Supplementary Textual Material

in

Chemistry

for

Class XI
&
Class XII

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Unit 5: States of Matter

5.7.1 KINETIC ENERGY AND MOLECULAR SPEEDS

As you have studied in the previous section the molecules of a gas are always in motion and are colliding with each other and with the walls of the container. Due to these collisions the speeds and the kinetic energies of the individual molecules keep on changing. However at a given temperature, the average kinetic energy of the gas molecules remains constant.

If at a given temperature, n_1 molecules have speed v_1, n_2 molecules have speed v_2, n_3 molecules have speed v_3, and so on. Then, the total kinetic energy (E_K) of the gas at this temperature is given by

$$E_K = \frac{1}{2} m \left(n_1 v_1^2 + n_2 v_2^2 + n_3 v_3^2 + \ldots\ldots\right)$$

where m is the mass of the molecule.

The corresponding average kinetic energy ($\overline{E_K}$) of the gas will be

$$\overline{E_K} = \frac{1}{2} \frac{m \left(n_1 v_1^2 + n_2 v_2^2 + n_3 v_3^2 + \ldots\ldots\right)}{\left(n_1 + n_2 + n_3 + \ldots\ldots\right)}$$

If the following term

$$\frac{\left(n_1 v_1^2 + n_2 v_2^2 + n_3 v_3^2 + \ldots\ldots\right)}{\left(n_1 + n_2 + n_3 + \ldots\ldots\right)} = c^2$$

Then the average kinetic energy is given by

$$\overline{E_K} = \frac{1}{2} m c^2$$

where *c* is given by

$$c = \sqrt{\frac{(n_1v_1^2 + n_2v_2^2 + n_3v_3^2 + \dots\dots\dots)}{(n_1 + n_2 + n_3 + \dots\dots\dots)}}$$

This *'c'* is known as **root-mean-square speed.** As the name implies, to calculate *c,* first take the squares of the individual speeds, then their mean and finally the square root of the mean.

It can be shown that c is related to temperature by

$$c = \sqrt{\frac{3RT}{M}}$$

The average kinetic energy depends only on absolute temperature and is related to absolute temperature by the expression

$$\overline{E_K} = \frac{3RT}{2N_A} = \frac{3}{2}kT$$

where k = Boltzmann constant = 1.38×10^{-23} J K^{-1}

In the case of gases, one also talks of two other speeds, namely, average speed and most-probable speed.

The **average speed ($\bar{c}$)** at a given temperature is the arithmetic mean of the speeds of different molecules of the gas. i.e,

$$\bar{c} = \frac{(n_1v_1 + n_2v_2 + n_3v_3 \dots\dots)}{(n_1 + n_2 + n_3 + \dots\dots\dots)}$$

where n_1 molecules have speed v_1, n_2 molecules have speed v_2, n_3 molecules have speed v_3, and so on.

The relationship between average speed and temperature T is given by

$$\bar{c} = \sqrt{\frac{8RT}{\pi M}}$$

The **most probable speed (c^*)** of a gas at a given temperature is the speed possessed by the maximum number of molecules at that temperature. Unlike average speed and root mean square speed, the most probable speed cannot be expressed in terms of the individual molecular speeds.

The most probable speed (c^*) is related to absolute temperature (T) by the expression

$$c^* = \sqrt{\frac{2RT}{M}}$$

Relationship between different types of molecular speeds

The three types of molecular speeds, namely, most probable speed (c^*), average speed ($\bar{c}$) and root mean square speed (c) of a gas at a given temperature are related to each other as follows:

$$c^* : \bar{c} : c = \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}}$$

$$c^* : \bar{c} : c = 1.414 : 1.596 : 1.732$$

$$c^* : \bar{c} : c = 1 : 1.128 : 1.224$$

For a particular gas, at a particular temperature,

$$c^* > \bar{c} > c$$

It follows from the above relationships that

$$Average\ speed\ (\bar{c}) = 0.921 \times Root\ mean\ square\ speed\ (c)$$

$$Most\ probable\ speed\ (c^*) = 0.817 \times Root\ mean\ square\ speed\ (c)$$

Example:
Calculate the root mean square, average and most probable speeds of oxygen molecules at 27 ^{o}C.

