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# The separation of stable isotopes of carbon

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ABSTRACT. **The present state of work on the separation of carbon isotopes by diffusion, fractional distillation, chemical isotopic exchange, and the selective excitation and dissociation of molecules in electrical discharges or in the field of laser radiation has been examined. The characteristics of new laboratory and industrial assemblies for separating carbon isotopes have been described. Promising directions of study aimed at developing effective technological processes for separating carbon isotopes have been noted.**

**The bibliography contains 148 references.**

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## I. Introduction

Natural carbon consists of two stable isotopes: $^{13}C$ (1.11%) and $^{12}C$ (98.89%). The $^{13}C$ isotope is now widely used in various branches of science and technology.

The stable isotopes of carbon are used in physics to study nuclear reactions, to determine nuclear constants, to study the inelastic scattering of polarised protons, etc.[1–5] The heavy carbon isotope $^{13}C$ is particularly important for investigating the mechanisms of processes taking place in living organisms.

The development of NMR spectrometers and methods for determining the position of a $^{13}C$ tracer in complex organic compounds and even in biological materials without decomposing them has provided a powerful stimulus for devising effective methods for separating the stable isotopes of carbon and synthesising a wide range of isotopically substituted compounds, and for the development of different forms of $^{13}C$ NMR spectroscopy. It has made it possible to obtain rapidly valuable information on the structure and dynamics of the structural components and on the nature of the intracellular medium, the primary and secondary exchange paths in a culture medium, etc.[6]

A promising sphere of application of stable isotopes of carbon is in the identification of various types of functional breakdown in the organism: liver deficiency, breakdown of exchange processes in the liver, diabetes, oxygen starvation of the heart muscle, lung deficiency, etc. A large number of papers have been published on the diagnosis of metabolic breakdown due to the dysfunction of the endocrine and other organs, using compounds labelled with $^{13}C$.[7–12] In the USA, 2.5 kg of the $^{13}C$ isotope are used annually for medical research and diagnosis alone.[6]

The wide interest in the use of stable isotopes to study processes in living organisms is indicated by the large number of published papers on this topic (see for example the bibliography in Ref. 13 and the published proceedings of special symposia and conferences).[6,14–17]

The extensive use of carbon isotopes in turn is stimulating the further development of methods and technology for their separation. Extensive material has accumulated on the separation of carbon isotopes by traditional methods such as the chemical exchange, fractional distillation, and diffusion of gaseous compounds of carbon, etc. In the last ten years, studies of the possible separation of carbon isotopes using lasers have shown that this method is highly effective for large-scale production.

## II. Separation by diffusion

Methods for separating carbon isotopes by diffusion include diffusion through a porous membrane and diffusion in a stream of vapour.

The separation of isotopes using porous partitions results from the fact that the relative frequency with which the molecules of the components being separated enter the small openings is inversely proportional to the square root of their molecular weight. Since the separation effect of a single diffusion step is small, gas-diffusion cascades are usually employed, as illustrated schematically in Fig. 1. Part of the stream being separated, entering the gas-diffusion stage, passes through the partition, while the other part (the heavy fraction) does not. The heavy gas fraction, with the higher molecular weight, is taken to the next stage in the direction of the tail of the cascade. The light fraction, after moving through the partition into the higher-pressure region, is passed by the compressor to the next stage in the direction of the head of the cascade.[18]

Carbon-13 enrichment by a factor of 6.6 has been achieved by diffusion through a porous membrane in a cascade of 35 single stages.[19] The material used in the diffusion cascade was methane, whose molecules, containing different carbon isotopes, have a greater relative difference in mass than any other gaseous compound of carbon. Later,[20] a heavy methane fraction containing about 16% $^{13}CH_4$† was obtained in the assembly after operation for 12 h.

The porous partition can be replaced by a stream of mercury vapour, through which diffusion takes place.[21–23] The separate stages of this cascade are mercury diffusion pumps, which move the lighter component slightly faster than the heavy component. An advantage of this cascade is the use of the diffusion pump simultaneously as the generator of the original mixture, the assembly

† Here and subsequently the concentrations of the isotopes are given in at. %.

for the fractionation, and the pump for moving the richer and depleted fractions from one stage to another.

Separating pumps with an output of 1 $cm^3$ per day at a pressure of 266.6 Pa gave an enrichment in $^{13}CH_4$ of up to 12.4% relative to the natural concentration.[23] An experimental assembly consisting of 51 pumps has also been described.[24-26] The starting material was methane with the natural concentration of $^{13}C$. At a pressure of 213–266 Pa after operation for 30 h at a rate of 300 $cm^3$ per day, a heavy methane fraction containing 30–32% $^{13}CH_4$ was obtained.

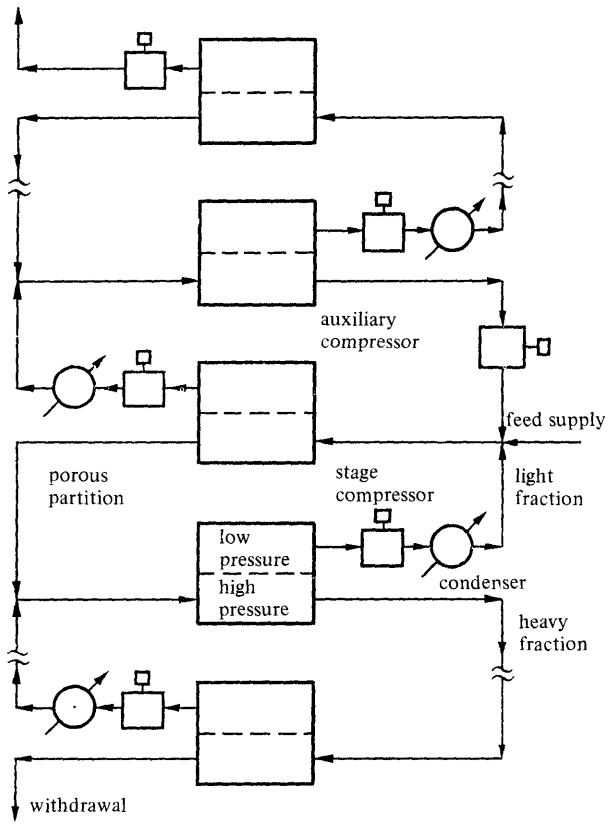



**Figure 1.** Schematic diagram of a gas-diffusion cascade.

The main disadvantage of the first diffusion cascade assemblies was their low output, which made it possible to obtain only tracer quantities of highly-enriched isotope fractions.

The problem of developing highly efficient assemblies with a high specific productivity was solved by using high pressures (1333 Pa).[26,27] $^{13}C$ concentrations of 88% and 70.2% were obtained at take-off rates of 30 $cm^3$ per day and 200 $cm^3$ per day respectively in a cascade consisting of 70 separating pumps. The starting material was methane with a $^{13}C$ concentration of 2.7%. The average separation coefficient in one stage was 1.086, that is it was slightly lower than that of analogous assemblies operating at pressures of 133–266 Pa (usually 1.1).

