EWCE 105
Environmental Chemistry

Lecture 7

Instructor
Maj Kazi Shamima Akter, Ph.D, Engrs
Department of EWCE, MIST

Lecture Outlines

Topics	Sub-Topics	References
Alkalinity and Acidity	• Alkalinity and acidity of carbonate containing water • Concept of pH • Capacity diagram (pH contour in alkalinity – CT diagram) • Significance and control on pH for natural water	1. **Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters** **Authors:** Werner Stumm and James J Morgan 3rd ed., Hoboken : Wiley, 2012

Alkalinity

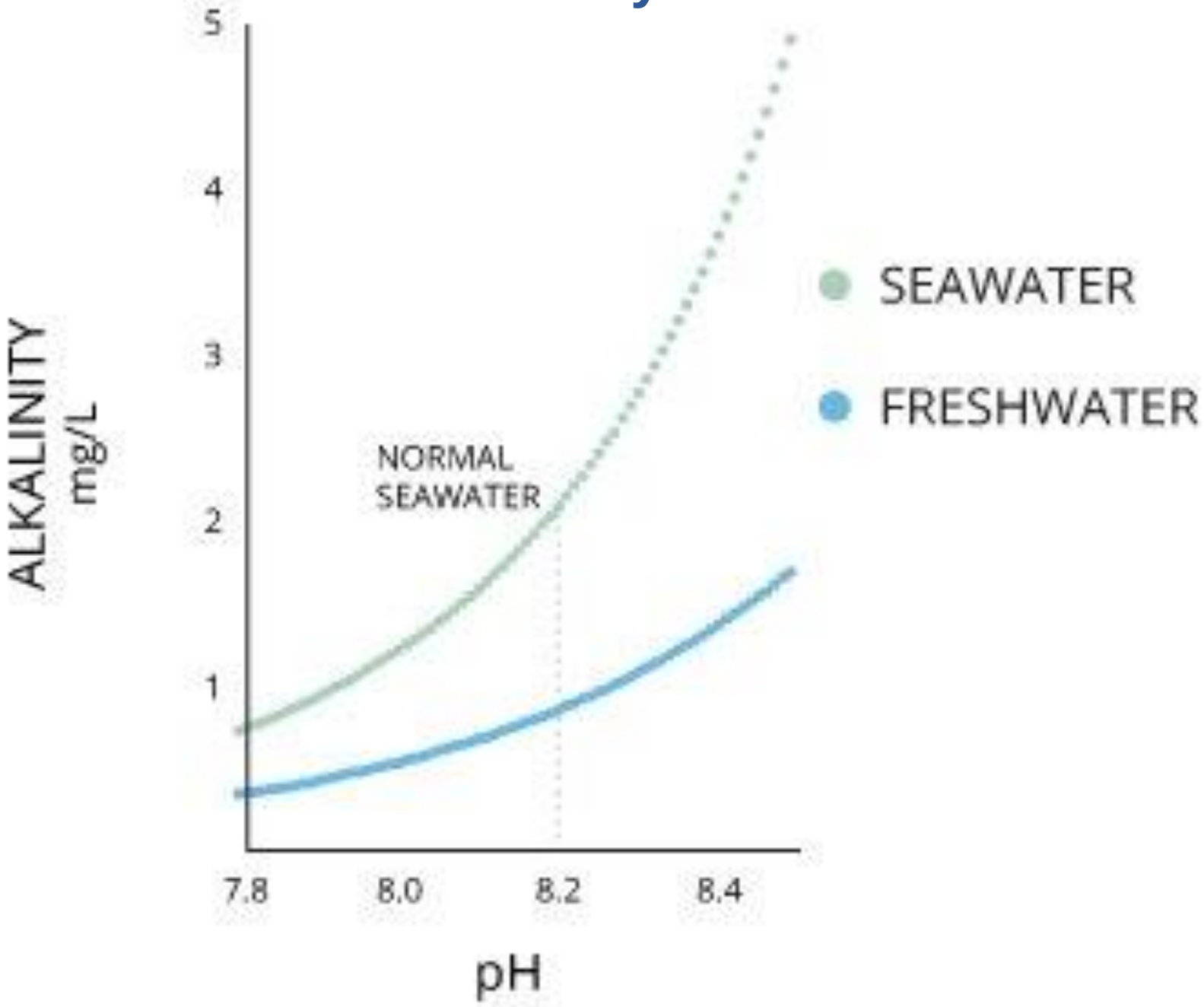
- The capacity of water to accept H^+ ions (protons) is called alkalinity.
- Alkalinity is a measure of strong acid required to attain the pH that the water would have if all the inorganic carbon was added as H_2CO_3 (i.e., pH ≈ 4.5).
- If pH of a solution is greater than 4.5, it has alkalinity, i.e., acid neutralizing capacity.

Alkalinity

Alkalinity is generally expressed as two types as follows –

- Phenolpthalein alkalinity, corresponding to titration with acid to the pH at which HCO_3^- is the predominant carbonate species (pH 8.3)
- Total alkalinity corresponding to titration with acid to the methyle orange endpoint (pH 4.3), where both HCO_3^- and CO_3^{2-} species have been converted to CO_2.

