

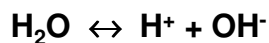
# GEOL 414/514

## ACIDS AND BASES

### Chapter 5

## LANGMUIR

## SIGNIFICANCE & MEASUREMENT OF pH



$$K_w = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = 10^{-14.00}$$

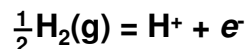
$$\text{pH} = -\log [\text{H}^+]$$

Most reactions involve or are controlled by pH:

1. Aqueous acid-base equilibria (hydrolysis, polymeriz'n)
2. Adsorption,  $\text{H}^+$  &  $\text{OH}^-$  compete with other ions
3. Formation of metal-ligand complexes ( $\text{H}^+$  &  $\text{OH}^-$  compet'n)
4. Oxidation-reduction rea'ns ( $\text{H}^+$  again)
5. Solubility & rate of mineral dissolution

## SIGNIFICANCE & MEASUREMENT OF pH

- Ultimate reference for pH & Eh measurements is H<sub>2</sub> electrode - bubble H<sub>2</sub> over Pt electrode



$$\begin{aligned} E &= E^\circ - \frac{RT}{nF} \ln \frac{[\text{H}^+]}{[\text{P}_{\text{H}_2}]^{1/2}} \\ &= E^\circ - 2.303RT/nf \log \frac{[\text{H}^+]}{[\text{P}_{\text{H}_2}]^{1/2}} \end{aligned}$$

- Cannot conveniently use the H<sub>2</sub> for routine measurements; use a glass electrode (pH) with a reference electrode - usually a Ag-AgCl or Hg-Hg<sub>2</sub>Cl<sub>2</sub> cell. Using a buffer solution, pH determinations are made

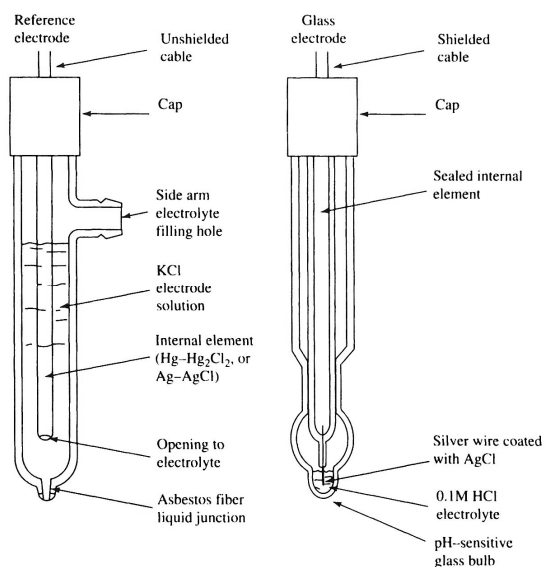
## SIGNIFICANCE & MEASUREMENT OF pH

- The pH of the unknown is obtained from:

$$\text{pH}_x = \text{pH}_b + \frac{(E_x - E_b)}{1.984 \times 10^{-4} \text{ V}}$$

- The electrodes measure voltages which the pH meter converts and displays as pH units
- The most important function of the reference electrode is to provide known and stable reference voltage
- There is a liquid junction potential due to the nature of the reference electrode - may be important in solutions of very low *I*

## GLASS (pH) AND REFERENCE ELECTRODES



## ACIDS AND BASES

### CHEMICAL DEFINITIONS

- **Acid:** has sour taste; liberates H<sup>+</sup> (H<sub>3</sub>O<sup>+</sup> in solution)  
- a substance which contains hydrogen which gives free H<sup>+</sup> when dissolved in water  
$$\text{HCl} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Cl}^-$$
- **Base:** water solution has soapy feel; has bitter taste  
- a substance containing the OH group that yields OH<sup>-</sup> on dissolving in water
- **Alkali:** generally means a soluble strong base
- **Alkaline (basic):** a solution containing appreciable OH<sup>-</sup> or capable of forming such a solution

## ACIDS AND BASES - 2

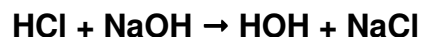
### GEOLOGIC USAGE

- The terms acid, base & alkali have wide and varied meanings in geology
- Many oxides of nonmetals dissolve in H<sub>2</sub>O to form acids
- Term “acid oxide” used for nonmetallic oxide regardless of solubility (SiO<sub>2</sub> & rocks with high % SiO<sub>2</sub>)
- Term “basic oxide” used for any metal oxide
- Text (& this course) uses strict chemical definitions
- Quartz-rich rock is felsic or silic
- So-called basic rocks are mafic
- Rocks rich in Na or K are called alkalic or alkaline

