THE MASS SPECTROMETER

By HAROLD W. WASHBURN

THE advent of World War II imposed many problems on the petroleum and chemical industries which required more rapid and accurate analyses on their raw, intermediate and final products. The methods used at the beginning of the war were too slow, required too much man power and did not give sufficient information. The contribution of the newer physical instruments in solving these problems is now a matter of record. One of the major problems which had to be successfully solved was the transformation of instruments of the research laboratory type into practical routine instruments which could be operated by the personnel available and under the conditions existing in the industrial routine analytical laboratory.

The newest of the new physical analytical instruments applied to the industry is the mass spectrometer. It is the purpose of this article to describe briefly what the mass spectrometer is and how it works, and to point out the fields in which it has been advantageously employed.

HISTORY

The mass spectrometer was originally designed for accurate determinations of the relative abundance of isotopes. It thus served as a companion instrument to the

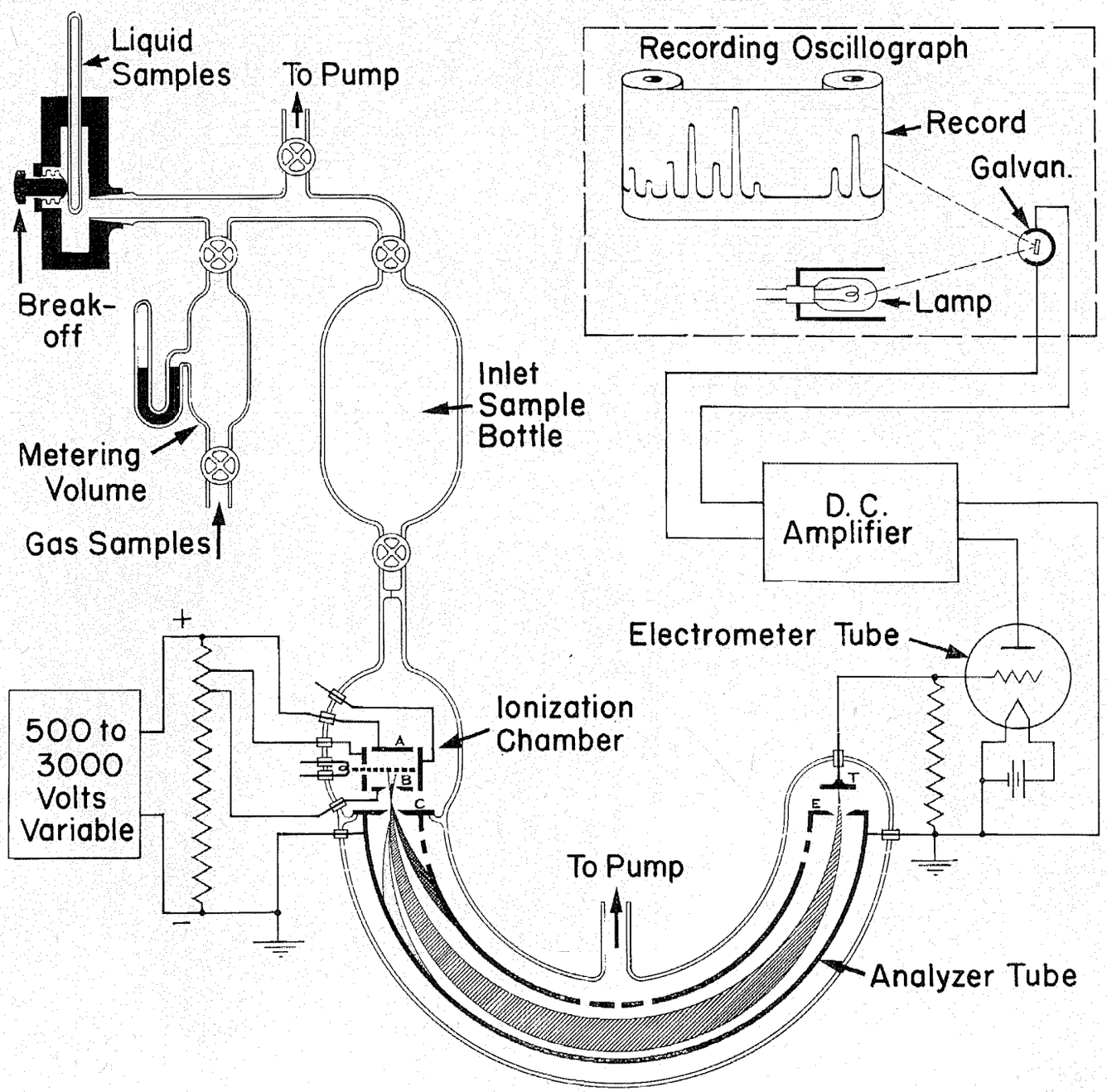

FIG. 1. Diagrammatical sketch of a mass spectrometer and associated apparatus as used for the analysis of gas and liquid mixtures.