Alkalinity

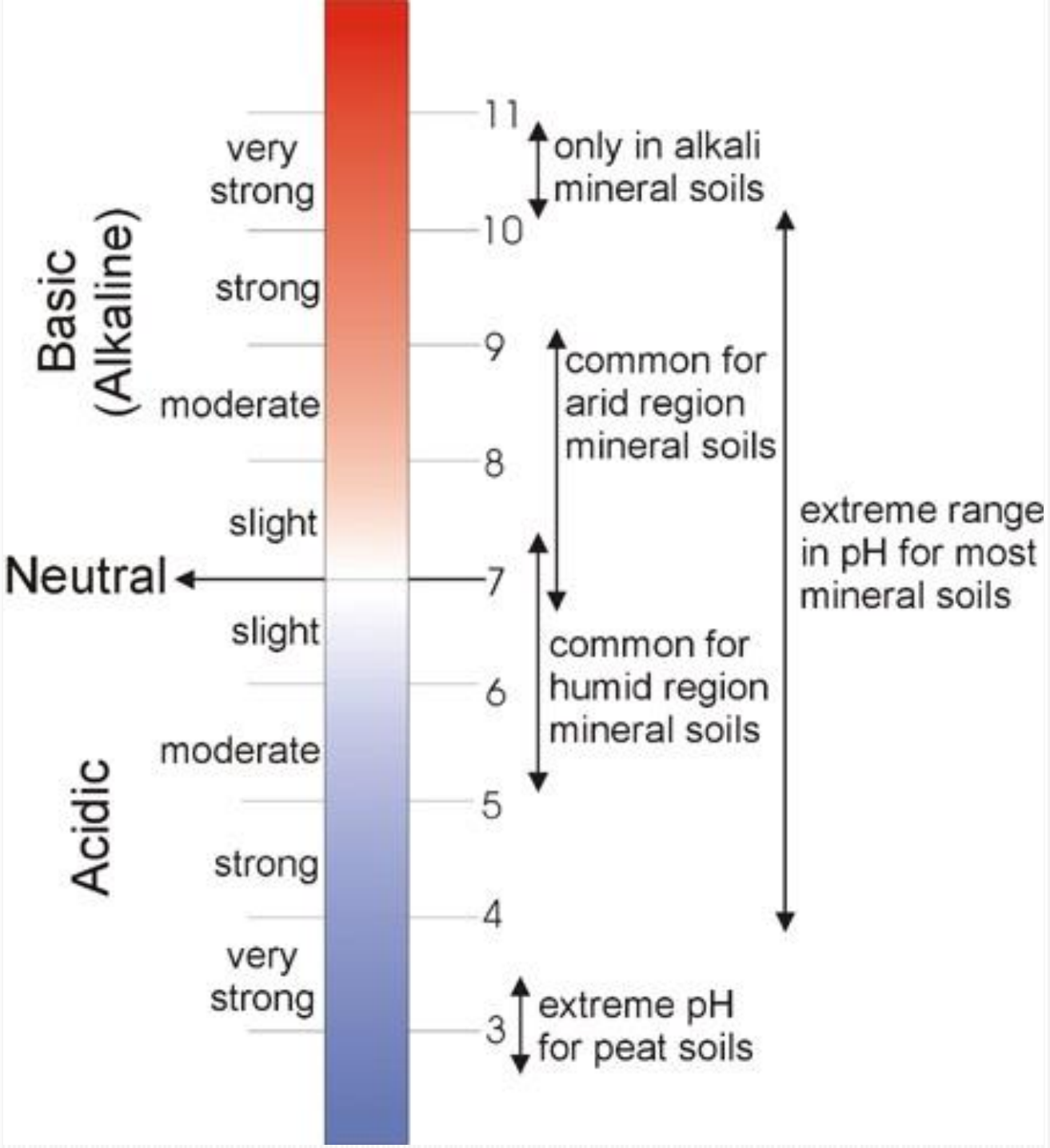

ALKALINITY
mg/L
5
4
3
2
1
NORMAL
SEAWATER
7.8
8.0
8.2
8.4
pH
SEAWATER
FRESHWATER

Acidity

- Acidity is a measure of strong base required to attain the pH that the water would have if all the inorganic carbon was added as Na_2CO_3 (i.e., pH ≈ 10.5).