## ACIDS AND BASES - 3

### THE pH

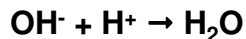
- Neutralization reactions



- More strictly:



- More simply, since Na<sup>+</sup> & Cl<sup>-</sup> are unaffected:



- Dissociation of H<sub>2</sub>O:  $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$

$$K_{\text{H}_2\text{O}} = [\text{H}^+][\text{OH}^-] = 10^{-14}$$

- The product, [H<sup>+</sup>][OH<sup>-</sup>], is constant for ALL H<sub>2</sub>O solutions

## ACIDS AND BASES - 4

### DISSOCIATION CONSTANTS OF WEAK ACIDS

- Strong acids: complete ionization in dilute solutions; HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>
- Weak acids: only slight ionization; H<sub>2</sub>CO<sub>3</sub>



and



$$\frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = K_1 = 10^{-6.4} = 4.2 \times 10^{-7}$$

$$\frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = K_2 = 10^{-10.3} = 5.0 \times 10^{-11}$$

These are  
dissociation  
constants

## ACIDS AND BASES - 5

### DISSOCIATION CONSTANTS OF WEAK ACIDS

- Calculate pH of 0.01 *m* H<sub>2</sub>CO<sub>3</sub>
- 0.01 *m* refers to the total carbonate conc

$$[\text{CO}_3]_{\text{total}} = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

- Set up an equation to express electrical neutrality:

$$[\text{H}^+] = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$$

- The coefficient of 2 before [CO<sub>3</sub><sup>2-</sup>] is necessary because each mol of a divalent ion is equivalent to 2 mols of negative charge
- Also remember [H<sup>+</sup>][OH<sup>-</sup>] = 10<sup>-14</sup>
- Now have 5 equations and 5 unknowns: ready to solve?

## ACIDS AND BASES - 6

### DISSOCIATION CONSTANTS OF WEAK ACIDS

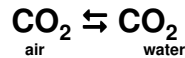
- Calculate pH of 0.01 *m* H<sub>2</sub>CO<sub>3</sub>, con't
  - We will make some assumptions to simplify the cal'n:
    - 1a -  $K_2$  of H<sub>2</sub>CO<sub>3</sub> < 10,000 x  $K_1$
    - 1b - CO<sub>3</sub><sup>-2</sup> arises only from 2<sup>nd</sup> ionization of H<sub>2</sub>CO<sub>3</sub> so [CO<sub>3</sub><sup>-2</sup>] should be small in relation to H<sub>2</sub>CO<sub>3</sub> and HCO<sub>3</sub><sup>-</sup>
  - 2 - [OH<sup>-</sup>] << [H<sup>+</sup>] (there is an acidic solution)
- therefore, set [H<sup>+</sup>] = [HCO<sub>3</sub><sup>-</sup>]
- reduce  $K_1$  Eq'n to  $[H^+]^2 / [H_2CO_3]$  (15)
- reduce [CO<sub>3</sub>]<sub>total</sub> Eq'n to  $[H_2CO_3] + [H^+] = 0.01$

## ACIDS AND BASES - 7

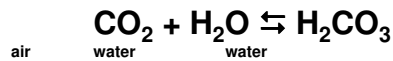
- Assumption 3: H<sub>2</sub>CO<sub>3</sub> is a weak acid, the H<sup>+</sup> from the ionization of H<sub>2</sub>CO<sub>3</sub> is small in comparison to the amount of H<sub>2</sub>CO<sub>3</sub>
- using Eq'n 15:
- $$[H^+]^2 = 0.01 * 10^{-6.4}$$
- $$[H^+] = 10^{-4.2} \text{ m}$$
- $$\text{pH} = 4.2$$
- To test assumptions:
- $$[HCO_3^-] = [H^+] = 10^{-4.2} \text{ m}$$
- $$[OH^-] = [10^{-14}] / [H^+] = 10^{-9.8}$$
- $$[CO_3^{-2}] = 10^{-10.3} [HCO_3^-] / [H^+] = 10^{-10.3}$$