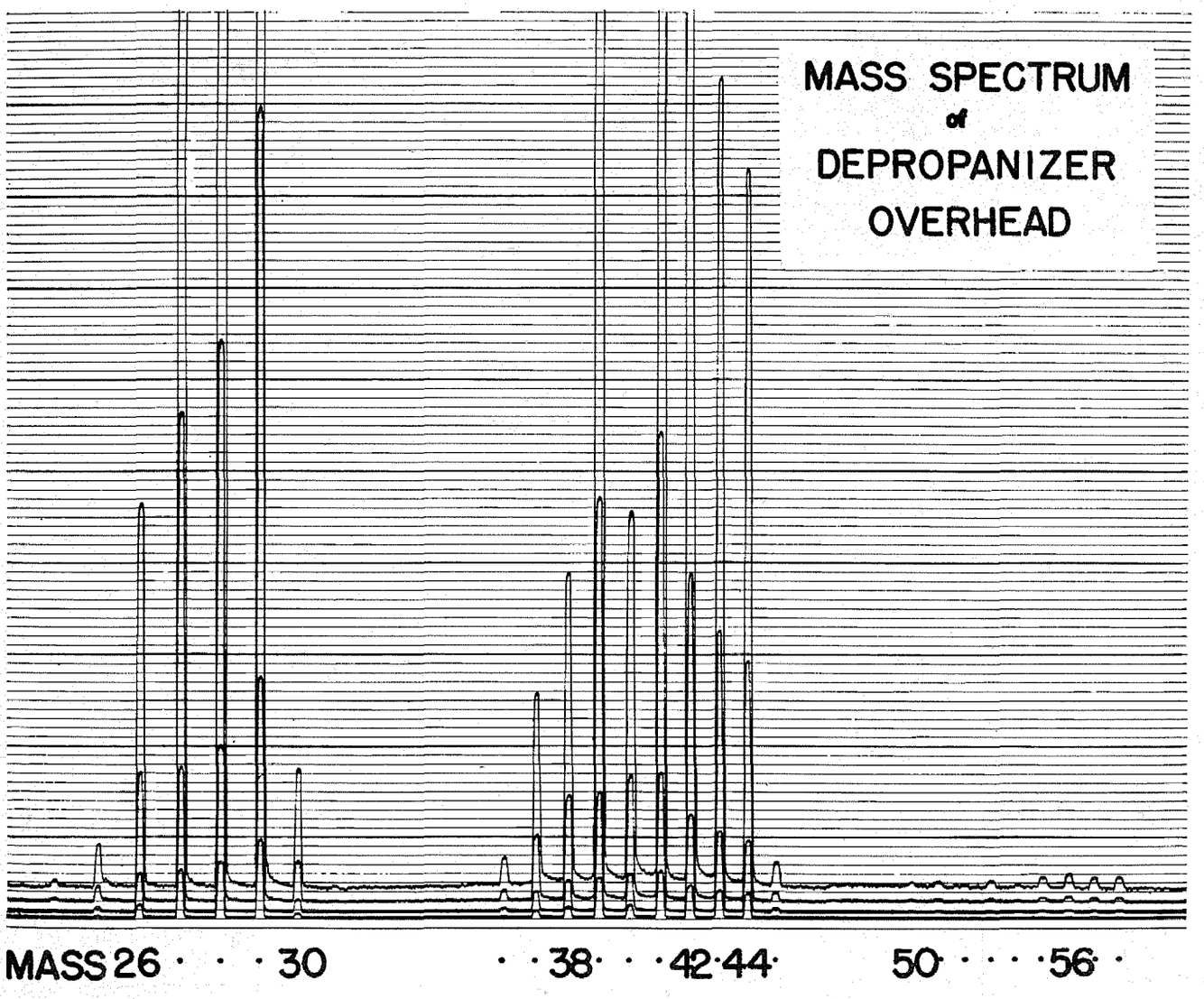

FIG. 2. Automatic record of depropanizer overhead mass spectrum, in which four galvanometers record peaks simultaneously at four sensitivity levels to insure accurate measurement over a large range of magnitudes. This record of a depropanizer overhead shows a 58 peak of 0.9 divisions, which means that the concentration of the key component, iso-butane, is 2.3 per cent.

mass spectrograph, a similar instrument but designed for accurate determination of isotopic mass rather than relative abundance. The data on isotopic mass and relative abundance obtained by these two instruments have been used for some of the most accurate atomic weight determinations available today.

The mass spectrometer is the much simpler instrument of the two, a fact which is partly responsible for its varied use today as an analytical tool. In the 1930's some members of the California Institute of Technology faculty foresaw the possibilities of the mass spectrometer and initiated the development of an instrument for use as a general analytical tool.

In the late 1930's, Dr. Robert A. Millikan, upon learning that Consolidated Engineering Corporation had decided to begin the development of a mass spectrometer which would be capable of analyzing complicated hydrocarbon mixtures, suggested that the California Institute instrument be loaned to Consolidated for preliminary experiments. After four years of intensive research by Consolidated which included the development and the building of two mass spectrometers, an instrument was produced for use in industrial laboratories. Today this instrument is used widely in the petroleum and chemical industries both as a routine control instrument and as a development laboratory analytical tool.

WHAT THE MASS SPECTROMETER DOES

