}$ are now used
- These two expressions are equal.

Expression of results
Solid Samples

- % (wt/wt) = cg/g
- ppt (wt/wt) = mg/g
- ppm (wt/wt) = mg/Kg
- ppb (wt/wt) = μg/Kg

Expression of Results
Liquid Samples

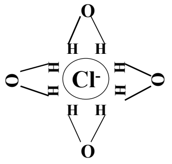
- % (wt/vol) = cg/ml
- ppt (wt/vol) = mg/ml
- ppm (wt/vol) = mg/L
- ppb (wt/vol) = ug/L

Nature of Water

- Hydrogen bonding
  - Adhesion and cohesion
- High dielectric constant
- Unique physical-chemical characteristics
  - Melting and boiling points

Hydration/Hydrolysis

- Hydration - ordered arrangement of water (dipole) around solute particles



Hydration/Hydrolysis

- Stability of cation hydration spheres
  - Enthalpy (ΔH_h) and Entropy (ΔS_h) of Hydration

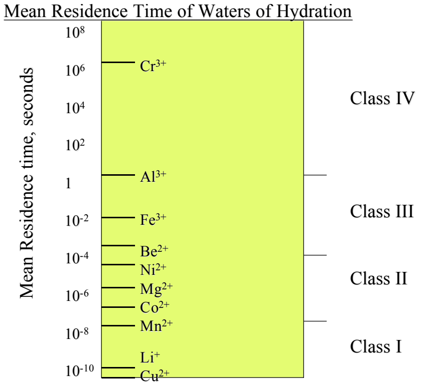
$M^{m+}_{(g)} + nH_2O_{(l)} \text{--->} [M(H_2O)_n]^{m+}_{(aq)}$

  - Mean residence time of waters of hydration (ligand exchange rates)

Enthalpy of Hydration for Select Metal Cations

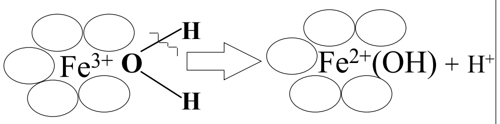
Ion	r, pm	ΔH_h
H^+	---	-1091 kJ mol^{-1}
Li^+	90	-515
Na^+	116	-405
K^+	152	-321
Rb^+	166	-296
Cs^+	181	-263
Be^{2+}	59	-2487
Mg^{2+}	86	-1992
Ca^{2+}	114	-1592
Sr^{2+}	132	-1445
Ba^{2+}	149	-1304
Ra^{2+}	162	-1259

Mean Residence Time of Waters of Hydration



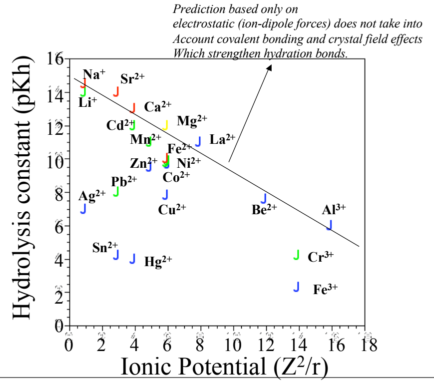
Hydration/Hydrolysis

- Hydrolysis - chemical reaction involving the splitting of the water molecule. Hydration taken to the “extreme”



Hydration/Hydrolysis

- Ions of small size and high charge tend to hydrate most strongly and have the largest hydrolysis constants
  - strong electric fields
  - most energenic bonding between water dipoles and ions



Prediction based only on electrostatic (ion-dipole forces) does not take into Account covalent bonding and crystal field effects Which strengthen hydration bonds.

