Acidity

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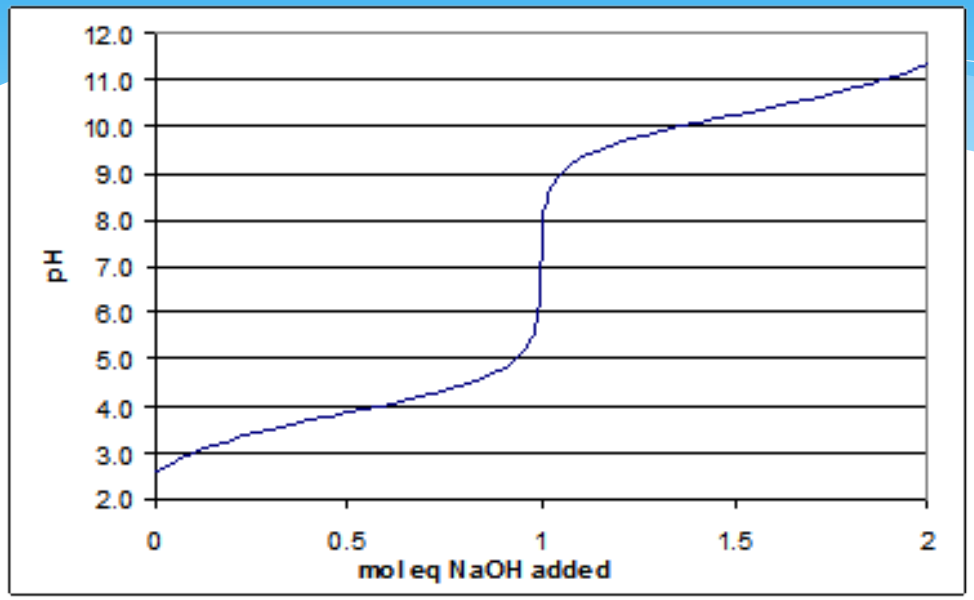
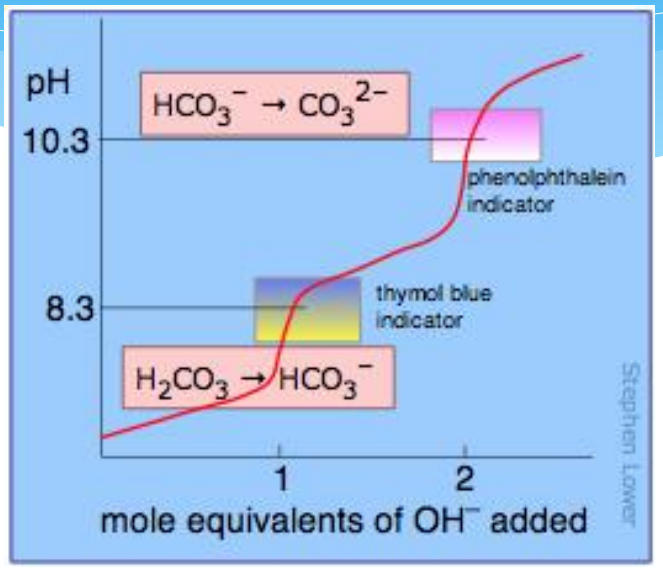
Acidity

* Carbon dioxide / bicarbonate system in waters→buffer
* Acidity is the ability of water to neutralize bases.
* All waters having a pH<8.5 contain acidity

* Phenolphthalein end point is taken as the ref point (8.2-8.4)
* Acidity of natural water is caused by CO_2 or by strong mineral acids.