The mass spectrometer is an electronic instrument which obtains data which are called mass spectra. The mass spectrum of a substance may be defined as the relative abundance of ions formed at different masses (molecular weights) by some sort of ionization process. In the type of instrument to be described in this article the ionization process is accomplished by bombarding with electrons the vapor of the substance for which a mass spectrum is to be obtained. The ions thus formed are segregated into a fan of beams by electric and magnetic fields. Each beam in the fan is composed of ions of one mass (molecular weight) only. The relative number of ions in each beam is automatically recorded by sweeping the beams past a target which has connected to it an amplifier and recording oscillograph. These processes are represented schematically in *Fig. 1*. In this diagram, for simplicity, there are shown only three

ion beams emerging as a fan from the ionization chamber. In practice these may be from 50 to 100. An automatically recorded mass spectrum of a refinery absorption plant de-propanizer overhead is shown in *Fig. 2.*

The mass spectra obtained in this manner are functions of the types of molecules in the vapors introduced into the instrument. This correlation between the mass spectra and the substances introduced permits the attainment of information from the mass spectra which may be used for obtaining either theoretical information on the properties of the molecules or practical information such as the concentration of each kind of substance present in a mixture.

APPLICATIONS TO INDUSTRIAL PROBLEMS

For purposes of discussion the applications will be divided into three categories:

1. Accurate quantitative analysis of gas or liquid mixtures containing as many as 10 to 20 components. (These analyses can be performed on extremely small samples. For example, if desirable, analyses can be made on samples as small as .001 to .01 cc. of vapor at standard pressure and temperature.)
2. Determination of kinetics and mechanism of chemical reactions.
3. Determination of the chemical processes which occur in metabolism processes.