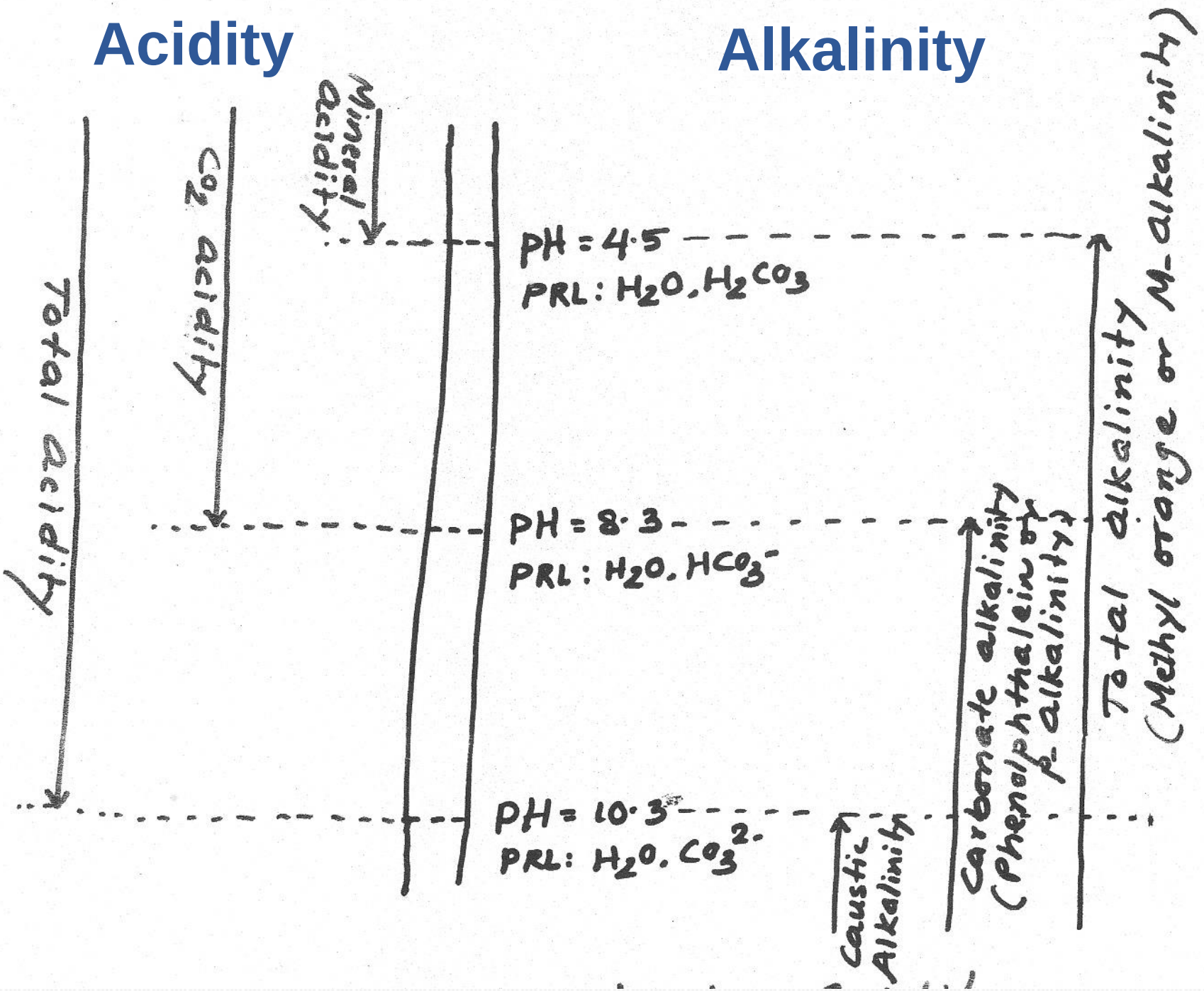
- If pH of a solution is less than 10.5, it has acidity, i.e., base neutralizing capacity.

Alkalinity and Acidity



Acidity

Alkalinity



Alkalinity and Acidity

Expressions for alkalinity, acidity:

(alkalinity) = Σ(Species that lose H+ wrt PRL)
$- \Sigma$(Species that gain H+ wrt PRL)

(acidity) = Σ(Species that gain H+ wrt. PRL)
$- \Sigma$(species that lose H+ wrt PRL)

where, PRL $\equiv$ H_2O, species which is dominant at the reference pH (e.g., 4.5 for total alkalinity, 8.3 for carbonate alkalinity).

Acidity and Alkalinity

Thus, total alkalinity,

PRL: H_2CO_3, H_2O

$$(alk) = (HCO_3^-) + 2(CO_3^{2-}) + (OH^-) - (H^+)$$
$$= C_T(\alpha_1 + 2\alpha_2) + (OH^-) - (H^+)$$
$$= f(pH, C_T).$$

And, total acidity,

PRL: CO_3^{2-}, H_2O

$$(acy) = (HCO_3^-) + 2(H_2CO_3) + (H^+) - (OH^-)$$
$$= C_T(\alpha_1 + 2\alpha_0) + (H^+) - (OH^-)$$
$$= f(pH, C_T).$$