Solution:

Given data:
Molar mass of oxygen, M = 32 g mol^{-1} = 0.032 kg mol^{-1}
Temperature, t = 27 ^{o}C ⇒ *T* = (27 + 273) K = 300 K

Expressions to be used:

Root mean square speed, $c = \sqrt{\frac{3RT}{M}}$

Average speed, $\bar{c} = \sqrt{\frac{8RT}{\pi M}}$

Most probable speed, $c^* = \sqrt{\frac{2RT}{M}}$

Actual calculations

Root mean square speed,

$$c = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3(8.314\,\mathrm{J\,K^{-1}mol^{-1}})(300\,\mathrm{K})}{(0.032\,\mathrm{kg\,mol^{-1}})}} = 483.6\ \mathrm{m\,s^{-1}}$$

Average speed,

$$\bar{c} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8(8.314\,\mathrm{J\,K^{-1}mol^{-1}})(300\,\mathrm{K})}{(3.14)(0.032\,\mathrm{kg\,mol^{-1}})}} = 445.6\ \mathrm{m\,s^{-1}}$$

Most probable speed,

$$c^* = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2(8.314\,\mathrm{J\,K^{-1}mol^{-1}})(300\,\mathrm{K})}{(0.032\,\mathrm{kg\,mol^{-1}})}} = 394.8\ \mathrm{m\,s^{-1}}$$

5.7.2 MAXWELL-BOLTZMANN DISTRIBUTION OF MOLECULAR SPEEDS

The speeds of the individual molecules of a gas do not remain constant. They keep on changing due to inter molecular collisions and due to collisions with the walls of the container. However, at a given temperature, the distribution of molecular speeds remains constant. This distribution of molecular speeds is given by Maxwell-Boltzmann distribution law.

For a given gas, at a given temperature, the distribution curve of molecular speeds is shown in Figure 5.7.1

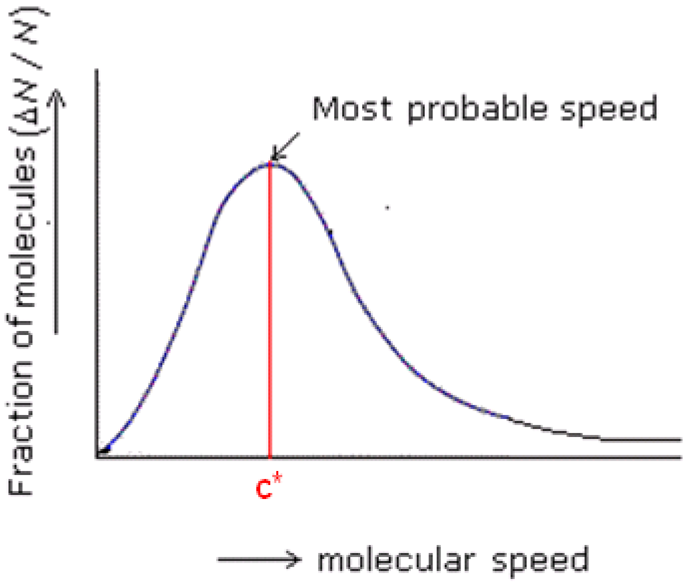

Figure 5.7.1. Maxwell Boltzmann distribution curve

You can see from the distribution curve that it is the plot of molecular speed vs the fraction of molecules. The important features of this distribution curve are:

(i) The fraction of molecules having too low or too high speeds is very small.

(ii) There is a certain speed for which the fraction of molecules is maximum. This speed is known as **most probable speed**.

(iii) The most probable speed of a gas, is the speed possessed by the maximum number of molecules of the gas at a given temperature and it corresponds to the peak of the curve.

Since the most probable speed (c^*) is related to absolute temperature T by the expression

$$c^* = \sqrt{\frac{2RT}{M}}$$

It means that at the same temperature, lighter gases shall move faster than heavier gases as is evident from the distribution curves of chlorine and nitrogen gases in Figure 5.7.2.