## EXAMPLE: CO<sub>2</sub> IN H<sub>2</sub>O

- The example of H<sub>2</sub>, Cl<sub>2</sub> & HCl involved a single phase, or homogeneous system
- A heterogeneous system, involving substances in different states, is geologically common



- Then:



$$K = \frac{[\text{H}_2\text{CO}_3]}{[\text{CO}_2][\text{H}_2\text{O}]}$$

- The equilibrium will respond to increased P<sub>CO<sub>2</sub></sub> (add CO<sub>2</sub>), decreased P<sub>CO<sub>2</sub></sub> (heat, create vacuum)

## EXAMPLE: CO<sub>2</sub> IN H<sub>2</sub>O

- Solubility of CO<sub>2</sub> = 0.76 L/L H<sub>2</sub>O at t = 25 °C, P<sub>CO<sub>2</sub></sub> = 1 bar
- 0.75 L CO<sub>2</sub>; 0.76L/24.5 L/mole = 0.31 moles CO<sub>2</sub>
- [Notice that H<sub>2</sub>O = 1000/18.016 = 55.5 m]
- For CO<sub>2</sub> above: K = [H<sub>2</sub>CO<sub>3</sub>]/[CO<sub>2</sub>] = 0.031/1 = .031 ≈ 10<sup>-1.5</sup>
- How much H<sub>2</sub>CO<sub>3</sub> in water exposed to ordinary air?
- Air contains 0.03% CO<sub>2</sub> by volume; volume fraction = 0.0003 & partial pressure = 0.00003 bar

$$K = 0.031 = [\text{H}_2\text{CO}_3] / 0.0003$$

$$[\text{H}_2\text{CO}_3] = 0.031 \times 0.0003 = 10^{-1.5} \times 10^{-3.5} = 10^{-5} \text{ m}$$

## EXAMPLE: CO<sub>2</sub> IN H<sub>2</sub>O

- What is pH of rainwater, assuming that acidity is only from CO<sub>2</sub> at P<sub>atm</sub>?



- Assume that the second K<sub>d</sub> is not important

$$K = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$

$$4.7 \times 10^{-7} = \frac{[\text{H}^+][\text{HCO}_3^-]}{2.04 \times 10^{-5}} \quad [\text{H}^+] = [\text{HCO}_3^-]$$

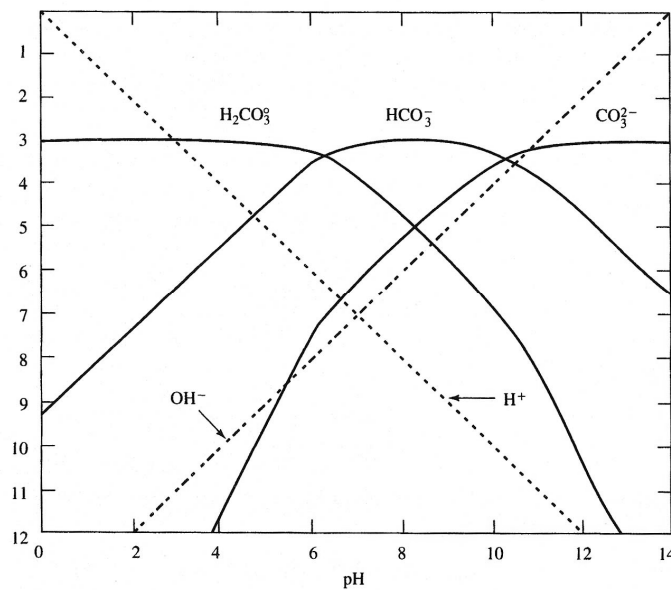
$$(4.7 \times 10^{-7}) * (2.04 \times 10^{-5}) = [\text{H}^+]^2$$

$$[\text{H}^+]^2 = 8.57 \times 10^{-12}$$

$$[\text{H}^+] = 2.92 \times 10^{-6}$$

$$\text{pH} = 5.53$$

## CARBONATE SPECIES IN SOLUTIONS



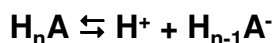


## ESTIMATING IONIC CONCENTRATIONS

- It is very often desirable to determine the ionic conc and ion distribution in natural systems
- We can use dissociation and hydrolyses equations, and associated  $K_{eq}$ , to determine the major, minor and dominant species
- See the example of  $H_2CO_3$  in the text
- When  $pH < 6.4$  then  $H_2CO_3$  dominates
- When  $pH = 6.4 - 10.3$  then  $HCO_3^-$  dominates
- When  $pH > 10.3$  then  $CO_3^{2-}$  dominates
- The above is true for these pH ranges regardless of concentrations in solution & whether or not any other solutes are present