Carbonic Acid Titration Curve





* @ pH 7 considerable CO_2 remains to be neutralized.
* Carbon dioxide alone will not depress pH below 4
* For strong acid → neutralization is completed@ pH 4

Acidity in water is caused by:

* Carbondioxide
* Strong mineral acids

If there's H_2CO_3 pH doesn't drop below 4

If pH < 4 → Mineral acidity

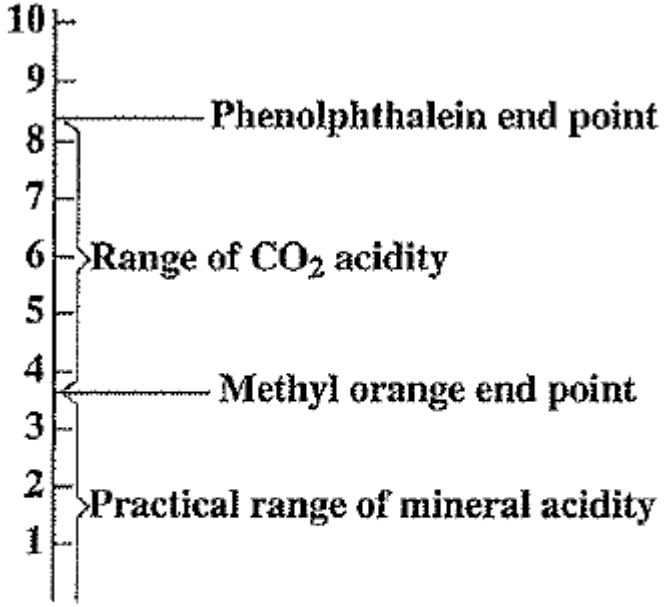


Figure 17.1
Types of acidity of importance in ordinary water and wastewater analysis, and the pH ranges in which they are significant.

Carbondioxide

* Normal component of natural waters
* Enters surface waters by
  * Absorption from atmosphere in accordance with Henry's Law
  * Biological oxidation of organic matter in polluted water

Henry's Law

Henry's Law, Solubility

$[x] = K P_x$ K: mM X(aq) per atm X

Gas	He	Ar	Xe	N_2	O_2	CO_2	NH_3
K	0.4	1.5	4.4	0.7	1.3	30	$> 10^4$

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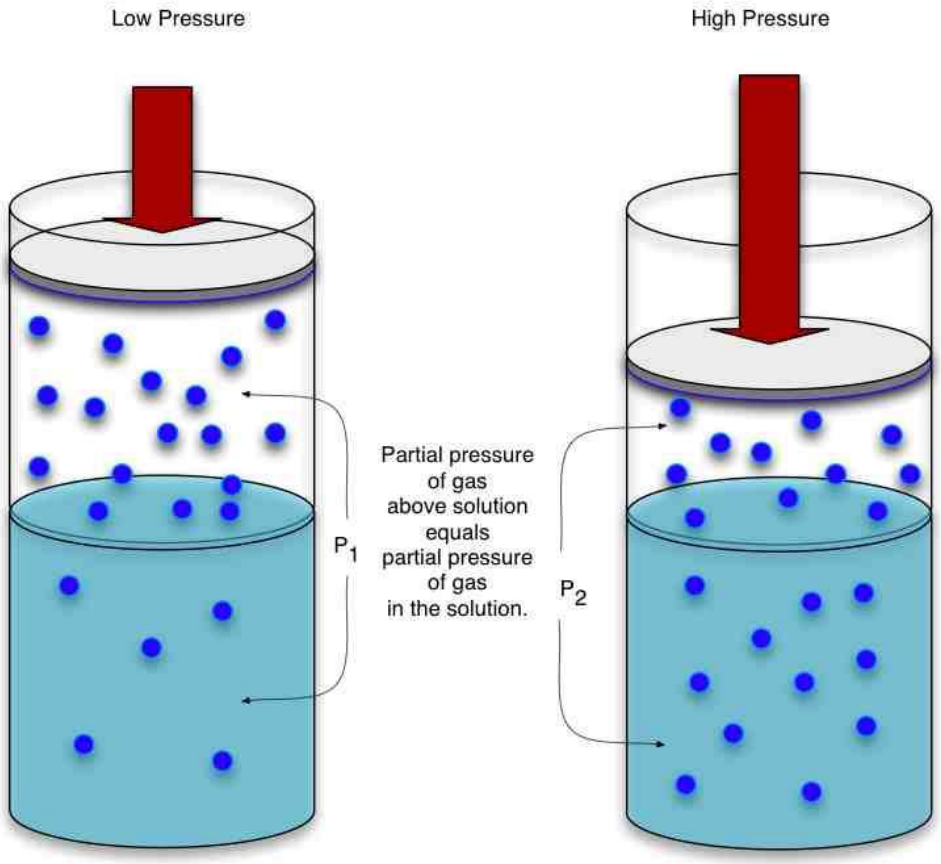
Henry's Law: Solubility of a gas in solution increases as the partial pressre of the gas above the solution increases.