A separating column using xylene vapour as auxiliary gas has been described.[28] On this column the enrichment in $^{13}C$ reached 2%. Subsequently, the combination of 10 diffusion columns of this type in a cascade gave an enrichment in $^{13}CH_4$ of up to 12% with an output of 500 $cm^3$ per day.[29]

Since the development of the first thermal diffusion column,[30] this method has been used fairly frequently to enrich natural methane for preparative purposes. The start of systematic studies in this field was probably made in Ref. 31, which gave the theoretical principles of the thermal diffusion method for the separation of a $^{12}CH_4-^{13}CH_4$ mixture. The essential feature of the thermal diffusion phenomenon is that when a temperature gradient is created in a mixture of several components, a concentration gradient is also produced.

The Clusius–Dickel thermal diffusion column consists of two vertically arranged surfaces, the space between which contains the mixture being separated. The temperatures of each surface are constant but different.[31] The temperature difference produces a concentration gradient in the horizontal direction. Simultaneously, as a result of the density difference in the mixture being separated, convective movement is produced close to the cold and hot surfaces; the less extensively heated stream of liquid or gas moves downwards, and the more extensively heated stream moves upwards, as shown schematically in Fig. 2. As a result, a counter-flow movement is established in the column, leading to repeated multiplication of the separation effect and to a change in the concentrations of the components of the mixture along the height of the column.

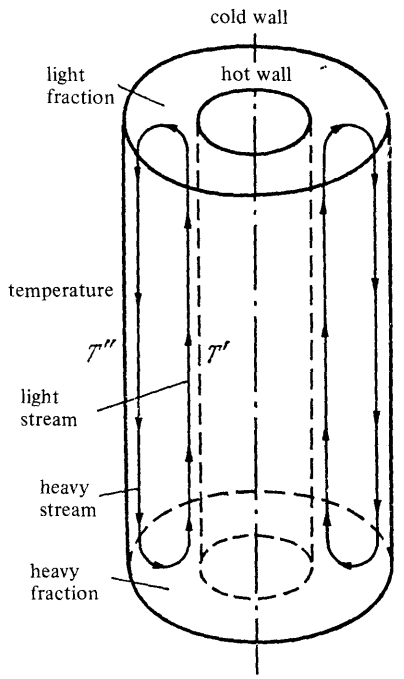



**Figure 2.** Diagram of a Clusius–Dickel thermal-diffusion column.

The principal gaseous compounds of carbon used to concentrate the $^{13}C$ isotope by thermal diffusion are methane and carbon monoxide (mainly the former).[32-42] The separation is carried out in thermal-diffusion columns with different dimensions at pressures from several Pa to atmospheric, and a temperature difference between the central tube (filament) and the outer wall of 573–673 K.

**Table 1.** Enrichment coefficients in the separation of carbon under liquid–vapour phase equilibrium conditions for different compounds.

| System | Temperature, K | $\varepsilon$ | Method of determination | Temperature dependence of the separation | Refs. |
|---|---|---|---|---|---|
| $^{12}CH_4 - {}^{13}CH_4$ | 90.5<br>111.8 | 0.0049<br>0.0010 | differential | $\varepsilon = 2.3\,(4.1986/T^2 + 0.0775T - 0.1959)$ | [53] |
| $^{12}CH_4 - {}^{13}CH_4$ | 90.5<br>97.5<br>111.8 | 0.0114<br>0.0108<br>0.0029 | Rayleigh distillation | $P_{^{12}CH_4}/P_{^{13}CH_4} = 0.0040 + 0.6689/T$ | [54] |
| $^{12}CH_4 - {}^{13}CH_4$ | 90.5 | 0.0125 | ditto | $P_{^{12}CH_4}/P_{^{13}CH_4} = 2.7526/T - 0.0180$ | [55] |
| $^{12}CH_4 - {}^{13}CH_4$ | 90.5<br>96.0<br>111.8 | 0.0055<br>0.0046<br>0.0029 | differential | $\varepsilon = 85.0/T^2 - 0.442/T$ | [56] |
| $^{12}CH_4 - {}^{14}CH_4$ | 90.5<br>111.8 | 0.0123<br>0.0085 | Rayleigh distillation | $\varepsilon = 1.1275/T - 0.0019$ | [57] |
| $^{12}C^{16}O - {}^{13}C^{16}O$ | 68.1<br>81.0 | 0.0125<br>0.0104 | ditto | $\varepsilon = P_{^{12}CO}/P_{^{13}CO} = 0.889/T - 0.0006$ | [58] |
| $^{12}C^{16}O - {}^{13}C^{16}O$ | 69.0<br>81.6<br>101.2 | 0.0131<br>0.0093<br>0.0062 | " | $P_{^{12}CO}/P_{^{13}CO} = 0.9954 \exp(1.447/T)$ | [59] |
| $^{12}C^{16}O - {}^{13}C^{16}O$ | 68.3<br>75.0<br>81.0 | 0.0109<br>0.0086<br>0.0070 | differential | $\varepsilon = 78.2/T^2 - 0.384/T$ | [56] |
| $^{12}C^{16}O - {}^{13}C^{16}O$ | 68.1<br>81.1 | 0.0120<br>0.0104 | ditto | | [56] |
| $^{12}C_2H_6 - {}^{13}C_2H_6$ | 130<br>147 | 0.0022<br>0.0012 | Rayleigh distillation | $P_{^{12}C_2H_6}/P_{^{13}C_2H_6} = 0.3985/T - 0.0021$ | [55] |
| $^{12}C_2H_4 - {}^{13}C_2H_4$ | 120<br>149 | 0.0014<br>0.0016 | ditto | | [55]<br>[60] |
| $^{12}CH_3OH - {}^{13}CH_3OH$ | 307.4 | 0.0002 | » | | [60] |
| $^{12}C_6H_6 - {}^{13}C_6H_6$ | 307.4 | 0.00025 | » | | [60] |
| $^{12}CH_3Cl - {}^{13}CH_3Cl$ | 307.4 | 0.0008 | » | | [60] |

A high concentration of $^{13}C$ in methane (99.8%) was achieved[34] in 2 weeks using a cascade consisting of nine columns with a total length of 24 m. The starting material was methane previously enriched in $^{13}C$ to 55–73%.

In thermal diffusion processes, the purity of the working material is particularly important. In the design of a ten-stage cascade in Ref. 42, therefore, provision was made for the continuous removal of impurities from the last stage; the concentration of impurities was determined from the thermal conductivity. After operation for 300 d, the cascade gave methane with a $^{13}C$ concentration of 96%.

In Ref.42 it was proposed that carbon monoxide be enriched in the $^{13}C$ isotope and then hydrogenated with electrolytic hydrogen with a deuterium concentration lower than $5 \times 10^{-5}$ % to eliminate the accumulation with the $^{13}CH_4$ molecules of the $CH_3D$ impurity present at a concentration of 0.06% in natural methane.[43] An assembly consisting of eight glass columns with internal diameter 12.1 mm and length 2.85 m, connected in series, has been described.[44] The starting material was $^{13}CH_4$ containing 55–70% $^{13}C$, obtained from enriched carbon monoxide. The process was carried out at a pressure of 94.5 kPa and a temperature of 673 K, and gave several litres of methane containing 99–99.8% $^{13}CH_4$. This complex separation scheme uses a large amount of energy, however, and is not justified economically.

