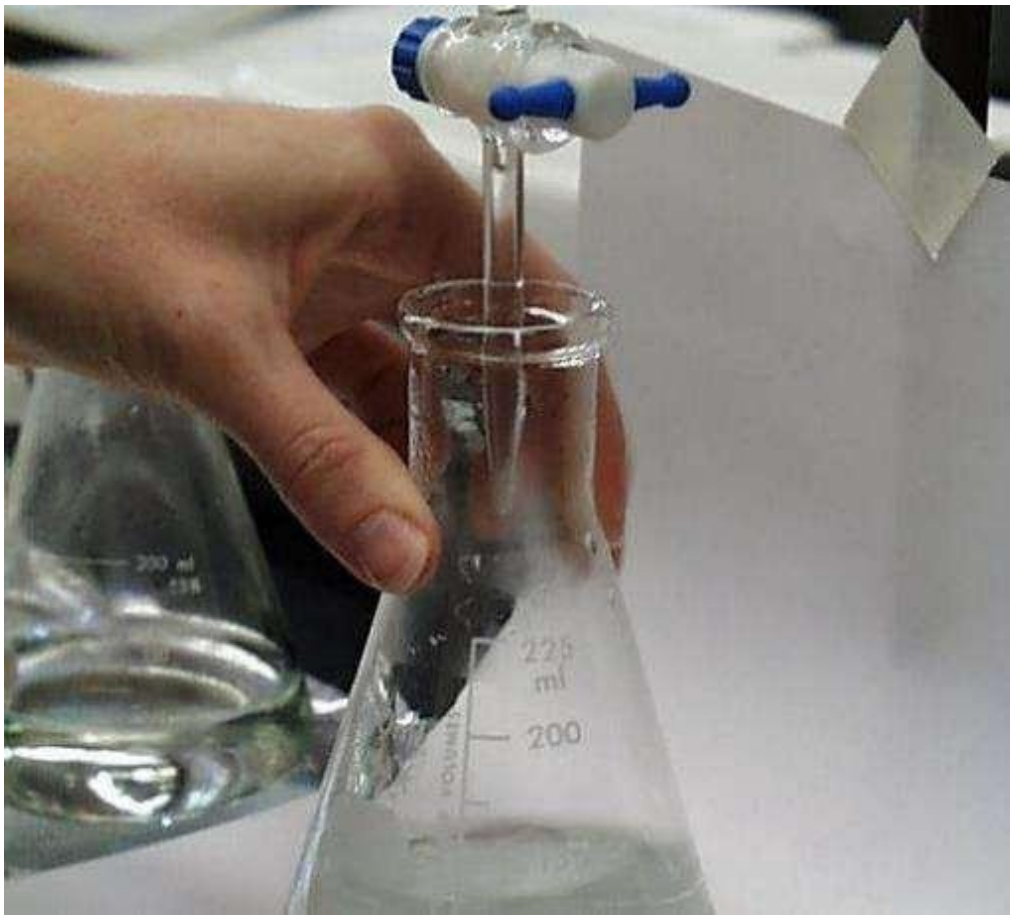
Experiment 5
Determination of CO_2 in water



Introduction:

Carbon Dioxide is present in water in the form of a dissolved gas. Surface waters normally contain less than 10 ppm free carbon dioxide, while some ground waters may easily exceed that concentration. Carbon dioxide is readily soluble in water. Over the ordinary temperature range (0-30°C) the solubility is about 200 times that of oxygen. Calcium and magnesium combine with carbon dioxide to form carbonates and bicarbonates.

Carbon dioxide does dissolve in water; however, the system is somewhat complex. First, the CO_2 dissolves according to:

CO_2 (g) = CO_2 (l)

At room temperature, the solubility of carbon dioxide is about 90 cm^3 of CO_2 per 100 ml of water (c_l/c_g = 0.8). Any water-soluble gas becomes more soluble as the temperature decreases, due to the thermodynamics of the reaction:

GAS (l) = GAS (g)

This effect is particularly large for gases like CO_2 that undergo specific reactions with water. Equilibrium is established between the dissolved CO_2 and H_2CO_3, carbonic acid.

CO_2 (l) + H_2O (l) = H_2CO_3 (l)

Carbonic acid is a weak acid that dissociates in two steps.

$$H_2CO_3 + H_2O \Leftrightarrow H_3O^+ + HCO_3^-$$
$$HCO_3^- + H_2O \Leftrightarrow H_3O^+ + CO_3^{2-}$$

The test for the determination of free carbon dioxide in water is based on the titration of a water sample with standard Sodium Hydroxide solution in the presence of phenolphthalein indicator. The CO_2 reacts with NaOH to form Sodium Bicarbonate with a consequent increase in pH. The reaction of NaOH with free CO_2 reaches completion at a pH of 8.3.

$$CO_2 + H_2O = H_2CO_3$$
$$H_2CO_3 + NaOH = HCO_3^- + Na^+ + H_2O$$
$$HCO_3^- + NaOH = CO_3^{2-} + Na^+ + H_2O$$

Environmental significance:

Aquatic plant life depends upon carbon dioxide and bicarbonates in water for growth. Microscopic plant life suspended in the water, phytoplankton, as well as large rooted plants, utilize carbon dioxide in the photosynthesis of plant materials; starches, sugars, oils, and proteins. The carbon in all these materials comes from the carbon dioxide in water.