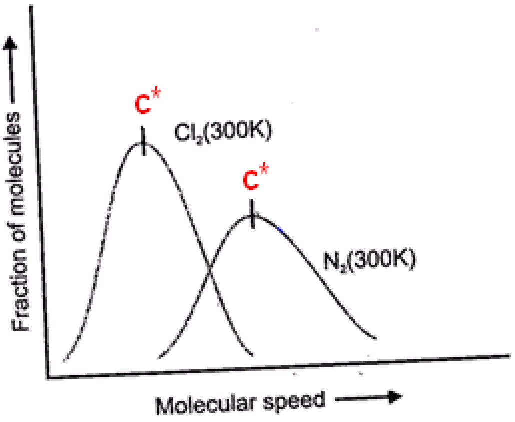

Figure 5.7.2. Maxwell Boltzmann distribution curves for chlorine and nitrogen gases at 300K

Effect of temperature

In Figure 5.7.3.are given the Maxwell Boltzmann distribution curves of a gas at three different temperatures T_1, T_2 and T_3 such that $T_1>T_2>T_3$.

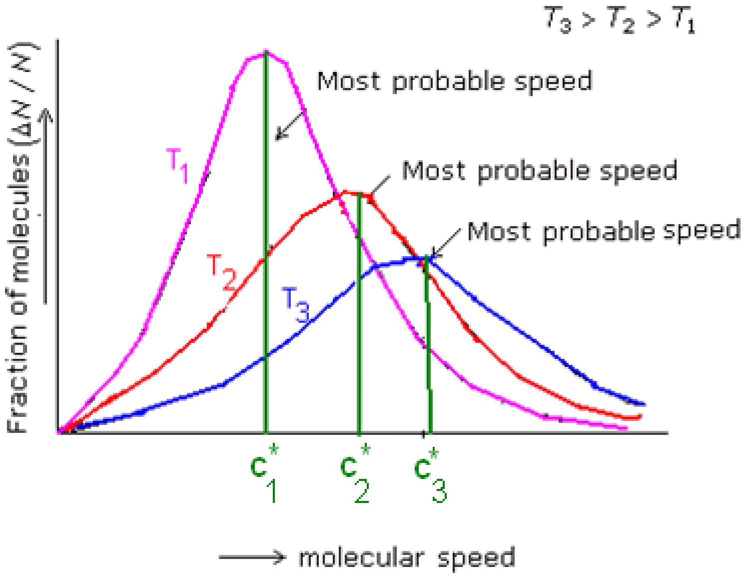

Figure 5.7.3. Maxwell Boltzmann distribution curves for a gas at three different temperatures

It can be seen from these distribution curves that as the temperature increases

1. The entire curve shifts towards right.
2. The most probable speed increases.
3. The fraction of molecules having most probable speed decreases.
4. The curve becomes broader in the middle range indicating that more molecules have speeds near to the most probable speed.
5. The fraction of molecules having higher speeds increases.
6. The fraction of molecules having lower speed decreases.

It may be noted that the total area under each of the curves remains the same as the sum of fractions of molecules remains unaltered on changing the temperature.

EXERCISE

1. Calculate (i) root mean square speed (ii) average speed and (iii) most probable speed of CO_2 molecules at 700 K .
2. A sample of a gas contains 15 molecules with a speed of 3 m s^{-1}, 25 molecules with a speed of 5 m s^{-1} and 30 molecules with a speed of 8 m s^{-1}. Calculate root mean square speed of these molecules.
3. Calculate the temperature at which the average speed of oxygen equals that of hydrogen at 20 K.
4. Calculate the temperatures at which the root mean square speed, average speed and the most probable speed of oxygen gas are all equal to 1500 m s^{-1}.

Answers

1. i. 629.92, m s^{-1} ii. 580.50 m s^{-1} iii. 514.33 m s^{-1}
2. 6.187 m s^{-1}
3. 320 K
4. T for root mean square speed= 2886 K,
   T for the average speed = 3399 K,
   T for most probable speed = 4330 K

Unit 6 : Thermodynamics

6.6.1 SECOND LAW OF THERMODYNAMICS

You have already studied in the previous sections that the first law of thermodynamics deals only with the law of conservation of energy and it gives no information about the criteria for feasibility of a given physical or chemical process. This law is always obeyed whether a given process occurs on its own or is made to occur with the help of an external agency. In any case the first law is valid in both the forward and reverse direction of the process. You have also learnt about the concept of entropy which is a measure of the randomness or the disorder in a system. This concept helps in explaining the spontaneity of the irreversible processes. For an irreversible process, the entropy of the system and surroundings taken together i.e. of the universe increases, while for a process at equilibrium it remains constant. This conclusion is of great importance as it helps us to predict whether a given process can take place spontaneously or not. Since all processes in nature occur spontaneously i.e. irreversibly, it follows that the entropy of the universe is increasing continuously.