In thermal diffusion, the separation factor depends on three main features: the temperature difference between the hot and cold walls, the molecular masses of the components of the gas being separated, and the properties of the molecules themselves. Methane has the highest relative differences in the masses of the isotopic molecules of all known gaseous compounds of carbon, but it is less thermally stable than carbon monoxide, and decomposes appreciably even at 700 °C. Thus the replacement of methane by carbon monoxide and hence an increase in the temperature difference should increase the efficiency of the thermal-diffusion column. Carbon monoxide was apparently first used instead of methane in thermal diffusion in Ref. 45. A column of length 5 mm and diameter 12 mm gave a separation factor of 5.85 at an optimum CO pressure of 71 581 Pa. Carbon monoxide was also used as the starting material in Refs. 46 and 47.

Comparison of the results obtained by the thermal diffusion of methane and carbon monoxide showed that the use of CO as the working gas makes it possible to decrease the volume of the assembly, but the consumption of electrical energy is appreciably higher.[47] Because of this the toxicity of CO, methane has definite advantages over carbon monoxide as the working gas. This probably explains why methane is used in the great majority of cases. Thermal diffusion has also been used to concentrate the $^{14}C$ isotope.[48–50]

Calculations of the cost of production[51,52] by thermal diffusion and the diffusion of methane through a porous partition showed that these methods are economically profitable only at a level of production of 100–200 g $^{13}CH_4$ with a concentration up to 60%.

Disadvantages of all methods for separating isotopes by diffusion are their low efficiency, which is related to the need to work at a low gas pressure, and the large amount of energy required by the process. According to Ref. 31, the power required to produce $CH_4$ enriched to 20% in the $^{13}C$ isotope by thermal diffusion is 6700 kW. h $g^{-1}$ $^{13}C$. It is therefore appropriate to use diffusion methods only in combined separation processes in the final stages of the concentration to obtain $^{13}C$ with an enrichment > 99%.

## III. Fractional distillation

The separation of isotopes by fractional distillation is based on the isotopic effects appearing as a difference in the saturated vapour pressures of the components when the liquid–vapour equilibrium is

reached. The magnitude of the elementary separation factor α in fractional distillation (α is the ratio of the quantities of the isotopes present in the two phases in equilibrium) is determined chiefly by the properties of the isotopic molecules and by the nature of their interaction in the condensed phase. The lack of a well developed theory of the liquid state creates certain difficulties, however, in the selection of compounds suitable for separating isotopes by this method. Analysis of published data shows that the selection of carbon compounds giving acceptable values of α is restricted to the first members of the homologous series of saturated aliphatic hydrocarbons and carbon monoxide.[53-59] Table 1 gives the enrichment factors ($\varepsilon = \alpha - 1$) for carbon isotopes at the vapour pressure equilibrium. These data show that of the compounds studied, only methane and carbon monoxide are promising for separating carbon isotopes by fractional distillation. The factors α have been determined by Rayleigh distillation with equilibrium evaporation of the compounds $C_2H_6$, $C_2H_4$, $CH_3OH$, $C_3H_8O$, $CH_3Cl$, $CCl_4$, and $C_6H_6$.[60-65] The separation factors for methane, found by Rayleigh distillation, agree with one another, but their absolute values are greater than the values of α obtained by the differential method. These discrepancies may be due to the insufficient purity of the specimens used to determine α in Refs. 53 and 56.

The separation of carbon isotopes by the fractional distillation of carbon monoxide on a glass laboratory column with internal diameter 17 mm and height of the packed layer 134 cm at a pressure of 66 650 Pa and a reflux density of 7 $cm^3(cm.\,min)^{-1}$ has been studied.[58] The packing consisted of stainless steel spirals with dimensions 1.5 × 2 mm, prepared from wire with a diameter of 0.2 mm. A steady state was established in about 5 h. The lowest value of the height equivalent to a theoretical plate (HETP) was 4 cm. The HETP on a metal column with internal diameter 17 mm and height 370 cm with the same packing as in the experiments on the glass column was 2.7 cm. In the opinion of the authors cited,[58] the reason for this difference in the HETP values is that the process in the glass column was insufficiently adiabatic.

The results of the experiments on the metal column[56] agree with experimental data[66] on the separation of carbon isotopes on a column with the same geometric dimensions and the same packing. In Ref. 66 the steady state was established in 50 h, and the maximum separation factor (overall separation factor) was 3.67. The height equivalent to a theoretical plate, calculated from this value and $\alpha = 1.01$, is 2.82 cm. Experiments were also carried out on a 12-metre column consisting of an exhaustion section with length 2 m and diameter 25 mm and a lower concentration section. The concentration section consisted of two parts: a lower part with length 5 m and internal diameter 17 mm, and an upper part with length 5 m and diameter 25 mm. All the sections of the column were made of stainless steel, and the packing consisted of triangular spirals with dimensions 1.5 × 2 mm, prepared from wire with diameter 0.2 mm. For a separation factor of 67.8, achieved in 52 days, an approximate estimation of the HETP gave the value 2.2 cm. About 82 g of product with a $^{13}C$ concentration of 10–20% was obtained.

A three-column cascade with a total length of 36 m, with an output of 0.13 mol per day, for obtaining carbon monoxide with a $^{13}C$ concentration of 60% has been described.[67-69] Prolonged use of the experimental assembly revealed a number of unsatisfactory features, mainly in the system used to purify the original carbon monoxide. After purification, the concentration of $CO_2$ in the CO supply stream was only 0.003%, but even this amount gradually led to contamination of the packed part of the assembly. Experiments showed that for this assembly the optimum pressure was 86.6 kPa.

The parameters of a pilot plant for obtaining $^{13}C$ were also given in Ref. 69. The separation part consisted of a three-section cascade with a total length of 74 m and an output of 8.3 g $^{13}C$ per day. This cascade gave a $^{13}C$ enrichment of 90–92%. A period of use confirmed the high productivity and reliability of the assembly, resulting from the use of small-diameter columns connected in parallel in the first section and the positioning of the column of the third section among the columns of the first section (Fig. 3).

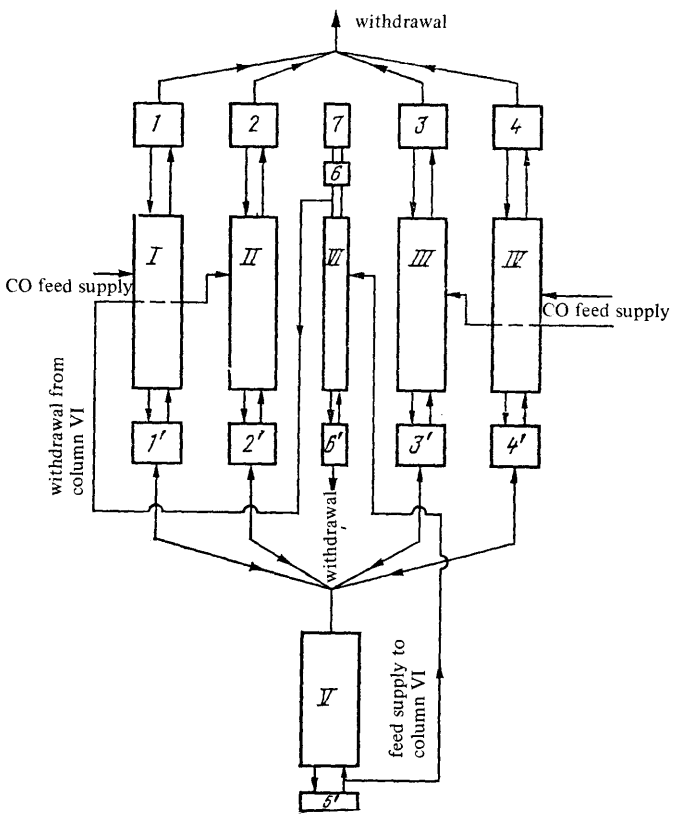



**Figure 3.** Schematic diagram of a pilot-plant assembly for obtaining the $^{13}C$ isotope by the fractional distillation of carbon monoxide: *I, II, III, IV*, columns of the first section; *1, 2, 3, 4*, condensers of the columns of the first section; *1', 2', 3', 4'*, evaporators of the columns of the first section; *V*, column of the second section; *5'*, evaporator of the column of the second section; *VI*, column of the third section; *6*, main condenser of the third section; *6'*, evaporator of the third section; *7*, intermediate condenser of the third section.