Acidity and Alkalinity

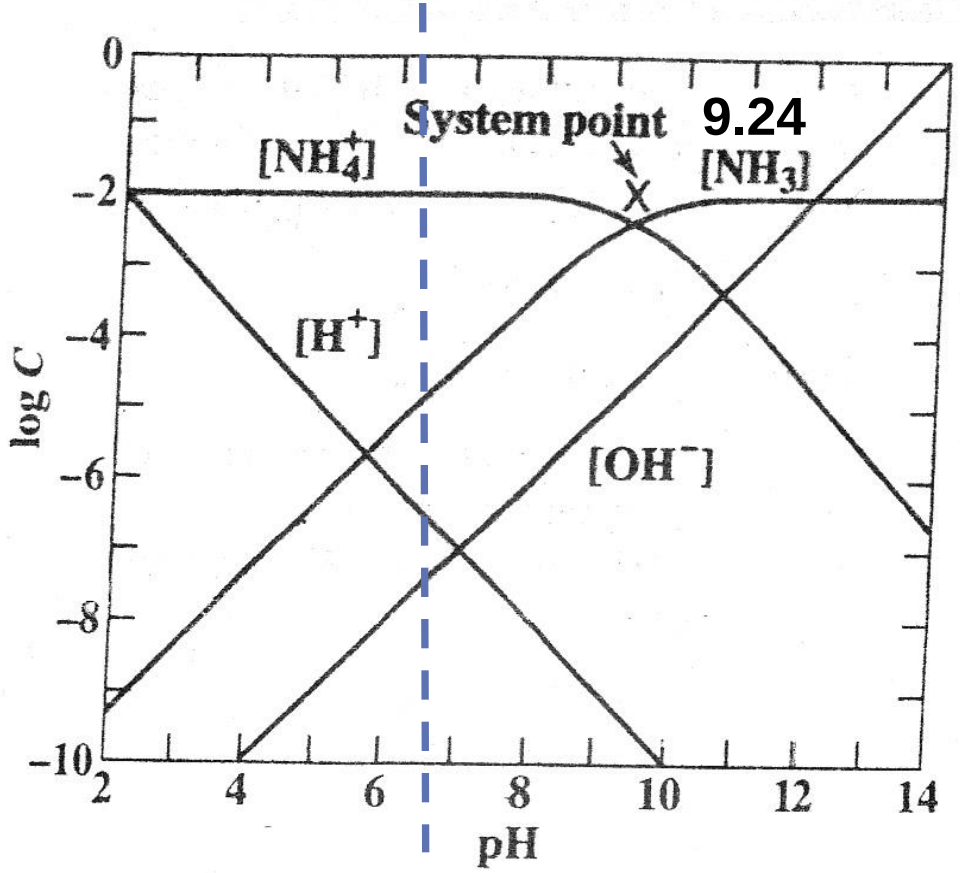
Similarly one can write expressions for other acidities, alkalinities.

These definitions can be extended to include other species that can contribute to alkalinity:

Acidity and Alkalinity

Ex. In addition to carbonate system, you have NH_4^+-NH_3 in water. Write down the expression for alkalinity.

So,



for this system
PRL for alkalinity:
H_2O, NH_4^+.

$(alk) = (NH_3) + (OH^-) - (H^+)$

If we include carbonate system,

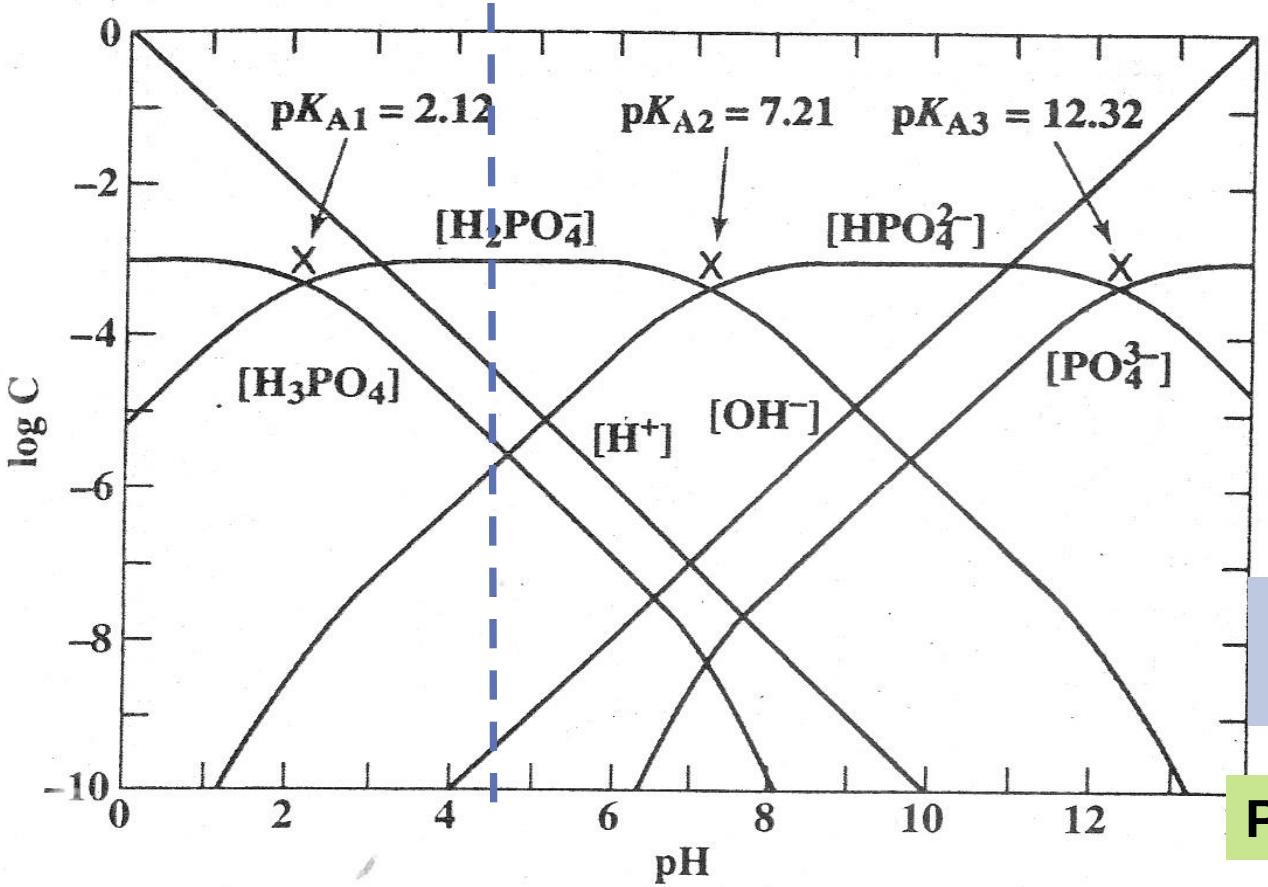
$(alk) = (HCO_3^-) + 2(CO_3^{2-}) + (NH_3) + (OH^-) - (H^+)$