Concept of Activity

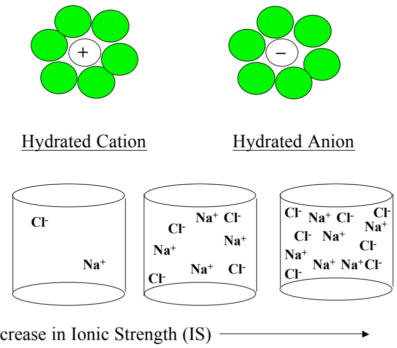
- Aqueous systems always strive toward electroneutrality
- Ions of opposite charge tend to surround and stabilize any particular ion in solution
- Long-range (>0.5 nm) are termed non-specific electrostatic interactions

Concept of Activity

- Non-specific Interactions cause non-ideal behavior of solutes which increase with:
  - – valence
  - – Number or concentration
- Ionic Strength (IS) = $1/2 \Sigma C_i Z_i^2$

Example

- Calculate the ionic strength of 0.005M NaCl and 0.005M $CaCl_2$



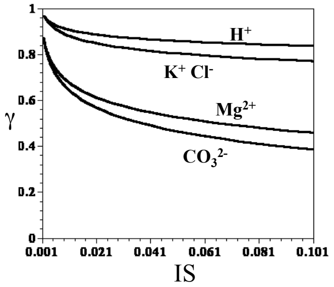
Concept of Activity

- In soil solutions these interactions reduce actual concentration of ions
- Solutes can be treated ideally by considering activity
- Ideal gas analogy
- $a_i = \gamma_i c_i$

Concept of Activity

- What would be the activity coefficient of an ideal solute?
- Deviation from 1 expresses the non ideal behavior of solutes
- Activity coefficient approaches 1 at infinite dilution:
  - $\lim_{M \to 0} \gamma = 1$

Ion Activity Coefficient vs. IS



Values of Single-Ion Activity Coefficients for Common Soil Ions

	IS				
Ion	0.001	0.005	0.01	0.05	0.1
H^+	0.967	0.933	0.914	0.86	0.83
Na^+	0.964	0.928	0.902	0.82	0.775
HCO_3^-, $H_2PO_4^-$	0.964	0.927	0.901	0.815	0.77
OH^-, F^-, MNO_4^-	0.964	0.926	0.90	0.81	0.76
K^+, Cl^-, NO_2^-, NO_3^-	0.964	0.925	0.899	0.805	0.755
Cs^+, NH_4^+	0.964	0.924	0.898	0.80	0.75
Mg^{2+}	0.872	0.755	0.69	0.52	0.45
Ca^{2+}, Cu^{2+}, Zn^{2+}, Fe^{2+}	0.87	0.749	0.65	0.485	0.405
Cd^{2+}, S^{2-}	0.868	0.744	0.67	0.465	0.38
Pb^{2+}, CO_3^{2-}, MoO_4^{2-}	0.867	0.742	0.665	0.455	0.37
SO_4^{2-}, SeO_4^{2-}, HPO_4^{2-}	0.867	0.74	0.66	0.455	0.355
Al^{3+}, Fe^{3+}, Cr^{3+}	0.73	0.54	0.455	0.245	0.18
PO_4^{3-}	0.725	0.505	0.395	0.16	0.095

Calculation of Activity Coefficients

- Different empirical equations are used depending on the IS of the soil solution
- Debye-Hückel (IS < 0.005)
- Extended Debye-Hückel (IS < 0.10 M)
- Davies (IS< 0.50 M)

Extended Debye-Hückel

$$\log \gamma_i = -A Z_i^2 \left[\frac{I^{1/2}}{1 + B a_i I^{1/2}} \right]$$

where:
A is a constant and is related to the dielectric constant of water (A= 0.5 at 298 K), B is also a constant related to the dielectric constant of water (B= 0.33 at 298 K), a is related to the size of the hydrated ion (in Angstroms), Z refers to the charge of the ion, and
I is ionic strength.

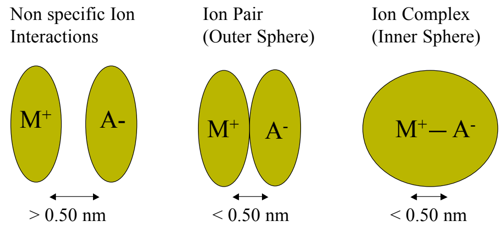
Other Interactions between solutes

- Presence of *ligands* (inorganic and organic) in soil solutions
- Ion Pairs
- Ion complexes
- Closer range (< 0.5 nm)