It is difficult to obtain high concentrations of $^{13}C$ by the fractional distillation of CO, because of the presence of the heavy oxygen isotope $^{18}O$ in the carbon monoxide.[67-69] Natural carbon monoxide is a $^{12}C^{16}O + {}^{13}C^{16}O + {}^{12}C^{18}O$ mixture. According to Ref. 56, the difference between the partial vapour pressures of

$^{12}C^{18}O$ and $^{13}C^{18}O$ is so small ($\alpha$ = 1.002 at 74.4 K) that fractional distillation in a column leads to the practical separation of only $^{12}C^{16}O$ from the binary $^{12}C^{18}O$ + $^{13}C^{16}O$ mixture. It can readily be shown that if it is assumed that the pressures of $^{12}C^{18}O$ and $^{13}C^{16}O$ are equal, the maximum enrichment in $^{13}C$ cannot exceed 95%. The further concentration of $^{13}C$ by this method requires an additional column. Thus on an industrial assembly with an annual output of 1.5 kg $^{13}C$, further enrichment of the product from 95% to 97.7% was achieved by the fractional distillation of the enriched $^{12}C^{18}O$ + $^{13}C^{16}O$ mixture in an additional column.[70] It is possible to carry out the catalytic exchange reaction[56,71]

$$^{13}C^{16}O + {}^{12}C^{18}O \rightleftarrows {}^{13}C^{18}O + {}^{12}C^{16}O. \quad (1)$$

Up to the present, however, low-temperature catalysts for effective homomolecular exchange according to reaction (1) have not been found, so that on existing assemblies the $^{13}C$ concentration does not exceed 95%. Of these assemblies, mention must be made of a cascade operating in the Los Alamos research laboratory (USA), consisting of twelve parallel columns with diameter 2.54 cm and length 12 m (first stage), four parallel columns with diameter 2.54 cm and height 6.1 m (second stage), and one column with diameter 2.54 cm and length 24.4 m (third stage). The HETP for an input of 0.09 mol min$^{-1}$ is 2.5 cm. The assembly produces 10.2 g of 92.4% $^{13}C$ per day.[51]

In Ref. 58, methane was used to separate carbon isotopes by fractional distillation. The experiments were carried out on the same column as the fractional distillation of CO, at a working pressure of 34 658 Pa. The steady state was reached in 7.5 h, and the HETP, calculated from $\alpha$ = 1.0108 and the maximum separation factor of 1.34, was 4.9 cm.

A comparative estimation of the efficiency of the fractional distillation of methane and carbon monoxide, carried out in Ref. 58 using the data from Ref. 46, showed that the use of methane to obtain $^{13}C$ with a concentration of 60–70% is economically less favourable. The applicability of this conclusion to the range of higher $^{13}C$ concentrations apparently requires special study. It may be noted that the use of methane requires the use of condensers of more complicated design, since the normal boiling point of liquid nitrogen is much lower than the freezing point of methane.

## IV. Chemical isotopic exchange

Chemical isotopic exchange, proposed in the mid-nineteen-thirties,[72] is an effective method for separating the isotopes of light elements. It occupies a unique position, on the one hand because of the wide variety of reactions and compounds which can be used to separate isotopes and on the other hand because it is comparatively inexpensive. The production of isotopes by chemical exchange is based on the use of thermodynamically reversible separation processes in two-phase systems. In these systems there are deviations from the equally-probable distribution of the isotopes between the phases present in thermodynamic equilibrium. The isotopic effect is characterised quantitatively by the elementary separation factor $\alpha$.

### 1. The bicarbonate method

One of the first reactions used to separate carbon isotopes was the exchange reaction between carbon dioxide and aqueous solutions of alkali metal bicarbonates:[73]

$$^{13}CO_2(\text{gas}) + H^{12}CO_3^-(\text{liquid}) \rightleftarrows {}^{12}CO_2(\text{gas}) + H^{13}CO_3^-(\text{liquid}). \quad (2)$$

At equilibrium, however, aqueous solutions of bicarbonates contain not only $HCO_3^-$ ions but also carbonate ions and molecules of dissolved $CO_2$, so that the main exchange reaction (2) is accompanied by exchange reactions between the $CO_2$ in the gas phase and the $CO_2$ dissolved in the liquid phase, and also between $CO_2$ and carbonate ions.[74,75] At 298 K the separation factors for the carbon isotopes in these reactions are 1.013, 1.0008, and 1.0077 respectively.[75] The overall effective separation factor under different specific conditions depends on the mole fraction of each compound in the solution, and according to Ref. 73 is 1.012 at 298 K and a pressure $P_{CO_2}$ = 101 308 Pa. With increase in temperature to 313 K, $\alpha$ decreases to 1.008.[75]

Despite the comparatively high separation factor and the simplicity of stream reversal, which is brought about by decomposing the bicarbonate with sulphuric acid, the bicarbonate method suffers from a serious disadvantage, namely the low rate of isotopic exchange.[73,76,77]

The influence of the material and geometric form of the packing on the efficiency of a column using the bicarbonate method has been studied.[78] At 293 K and a rate of supply of 20% potassium bicarbonate solution of 4 ml min$^{-1}$, in a two-metre column with diameter 16 mm filled with an aluminosilicate catalyst, the HETP was 53 cm. This agrees with the value obtained in another study[47] using a similar catalyst.

The addition to the aqueous potassium bicarbonate solution of acetone, in which the solubility of carbon dioxide is 7 times that in water, increases the separation of the carbon isotopes.[75,79,80] The optimum concentration of acetone in water is 5 vol.%.

The bicarbonate method uses large quantities of reagents for stream reversal. A method of separation using the bicarbonate of 2-aminoethanol instead of alkali metal bicarbonates does not suffer from this disadvantage.[81] Stream reversal in this case is achieved by simple thermal decomposition of the bicarbonate of 2-aminoethanol to the original $CO_2$ and 2-aminoethanol, and the 2-aminoethanol solution, saturated with $CO_2$ in an absorber, is returned to the cycle. This eliminates almost completely the irreversible consumption of reagents, and the expenditure on stream reversal reduces mainly to the cost of electrical energy. The effective carbon isotope separation factor when the bicarbonate of 2-aminoethanol is used is approximately the same as for isotopic exchange between $CO_2$ and alkali metal carbonates.[82]

The influence of temperature and the concentrations of the bicarbonate of 2-aminoethanol and the added catalyst carbonic anhydrase on the efficiency of the column was studied.[83] The experiments were carried out on a column with length 6 m and internal diameter 15 mm. The packing consisted of activated carbon and ShCM grade silica gel with a particle size of 2.5–3.5 mm. Neither silica gel nor activated carbon catalyses isotopic exchange between the bicarbonate of 2-aminoethanol and $CO_2$. With increase in temperature from 5 °C to 50 °C, the degree of separation passes through a maximum at 20 °C. The optimum 2-aminoethanol concentration is 0.9–1.0 M. The HETP decreases by a factor of 1.3–1.5 when an alcohol–chloroform specimen of carbonic anhydrase (1–10%) is added, and is 65–80 cm, depending on the catalyst concentration.