pH = 4.5, Ref pH for total alkalinity

Acidity and Alkalinity

Ex. If you have orthophosphates in water, what would be the expressions for alkalinity.

Soln.



pH = 4.5, Ref pH for total alkalinity

PRL: H_2O, $H_2PO_4^-$

$$\therefore (alk) = (HPO_4^{2-}) + 2(PO_4^{3-}) - (H_3PO_4) + (OH^-) - (H^+)$$

Acidity and Alkalinity

(1) Acidity and Alkalinity are conservative properties.

Water A: $(Alk) = 10^{-3}\ M$

Water B: $(Alk) = 5 \times 10^{-3}\ M$

If A and B are mixed (1:1), for the mixture, $(Alk) = 3 \times 10^{-3}\ M$.

Alk of the mixture A and B = $(1 \times 10^{-3} + 5 \times 10^{-3}) / 2$

$= 3 \times 10^{-3}$ M

Acidity and Alkalinity

- Alkalinity is unaffected by addition or subtraction of CO_2.
- Alkalinity is the acid neutralizing capacity of a solution. Hence if acid (CO_2) is added to or withdrawn from the solution, alkalinity of the solution will be unaffected.
- Similarly, acidity is unaffected by addition or subtraction of CO_3^{2-}.
- Acidity is the base neutralizing capacity of a solution. Hence if a base (CO_3^{2-}) is added to or withdrawn from the solution, acidity of the solution will be unaffected.

Alkalinity

- In natural waters below pH ≈ 8.3, HCO_3^- is usually the only significant base.

- Bicarbonate alkalinity in water is derived from two sources:

(i) Weathering of silicate and carbonate minerals by carbonic acid, for example –

$$2KAlSi_3O_8 + 2H_2CO_3 + 9H_2O = Al_2Si_2O_5(OH)_4 + 2K^+ + 4H_4SiO_4 + 2HCO_3^-$$

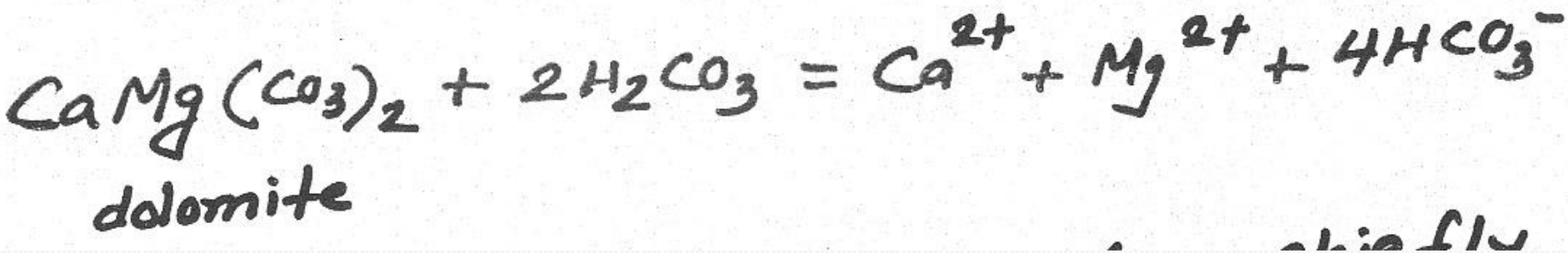
K-feldspar

Kaolinite clay

Silicic acid

Alkalinity

(ii) The dissolution of carbonate minerals



- In most waters, alkalinity is due chiefly to bicarbonate ions, and to a minor extent, carbonate ion.

- Alkalinity is usually expressed as mg/L as $CaCO_3$.

(alk) mg/L as $CaCO_3$ = (alk) meq/L × 50.04

= (alk) moles/L × 100.08

Acidity

Higher acidity is significant and undesirable, because –

- Acidity gives water a greater capacity to attack geologic materials (thus it accelerates rock weathering). So, it is usually accompanied by higher TDS (Total Dissolved Solids), including hardness.

- Acidity increases the solubilities of hazardous substances, such as heavy metals, and is corrosive and toxic to fish and other aquatic forms.

- Acidity thus limits the use of water without its extensive treatment due to high TDS, high metals and low pH.

Buffer

- Buffers may be defined as substances in solution that offer resistance to changes in pH as acids and bases are added to or formed within the solution.

- Buffer solutions usually contain mixtures of weak acids and their salts (conjugate base) or weak base and their salts (conjugate acids).

