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A CHEMICAL METHOD

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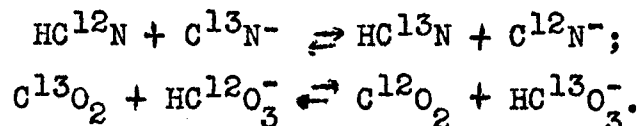
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THE CONCENTRATION OF THE HEAVY ISOTOPES OF CARBON BY A CHEMICAL METHOD

[This is a translation of an article written by Yu. K. Shaposhnikov in Zhurnal Fizicheskoy Khimii (Journal of Physical Chemistry), Vol XXXII, No 4, Moscow, 1958, pages 896-874.]

For the concentration of heavy isotopes of carbon, various methods are in use: thermodiffusion, fractional distillation and isotope exchange [1]. The two latter methods are suitable for obtaining large quantities of compounds enriched by C^{13} .

There are two reactions [2-3] used at the present time as a method for the separation of carbon isotopes:

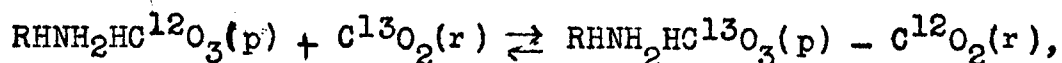


A substantial defect of the bicarbonate method appears to be the slow rate of the carbon dioxide hydration [3-5] limiting the entire separation process. In addition to that, when the bicarbonate and cyanide methods of C^{13} concentration are used there is a substantial loss of these substances and the sulfuric acid. The acid is needed for decomposition of the salts in the heater in order to separate HCN and CO_2 returning into the exchange column.

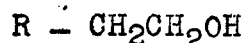
The work of Shchennikova [6] disclosed that an aqueous solution of monoethanolamine bicarbonate can be used as a working solution in the bicarbonate method of C^{13} concentration since it decomposes with separation of CO_2 at ordinary boiling [7-9]. Therefore, when this method is used, there is no necessity for using sulfuric acid. In Addition, the spent solution of monoethanolamine can be returned again into the exchange column by converting it first into a solution of monoethanolamine bicarbonate. The introduction into this solution of a ferment -- carbonic anhydrase in the form of an alcohol-chloroform solution -- according to our experiments materially increases the speed of the process and consequently is a factor of the column separation.

Experimental Part

Isotope exchange in a solution of a monoethanolamine bicarbonate can be presented by the following overall equation:



where



The carbon isotope exchange takes place in a counter-flow column. A solution of monoethanolamine bicarbonate is fed into the upper part of the column. The monoethanolamine bicarbonate trickled through the packing in the column and entered into the evaporating column with the heater where the process of regeneration of CO_2 from the monoethanolamine was taking place. Separated carbon dioxide, freed from water vapors in a condenser, entered into the exchange column below. As a result of multiple repetitions of the exchange reaction between the gas and the liquid phases in the column, the solution of monoethanolamine bicarbonate flowing downward along the packing became somewhat enriched with heavy isotope of carbon.

In our work we used radioactive isotope C^{14} as an indicator. For the measurement of activity of samples containing C^{14} we used a measuring device of the inner filling type [10]. The value of the obtained enrichment with C^{14} was determined by a ratio $F = A/A_0$ (the activity of solutions at the bottom of column A and the original solution A_0). The carbon dioxide does not regenerate fully from the monoethanolamine solution in the heater with the evaporating column. The quantity of carbon dioxide remaining in the solution was determined by the method of isotope dilution (6).

From the data dealing with the solubility of carbon dioxide in the boiling solution of monoethanolamine and from its content in the original solution the separation P was calculated according the formula-

$$P = \frac{\alpha}{L} \cdot 100\%$$

where α — solubility of CO_2 in a boiling monoethanolamine,
L — content of CO_2 in the original solution determined by

valumetric meter [11]. The relative error of determining the factor of the column separation was accepted by us to be equal to 3%.

The errors of determining the amount of the separating were a sum of errors in measuring the amounts of L and R .

Considering all factors, the relative error of separating CO_2 from the heater does not exceed $\pm 10\%$.

Discussion of Results

The separating ability of the column depends on this series of factors: concentration of the working solution; temperature in the exchange column; rate of feeding the working solution; shape of the packing and the presence in the solution of different quantities of the catalyzer carbonic anhydrase ferment.

The effect of the monoethanolamine bicarbonate concentration on the value of the separation factor was studied in a series of special experiments.