This important statement i.e. "*in any spontaneous process, the entropy of the universe (system and surroundings) always increases*" is also known as **the second law of thermodynamics.**

$$\Delta \mathbf{S}_{\text{Universe}} = \Delta \mathbf{S}_{\text{system}} + \Delta \mathbf{S}_{\text{surroundings}}$$

Specifically it means that

If $\Delta \mathbf{S}_{\text{Universe}} > 0$, the reaction is spontaneous

If $\Delta \mathbf{S}_{\text{Universe}} < 0$, the reaction is non-spontaneous

If $\Delta \mathbf{S}_{\text{Universe}} = 0$, the reaction is at equilibrium

Since chemists are generally more interested in the system (reaction mixture) than the surroundings, it is therefore more convenient to restate the second law in terms of the thermodynamic properties of the system, without regard to the surroundings. As already described in the previous section, this is possible through the Gibbs free energy G which for a system is defined as **$G = H - TS$**. In terms of this thermodynamic property, the **second law of thermodynamics** can be restated as *in any spontaneous process at* *constant temperature and pressure, the free energy of the system (*ΔG_{system}*) always decreases.* According to this definition

If $\Delta G_{system} < 0$, the reaction is spontaneous

If $\Delta G_{system} > 0$, the reaction is non-spontaneous

If $\Delta G_{system} = 0$, the reaction is at equilibrium

6.8. THIRD LAW OF THERMODYNAMICS

The third law of thermodynamics is concerned with determination of entropy. It states that **a substance which is perfectly crystalline at absolute zero of temperature has an entropy of zero.** In a perfect crystal at absolute zero of temperature, each constituent of the crystal (atom, molecule or ion) is at the proper crystal lattice site and it therefore has the lowest energy. This means that this particular state is of perfect order, i.e, has zero disorder and hence zero entropy.

Using zero value of entropy at absolute zero for a perfectly crystalline substance as the reference point (initial state), one can calculate absolute value of entropy of the substance in any state (solid, liquid or gas) at any temperature by calculating ΔS for the process/es in going from the initial state to the state of the substance for which entropy is to be calculated.

However there are certain substances which possess certain entropy even at absolute zero. This entropy is known as **residual entropy**. The origin of residual entropy can be explained on the basis of the disorder which remains at absolute zero in certain crystals composed of AB types of molecules where A and B are similar atoms (as in CO). In such substances, there is a very little energy difference between "…AB AB AB…" and "..…AB BA BA AB….." and other arrangements so that the molecules adopt the orientations AB and BA at random in the solid. This gives rise to some disorder, also known as *frozen disorder,* and consequently residual entropy. For example in case of CO, the measured residual entropy is 5 J K^{-1} mol^{-1} which is close to the value expected for a random structure Figure 1 (B) of the form "……CO CO OC CO CO OC OC…".

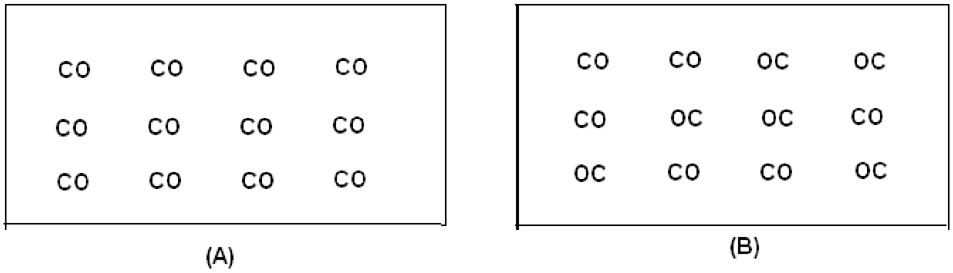

Figure 1. Alternative molecular arrangements for CO (A) Perfect crystal (B) Actual crystal