Buffer Capacity

- The concept of buffer capacity is very important in aqueous/ environmental studies.
- The buffer concept helps us to understand what reactions control the pH of natural waters including soil water.
- The standard buffer solutions used in pH electrode calibration are designed to have maximum buffer capacities to assure that their pH values are as constant as possible.

Significance of pH

Most reactions in gas/water/rock systems involve or are controlled by pH of the system, such as –

- Aqueous acid-base equilibria including hydrolysis and polymerization

- Adsorption, because protons (H^+) compete with cations and OH^- ions compete with anions for adsorption sites. Also surface charge of most minerals is pH dependent.

- Formation of metal-ligand complexes, because H^+ compete with metal ions to bond the weak acid anions, and OH^- competes with other ligands that would form complexes.

Controls on pH of Natural Water

- Lowest pH values (1 to 3) are usually associated with the products of FeS_2 weathering, which generates strong acids (H_2SO_4, HSO_4^-) and acid cations (e.g. Fe^{3+}).

- The pH of acid rain, which is sometimes below 3, may affect the presence of H_2SO_4, HNO_3 and HCl acids.

Controls on pH of Natural Water

- In natural waters having pH values between about 4.5 and 7, the acids are weak and usually include H_2CO_3 and smaller amounts of organic acids (e.g. fulvic acid).

- In near surface environment, these acids derive chiefly from organic decay and in case of H_2CO_3, from plant root respiration as well.

Capacity Diagram - Alkalinity

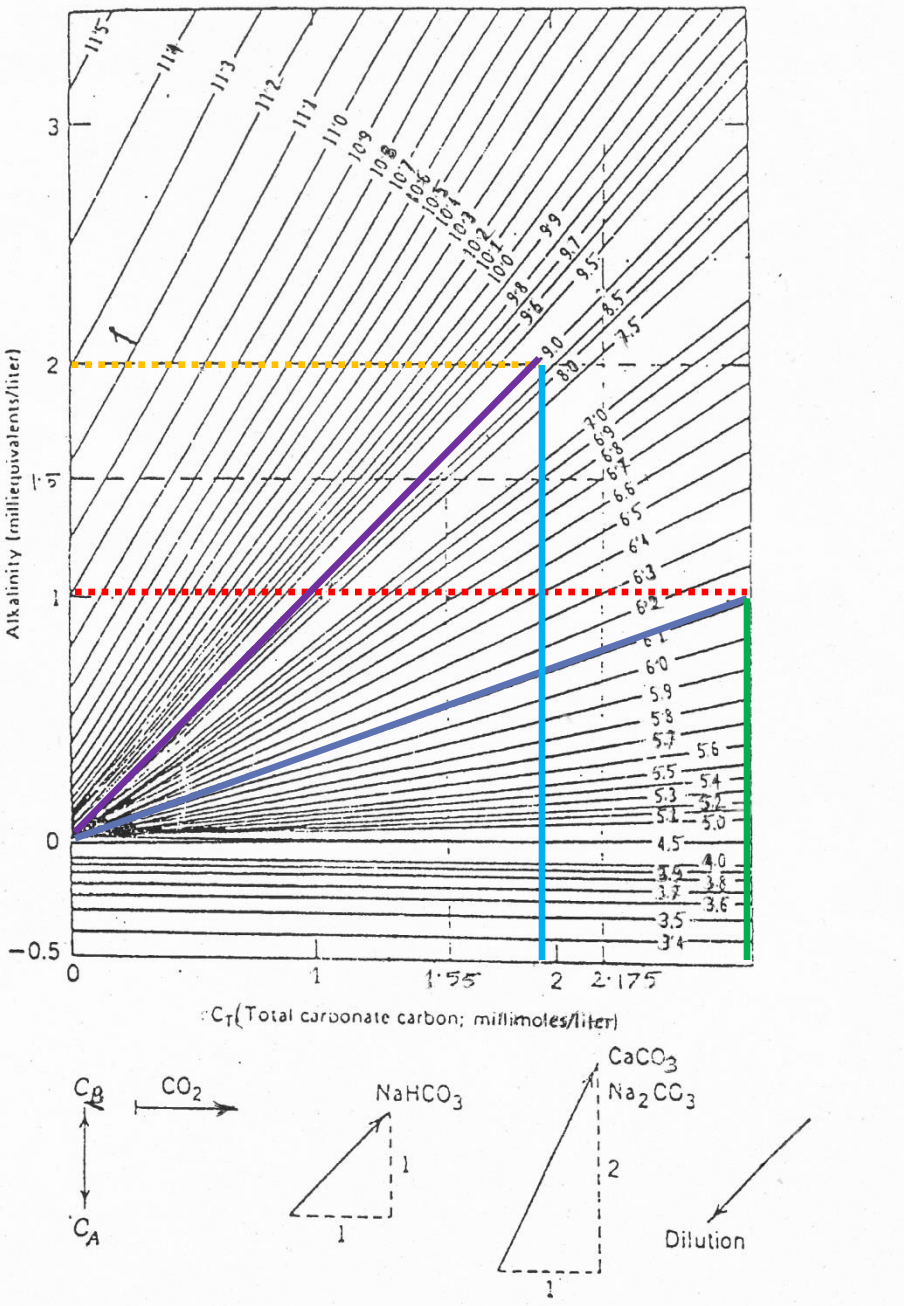


Figure 4.5. pH contours in alkalinity-versus C_T diagram. The point defining the solution composition moves as a vector in the diagram as a result of the addition (or removal) of CO_2, $NaHCO_3$, and $CaCO_3$ (Na_2CO_3) or C_B and C_A. (After K. S. Deffeyes [2].)