* Groundwaters are high in CO_2 → since it is not free to escape to atmosphere.

30-50 mg /L can be found.

* For groundwater that do not contain Ca, Mg

* Ca, Mg neutralize the CO_2 through formation of bicarbonates.

$$CO_2 + CaCO_3 \rightarrow Ca^{2+} + 2HCO_3$$

Mineral acidity

* Present in many industrial wastewaters
  * Particularly from metallurgical industry
  * Some from the production of synthetic organic compounds
  * Drainage from abondoned mines
  * Salts of heavy metals especially trivalent metal ions (e.g. Fe(III), Al(III) hyrdolize in water to produce mineral acidity

$$FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3(s) + 3H^+ + 3Cl^- \qquad (17.4)$$

Significance of CO_2 and Mineral Acidity

Not very important for public health.

CO_2 in malt and carbonated beverages higher than natural waters.

If water contain mineral acidity

→ unpleasant taste

→ no consumption

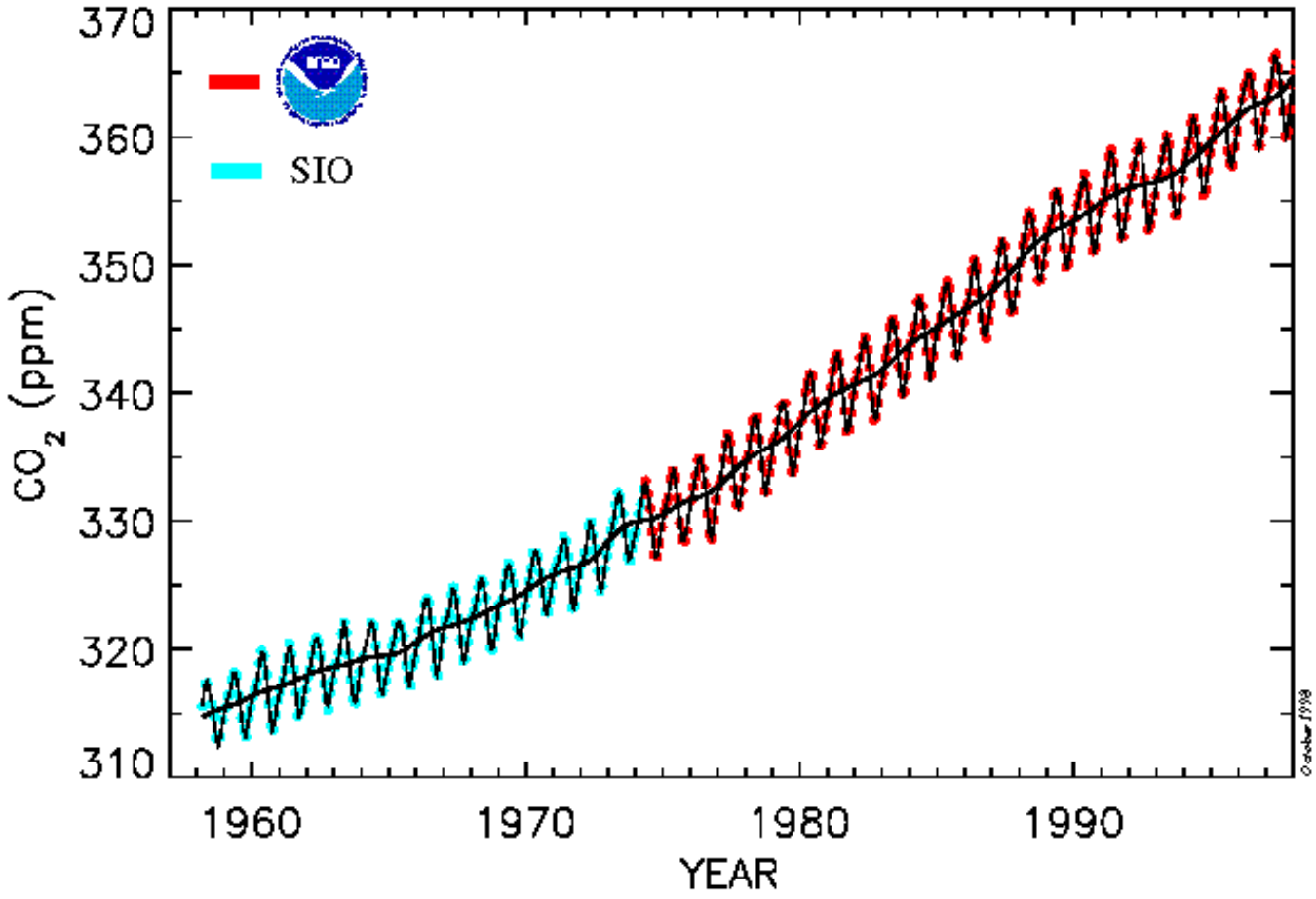
Acidic waters → corrosive characteristics