EXERCISE

1. State Second Law of Thermodynamics.

2. Write the conditions in terms of ΔH and ΔS when a reaction would be always spontaneous.

3. When $\Delta H > 0$ and $\Delta S < 0$, a reaction is never spontaneous. Explain.

4. Comment on the spontaneity of a reaction at constant temperature and pressure in the following cases
   (*i*) $\Delta H < 0$ and $\Delta S > 0$
   (ii) $\Delta H > 0$ and $\Delta S < 0$
   (iii) $\Delta H < 0$ and $\Delta S < 0$
   (iv) $\Delta H > 0$ and $\Delta S > 0$

5. State third law of thermodynamics.

6. Explain the term residual entropy.

Unit 7: Equilibrium

7.12.1 pH OF BUFFER SOLUTIONS : HENDERSON - HASSELBALCH EQUATION

As you have already learnt in the previous section a buffer solution is a solution which resists change in its pH on the addition of small amount of acid or a base. Most of the important buffer solutions generally consist of mixtures of weak acids and their salts or weak bases and their salts. These buffer solutions are known as **acidic buffers** and **basic buffers** respectively. If the pH of the buffer solution is less than 7, it is called an acidic buffer and if the pH of the buffer solution is greater than 7 it is called a basic buffer. Examples of some acidic and basic buffers are as given below

Acidic buffer	**Basic buffer**
1) Acetic acid and sodium acetate	1) Ammonium hydroxide and ammonium chloride
2) Formic acid and sodium formate	2) Ammonium hydroxide and ammonium nitrate

pH of an acidic buffer

A very common example of an acidic buffer is a mixture of acetic acid and sodium acetate. Acetic acid, being a weak acid, is very slightly dissociated, while sodium acetate being a salt is completely dissociated. The mixture thus contains acetic acid molecules as well acetate ions and sodium ions.

At equilibrium:

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

$$[H^+] = K_a \frac{[CH_3COOH]}{[CH_3COO^-]}$$

Taking the negative logarithm on both the sides, we get

$$-\log[H^+] = -\log K_a - \log\frac{[CH_3COOH]}{[CH_3COO^-]}$$

$$pH = pK_a - \log\frac{[CH_3COOH]}{[CH_3COO^-]}$$

$$pH = pK_a + \log\frac{[CH_3COO^-]}{[CH_3COOH]} \qquad \text{…………………(7.39)}$$

In general,

$$pH = pK_a + \log\frac{[Salt]}{[Acid]} \qquad \text{……………………(7.40)}$$

It may be noted that the concentration of the acetate ions is taken to be almost equal to the concentration of the salt because the acetate ions coming from fully dissociated salt (here sodium acetate) suppress the ionization of the weak acid (acetic acid).

This equation (7.40) is called ***Henderson- Hasselbalch equation.*** According to this equation, the pH of an acidic buffer consisting of a mixture of a weak acid and its salt depends on the pK_a of the acid, and the concentrations of the salt and acid in the mixture.

If concentration of the salt is equal to that of the acid, then $pH = pK_a$

Buffer action of Acidic buffer

The buffer action of an acidic buffer consisting of a mixture of acetic acid and sodium acetate can be explained in the following way. If we add small amount of HCl to the buffer solution it will ionise to give H^+ ions. These combine with CH_3COO^- ions to form weakly ionized acetic acid.

$CH_3COO^-(aq) + H^+(aq) \rightarrow CH_3COOH(aq) + H_2O(l)$

Since H^+ ions get neutralised by CH_3COO^- ions, there will be no change in pH. On the other hand, if we add a few drops of NaOH to the buffer solution, it provides OH^- ions which are neutralized by the acetic acid present in the mixture.

$OH^-(aq) + CH_3COOH(aq) \rightarrow CH_3COO^-(aq) + H_2O(l)$

Therefore the pH of the solution remains unchanged.

pH of a Basic Buffer

A very common example of a basic buffer is a mixture of ammonium hydroxide and ammonium chloride. Ammonium hydroxide being a weak base is very slightly dissociated, while ammonium chloride being a salt is completely dissociated. The mixture thus contains ammonium hydroxide molecules as well as ammonium ions and chloride ions.