The bicarbonate method for separating carbon isotopes can compete with the fractional distillation of CO only when catalysts capable of giving comparable HETP are found.

## 2. The carbamate method

In the early nineteen-sixties it was established[84] that the salt-like carbamates formed by the reaction of secondary amines with $CO_2$ in anhydrous organic solvents may be promising for separating carbon isotopes by the isotopic exchange reaction:

$$^{13}CO_2(gas) + R_2N^{12}CO_2^-(liquid) \rightleftarrows R_2N^{13}CO_2^-(liquid) + {}^{12}CO_2(gas). \quad (3)$$

The product of the reaction of the amine with $CO_2$ is thermally unstable, so that stream reversal in the carbamate system is achieved by simple heating, and the separation can be carried out using the simple scheme shown in Fig. 4.

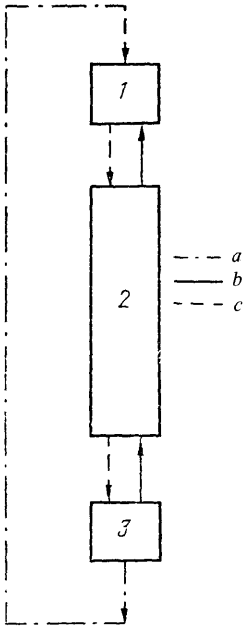



**Figure 4.** Schematic diagram of the separation of carbon isotopes by the carbamate method: *1*, absorber, *2*, exchange column, *3*, desorber, *a*, stream of complex former (amine + solvent), *b*, stream of gas ($CO_2$), *c*, stream of complex (amine + solvent + $CO_2$).

The presence of moisture in the solvent can produce a radical change in the nature of the product obtained by the reaction of $CO_2$ with a secondary amine. The reactions taking place in this case are probably accompanied by the reaction of water to give carbonates.

A column with length 196 cm and internal diameter 10 mm, containing stainless steel Helipak packing, was used to determine the degree of separation of carbon isotopes under identical conditions (reflux density, amine concentration, temperature) using fifteen different amine solutions in methanol.[85] The degree of separation of $^{13}C$ decreased in the order isobutylamine > 2-aminoethanol > n-butylamine. The optimum concentration of the solution of n-butylamine in methanol is 1–1.2 M, and the optimum temperature 298 K. Further increase in the n-butylamine concentration is inappropriate, because of the appreciable deterioration in mass transfer as a result of the increase in the viscosity of the solution.

The hydrodynamic characteristics of the system were improved using a whole series of non-aqueous solvents[86,87] having a lower viscosity and greater solvent power for carbamate, compared with methanol. The best of these was triethylamine (TEA). Of the amines, di-n-butylamine (n-DBA) has the most favourable characteristics. In the Mound Laboratories (USA), data obtained for solutions of n-DBA in TEA were used to construct and operate a five-stage cascade in which $CO_2$, previously enriched to 20% in $^{13}C$, gave 4 g $^{13}C$ per day with 90% enrichment.[88] The incomplete stream reversal when TEA is used as solvent lowers considerably the efficiency of the separation of the isotopes in the carbamate system.[51]

Pyridine and triethylamine have been used as solvents, and dibutylamine as the amine.[89] Experiments showed that solutions of dibutylamine in triethylamine with a water concentration $\geqslant 0.1\%$ are unsuitable for the separation, because of the formation of an insoluble precipitate in the desorber and in the column. On a column with diameter 2.5 cm and length 100 cm, the greatest separation factor (1.77) was achieved using a 1 M solution of n-DBA in TEA. With increase in the molarity of the solution, the separation deteriorated, due to the increase in the viscosity of the liquid phase. Triethylamine has a number of disadvantages as solvent: 1) the high saturated vapour pressure of TEA under the working conditions in a prolonged separation process leads to extensive loss of solvent and requires the use of special assemblies to keep the composition of the liquid phase constant; 2) preliminary drying of the solvent is essential; and 3) quantitative stream reversal in the desorber cannot be achieved when TEA is used.

A search has therefore been carried out for a more effective solvent which would satisfy the following requirements: low viscosity and boiling point; good solvent power for carbamate; low surface tension; chemical inertness and thermal stability; comparatively low vapour pressure; low physical solvent power for $CO_2$ and low solvent power for water; low cost; and availability. From these properties, octane was selected as solvent for di-n-butylamine.[89] On a column with length 100 cm and diameter 2.5 cm, using a 1 M solution of n-DBA in octane, the separation factor was 1.93, which is slightly greater than that for triethylamine, for which the separation factor was 1.77. Moreover, when octane was used, the time taken for the assembly to reach the steady state was reduced by 30%. The dependence of the degree of separation on the reflux density for the 2 M n-DBA–octane–$CO_2$ system was studied on a large-scale metallic laboratory assembly (length of packed column 250 cm, diameter 56 mm). The highest separation factor, 2.4, was achieved at a reflux density of 1 ml $cm^{-2}$ $min^{-1}$.

**Table 2.** Influence of temperature on the value of $\alpha$ and the degree of separation of carbon isotopes in the system formed by $CO_2$ and a solution of n-DBA in octane.[90]

| Temperature, K | $\alpha$ | Reflux density ml $cm^{-2}$ $min^{-1}$ | Degree of $^{13}C$ separation | Time to reach steady state, h | HETP, cm |
|---|---|---|---|---|---|
| 298 | 1.0100±0.0003 | 0.840 | 1.67 | 48 | 1.94 |
| 318 | 1.0075±0.0004 | 1.070 | 1.60 | 30 | 1.62 |
| 333 | 1.0060±0.0003 | 1.170 | 1.46 | 25 | 1.61 |

When the separation was carried out for 60 d using the same working mixture, the concentration of moisture in the liquid phase did not increase, and remained at 0.03%. Thermal phase reversal at

the lower end of the assembly was achieved by boiling the liquid phase at 131 °C. The loss of $CO_2$ did not exceed 5 μg $ml^{-1}$.

The influence of temperature on the separation of carbon isotopes using the system formed by $CO_2$ with a solution of n-DBA in octane was studied on a column with diameter 2.5 cm and length 100 cm at different reflux densities calculated to give the same carbon dioxide flux at all temperatures.[90] Table 2 shows that α decreases regularly with increase in temperature. Increase in temperature above 318 K is not appropriate. Because of the appreciable dependence of the HETP on temperature in the range 298–318 K, the decrease in α is compensated by the decrease in the HETP and by the decrease in the accumulation time of the isotopic product.