## WEAK ACIDS - 1

General Equation for a weak acid:



$$[H^+] = (\sum A * K_1)^{1/2}$$

$K_2$  is generally  $10^4 - 10^6 < K_1$

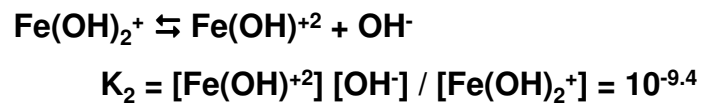
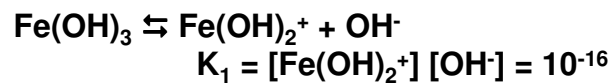
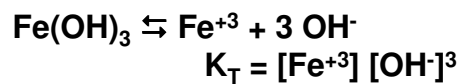
Must use caution, must be sure that  $K_2 < 10^4 K_1$

- A. If  $K_1$  is  $10^{-1}$  to  $10^{-2}$ , then acid is moderately weak, NOT a weak acid and generalization does not hold
- B. In some cases ionization of  $H_2O$  might give a pH lower than a very weak acid
- C. Use pH of  $H_2O$  in equilibrium with  $CO_2$  in air (5.7) as a lower limit for calculation for weak acid – below this point, pH is controlled by substance in  $H_2O$

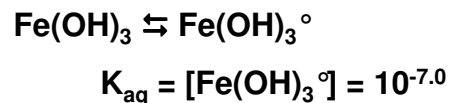
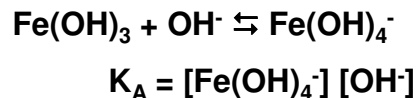
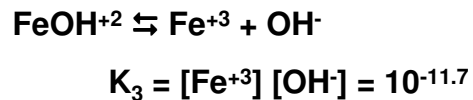
## WEAK ACIDS - 2

### Dissociation Constants of Hydroxides

- Strong bases ionize completely (as do strong acids)  
KOH, NaOH, NH<sub>4</sub>OH
- Most other hydroxides of interest in Geology are only slightly soluble & do not follow the analogy of weak acids
- Example:



## WEAK ACIDS - 3



- In a natural system, there may also be Fe(OH)<sub>2</sub> present; ionization and speciation of this form would also have to be considered

## HUMIC AND FULVIC ACIDS

- Soil humic substances (60-80% SOM):
  - fulvic acid - low M.W., sol in acid or base
  - humic acid - med M.W., sol in base, insol acid
  - humins - highest M.W., insol in acid or base
- Soil nonhumic substances: carbohydrates, proteins, peptides, amino acids, fats, waxes
- Humic substances are acidic, dark-colored, partially aromatic, M.W.'s range from 100's -1000's g FW<sup>-1</sup>
- Aquatic humic substances:
  - polyelectrolytic acids that can be isolated from water by sorption onto XAD or weak-base exchange resin;
  - M.W., 500-5000 g/mol
  - humic & fulvic acids