Corrosive factor in most waters → CO_2

in industrial wastes ; mineral acidity

* CO_2 content is also important in lime-soda ash softening,
* In biological treatment pH must be maintained (6.0-9.5). Amount of chemicals are calculated based on acidity values.
* Combustion of fossil fuels → Nitrogen oxides
  +Sulfur oxides
* When mixed with rain → forms sulfuric and nitric acids.
* Acid rain also cause leaching of chemicals (aluminum) from soil.

- $P_{CO2} = 10^{-3.5}$ yields pH = 5.66
  - What is $10^{-3.5}$? 316 ppm CO_2
- What is today's P_{CO2}? ~368 ppm = $10^{-3.43}$
  - pH = 5.63



pH of Global Precipitation

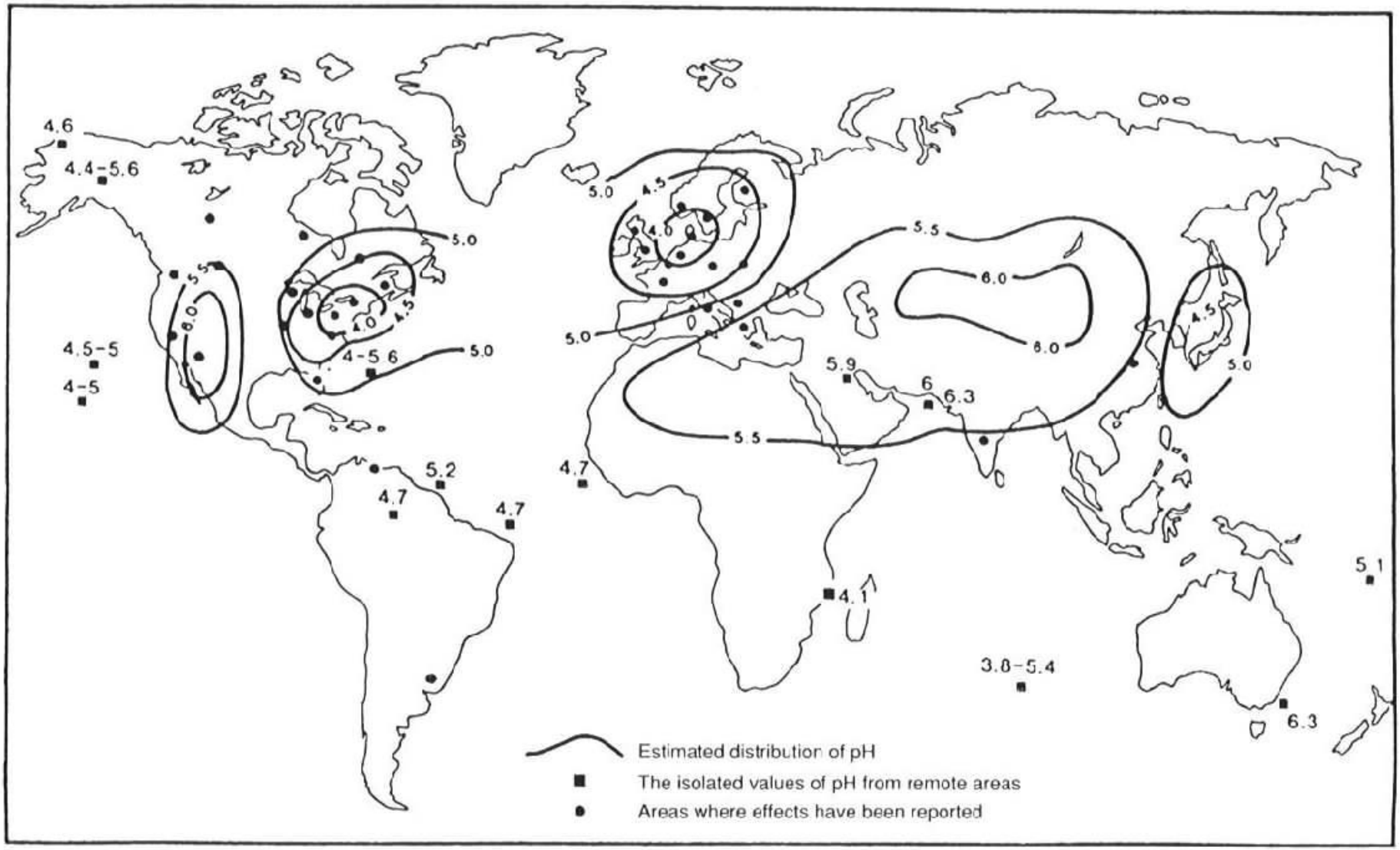


FIGURE 20.19 Map of the global pattern of precipitation acidity as determined by the Background Air Pollution Monitoring Program of the World Meteorological Organization (after Whelpdale and Miller, 1989).

Acidity measurement

* Calculation from pH and alkalinity
* Titration method

Methods of Measurement

* Measured with standard alkaline solutions.
* Mineral acids → Titration to pH 3.7 (methyl orange end point) **(methyl orange acidity)**
* Titration till phenolphthalein end point (pH 8.3) → Mineral acidity + acidity due to weak acids.