ANALYSIS OF GAS AND LIQUID MIXTURES[4]

The mass spectrometer method employed for mixture analysis may be called the superposition method. In this method of analysis the energy of the bombarding electrons is made sufficiently high so that a large percentage of the molecules which undergo ionization are in addition broken into fragments. Therefore, if a pure substance is introduced into the mass spectrometer ionization chamber, ions of several different masses will be formed, and it is found that the relative abundance of the ions at these different masses is a function of the structure of the molecules of which the substance is composed. The mass spectrum of a substance may therefore be considered as a fingerprint from which that substance can be recognized.

The commercial mass spectrometer has been developed so that the mixture mass spectrum is a linear superposition of the mass spectra of the components in the mixture. The analysis consists of the unraveling of the composite mixture spectrum into the spectra of the mixture components. The attainment of linear superposition greatly simplifies the determinations of the composition of the mixture from its mass spectrum.

[4]A more complete discussion of this subject by the author may be found in *Industrial and Engineering Chemistry*, Analytical Edition, *17*, p. 74, (February 15, 1945).

Since no exhaustive tests have been made on the types of mixtures which can be successfully analyzed by this method, it is impossible at this time to give a comprehensive outline of the types of mixtures to which this method is adaptable. However, it is possible to state the types of mixtures to which this method has been successfully applied.

One of the major analytical problems in the chemical industry is the analysis for small impurities in intermediate products. The mass spectrometer is particularly well adapted to this type of problem. For example, it is possible to detect as small a quantity as 0.003 per cent diethylbenzene in ethylbenzene, an analysis which is of importance to the synthetic rubber industry. No other analytical method has been successful in performing this analysis.

The mass spectrometer method of analysis, at present, is conceded to be the most satisfactory method for analyzing light hydrocarbon mixtures; for example, mixtures containing hydrogen, carbon monoxide, nitrogen and paraffinic and olefinic hydrocarbons containing one to five carbon atoms can be analyzed without any preliminary fractionation. Mixtures of this type are encountered in many places in the petroleum refinery. One of the output streams from a catalytic cracking unit, for example, contains 15 or more components in this range.

The analysis time for this type of mixture with the mass spectrometer is 30 minutes, instrument time, and one and one-half hours, computing time. This computing time may be reduced to 30 minutes if an electronic computer is available. The complete analysis of this mixture by methods used prior to the advent of the mass spectrometer required about eight hours. The time has, therefore, been reduced to one-eighth the previous time. This increased speed in analysis has permitted refinery operators to maintain closer control of their operation. Hence, there is an improvement both in efficiency and in the quality of the product.

A third type of problem to which the mass spectrometer is just beginning to be applied is the analysis of a mixture containing as many as six isomeric octanes. This permits the analysis of fractionated cuts of alkylates. To date such analyses have been used mainly in