## FTIR SPECTRA OF HUMIC & FULVIC ACIDS

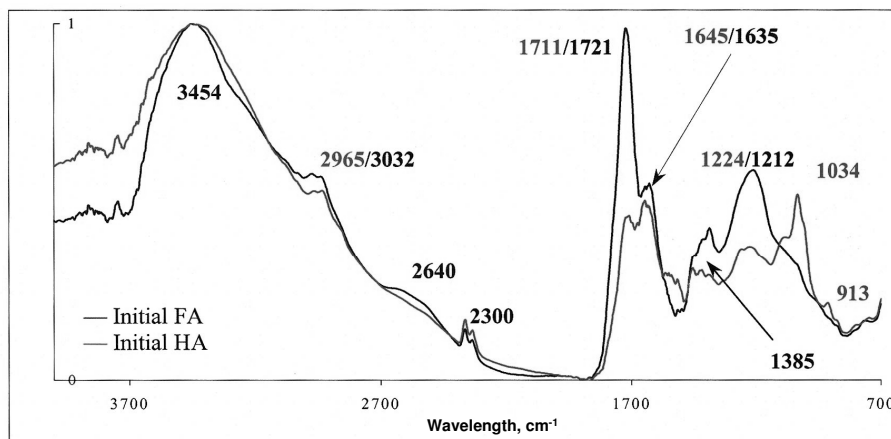
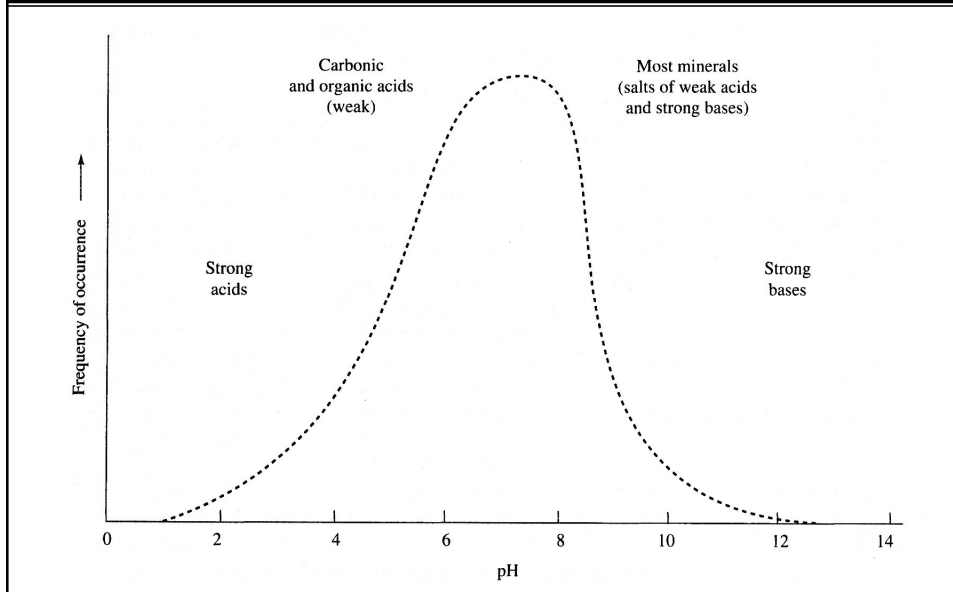


Fig. 7. Initial FTIR spectra of Dismal Swamp humic and fulvic acids.

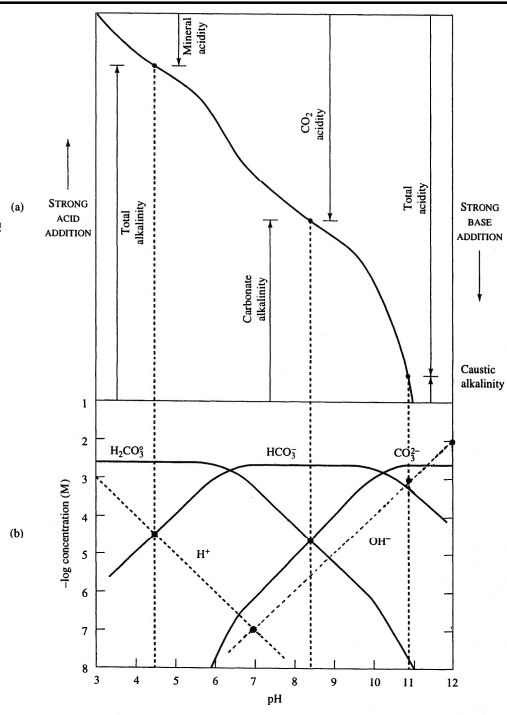
Isolated using XAD resin, humic & fulvic sep'd with resins