* Total acidity → (**phenolphthalein acidity**)

Analysis of CO_2

* Special precautions are required for sample collection, handling, and analysis of CO_2.
* If CO2 is of important consideration→Partial pressure of CO_2 in water is greater that in the atm→avoid exposure to air
* If possible analyze at the point of sampling
* Collect sample by using submerged tubes, fill completely , leave no air pockets → keep the temp. same.

Calculation from pH and Alkalinity

* Amount of CO_2 can be calculated using ionization eqn. for carbonic acid.
* When pH<8.5

$$\frac{[H^+][HCO_3^-]}{[H_2CO_3^*]} = K_{A1} \qquad (17.7)$$

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

$$CO_2 + H_2O \text{ <--> } H_2CO_3$$

* [H2CO3*]=Molar concentration of carbonic acid + Free CO2
* $[H_2CO_3] \cong [CO_2]$ since CO2 is 99% of the total

Example :

$K_{A1} = 4.3*10^{-7}$, $[H^+] = 10^{-7}$, $[HCO_3^-] = 4.3*10^{-3}$

$[CO_2] = 10^{-7}*4.3*10^{-3} / (4.3*10^{-7}) = 10^{-3}$ mol/L

= 44 mg /L

* Limitations of the calculation procedure:
  * Dissolved solids concentration should be shown→gravimteric methods or conductivity
  * pH must be measured very accurately
    * An inaccuracy of 0.1 in pH→carbon dioxide error of 25%

