

CHEMISTRY

M.Sc Sem-2

Unit 1: Nuclear Chemistry

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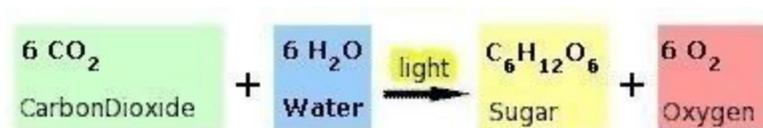
Tracer Technique

Radioactive isotopes have been found to be highly useful in understanding the mechanism of certain reactions as well as certain processes in the medicine industry, agriculture, biology etc. The technique employed is known as pressure technique and the radioactive isotope used for such works are known as tracers or labelled elements.

The tracer elements are mixed with the ordinary compounds and their presence is later on detected by sensitive instruments.

Applications of tracer techniques:

1. In understanding the mechanism of photosynthesis.
 - a. Photosynthesis in plants involves the following reactions.



In one of the experiments a small amount of the radioactive carbon dioxide was introduced with natural carbon dioxide. It was found that oxygen which is formed along with sugar comes from water and not from CO₂. Accordingly the correct reaction is written as



2. The solubility of sparingly soluble salt can also be determined by the tracer technique.
3. Medicine: Common salt containing the radioactive sodium isotope(Na^{*}) is introduced into the blood of a wounded patient to find out whether the blood is reaching the wound.

4. Agriculture: Radioactive phosphorus P^{32} has been used to trace the uptake of phosphorus by plants.

Neutron Activation Analysis

It is a method to determine the fresh quantity of elements present in the sample. The element to be determined is made radioactive which is the measure of the mass of the element originally present in the sample.

Modified comparator method

The sample is irradiated by neutrons in a nuclear reactor under flux for a fixed period. The sample becomes radioactive because of the (n, γ) reaction. The Gamma(γ) ray peaks are measured by a multi channel analyser. It is compared to the peaks of known quantities of a known sample. The composition of the unknown sample is computed from the activity charts.

Advantage

A highly sensitive method which permits the determination of microquantity of elements present in the sample.

Applications

1. In estimating traces of undesirable impurities. Eg: Oxygen in steel
2. For estimating the amount of trace elements. Eg: (Zn, Cu, Mn, Co etc) in plants and animals
3. In dating geological specimens.
4. Composition of the surface of the moon has been analysed with the help of this method.

Nuclear Shell Model

Research revealed that those nuclei are more stable than their neighbours. whose protons or neutron numbers are equal to one of these numbers(2, 8, 20, 50, 82, 126). These numbers are known as magic numbers. In this model the magic numbers are interpreted as forming a complete shell of neutrons or protons analogous with an electronic shell. A nucleus which has a filled shell is more stable than one which has unfilled shells.

Evidence

1. Tin with $Z=50$ has 10 stable isotopes which is more than any other element.
2. Radioactive atoms by emitting alpha particles attain stability with magic number totals.

Liquid Drop Model

Bohr suggested that the nucleus is analogous with a small electrically charged drop of liquid. The following analogies hold.

1. The drop is spherical. The nucleus is also assumed to be spherical.
2. The density of a drop and nucleus is independent of their size.
3. The surface tension of a drop is similar to the potential barriers effect at the surface of the nucleus.
4. Both the molecules in the drop and nucleons in the nucleus interact only with their closest neighbours.
5. If energy is given to the drop, its molecules evaporate. Similarly, if energy is given to the nucleus by bombarding with a particle, a compound nucleus is found which emits nucleons.
6. If a drop is made to oscillate, it tends to separate into two parts of equal size. Similarly, in the fission process, a nucleus breaks up into 2 fragments of roughly equal size.

Consequences

$$\begin{aligned}\text{Mass number } A &= \text{mass of the nucleus} \\ &= \text{volume} \times \text{density} \\ &= \frac{4}{3} \pi r^3 \times \rho \text{ (where } r = \text{radius of nucleus)} \\ \text{or } r^3 &\propto A \\ \text{or } r &\propto A^{1/3}\end{aligned}$$

The liquid drop model is very useful in the study of nuclear fission and fusion.

Drawbacks

The density and surface tension of the nuclear fluid have fantastic values.

Isotope dilution method

Isotope dilution analysis is very useful in analytical chemistry. This is a technique which is suitable where a compound can be isolated in a pure state but only with poor yield. The technique consists of adding a known amount of the pure compound containing an active isotope to the unknown and thoroughly mixed with it. Now a sample of pure compound is isolated from the mixture and its activity is measured with the help of an electroscope. The amount of substance in the original material is then calculated.

In general isotope dilution is used to determine the yield of a product that is difficult to separate from its reaction mixture when separation of some of the product from its mixture is possible but quantitative separation of all the products is not possible, the yield can also be calculated by making use of the technique of isotopic dilution.

Let us consider a solution containing M gm of a compound which is to be determined. A portion of the same compound which is tagged with a radioactive isotope is now added to the solution. Suppose the weight of the added portion be m gm, and its activity is A cpm and specific activity = A/m.

Let after complete and throughout mixing, w gms of this compound is isolated in a pure state and its activity and specific activity B cpm and (S=B/w) respectively.

Now assuming loss by decay to be negligible, the total amount of activity after mixing must be the same as before. Thus, it follows that $S_0 m = (M+m) \cdot S$

$$M = w(A/B) - m \quad - \text{(#1)}$$

Now if the added material is highly active, then the amount added m can be very small compared to M.

Hence equation (#1) becomes

$$M = w(A/B) \quad - \text{(#2)}$$

$$\text{But } M = A(w/B) - m = A(1/S) - m \quad - \text{(#3)}$$

$$\text{Since } w/B = 1/S$$

(#3) is evidently a straight line having a slope A and intercept m. The calculation may be made clear by the following example.

Suppose we have to determine the amount of glycine in the mixture with other amino acids. Isotopic dilution analysis is the most appropriate technique in this case, because glycine can be isolated chemically, but only with a pure low yield. A sample of glycine which contains an atom of C¹⁴ in perhaps, 1 in every million of its molecules, is first synthesised commercially. A 0.5 gm portion of this active preparation, whose specific activity corrected for background is 25000 cpm per gm is mixed with unknown substance. Suppose 0.2gm of pure glycine having an activity of 1250 counts per 10 min is obtained from the mixture. The specific activity corrected for the background of the pure glycine is 100 counts per 5 min. Thus the data may be summarised as follows.

$$M = 0.5\text{gm}$$

$$w = 0.2\text{gm}$$

$$A = mS_0 = 12500 \text{ cpm}$$

$$S_0 = 25000 \text{ cpm per gm}$$

$$B = 1250/10 - 100/5 = 105 \text{ cpm}$$

Substituting in (#3),

$$M = w(A/B) - m = (0.2 \times 12500)/105 - 0.5 = 23.3 \text{ gm}$$

is the required weight of glycine in the sample.

Advantages

There are several advantages of this method. Some of them are:

1. The method is an absolute one and no corrections are therefore needed to obtain the final result.
2. The method is very sensitive.
3. Accuracy is of the order of 1% or higher.
4. In this method it is not necessary to separate the constituents. If during processing, part of one isotope is lost, at the same time an equal portion of the other isotope would be lost as they cannot be chemically separated.
5. Simple mass spectrometers can be used as the method does not depend upon a particular source.

However, till date the following elements cannot be determined by this method:

Fluoride, Aluminium, Manganese, Scandium, Cobalt, Phosphorus, Gold etc