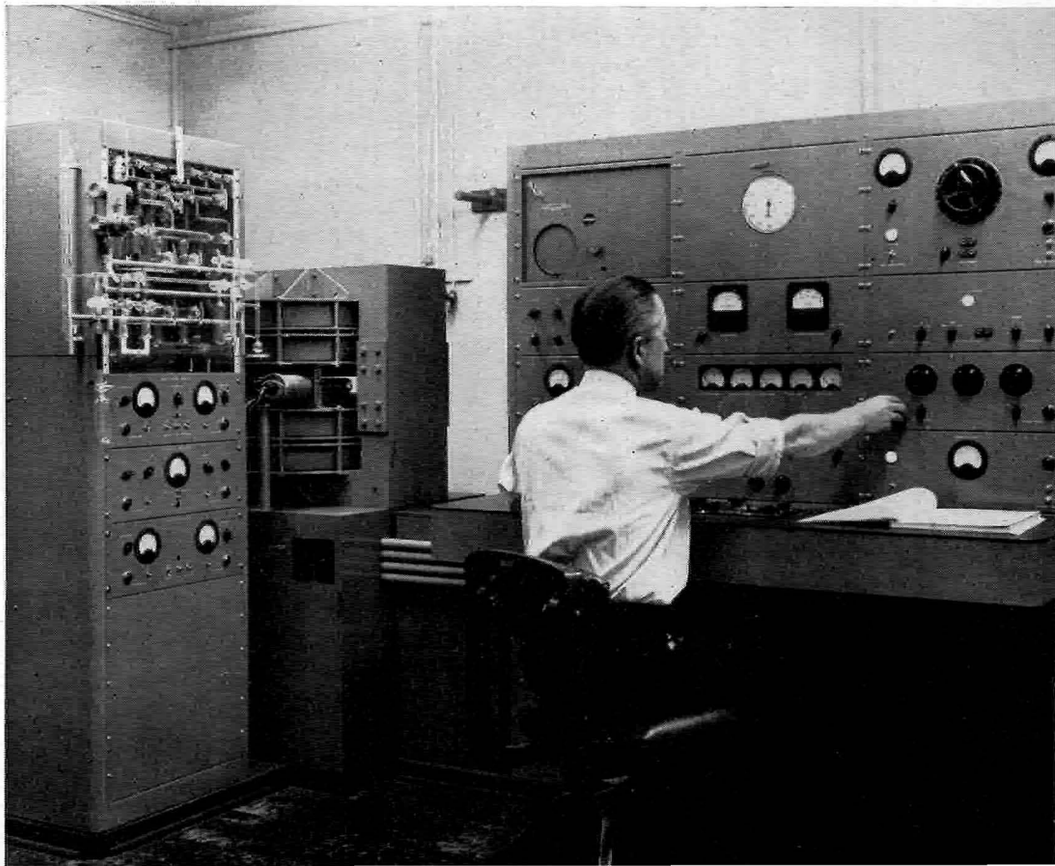

FIG. 3:

Typical mass spectrometer installation in operation.

$$CO_2 + H_2O + h\nu \xrightarrow{\text{chlorophyll}} O_2 + \left(\frac{1}{n}\right)(C \cdot H_2O)n$$

Expt.	Substrate	Time between dissolving $KHCO_3 + K_2CO_3$ & start of O_2 collection (min.)	Time at end of collection (min.)	H_2O	% O^{18} in HCO_3^- $CO_3^=$	O_2
1	0.09M	0		.85	.20	
	$KHCO_3$+	45	110	.85	.41	.84
	0.09M	110	225	.85	.55	.85
	K_2CO_3	225	350	.85	.61	.86
2	0.14M	0		.20		
	$KHCO_3$+	40	110	.20	.50	.20
	0.06M K_2CO_3	110	185	.20	.40	.20
3	0.06M	0		.20	.68	
	$KHCO_3$	10	50	.20		.21
	0.14M K_2CO_3	50	165	.20	.57	.20

FIG. 4. Study of photosynthesis by isotope tracer techniques.

the development laboratory in improving refinery processes. They may, however, prove to be important in control operation in the future, since the alkylate is one of the end products of aviation gasoline manufacture.

Preliminary experiments indicate that the mass spectrometer may be used to analyze mixtures containing oxygenated compounds and chlorinated compounds. Analysis of mixtures containing these compounds is of considerable interest to the chemical industry as well as the petroleum industry, since many intermediate products contain these substances.

In addition to the advantages of speed and additional information which it provides, the mass spectrometer method is unique in permitting the analysis of extremely small samples. Samples of gas as small as one-thousandth of a cubic centimeter can be analyzed. An important application requiring this feature is the analysis of gases in thermionic vacuum tubes.

KINETICS AND MECHANISM OF REACTION

An application of the mass spectrometer to pure research is illustrated by its employment in studies of kinetics and mechanism of reaction. Its application to this field has followed two different attacks: (a) Small samples are withdrawn from the reaction chamber during the reaction and analyzed. (b) Heavy isotope tracer techniques are employed.