# CONTROLS ON pH OF NATURAL WATERS

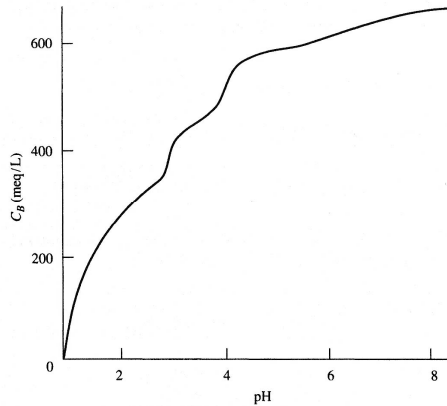


# ACIDITY & ALKALINITY DETERMINATION

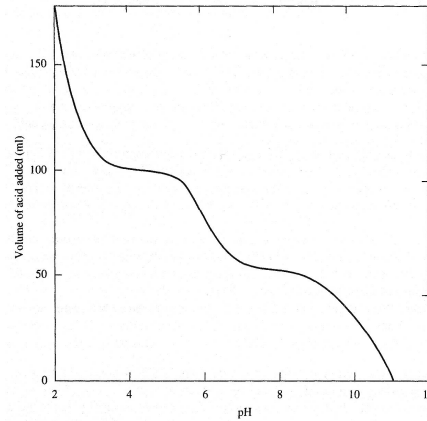
Titration curve on same scale with carbonate species figure



## EXAMPLE TITRATION CURVES



**Titration of acid U mill-tailings solution with NaOH**



**Titration of total carbonate with HCl**

## BUFFERS

- Buffers resist change in pH when either an acid or a base is added to them
- Seawater is a good buffer, generally maintains a pH from 8.1 to 8.3
- In lab, we will compare the buffering action of seawater to that of other aqueous solutions
- Examine a system of 0.01 *m* H<sub>2</sub>CO<sub>3</sub> & 0.01 *m* NaHCO<sub>3</sub>:
- Important species, HCO<sub>3</sub><sup>-</sup> & H<sub>2</sub>CO<sub>3</sub> are both = 0.01 *m*, pH = 6.4, or
- $[H^+] = [H_2CO_3] / [HCO_3^-] * K_1 = 0.01/0.01 * K_1$   
 $K_1 = 10^{-6.4} m$

## BUFFERS - 1

$\text{H}_2\text{CO}_3$  &  $\text{NaHCO}_3$  example continued:

1. Add acid:  $\text{H}^+ + \text{HCO}_3^- \rightarrow \text{H}_2\text{CO}_3$ 
  - the ratio of  $[\text{H}_2\text{CO}_3] : [\text{HCO}_3^-]$  changes which does change the  $[\text{H}^+]$  but not very much unless the ratio is greatly changed;
  - change ratio from 1 to 2, pH changes from 6.4 to 6.1
- Add base:  $\text{OH}^- + \text{H}_2\text{CO}_3 \rightarrow \text{HCO}_3^- + \text{H}_2\text{O}$ 
  - change ratio in opposite direction, pH changes from 6.4 to 6.7

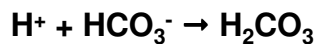
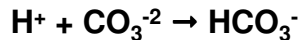
## BUFFERS - 3

- Generally, a buffer consists of approximately equal amounts of a weak acid and a salt of the acid. The pH maintained is determined by the  $K_d$  of the acid.
- Mixtures of bases and corresponding cations are also efficient buffers
- Carbonates:  
$$\text{CaCO}_3 + \text{H}^+ \rightleftharpoons \text{Ca}^{+2} + \text{HCO}_3^-$$
or  
$$\text{Ca}^{+2} + \text{HCO}_3^- + \text{OH}^- \rightleftharpoons \text{CaCO}_3 + \text{H}_2\text{O}$$
- The  $\text{HCO}_3^-$  plays an important role in buffering:  
$$\text{HCO}_3^- + \text{H}^+ \rightarrow \text{H}_2\text{CO}_3$$
$$\text{HCO}_3^- + \text{OH}^- \rightarrow \text{CO}_3^{-2} + \text{H}_2\text{O}$$

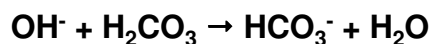
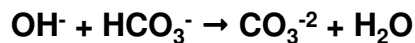
## BUFFERS - 4

- For sea water:

add H<sup>+</sup>:



add OH<sup>-</sup>:



and

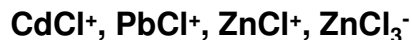


## ELECTROLYTE SOLUTIONS & ION-ION ASSOCIATIONS

- In electrolytic solutions, some ions & molecules form combinations, called complexes. Many of these are commonly referred to as ion pairs.
- They behave as a unit and are treated as a thermodynamic entity.

### Chloride complexes

- Formation is common with many types of cations, especially transition metals, over a wide range of geochemical conditions



Ion sorption, mobility, volatility affected