Conversion of Isotopically Enriched CO_2 to CO

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Current interest in the synthesis of organic compounds containing isotopic tracer atoms makes it desirable to convert carbon dioxide enriched in C^{13} or C^{14} into other useful compounds. A simple method of converting C^*O_2 to C^*O would be useful in the synthesis of labeled methyl alcohol[1] and labeled sodium formate. A satisfactory method was found to be the reduction of CO_2 with hot zinc as used by the authors (*3*) in the concentration of CO_2 enriched in C^{13}. This method of concentrating C^{13} made use of the isotopic exchange reaction $C^{13}O + C^{12}O_2 \rightleftarrows C^{12}O + C^{13}O_2$ in conjunction with thermal diffusion which produced countercurrent flow of CO_2 and CO. The $C^{13}O_2$ produced by isotopic exchange at the hot wire is transported toward the bottom of the column, where it must

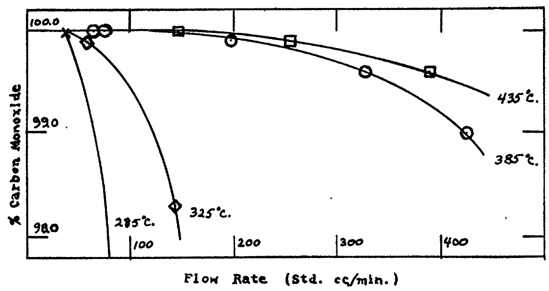

FIG. 1. Effect of flow rate and temperature on percentage conversion of CO_2 to CO.

be converted to $C^{13}O$ if total reflux is to be established. This conversion was accomplished by circulating the CO_2 through zinc powder at about 400° C. (*1*). It was found advantageous to support the zinc dust on asbestos fiber to give greater porosity and to prevent clogging. Small pellets about 6 mm. in diameter were made from a moistened mixture containing 95 per cent by weight zinc dust and 5 per cent asbestos fiber of the type used for Gooch crucibles. These were dried at 110° C. for 24 hours before being placed in the converter. Spectrographic examination of the zinc (technical grade) showed the presence of Pb, Cu, and Sn as impurities.

In order to study the efficiency of conversion of CO_2 to CO under various conditions, 50 grams of the zinc pellets were placed in a 15-cm. length of Pyrex tubing 25 mm. in diameter. A Chromel-Alumel thermocouple was attached to the outside wall, and the converter was then placed in a furnace. Carbon dioxide at atmosphere pressure was passed through the converter at several rates of flow at each of the following temperatures: 435° C., 385° C., 325° C., and 285° C. The result are given in Fig. 1, in which the percentage conversion at each temperature is plotted against the flow rates.

An Orsat apparatus was used to measure the concentration of CO to ± 0.2 per cent. These results indicate that a yield of 99–100 per cent CO can be obtained at temperatures between 385° and 435° C. with flow rates as high as 400 cc./minute. Convenient operating conditions seem to be a temperature of 400° C. and a flow of about 100 cc./minute. This will assure a conversion of 99.5 per cent for a single passage through the converter. The CO_2 may be forced through the converter by means of pressure or drawn through with a Toepler pump arrangement. About 15 l. was converted for use in the chemical exchange column without any loss in efficiency of the converter.

The available quantity of isotopically enriched CO_2 is frequently small; consequently, a method of converting smaller volumes of CO_2 is desirable. Suitable arrangements are

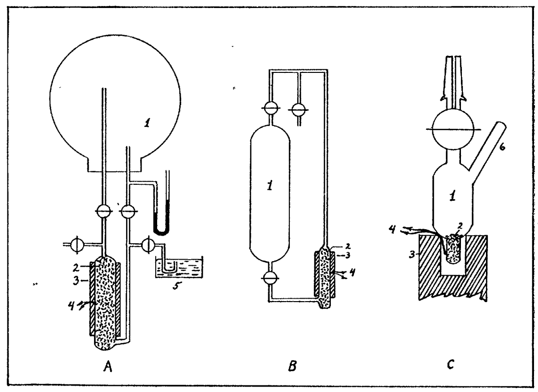

FIG. 2. Apparatus for conversion of isotopically enriched CO_2 to CO: (1) sample container; (2) zinc-asbestos mixture; (3) furnace; (4) thermocouple leads; (5) mercury trough for collecting samples; (6) inlet for introducing zinc-asbestos mixture.

illustrated in Fig. 2 (B, C) for use with conventional-type sample tubes. The apparatus shown in Fig. 2(A) was used to measure the efficiency of the converter when connected to a closed system in which the samples are frequently stored. The converter was attached in a vertical position to the two glass tubes leading into the 2-l. bulb which contained CO_2 at a pressure of about 80 cm. Hg.

After evacuating the converter, the furnace was adjusted to the desired temperature and the stopcocks opened. Convection up through the converter acts to recirculate the gas from the bulb through the zinc pellets. Small samples (0.5 cc.) were withdrawn periodically and analyzed with a Blacet-Leighton microgas analysis apparatus (A. H. Thomas Company). Experiments at 425° and 480° C. (Fig. 3) showed that practically complete conversion was obtained in 5–6 hours. The fact that no significant change in total pressure occurred indicates that very little, if any, CO is lost by decomposition.

[1] See, for example, the high-pressure synthesis of deuteromethyl alcohol from CO and D_2 by J. E. Zanetti (du Vigneaud, V., Chandler, J. P., Cohn, M., and Brown, G. B. *J. biol. Chem.*, 1940, **134**, 787).