Other Interactions between solutes

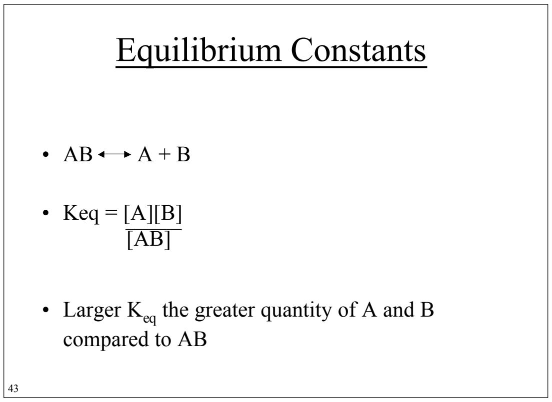
- Ion Pair - waters of hydration retained (outer-sphere complexes)
- Ion Complexes - lose some waters of hydration (inner-sphere complexes)

Reactions Responsible for the Non-Ideal Behavior of Solutes



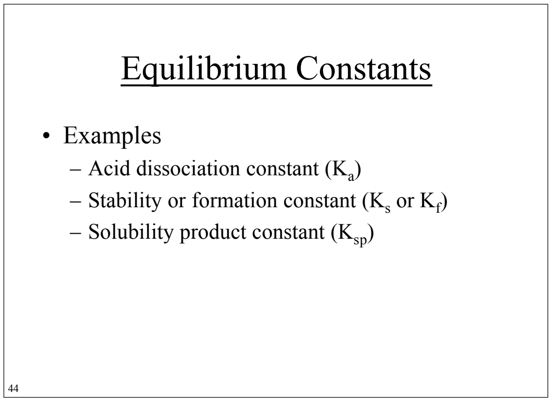
Ion Pairing/Complexation

- Cations/Anions have high charge (>2)
- Inorganic anions (other than NO_3^- and Cl^-)
- Presence of transition metals/neutral or anionic organic molecules
- High concentration of complexing ligands
- High pH and the presence of polyvalent (e.g. +2 or +3) cations



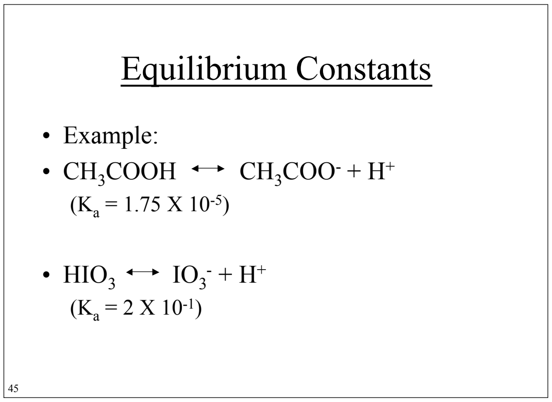
Equilibrium Constants

- AB ↔ A + B
- $Keq = \frac{[A][B]}{[AB]}$
- Larger K_{eq} the greater quantity of A and B compared to AB



Equilibrium Constants

- Examples
  - Acid dissociation constant (K_a)
  - Stability or formation constant (K_s or K_f)
  - Solubility product constant (K_{sp})



Equilibrium Constants

- Example:
- $CH_3COOH \leftrightarrow CH_3COO^- + H^+$
  ($K_a = 1.75 X 10^{-5}$)
- $HIO_3 \leftrightarrow IO_3^- + H^+$
  ($K_a = 2 X 10^{-1}$)

Equilibrium Constants

- Often K_{eq} will be expressed as pK
- Similar to pH which is the $-\log[H^+]$
  - pK = -log(K)

Equilibrium Constants

- pKa
  - HIO_3 = 0.77
  - HOCl = 7.96
  - HOAc = 4.75
  - $C_6H_4(OH)COOH$ = 3
- Rank the above acids from weakest to strongest

Solubility Product

- Equilibrium constant relating solubility of a substance and the conc. of its ionization products:
- $AgCl_{(s)} = Ag^+ + Cl^-$ $K_{sp}=[Ag^+][Cl^-]$
- $CaCl_{2(s)} = Ca^{2+} + 2Cl^-$ $K_{sp}=[Ca^{2+}][Cl^-]^2$