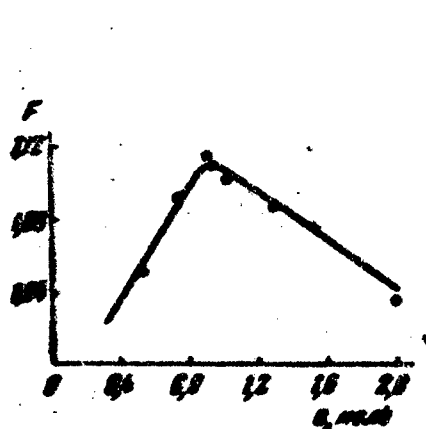


Fig. 1. Relationship between the factor of the column separation and the concentration of monoethanolamine bicarbonate.

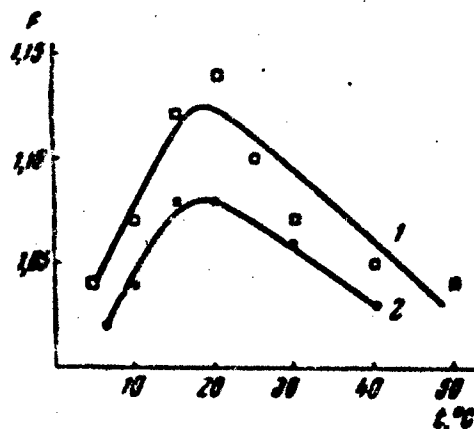


Fig. 2. Relationship between the factor of the column separation and the temperature: 1-0.95 mole/b; 2-1.50 mole/b.

Investigations were conducted with a 2.8m column with an inner diameter of 12 mm. For packing an activated carbon was used in sizes of grains 1.5-2.0 mm. The temperature was maintained within the limits 18-20°C. The results of experiments to determine the ratio between the separation factor and the concentration of the monoethanolamine

bicarbonate solution are shown in Fig 1, from which it is apparent that the separation factor of the column has a maximum value at the monoethanolamine bicarbonate concentration 0.9-1.0 mole/l.

In addition, these series of experiments proved that the relative losses of the carbon dioxide in the boiling solution of monoethanolamine bicarbonate increase with the decrease of the concentration of the working solution though the solubility of CO_2 in a boiling solution of monoethanolamine remains constant. (0.7 ml CO_2 /ml. solution).

The experiments conducted by us indicate that the value of the separation factor of the column depends also on the temperature in the column. This relationship was determined for four concentrations of monoethanolamine bicarbonate solution 0.65; 0.95; 1.15 and 1.5 mole/l at intervals of 5.0 - 50.0°C. Some of the experimental data is shown in Fig. 2. The maximum value of the column separation factor is within the limits of 15 - 25°C for all studied concentrations. The obtained relationships between the column separation factor and the concentration of the monoethanolamine bicarbonate solution and the temperature in the exchange column follow from the Cohen formula [12]. In the case when the separation is not equal to zero,

$$F_p = \frac{(1-p) + \theta}{(1-p)(e^{\theta})^{-(1+\alpha)} + \theta}.$$

Here F_p - is a factor of the column separation at the separation equal p , α - a single stage separation factor:

$$\theta = \frac{p}{\alpha - 1} \quad \text{и} \quad \alpha = \frac{kcc'}{2L} (\alpha - 1) Z.$$

c' - bicarbonate concentration in a solution; c - concentration of carbon dioxide in gas; k - constant directly depending on the rate of the isotope exchange; Z - height of the column; L - rate of flow of the working solution in the column.

When separation is zero the separation factor has the following value:

$$F_{p=0} = e^{\theta} = e^{(kcc'/L)(\alpha-1)Z}.$$

From this expression it is apparent that the separation factor increases with the increase of the bicarbonate concentration in a solution and the concentration of

the carbon dioxide in gas. The decrease of the value of F while the concentration of the working solution is in excess of 0.9 - 1.0 N can be explained by the fact that the speed constant of the isotope exchange diminishes its value. Therefore, the resulting effect of these two values shows that the separation factor of the column has a maximum value at a definite concentration of the monoethanolamine bicarbonate solution. With the increase of the temperature in the exchange column the speed constant of the isotope exchange increases, and a concentration of bicarbonate in the solution and, consequently, CO_2 in the gas decreases. The effect of changeability of these two values explains the presence of maximums in connection with the temperature dependency of the separation factor of the column.

In the present work we compared the results of the column work filled in with an activated carbon and silica gel as packing. The silica gel was marked ChSM; the size of grain was 2.5 - 3.5 mm.

As a result of these experiments it was established that silica gel as well as activated carbon do not possess catalytic qualities with relation to the isotope exchange between the bicarbonate-ion and the carbon dioxide.

Experiments were conducted in a column 6 m. long with an inner diameter of 15 mm. at 18 - 20° C. The separation factor of the column with carbon packing is equal to 1.17 and, with silica gel packing, to 1.25. The increase in the value of the separation factor for silica gel packing in comparison with the activated carbon can be explained by a greater grip of the liquid on the surface of the silica gel.