Methyl Orange Acidity

* If pH < 4 → contain mineral (methyl orange) acidity
* Mineral acids are neutralized @ pH 3.7
* Bromphenol blue has sharper color change.
* E.W $_{CaCO_3}$ = 50
* N/50 NaOH is used 1mL = 1 mg acidity
* Results are reported as $CaCO_3$

Phenolphthalein Acidity

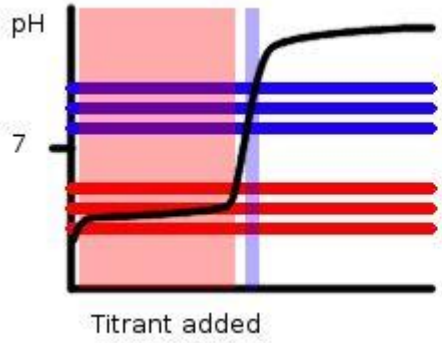
* Total acidity = mineral acidity + from weak acids
* Weak acids are neutralized at pH 8.3
* Phenolphthalein or metacresol purple indicators are used
* Titrant: N/50 NaOH
* Results are expressed as $CaCO_3$.

Application of Acidity Data

* CO_2 determination for public water supplies considered for the selection of treatment methods.
* Corrosion control
* Softening
* Industrial wastes → Mineral acidity must be neutralized before discharge

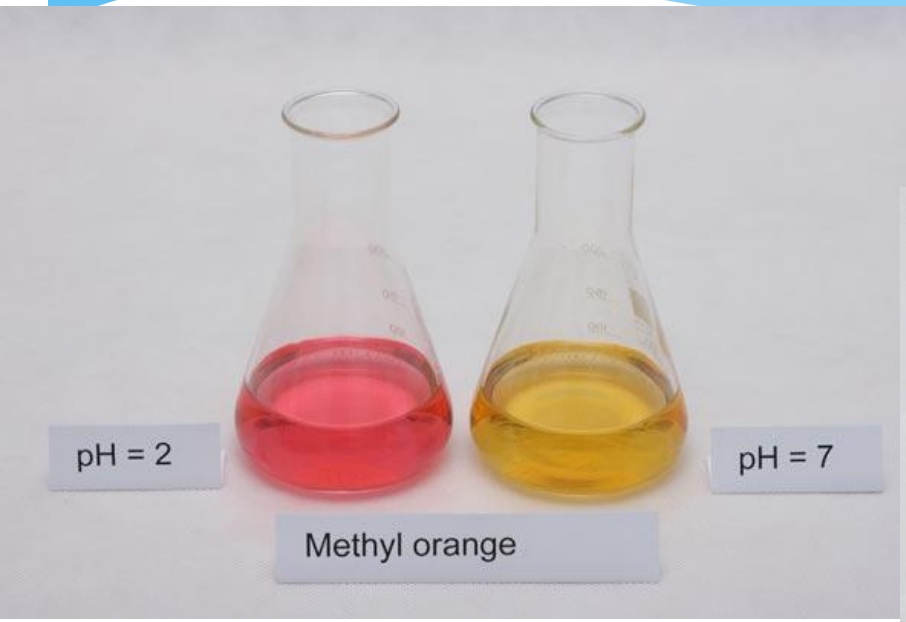
Acidity = $N*V_{titrant}*50*1000 / (\text{ mL sample})$

$E.W_{CaCO_3} = 100/ 2 = 50$ g/eq



The solid horizontal lines show the range of pH in which Phenolphthalein (blue) and Methyl Orange (red) changes color. The middle line represents the pKa while the two outer lines represents the end or start of color change.

The pink and light blue highlight shows the range in which color change will occur based on the amount of titrant added.



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Phenolphtalein endpoint