The results of published studies[89,90] were used to calculate versions of a cascade assembly for obtaining highly concentrated $^{13}C$. To obtain a $^{13}C$ concentration of 99% with α = 1.01, approximately 1400 theoretical separation stages are required. It was found most suitable to use a four-column cascade, with minimum total volume and minimum time to reach the steady state (about 53 d). It was shown that for a calculated assembly operation time of 300 days per year, half of the expenditure is for the starting materials (amine and solvent).

## 3. The cyanide method

The exchange between hydrogen cyanide and alkali metal cyanide solutions is one of the most effective methods for separating carbon isotopes. The concentration of $^{13}C$ by the reaction

$$H^{12}CN(gas) + Na^{13}CN(liquid) \rightleftarrows H^{13}CN(gas) + Na^{12}CN(liquid) \quad (4)$$

takes place in the gas phase, and the calculated separation factor α is 1.026–1.030 at 298 K.[91–93] A slightly higher value of α (1.035) is obtained for the separation of $^{12}C$ and $^{14}C$.[94] The effective separation factor is lowered to 1.013[91] as a result of exchange between gaseous HCN and hydrogen cyanide absorbed by the NaCN solution. For this last reaction, α = 0.995.

A two-stage cascade with a total length of 19.5 m gave 20 g of carbon containing 25% $^{13}C$.[93] The column diameter was 22 mm in stage I, and 10 mm in stage II. The working pressure in the lower part of the column was 166 652 Pa. The column of stage I was supplied with sodium cyanide formed by neutralising the ascending stream of HCN with NaOH solution in the absorber.

A cascade consisting of two columns was used to study the influence of pressure and the NaCN concentration on the efficiency of the separation.[95] The diameters of the columns of stages I and II were 24.8 mm and 14.4 mm respectively, and the height of each column was 2.5 m. The optimum concentration of the solution was 4.5 M, and the optimum pressure 166 625 Pa. Later,[96] the data from Ref. 95 were used to construct a four-stage cascade with a total length of 13 m, with packing consisting of Fenske glass spirals with diameter 4 mm. The output of the cascade was 0.16 mol $^{13}C$ per day.

The exchange reactions taking place in a liquid–liquid system between cyanohydrins in the organic phase and aqueous potassium cyanide solutions have also been studied:[97]

$$R_2C(OH)^{12}CN + K^{13}CN \rightleftarrows R_2C(OH)^{13}CN + K^{12}CN. \quad (5)$$

The high lability of the cyanide groups of the cyanohydrins leads not only to high separation factors (1.035–1.040) but also to a fairly high rate of isotopic exchange.

In addition to its advantages (a high separation factor and medium HETP), the cyanide method also has a number of significant disadvantages, primarily the extreme toxicity and the high cost of cyanides, and their tendency to polymerise with blockage of the packing. Moreover, the need to work at a reduced pressure reduces the carrying power of the column and hence its productivity. Changing to columns with a large diameter leads to a sharp increase in the HETP. These disadvantages make the process unsuitable for obtaining $^{13}C$ on the industrial scale.

## 4. Ion exchange and other methods of separation

The first publications on the separation of isotopes on ion exchange resins appeared in the mid-nineteen-fifties,[98] when a carbon isotopic effect was detected in the separation of $^{14}C$-labelled amino-acids on cation exchange resins. The effect depended significantly on the position of the tracer in the aminoacid molecule. The presence of the $^{14}C$ isotope in a position at a distance from the ionogenic groups had no influence on the ion exchange properties of the acid.

In the separation of carbon isotopes using hydrogen cyanide, a separation factor close to 1.01 was obtained.[99] The process was carried out by depositing a band of cyanide ions on Dowex-2 anion exchange resin and displacing the band with dilute solutions of hydrochloric and acetic acids. No further studies were carried out, however, because of the high volatility and toxicity of hydrogen cyanide.

Subsequently, carbon isotopes were separated using formate ions,[100,101] deposited on the strongly basic Dowex-2 resin in the acetate form. When the band was displaced with hydrochloric acid solution, its leading edge was enriched in the heavy isotope. With increase in temperature from 279 K to 308 K, α decreased from 1.0062 to 1.0032.

Analysis of the experimental data showed that the use of ion exchange resins with a very high degree of cross-linking does not always lead to an increase in the efficiency of the separation, since there is a simultaneous increase in the dehydrating action of the resin on the ions. Moreover, increase in the degree of cross-linking (the concentration of divinylbenzene in the resin) may lead to a deterioration in mass transfer. In the separation of sulphur isotopes in a band of bisulphite ions in a column of Dowex-2 × 10 anion exchange resin in the acetate form, carbon isotopes were also separated at the boundary between the bisulphite and acetate ions.[102] The heavy $^{13}C$ isotope was concentrated in the solution. The separation factor α was approximately 1.0016.

A combined method for the simultaneous separation of sulphur and carbon isotopes on Wofatit-150 [?Ambeslite IR-20 (Ed. of Translation)] ion exchange resins with displacement of $CN^-$ and $HSO_3^-$ with sulphuric acid solution has been described .[103,104]

The use of ion exchange processes to separate carbon isotopes has not yet gone beyond laboratory studies. Nevertheless, in a number of cases, ion exchange can probably compete with traditional methods, particularly for isotopes of elements of medium mass, whose separation by chemical exchange or fractional distillation is difficult. The most promising methods involve ion exchange using counter-current movement of the phases analogous to that in the two-phase separation processes of fractional distillation and chemical isotopic exchange.

Of other chemical exchange systems used to separate carbon isotopes, mention may be made of systems based on carbonyl complexes. The complexes of CO with $Ag_2SO_4$ (in concentrated $H_2SO_4$), CuCl (in concentrated HCl), $CuSO_4$ (in concentrated $H_2SO_4$), di-n-propylamine, $Cu_2Cl_2.8NH_4Cl$, etc. have been tested.[105] The most suitable for the exchange reaction was found to be the $Cu_2(CO)Cl_2.8NH_4Cl-CO$ system, for which at 20 °C α = 1.016 and the half-exchange time is ~5 s. The stream reversal in the desorber

at 140 °C was quantitative (>99.99%).[105] A characteristic feature of the liquid phase of this system is the formation, on contact with atmospheric oxygen, of a sparingly soluble precipitate which blocks the packing in the column and disrupts its operating conditions. Technological difficulties probably represent the main obstacle to the industrial application of this system.

The simultaneous separation of carbon and sulphur isotopes by chemical exchange between carbon disulphide and potassium xanthate ($S=C(OR)SK$) [106,107] has not found practical application, probably because of its high cost.

## V. Isotopic effects in electrical discharges

In many countries in recent years, considerable attention has been paid to methods for separating stable isotopes based on the selective excitation of atoms and molecules in electrical discharges.[108,109]

Isotopic effects in the synthesis and dissociation of molecules in gas discharges had been observed even earlier, but they were slight. Thus it was shown[110-112] that in the dissociation of carbon dioxide in a silent discharge, the heavy $^{13}C$ isotopes of carbon accumulate in the undissociated $CO_2$ molecules. The degree of separation is independent of the power of the discharge and the rate of flow and pressure of the gas in the discharge tube, and its average value is $1.028 \pm 0.008$. A study of the redistribution of the isotopes in the dissociation of carbon dioxide in a glow discharge showed that, as in the silent discharge, the carbon monoxide formed has a lower concentration of the heavy $^{13}C$ isotope, and the undissociated carbon dioxide fraction is enriched in $^{13}C$ by an average factor of $1.020 \pm 0.008$.[113] Analysis of the mechanisms of the dissociation of carbon dioxide in glow[114] and silent[115-118] electrical discharges indicates that the dissociation passes through a number of stages with the formation as intermediate products of oxygen and ozone, which also accumulate in appreciable quantities in the final products.