For the increase in the rate of the isotope exchange between the bicarbonate-ion and the carbon dioxide, we utilized carbonic anhydrase. These experiments were conducted in a column 6 m. long and inner diameter 15 mm. with packing of silica gel (size of grain: 2.5 - 3.5 mm.) at room temperature. For all experiments we used 1.02 mol/l. monoethanolamine bicarbonate solution. The rate of feeding the working solution into the column was 0.57 m./min. CM^2 . The carbonic anhydrase was added to the working solution in quantities of 1 to 14.3%.

The results of these experiments are shown on dr.

3 - 5.

It is apparent from these experiments that an addition of carbonic anhydrase to the working solution increases the separation factor of the column. The carbonic anhydrase influences the factor even if the enzyme solution is diluted 100 times. With a further increase of the concentration of

the alcohol-chloroform preparation of the carbonic anhydrase in the working solution, the separation coefficient of the column increases (Fig. 4). A 10% concentrate of the ferment in the working solution produces a maximum value of 1.4 for the column separation factor; that is, increases the factor 100% in comparison with the value of the factor obtained in experiments without the addition of enzyme to the working solution.

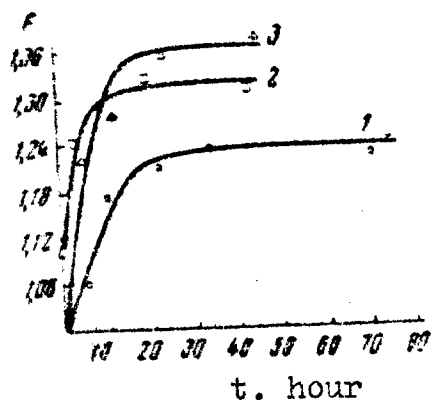


Fig. 3. Relationship between the column separation factor and the time: 1 - without addition of ferment to the working solution; 2 - with addition of 1% of ferment to the working solution; 3 - with addition of 5% ferment to the working solution.

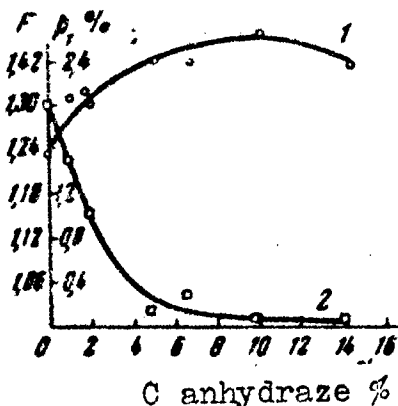


Fig. 4. Relationship between 1 - the column separation factor and 2 - the separation CO₂ from the monoethanolamine and the concentration of the carbonic anhydrase solution in the working solution.

Further increase of the enzyme not only failed to increase the separation factor of the column but actually decreased it for two reasons: strong dilution of the working solution with ferment destroys the conditions for obtaining a maximum separation, because the concentration of the monoethanolamine bicarbonate solution is reduced; the increase in the concentration of the ferment solution is not necessarily connected with its enzyme activity.

It is apparent from Fig. 4 that with the increase of the concentration of the preparation of carbonic anhydrase in a monoethanolamine bicarbonate solution, the separation of CO₂ from the working solution, flowing from the heater, decreases to an insignificant value of 0.1%.

From the data obtained from Fig. 5, it follows that

an addition of small quantities of ferment results in an increase of the separation factor of the column from 1.24 to 1.30 - 1.32, at the time when the separating of CO_2 from the boiling monoethanolamine solution flowing from the heater remains constant.

With the increase of the ferment concentration in the working solution the separation factor of the column increases but the separation is decreased. Therefore, the increase of the separation factor of the column is conditioned not only by a specific action of the carbonic anhydrase, that is, the ability to speed up the hydration of the reaction and dehydration of CO_2 in the column, but also by diminishing the separation of the carbon dioxide from the monoethanolamine solution flowing from the heater.

The relationship between the separation factor of the column and the time shown on Fig. 3 does not answer the question: does the use of carbonic anhydrase as a catalyst lead to a decrease of the time for reaching equilibrium in the column inasmuch as simultaneously the separation factor of the column also increases? But with the increase of the separation factor, the time for reaching a stationary condition in the column increases. Therefore, for comparison it is necessary to select such conditions that the separation factor of the column without the presence of the ferment in the working solution would be equal to the separation factor with the addition of the enzyme to the working solution. For this purpose we selected a column 10 m. long and of a 12 mm inner diameter. Silica gel marked ChSM, diameter of grain 2 - 2.5 mm. was used as packing. The experiment was conducted at room temperature.