The fact that the mass spectrometer is capable of analyzing such extremely small samples makes possible the withdrawal and analysis of samples from a reaction chamber while the reaction is taking place, and thus determining the composition of the mixtures in the chamber without in any way disturbing the reaction. The employment of automatic recording permits the necessary data to be recorded within from two to 10 minutes, depending on the particular analysis which is to be made. Therefore, the sampling procedure may be either intermittent, drawing samples at intervals of two to 10 minutes, or continuous, using a constant flow method with a flow of 10 microliters every two or 10 minutes.

An example of a kinetic study made by this method is given in a publication by Leifer and Urey[1]. In these experiments the authors ran a continuous analysis of the gases withdrawn from the reaction vessel during the thermal decomposition of dimethylether and acetaldehyde.

An advantage of this method of studying the kinetics is its ability to detect and quantitatively determine stable intermediate substances that are formed during the reaction. The publication of Leifer and Urey illustrates this advantage in their quantitative determination of the formation of formaldehyde as a stable intermediate in the thermal decomposition of dimethylether.

The determination of the mechanism of reaction by heavy isotope tracer techniques has been widely used by biochemists. A simple example which illustrates the method is given in an article by Rubin[2]. This article describes simple experiments for determining whether the oxygen liberated by photosynthesis comes from the carbonate ion or from the water. The information in this article may be briefly summarized as follows: The reaction which takes place in photosynthesis can be represented by the equation shown at the top of *Fig. 4*. This equation in no way indicates whether the liberated oxygen comes from the CO_2 or from the H_2O.

Two experiments were performed to determine from which of these two substances the oxygen is liberated. In the first experiment young chlorella cells were suspended in heavy oxygen water containing ordinary potassium bicarbonate. In the second experiment algae

[1]Leifer, E. and Urey, H. C., *J. Am. Chem. Soc., 64,* pp. 994-1001 (1942).
[2]Rubin, S. and Randall, M. F., *J. Am. Chem. Soc., 63,* p. 877 (1941).

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No wonder America's glycerine-containing kitchen fats were called to war!

GLYCERINE IN INDUSTRY

In versatility, glycerine keeps pace with its companion product, soap. Industry of wide range and variety, for peace and for war, depends on glycerine's important qualities. *X*-ray, V-mail, and movie film, waterproof bonding cements, printing inks, and anti-freeze solutions —all require glycerine in their manufacture. Glycerine's hygroscopic quality makes it an ideal moisture-retaining agent in cigarettes and gives it importance in food processing and preservation.

During the past few years many new applications for glycerine have developed in plastics, cellophane, safety glass and rayon.

SOAP AND THE FUTURE

Americans like to wash. They like themselves, their possessions, and their surroundings to be clean. They like cleanliness in their stores and amusement places, and on their trains, ships, and planes. Therefore, it's easy to prophesy that soap will continue to be used to wash everything that's washable. Soap's unusual applications—from lubricating that sticky drawer in the bureau to performing an important role in synthetic rubber—also are likely to continue to increase.

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were allowed to carry on photosynthesis in ordinary water and heavy oxygen potassium bicarbonate and carbonate.

In these experiments the determination of the excess O^{18} in the water was accomplished by first equillibrating the water with CO_2 and then running the CO_2 through the mass spectrometer. To determine the excess O^{18} in the carbonate ions a precipitate of calcium carbonate was formed and then calcined to liberate CO_2 which was run through the mass spectrometer. The O_2 was run directly through the mass spectrometer.

The results show that when the water contained excess heavy oxygen isotope, the liberated oxygen also contained excess heavy oxygen isotope; but when the carbonates contained the excess heavy oxygen isotope, the liberated oxygen did not contain excess heavy oxygen isotope. The liberated heavy oxygen must, therefore, have come from the water and not from the bicarbonate contained in the water.

CHEMICAL PROCESSES IN METABOLISM

There are many examples in the literature showing the application of the heavy isotope tracer techniques to metabolism studies. The field which seems to be the most fruitful, at this time, is that of intermediary metabolism; that is, the mechanism of the breakdown and synthesis of proteins, fats and carbohydrates and their introconversion, as well as the effects of vitamins and hormones thereon. The usual procedure in this isotope tracer work is to submit a labeled substance to a biological reaction either in an intact animal or in an isolated tissue or extract, and then to isolate the products and determine their heavy isotope content.