Solubility Product

- IAP = $[A^-]^n[B^+]^m$
- $IAP/K_{sp} < 1$ *undersaturation*
- $IAP/K_{sp} = 1$ *saturation*
- $IAP/K_{sp} > 1$ *supersaturation*

Solubility Product

- Common Ion Effect

Solubility of a salt is less

- Diverse Ion Effect

Solubility of a salt is greater

Example

- What must be the conc. of added Ag^+ to reach saturation of AgCl in a 1×10^{-3} M solution of NaCl (K_{sp} of AgCl = 1×10^{-10})

Acid-Base Equilibria

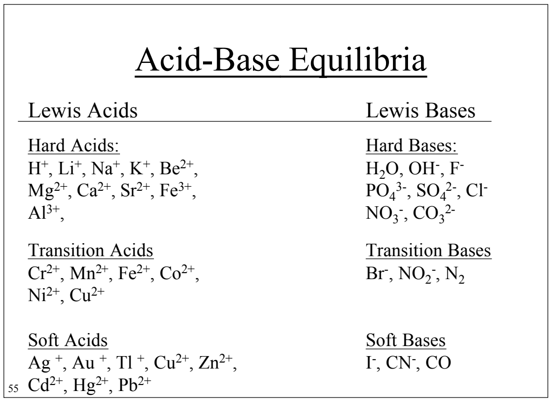
- *Arrhenius Theory*- acid ionizes in H_2O to give H^+, base ionizes to give OH^-
- *Bronsted Theory* - acid can donate a proton and a base can accept a proton
- *Lewis Theory* - acid is an electron pair acceptor and a base is an electron pair donor

Acid-Base Equilibria

- Hard/Soft Acid Base theory (Lewis Theory)
  - Hard Acid - high charge and small size
  - Soft Acid - low charge and large size

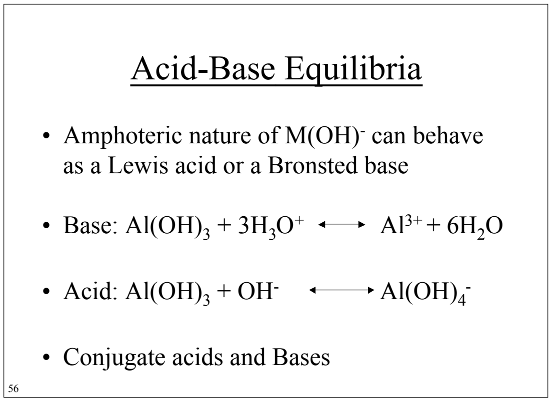
Acid-Base Equilibria

- Hard/Soft Acid Base theory
  - Hard Base - low polarizability and high electronegativity
  - Soft Base - high polarizability and low electronegativity



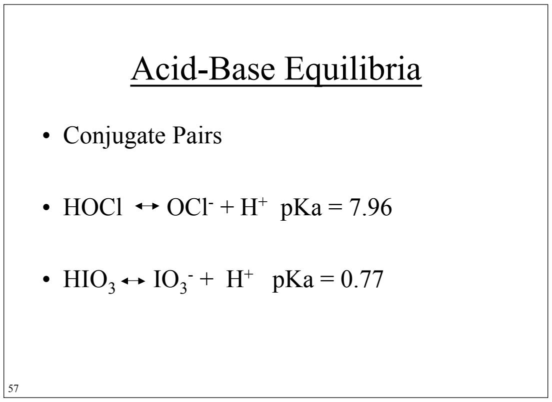
Acid-Base Equilibria

Lewis Acids	Lewis Bases
Hard Acids: H^+, Li^+, Na^+, K^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Fe^{3+}, Al^{3+},	Hard Bases: H_2O, OH^-, F^- PO_4^{3-}, SO_4^{2-}, Cl^- NO_3^-, CO_3^{2-}
Transition Acids Cr^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}	Transition Bases Br^-, NO_2^-, N_2
Soft Acids Ag^+, Au^+, Tl^+, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}	Soft Bases I^-, CN^-, CO