Problem Solving using Capacity Diagram

Two water mixed together:

Water 1: pH = 6.1
(alk) = 1×10^{-3} M
= 1.0 mM
} From Capacity diagram. (Fig 4.5)
C_T = 2.8 mM.

Water 2: pH = 9.0
(alk) = 2 mM
} From Capacity diagram
C_T = 1.9 mM.

For the mixture.

$$(alk) = \frac{1+2}{2} = 1.5 \text{ mM}$$

$$C_T = \frac{2.8+1.9}{2} = 2.35 \text{ mM}$$

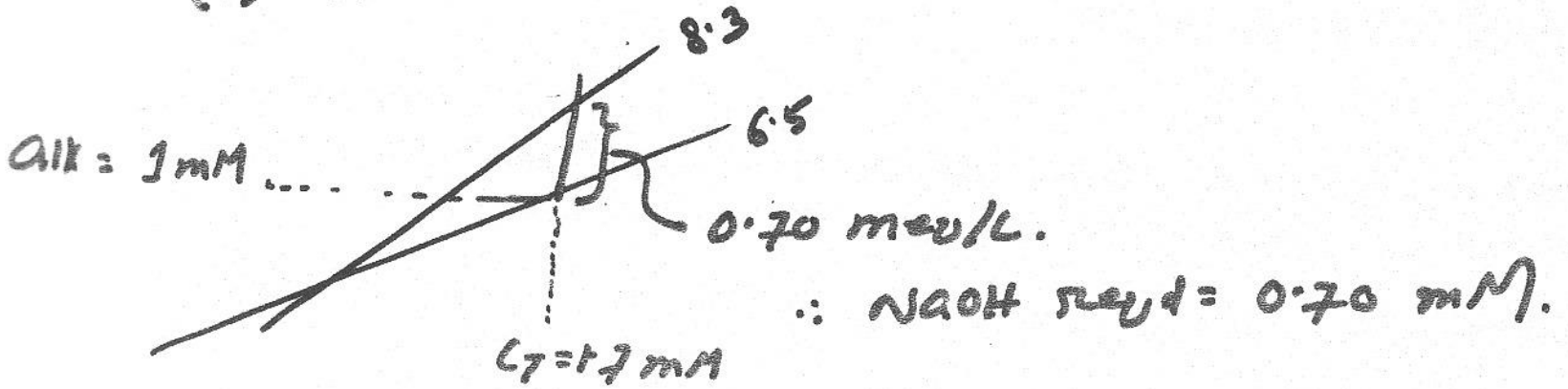
} From Fig 4.5
pH = 6.6
Answer.

Problem Solving using Capacity Diagram

Surface water: pH = 6.5, (Alk) = 1.0 mM } From Capacity diagram, C_T = 1.7 mM

Want to raise pH to 8.3:

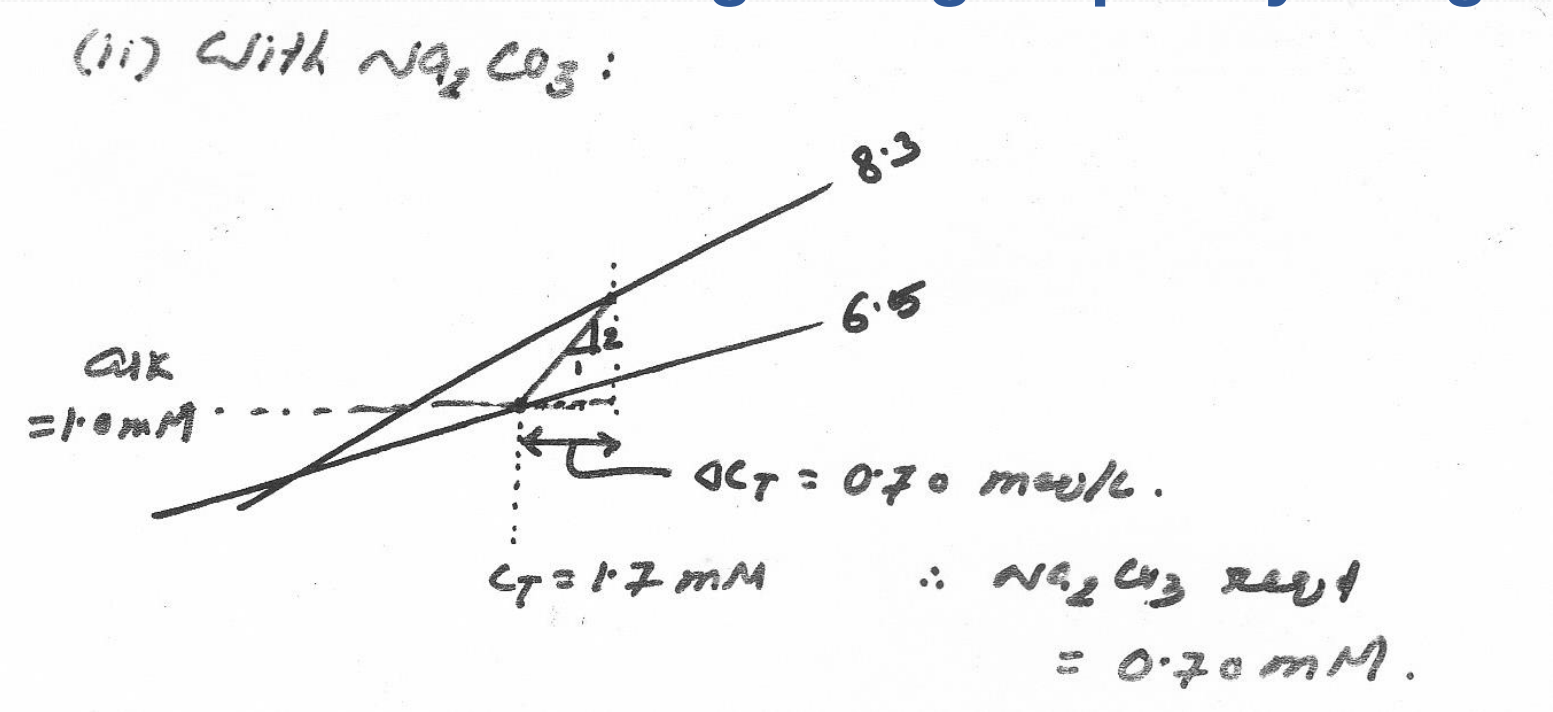
(i) With NaOH:



Note:

- Alkalinity indicates acid neutralizing capacity
- Amount of alkalinity = amount of base (NaOH) required to neutralize acid

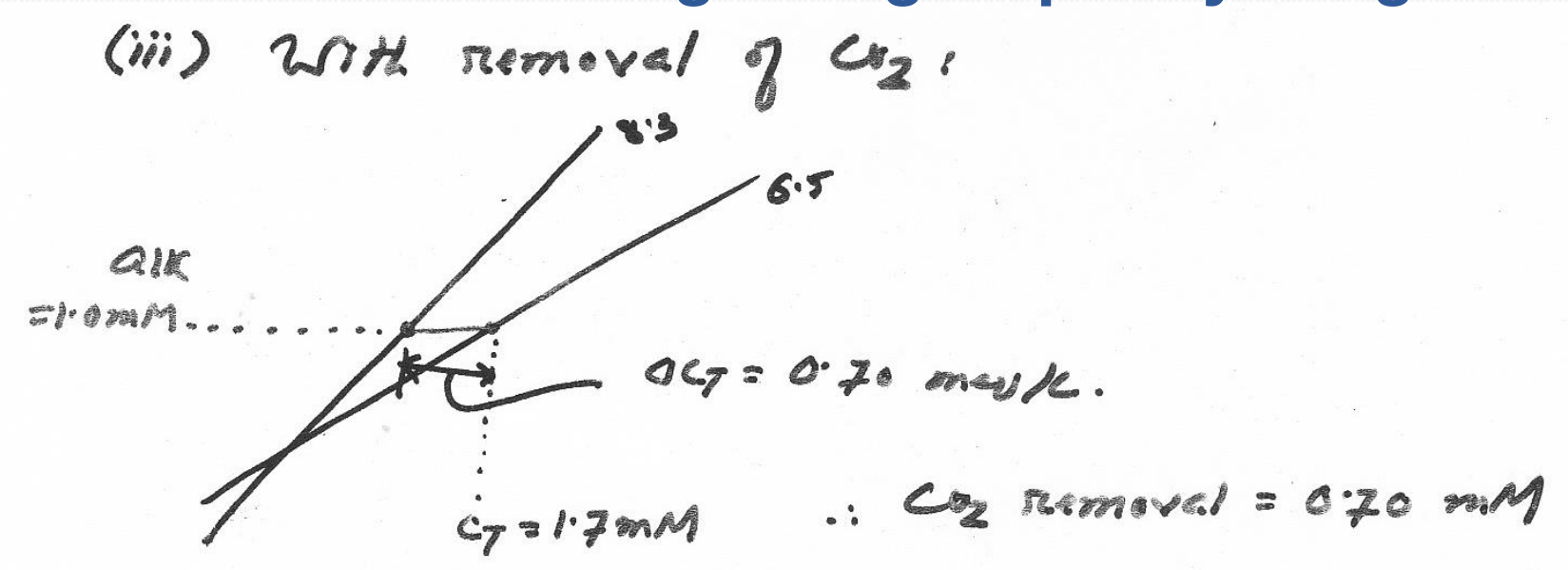
Problem Solving using Capacity Diagram



Note:

- $C_T = H_2CO_3 + HCO_3^- + CO_3^{2-}$
- When Na_2CO_3 is added to water, it will add HCO_3^- and CO_3^{2-} ions to the solution, hence alter the value of C_T. Thus the increase in C_T indicates the amount of Na_2CO_3 added to the solution.

Problem Solving using Capacity Diagram



Note:

- $C_T = H_2CO_3 + HCO_3^- + CO_3^{2-}$
- When CO_2 is removed from water, it will reduce the total decrease in C_T indicates the amount of Na_2CO_2 removed/ withdrawn from the solution.