A method has been proposed for separating isotopes by chemical reactions taking place under thermodynamically non-equilibrium conditions,[109,119] when the difference in the rate constants of the reactions involving different isotopic forms of the molecules may be considerable.[119]

The possibility of separating carbon isotopes in the reaction CO + CO taking place in an electrical discharge under different conditions (pulse, direct, alternating) has also been studied.[120,121] The chosen duration of the discharge pulse was much shorter than the vibrational-relaxational relaxation time. The pulse repeat frequency was 0.3 Hz, and its duration 5 μs. The experiments were carried out in a stream of gaseous CO at 298 K and 77 K in a reaction vessel consisting of a discharge tube with diameter 20 mm, length 300 mm, with molybdenum electrodes. The gas pressure in the reactor was varied from 133 Pa to 1330 Pa, and the flow rate from $10^{-2}$ litre $s^{-1}$ to 1 litre $s^{-1}$. The composition of the mixture before and after the reaction was determined mass-spectrometrically. The measurements showed that in the pulse discharge with the walls of the reactor cooled to liquid-nitrogen temperature, the average concentration of $^{13}C$ in the $C_2O$ formed reached 3.5%. No significant enrichment in $^{13}C$ was observed in the alternating and direct current discharges.

The presence of $C_2O$ in the reaction products apparently indicates that the mechanism of the reaction CO + CO in the pulse electrical discharge is analogous to that of the photolysis of CO using an iodine lamp (wavelength 2064 Å):[122]

$$CO^* + CO \rightarrow CO_2 + C, \quad (6)$$

$$C + CO \rightarrow C_2O, \quad (7)$$

$$C_2O + CO \rightarrow C_3O_2 \quad (8)$$

(CO* represents an excited CO molecule). Reaction (6) can take place in two directions:

$$^{13}CO + {}^{12}CO \rightarrow {}^{12}CO_2 + {}^{13}C \quad (9)$$

and

$$^{13}CO + {}^{12}CO \rightarrow {}^{13}CO_2 + {}^{12}C. \quad (10)$$

Since the experiments showed $^{13}C$ enrichment in the compound $C_2O$, which is formed with the participation of C, and not $CO_2$, reaction (9) apparently predominates.

The degree of separation of $^{12}C$ and $^{13}C$ in an electrical discharge is much greater than that in other single-stage processes. Because of the complexity of the accumulation of the products of the separation in the reactions in electrical discharges, and the large quantities of energy required for these processes, however, they still remain at the stage of laboratory studies.

## VI. Separation of isotopes using lasers

In the last ten years, the laser separation of isotopes (LSI) has been intensively studied in the Soviet Union and other countries. This is related to a number of potential advantages of the LSI method over traditional methods, namely the high selectivity of the elementary act of separation ($\alpha \gg 1$) resulting from the monochromatic nature of the laser radiation and the possibility of its preferential action on one isotopic form; the fairly low expenditure of energy per atom of the isotope separated (energy is required practically only to isolate the required isotope); the rapid attainment of the steady state of the process; and its universal character.

Of the forms of the LSI method known at present, the most suitable for practical application is the isotopically selective multiphoton dissociation (MPD) of molecules, based on the phenomenon of the selective decomposition of molecules under the influence of resonance infrared radiation. Experiments on isotopically selective MPD have been carried out for many isotopes, from the light (hydrogen) to the heavy (osmium) elements.[123]

The selectivity coefficient of the dissociation, which corresponds to the separation factor, is usually defined as the ratio of the effective rate constants of the dissociation of the molecules with different isotopic compositions in a single irradiation. This definition is close to that adopted in traditional methods for separating isotopes;[124] in both cases the value of $\alpha$ is a measure of the selectivity of the elementary act of the separation.

Although the processes of multiphoton excitation and dissociation of molecules under the influence of infrared radiation have potentially a high isotopic selectivity, there are a number of factors which may lower the separation factor considerably. One of the main factors is vibrational relaxation, as a result of which high selectivity is achieved at low pressures (not higher than 133 Pa).

The study of the isotopically selective dissociation of the $CF_3I$ [125] and $CF_3Br$ [126] molecules shows that carbon LSI has promising possibilities. These molecules are of interest since the dissociation energies of the weak C–I and C–Br bonds are only 2.3 eV and

2.8 eV respectively. The high isotopic selectivity is preserved at a comparatively high gas pressure (up to 670 Pa).[127] Since it is desirable to carry out the process at increased gas pressures to increase the productivity, the dependence of the selectivity of the MPD on pressure was studied for $CF_3I$,[125,128,129] $CF_3Br$,[130] $CF_2Cl_2$,[131] and $C_6H_5F$.[132] In all cases the selectivity of the dissociation decreased regularly with increase in the pressure of the gas used.

Experiments have shown that it is better to use molecules which are not too complex for separation by the LSI method, since the MPD of polyatomic molecules gives numerous fragments, and the isotopic selectivity is decreased. At the same time, complex molecules dissociate more readily under the influence of laser radiation, and higher energy densities are required for molecules containing few atoms.[123] In molecules containing few atoms, the density of the levels up to the dissociation energies is small. This, firstly, restricts the possibility of attaining an energy sufficient for decomposition of the molecule, and, secondly, decreases the rate of the intramolecular redistribution of the excitation energy. Collisions with the buffer gas, however, may change the rotational state of a molecule in the ground or excited state. Since simple molecules (HFCO, $CHF_3$, $CF_3I$, $CF_3Br$) may be promising for carbon LSI, the MPD of these compounds in the presence of large quantities of buffer gases (Ar, He, NO, $N_2$) has been studied.[133–135] The dependence of the effective rate constant of the dissociation on the pressure of the buffer gas has been studied. An appreciable decrease (by an order of magnitude or more) in the rate of the MPD of these molecules was observed with increase in the pressure of the buffer gases from $1.33 \times 10^3$ Pa to $26.6 \times 10^3$ Pa.

Even with the fairly high selectivity coefficients of the MPD of molecules, one enrichment cycle is insufficient to achieve a high concentration of the required isotope, and a multistage process is necessary.[129,133,134,136–138] In the field of a pulse $CO_2$ laser, $CF_3X$ molecules decompose by the reaction

$$CF_3X \rightarrow CF_3 + X \quad (X = I, Br, Cl)$$

to give molecules of $C_2F_6$ and halogen as final products. Since the $C_2F_6$ molecule does not absorb in the range of the radiation of the $CO_2$ laser, and its chemical transformation into $CF_3X$ is fairly complicated, the dissociation of $CF_3X$ may be carried out in the presence of, for example, acceptors of $CF_3$ radicals such as HBr and NO.[136] This gives $CF_3H$ and $CF_3NO$ molecules, which are then easily reconverted into the original compound $CF_3X$. When $CF_3NO$ is heated with an excess of Br to 200 °C, $CF_3Br$ is formed quantitatively in several minutes, so that one or several additional enrichment stages can be carried out.