Acid-Base Equilibria

- Amphoteric nature of $M(OH)^-$ can behave as a Lewis acid or a Bronsted base
- Base: $Al(OH)_3 + 3H_3O^+ \longleftrightarrow Al^{3+} + 6H_2O$
- Acid: $Al(OH)_3 + OH^- \longleftrightarrow Al(OH)_4^-$
- Conjugate acids and Bases



Acid-Base Equilibria

- Conjugate Pairs
- $HOCl \leftrightarrow OCl^- + H^+$ pKa = 7.96
- $HIO_3 \leftrightarrow IO_3^- + H^+$ pKa = 0.77

Acid-Base Equilibria

- Proton hydrolyzes in H_2O to H_3O^+
- Pure water ionizes slightly:
  $2H_2O \dashrightarrow H_3O^+ + OH^-$
- Self-ionization constant K_w:
  $K_w = [H^+][OH^-] = 1 \times 10^{-14}$

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Acid-Base Equilibria

- Strong vs. Weak Acid/Base

Strong: ionization is complete

Weak: ionization is incomplete

Strength is measured by the magnitude of the equilibrium constant (K_b or K_a)

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Acid-Base Equilibria

- Buffers - mixture of weak acid/base and its salt
- Henderson/Hasselbach Eq.
- $pH = pK + \log[salt]/[acid]$ *pK = -log[Ka]*
- $pH = pK + \log[COO^-]/[COOH]$

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Example

- Calculate the pH of a solution prepared by adding 10 ml of 0.10 M acetic acid to 20 ml of 0.10 M sodium acetate. $K_a = 1.73 \times 10^{-5}$

Redox Reactions

- Transfer of electrons
- Oxidation
  - losing and e-
- Reduction
  - gaining an e-
- $CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O$
- $FeS_{2(s)} + O_2 \leftrightarrow Fe(OH)_{3(s)} + SO_4^{2-}$

Miscellaneous Calculations

- Dilutions: $C_1V_1 = C_2V_2$
- Example: A 200 ml soil extract has a K= conc. of 3000 ppm. How many ml must one add to a 100 ml volumetric to obtain a final conc. of 500 ppm?

Miscellaneous Calculations

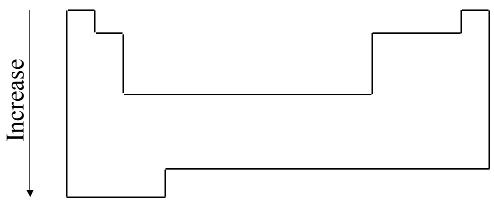
- Acid Dilution Problem
- How many ml of conc. H_2SO_4 (94%) are required to prepare 1 L of a 1 M solution?
- Density is 1.831 g cm^{-3}

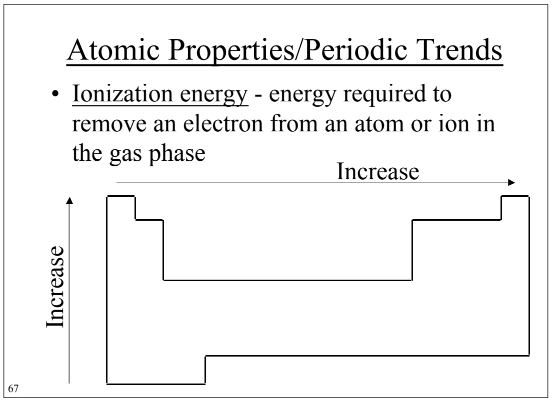
Miscellaneous Calculations

- Use dimensional analysis:

Atomic Properties/Periodic Trends

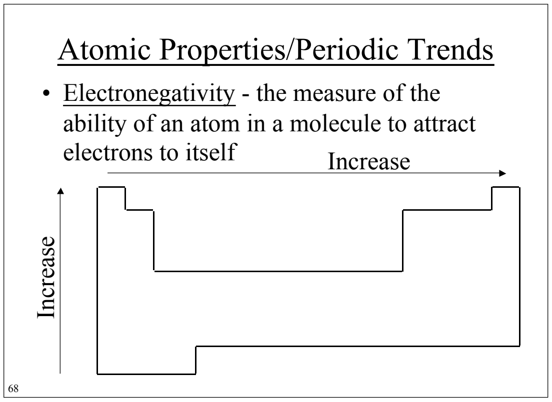
- Atomic Size (radii)