The solid curves represent the dependence of CO concentration on the time as obtained from the results of the following calculations. If x is the mole fraction of CO in a bulb (of volume V cc.) at a time t, then with a convective transport rate of T cc./minute upwards through the converter, the flow of CO_2 into the converter at time t is T(1 − x) cc./minute. Assuming complete conversion of the CO_2 in the mixture to CO, T(1 − x) also represents the increment in the flow of CO leaving the top of the converter at time t. The net increase in the number of cubic centimeters of CO in the vessel is then given by:

$$V \frac{dx}{dt} = T(1-x).$$

The solution of this equation for the boundary condition, x = 0 at t = 0, gives the following expression for the time dependence of the concentration of CO in the vessel:

$$x = 1 - e^{-Tt/V}.$$

The two solid curves in Fig. 3 were obtained by substituting convective flow rates of T = 35 cc./minute and T = 40 cc./minute in the above equation. It is therefore evident that the convective flow in the converter was approximately 35–40 cc./minute. Using this value for T, the percentage conversion at any time, t, can be calculated. It can be seen that

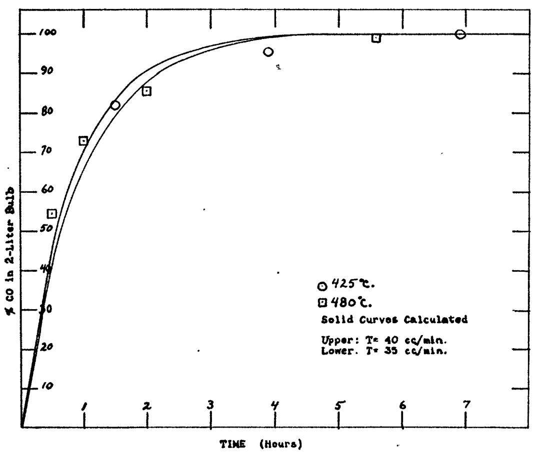

FIG. 3. Rate of conversion of CO_2 to CO in a closed system.

this method may readily be adapted to the determination of convective transports through different types of packed columns for engineering experiments.

To test the method for conversion of small samples, a 5-cc. reaction vessel containing about 1 gram of the powdered zinc-asbestos mixture, as illustrated in Fig. 2(C), was used in connection with a standard system (*2*) for obtaining CO_2 from $BaCO_3$. Carbon dioxide was liberated from 40 mg. of $BaCO_3$,[2] in which a mass spectrographic analysis showed 3 per cent of the carbon atoms to be C^{13}. After the sample was transferred to the reaction vessel, the zinc was heated to about 425° C. for two hours. Analysis with the microgas analysis apparatus showed 99 per cent conversion to CO. Mass spectrographic analysis showed that it contained 3 per cent $C^{13}O$.[3]

[2] The authors are indebted to Dr. A. V. Grosse of the Houdry Process Corporation for the barium carbonate enriched in C^{13}.

[3] Thanks are due to E. H. Mosbach for assistance with the mass spectrographic and gas analyses and to Miss M. Lamson for help with the spectrographic analyses.

The carbon monoxide may be converted back to carbon dioxide, if desired, by passing it through copper oxide heated to 400° C.

References

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A Kinesimeter for Studying the Spontaneous Activity of Small Animals

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With the increase in number of sympathomimetic amines in use and under investigation for their circulatory effects, it has become necessary to study their effects on central stimulation with ever-increasing accuracy.

Many types of activity recorders have been employed for this purpose and with varying degrees of results.

As early as 1898, Stewert (*6*) tested the effects of alcohol, diet, and changes in barometric pressure on the spontaneous activity of small animals. His method consisted of a squirrel cage made of wire mesh 18 inches in diameter and 20 inches in length. The animal's movements caused the cage to rotate. An eccentric coupled to the escapement mechanism of an alarm clock caused the revolutions to be registered by the second hand. Slonaker (*5*), using a slight modification of the same technique, studied the normal activity of the white rat at different ages. His findings showed that the greatest activity of the rat occurred when the animal was 87–120 days old.

The above method, of course, is suitable only for the type of research in which activity is studied for many days or weeks. For studies of activity due to the central nervous excitability of various drugs, involving only a few hours, a much more sensitive apparatus had to be developed.

Schulte, *et al.* (*4*) used a cage and spring suspension, coupled to a work adder by a string. As the animal's motions moved the cage, the work adder revolved. A signal magnet recorded these motions on a kymograph. This method has a decided advantage in that it takes into account both large and small motions and accumulates them. However, the cage is undamped and is free to oscillate in any direction.[1]

Abreu (*1*) used a cage suspended by a spring in which the movements were transmitted by a tambour-air system to a kymograph.

The above types of apparatus are best described by the term "jiggle" cages. Since they are all suspended on coiled springs, one movement of the animal results in from one to several movements of the cage. Both vertical and pendular movements may be transmitted to the recording devices.

[1] C. W. Geiter, of Frederick Stearns & Company, developed a method whereby a cage was suspended on a spring. As the animal's motions caused the cage to move up and down, a flag cut a beam of light, causing a photocell to operate a counter (unpublished).

Ross E. Hart, of Jefferson Medical School, Philadelphia, studied activity by means of transmitting the motions of an activity cage coupled to an air tambour writing on a kymograph. By this method activity can be judged roughly by inspection of the records (unpublished).