At equilibrium,

$NH_4OH(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$$

$$[OH^-] = K_b \frac{[NH_4OH]}{[NH_4^+]}$$

Taking the negative logarithm on both the sides, we get

$$-\log[OH^-] = -\log K_b - \log\frac{[NH_4OH]}{[NH_4^+]}$$

$$pOH = pK_b - \log\frac{[NH_4OH]}{[NH_4^+]}$$

$$pOH = pK_b + \log\frac{[NH_4^+]}{[NH_4OH]} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(7.41)$$

In general,

$$pOH = pK_b + \log\frac{[Salt]}{[Base]} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(7.42)$$

It may be noted that the concentration of the ammonium ions is taken to be almost equal to the concentration of the salt because ammonium ions coming from the fully dissociated salt (here ammonium chloride) suppress the ionization of the weak base ammonium hydroxide. This equation (7.42) is called ***Henderson- Hasselblach equation.***

Further, pH can be calculated easily from pOH using

$$pH + pOH = 14$$

Hence,

$$pH = 14 - pK_b - \log\frac{[Salt]}{[Base]}$$

$$pH = pK_a + \log\frac{[Base]}{[Salt]}$$

It may be noted that $pK_a + pK_b = 14$

Buffer action of basic buffer

The buffer action of a basic buffer consisting of a mixture of ammonium hydroxide and ammonium chloride can be explained in the following way. If a few drops of HCl are added to the buffer solution, it will ionise to give H^+ ion which will combine with OH^- ions to form H_2O.

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

Therefore, the addition of HCl will not change the pH. On the other hand, when a few drops of NaOH solution are added to the buffer solution, it would give OH^- ions. These OH^- ions combine with NH_4^+ ions present in the solution to form NH_4OH, which is only slightly ionised.

$$OH^-(aq) + NH_4^+(aq) \rightarrow NH_4OH(aq)$$

Hence, the addition of a base also will not change the pH.

EXERCISE

1. A certain buffer is made by mixing sodium formate and formic acid in water. With the help of equations explain how this buffer neutralizes addition of a small amount of an acid or a base.

2. A basic buffer is made by mixing ammonium hydroxide and ammonium nitrate in water. Explain how this buffer resists change in its pH on addition of a small amount of an acid or a base.

3. What would be the pH of a solution obtained by mixing 10 g of acetic acid and 15 g of sodium acetate and making the volume equal to 1 L. Dissociation constant of acetic acid at $25^{o}C$ is 1.75×10^{-5}.

4. A buffer solution contains 0.40 mol of ammonium hydroxide and 0.50 mol of ammonium chloride to make a buffer solution of 1 L. Calculate the pH of the resulting buffer solution. Dissociation constant of ammonium hydroxide at $25^{o}C$ is 1.81×10^{-5}.

Answers

3. pH = 4.80
4. 9.161

Class XII

Unit 16: Chemistry in Everyday Life

16. 4.2.1. ANTIOXIDANTS

Antioxidants are one of the important and necessary food additives. These compounds retard the action of oxygen on food thus reducing its speed of decomposition by oxidation. Hence they help in the preservation of food. These act as sacrificial materials, i.e. these are more reactive towards oxygen than are the materials they are protecting. They also reduce the rate of involvement of free radicals in the aging process.

Examples: The two most familiar antioxidants used are butylated hydroxy toluene (BHT) and butylated hydroxy anisole (BHA) (Figure 1). These phenolic compounds are added to preserve fats in packaged food. Oxygen reacts preferentially with BHA or BHT rather than oxidizing fats or oils, thereby protecting them from spoilage. The addition of BHA to butter increases its storage life from months to years. Sometimes, BHT and BHA are added in combination with citric or ascorbic acids to produce a more active synergetic effect.

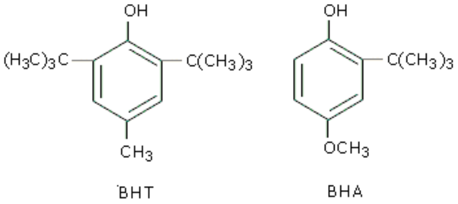

Figure 1: Butylated hydroxy toluene (BHT) and butylated hydroxy anisole (BHA)

Sulphur dioxide and sulphites (such as sodium sulphite, sodium bisulphite and sodium metabisulphite) are useful antioxidants for wine and beers, sugars syrups and cut, peeled or dried fruits and vegetables. They prevent or reduce their discoloration.

EXERCISE

1. Name one antioxidant commonly used to increase the storage life of butter.
2. Name one antioxidant used in wine and beers.