Some very interesting articles published by Schoenheimer[3] report the results of experiments in which normal adult rats were fed a labeled amino acid for a period of several days. The amino acid was labeled by synthesizing it with an excess of heavy isotope of nitrogen. At the end of this period the rats were killed and the various parts of the rats analyzed with the aid of a mass spectrometer for the labeled atoms.

There were only two important results. (1) Less than one-third of the nitrogen contained in the amino acids fed the rats was recovered in the excreta, although the total amount of excreted nitrogen was equal to that in the diet. This indicates that the other two-thirds of the labeled nitrogen had been assimilated into the tissues in exchange for normal nitrogen formerly present in the tissues. (2) It was observed that more than half of the nitrogen of the amino acids fed ended up in the body proteins. These two facts showed that the metabolism was much more efficient than previously supposed in incorporating the amino acids fed to the rat into the body protein. In other words, even though the excreted nitrogen was equal to that of the intake, only a small part of this excreted nitrogen passed in effect directly through the rat. Another important conclusion follows from the fact that the nitrogen incorporated in the proteins was

[3]Schoenheimer, R., Ratner, S. and Rittenberg, O., *J. of Bio. Chem., 130*, p. 703 (1939).

originally fed in the form of amino acids. This shows that the absorption process is a very extensive succession of chemical reactions and not a simple mixing process. It may be stated here that this information could not have been obtained by any other technique.

These results are very important in that they show the possibilities of this relatively new method of attack in aiding the medical profession to find out many new facts about body chemistry.

CONCLUSION

From this discussion it will be seen that the mass spectrometer is very versatile in its applications. It is expected that in the future it will become of increasing usefulness in the chemical and medical fields, as well as in fundamental physical research.

References

1. Leifer, E. and Urey, H. C., *J. Am. Chem. Soc., 64,* pp. 994-1001 (1942).
2. Rubin, S. and Randall, M. F., *J. Am. Chem. Soc., 63,* p. 877 (1941).
3. Schoenheimer, R., Ratner, S. and Rittenberg, O., *J. of Bio. Chem., 130,* p. 703 (1939).
4. Washburn, H. W., Wiley, H. F., Rock, S. M., Berry, C. E., *Indus. and Eng. Chemistry,* Anal. Edition, *17,* p. 74 (February 15, 1945).

C. I. T. NEWS

NOVEMBER MEETING

On November 15 the monthly meeting of the Alumni Association will be held at the Kaiser Steel Plant in Fontana. Dinner will be served cafeteria style at 5:30 P.M., following which a tour of the steel plant has been arranged. Donald R. Warren, of the Donald R. Warren Company, a Tech alumnus, is arranging this meeting. Mr. Warren did considerable design and construction work on the Kaiser plant. This promises to be a very interesting meeting, and a good attendance is expected. Notice of details will be sent in the usual manner.

ERNST MAAG '26 TAKES NEW POSITION

Ernst Maag, past president of the Alumni Association, has accepted a position as chief engineer for Latisteel, Inc., in Los Angeles, effective November 1. Mr. Maag has been with the Department of Building and Safety of Los Angeles County for the past 12 years.

Mr. Maag's affiliation with the County began in 1933 as district structural engineer. Through a series of promotions he became structural research engineer in 1941. Prior to serving with the County Mr. Maag was building inspector for Pasadena from 1926 to 1931, serving under Walter Putnam, head of the department. From 1931 to 1933 Mr. Maag was in charge of the testing laboratory on Morris Dam for the Pasadena Water Department. His new work with Latisteel, Inc., will be chiefly development and testing.

NEW APPOINTMENTS

The Board of Trustees has announced the following appointments to the Institute faculty:

J. R. Oppenheimer, Professor of Physics
Aladar Hollander, Associate Professor of Mechanical Engineering
A. P. Banta, Associate Professor of Sanitary Engineering