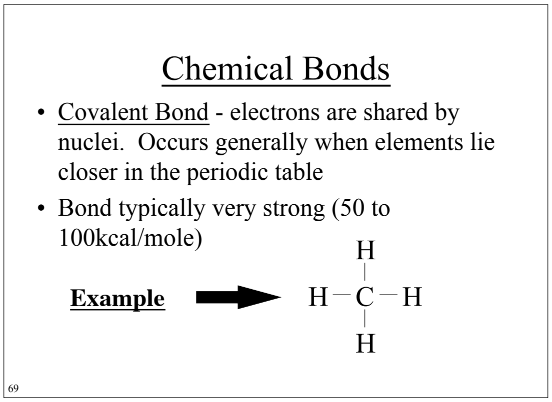
Atomic Properties/Periodic Trends

- Ionization energy - energy required to remove an electron from an atom or ion in the gas phase



Atomic Properties/Periodic Trends

- Electronegativity - the measure of the ability of an atom in a molecule to attract electrons to itself



Chemical Bonds

- Covalent Bond - electrons are shared by nuclei. Occurs generally when elements lie closer in the periodic table
- Bond typically very strong (50 to 100kcal/mole)

Example

CH_4

Chemical Bonds

- Ionic Bond (Polar bond) - electrostatic attraction between atoms of opposite charge, transfer of 1 or more electrons occurs (A + B ---> $A^+ + B^-$)

Chemical Bonds

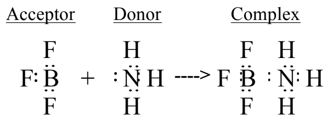
- Ionic Bond (Polar bond)
  - Bond orbital is strongly displaced
  - Generally involve metals from left of the periodic table and nonmetals from the right side
  - **Example** ----> NaCl (strength similar to covalent)

Chemical Bonds

- Ionic (e^- held by 1 atom) and covalent (e^- equally shared) bonds are extremes.
- Electronegativities vary:
  - Ionic bond - EN difference > 1.7
  - Polar covalent bond - EN difference 0.5 - 1.7
  - Nonpolar covalent bond - EN difference < 0.5

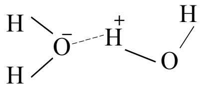
Chemical Bonds

- Coordinate covalent bond - both e$^-$ supplied by a donor atom while the other atom provides an accommodating orbital.
  - **Example** :



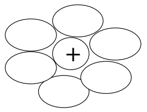
Chemical Bonds

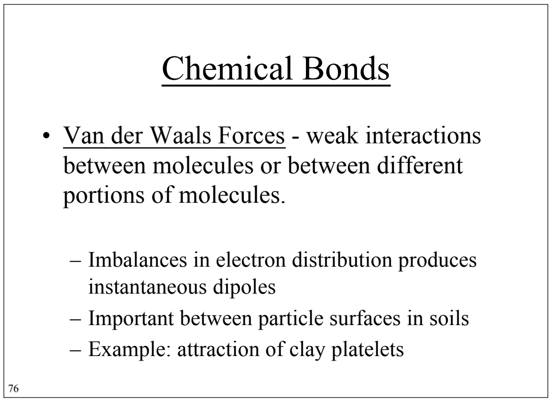
- Hydrogen Bond (dipole-dipole) - EN differences of elements form polar molecules (Unequal sharing of electrons).
- Hydrogen bonding occurs when H is bonded to F, O, N, Cl.
- Example:



Chemical Bonds

- Ion-Dipole Bond - many molecules posses a dipole (separation of charge). These molecules are attracted to ions. Weak.
- Example: Hydration of ions





Chemical Bonds

- Van der Waals Forces - weak interactions between molecules or between different portions of molecules.
  - Imbalances in electron distribution produces instantaneous dipoles
  - Important between particle surfaces in soils
  - Example: attraction of clay platelets