When the oxygen concentration in waters containing organic matter is reduced, the carbon dioxide concentration rises. The rise in carbon dioxide makes it more difficult for fish to use the limited amount of oxygen present. To take on fresh oxygen, fish must first discharge the carbon dioxide in their blood streams and this is a much slower process when there are high concentrations of carbon dioxide in the water itself.

Corrosion is the principal difficulty caused by carbon dioxide. This gas on solution in water produces carbonic acid, resulting in lowering of pH. With a decrease in pH, corrosive characteristics is induced in water, resulting in severe corrosion of heat exchanger, pipes, valves etc. Corrosion in boiler system takes place due to the presence of carbonate and bicarbonate although Carbon dioxide is not present in this case.

Guidelines:

Bangladesh Environment Conservation Rules (2023) does not set any limits for the presence of CO_2 in water.

Precaution:

Since excess CO_2, if present in water, easily escapes to the atmosphere, tests for presence of CO_2 in water should be performed immediately after collection of water sample, especially for ground water samples which usually contain high CO_2. If this is not possible, the sample bottle should be completely filled and capped and the sample should be kept at a temperature lower than that at which it was collected.

Where the free CO_2 of the water sample is high, there may be some loss of CO_2 to the atmosphere during the titration process. To check this, it is advisable to secure a second sample. Upon complete determination of CO_2 on the first sample, then take the second sample (100ml) and immediately add the full amount of N/44 sodium hydroxide solution used in the titration of the first sample. Add 10 drops of phenolphthalein indicator and if the sample remain colourless, add additional N/44 sodium hydroxide to the end point (till the slight pink colour appears) and accepting this second test as more accurate titration.

Apparatus:

1. Beaker
2. Measuring cylinder
3. Dropper
4. Stirrer
5. Burette

Reagent:

1. Standard N/44 Sodium Hydroxide
2. Phenolphthalein Indicator **

**An indicator is a substance that undergoes a change in color when the end-point of a titration is reached. Acid-base indicators are used to signal the end of acid-base titrations. An acid-base indicator is itself a weak acid (or its conjugate base).

Phenolphthalein is a commonly used indicator for titrations, and is a weak acid. The weak acid is colorless and its ion is bright pink. Adding extra hydrogen ions shifts the position of equilibrium to the left, and turns the indicator colorless. Adding hydroxide ions removes the hydrogen ions from the equilibrium which tips to the right to replace them - turning the indicator pink. The half-way stage happens at pH 8.3. Since a mixture of pink and colorless is simply a paler pink, this is difficult to detect with any accuracy.

Procedure:Take a 100 ml of sample in a beaker and add 10 drops of Phenolphthalein indicator. If a pink color develops, no carbon dioxide is present in the water sample.

1. Add N/44 sodium Hydroxide solution from a burette to the sample and stir gently until a slight permanent pink color appears as compared with distilled water. Record ml of sodium hydroxide used. Since excess CO_2, if present easily escapes to atmosphere, so tests should be performed immediately after collection of water sample. If this is not possible sample bottle should be completely filled and stoppered and be kept at a temperature lower than that at which it was collected.

Calculation:

Carbon dioxide (mg/L) =mL of N/44 NaOH used x Multiplying Factor (M.F.)

Where, M.F. = $\frac{Normality\ of\ NaOH \times Equivalent\ wt.of\ \mathrm{CO2} \times 1000}{mL\ of\ sample\ taken}$

Determination of CO_2 acidity:

Phenolphthalein acidity (often called CO_2 acidity) of water is defined as the amount of standard base (usually 1/50 N NaOH) required raising the pH of a sample of water to the phenolphthalein end point of 8.3. CO_2 acidity is expressed as $CaCO_3$ (calcium carbonate) required to neutralize H_2CO_3)

Hence, Acidity could be easily determined from the results of CO_2 determination as follows:

Phenolphthalein Acidity as mg/L $CaCO_3$ = $\mathrm{CO_2\,(mg/L)} \times \frac{50}{44}$

Assignment Questions:

1. Discuss the environmental significance of CO_2.
2. Why does groundwater contain higher carbon dioxide than surface water?
3. Why test for Carbon dioxide should be performed immediately after collection of water ?