Another method for cascading the laser separation process involves the use of $I_2$ and $Br_2$ molecules as acceptors. Thus the MPD of $CF_3I$ mixed with $Br_2$ led to the complete conversion of the original molecules to $CF_3Br$, and, on the other hand, the dissociation of $CF_3Br$ in the presence of $I_2$ led to the complete conversion of $CF_3Br$ into $CF_3I$.[133,134,137,138] The experiments showed that in the presence of acceptors the yield of the dissociation and the selectivity of the MPD may be not only preserved but in many cases increased. The dependence of the yield of the MPD of $CF_3I$ ($CF_3Br$) on the pressure of the acceptor is not monotonic, and has a clearly defined maximum, close to which the yield of the dissociation is higher than in the absence of the acceptor.

In principle, a high enrichment in the required isotope can be achieved by using laser radiation to 'burn off' from the starting material the molecules containing the isotope which is not required. In this separation scheme, the required isotope is concentrated in the residual products. For carbon, this method can effectively concentrate only the $^{12}C$ isotope, by 'burning off' from the mixture the small quantity of molecules containing the $^{13}C$ isotope. Gram quantities of $CF_3I$ with a $^{12}C$ concentration of 99.99% have been obtained in this way.[139]

To obtain a highly enriched $^{13}C$ fraction, a two-stage scheme is best. In the first stage, the $^{13}CF_3I$ molecule is dissociated, and in the presence of an acceptor a new compound $CF_3X$ is formed (X = Br, NO) with 20–30-fold enrichment in $^{13}C$. The $CF_3X$ is then transformed either into the original compound[137] or into a compound which undergoes isotopically selective dissociation under the influence of a $CO_2$ laser (for example $CF_3Br$).[133] The second stage involves the dissociation of the $^{12}CF_3X$ molecules. In this way it is possible to obtain a product with a $^{13}C$ enrichment of 90–99%.

The above results were obtained under single-pulse conditions. They were later reproduced[140,141] on a specially constructed assembly consisting of a pulse-periodic $CO_2$ laser with a kilowatt power level and a laser separating cell with transverse pumping of the working gas. The results obtained make it possible to proceed to the development of an industrial assembly for carbon LSI by isotopically selective MPD using $CF_3I$ or $CF_3Br$ molecules as the starting material.[140]

Analysis of the experimental data shows, however, that in addition to their advantages (the low dissociation energy of the carbon–halogen bond, and the high isotopic selectivity at a comparatively high gas pressure up to 600 Pa), halogen-substituted methane molecules have certain disadvantages: they decompose by a radical mechanism, and the primary act of dissociation of the $CF_3X$ molecules (X = I, Br) to a $CF_3$ radical and halogen is followed immediately by the start of secondary chemical reactions which lower the selectivity and the yield of the required isotope. Moreover, the isotopically enriched halogen-substituted hydrocarbons obtained as final products in these processes may find only limited application. The conversion of $CF_3X$ molecules into simple molecules (CO, $CO_2$) convenient for subsequent application involves technological difficulties and additional expense. A search has therefore been carried out for molecules whose isotopically selective dissociation will give products widely used in the synthesis of labelled compounds, and also in traditional methods of separation by low-temperature fractional distillation and exchange.[142] In particular, for carbon LSI it has been suggested that carbonyl-containing compounds, many of which give CO and $CO_2$ on decomposition, may be used. Moreover, in carbonyl-containing compounds, the C=O bond stretching vibrations (1700–1800 $cm^{-1}$) show large isotopic shifts (40–50 $cm^{-1}$),[143] and this is important for achieving a high isotopic selectivity in the MPD process.

It should be emphasised that the frequency of the C=O stretching vibration lies in the range of the generation of the $CO_2$ laser, which has not yet been used to separate isotopes, although its specific energy characteristics and the broad spectral composition of the radiation makes this a realistic possibility.[144–146] Carbonyl chloride $COCl_2$ enriched in $^{13}C$ and $^{18}O$ has been used to study MPD under the influence of pulse $CO_2$ laser radiation and to determine the yield of products and the selectivity with respect to carbon and oxygen simultaneously. The isotopic analysis of the dissociation product (CO) and the residual product ($COCl_2$) was carried out by mass spectrometry. The energy of the lasing pulse was ~0.5 J, and its duration ~5 μs. The irradiation of carbonyl chloride at a pressure of 66 Pa gave a selectivity of 4 with respect to carbon and oxygen.[147,148]

## VII. Summary

At the present time, the principal industrial method for obtaining the $^{13}C$ isotope is the low-temperature fractional distillation of carbon monoxide. Extensive studies of the fractional distillation of CO in counter-current laboratory, pilot-plant, and industrial packed columns with different diameters have given the optimum parameters of the technological separation process, providing a reliable basis for increasing their productive capacity and making it possible to arrange cascades of columns to reduce the time taken to achieve a given $^{13}C$ concentration. At the same time, the method involving low-temperature fractional distillation of CO has a number of disadvantages, of which the most significant are the comparatively low separation fator $\alpha$ and the high energy consumption associated with the large quantities of coolant used, the complexity of the technological equipment for the process, and the rigorous requirements for pure CO. These disadvantages, particularly the first, become important when the scale of $^{13}C$ production is increased.

Promising technical and economic characteristics are shown by processes for obtaining carbon isotopes by chemical isotopic exchange between carbon monoxide or dioxide and their molecular compounds with organic ligands. The main advantages of these systems, in addition to the comparatively high values of the factor $\alpha$, are the possibility of thermal enrichment of the streams and the fact that the separation can be carried out at room temperature. The carbamate system appears promising. The efficiency of the carbamate method of separation can be increased by using aliphatic hydrocarbons as solvents for the amines. The disadvantages of this method are, firstly, the need to use a large quantity of inert solvent, which requires an increase in the cross-section of the mass-exchange assembly and the processing of large streams. The main volume of the assembly and most of the material expenditure are associated with the first two stages of the cascade, where the $^{13}C$ concentration is increased to only 10%.

Another promising direction for the large-scale production of carbon isotopes is the laser method. The laser separation of carbon isotopes may in the near future compete with traditional methods such as fractional distillation and chemical isotopic exchange. An important task in the development of a technological LSI process is to find effective starting materials. To obtain a highly enriched required isotopic product, several cycles of the laser separation are usually required. After each separation stage it is necessary to convert the enriched product into the starting material or into compounds which absorb the energy of the $CO_2$ laser; this is often difficult and always requires the expenditure of energy and materials.

A method of separation using only lasers is probably not always the optimum method. It may be technologically appropriate to combine carbon LSI with traditional methods of separation, in particular chemical exchange and fractional distillation. In this combination, simple carbon-containing molecules (CO, $CO_2$, etc.) with a low degree of enrichment (up to 10–15 at.%), obtained in a single laser-separation cycle, can be subjected to further enrichment by traditional methods. This would make it possible to eliminate from cascade separating assemblies the first two stages, in which, as noted above, the greatest quantities of energy and materials are used, and this should lead finally to a significant decrease in the cost of carbon isotopes.

Important directions in the separation of carbon isotopes are still the development of rational technological schemes for combining separation processes and the search for less expensive starting materials, taking account of the possibility of using industrial waste products to give ecologically clean processes.

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