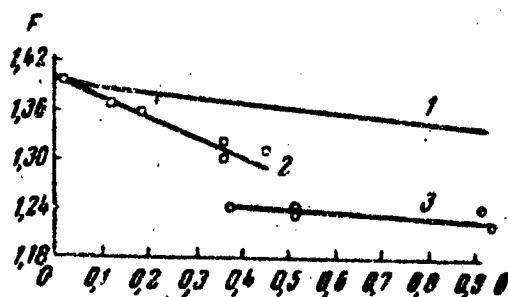


Fig. 5. Relationship between the separation factor and the amount of the separation: 1 - Calculated according to the Cohen formula [12]; 2 - obtained in experiments with the use of carbonic anhydrase; 3 - obtained in experiments without the addition of carbonic anhydrase to the working solution.

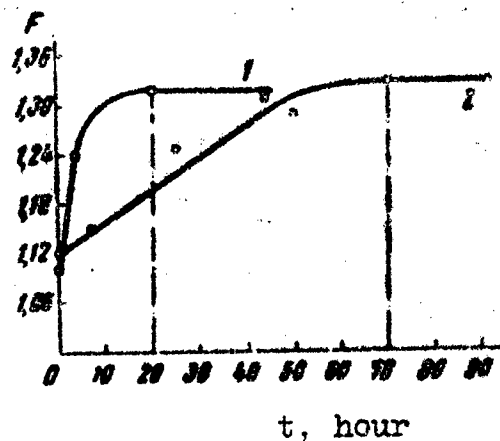


Fig. 6. Comparison of the time required to reach equilibrium in columns of different length: 1 - With the addition of 1% of ferment to the working solution in the column 6 m. in length; 2 - without the addition of ferment to the working solution in a column 10 m.

The rate of the flow of the working solution in the column was 0.62 ml/min. cm². The monoethanolamine bicarbonate concentration was equal to 1.03 mol/l. To the working solution 3% of etnyl alcohol was added to clarify a question: does the alcohol serve to diminish the separation of CO₂ from the monoethanolamine solutions flowing from the heater; while the alcohol-chloroform solution of carbonic anhydrazide is added to the monoethanolamine bicarbonate?

The results are shown on Fig. 6 by means of curve 2. For the purpose of comparison an experiment was conducted with an addition of 1% of carbonic anhydrazide to the working solution (Fig. 6, curve 1) in a 6 m. column. It is apparent from Fig. 6 that in this experiment an equilibrium was reached after 20 hrs. of the column work, and in the experiment with a column 10 m. high the stationary condition was reached only after 70 hrs. of uninterrupted work of the column. The separation of CO₂ taken from the heater with the solution of monoethanolamine in an experiment with an addition of 3% alcohol to the working solution decreased to the value of 0.3%.

Therefore, from the cited data it is apparent that in order to reach a separation factor equal to 1.32 - 1.33 the time for establishing equilibrium in a column was reduced in half. In addition, the experiment in column 10 M. indicated that the amount of the solubility of CO₂ in a boiling solution of monoethanolamine decreases with the addition of ferment to the working solution due to the

presence of alcohol in the preparation of the anhydrazide. The cited experiments support the fact that the rate of carbon isotope exchange between the carbonate-ion and CO_2 is limited by the speed of the hydration of the carbon dioxide. The value of VETT in experiments with addition of various concentrations of the carbonic anhydrazide to the working solution is within the limits 65 - 80 cm. considering that the single stage of the separation factor for the exchange of isotopes C^{12} - C^{14} between CO_2 and HCO_3^- ions is equal to 1.039 [13].

The separation factor of the column for the exchange of isotopes C^{12} - C^{13} will attain smaller value in comparison with the obtained values of F for the separation of isotopes C^{12} - C^{14} , because the single-stage separation factor during production of C^{13} is equal to 1.012 [14].

In conclusion the author wishes to express appreciation to I. A. Korshunov for his interest in the work and constant help in its execution.

CONCLUSIONS

1. Within the limits of the studied concentrations of an aqueous monoethanolamine solution (0.3 - 2.0 mol/l) the greatest separation of the carbon isotope took place when we used solutions with monoethanolamine bicarbonate concentrations of 0.9 - 1.0 mol/l.

2. The maximum separation factor for all studied concentrations of monoethanolamine bicarbonate solutions was obtained at 15 - 25°C.

3. An addition of carbonic anhydrazide to the monoethanolamine bicarbonate solution as a catalyzer during the processes of dehydration and hydration of CO_2 increases the value of the separation factor of the column and decreases the value of CO_2 separation.

4. An addition of alcohol to the monoethanolamine bicarbonate solution decreases the value of CO_2 separation 8 to 10 times.

5. An addition of carbonic anhydrazide to the working solution decreases the time for reaching equilibrium in the column at equal concentrations of the products.

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THE ENRICHMENT OF THE RARE CARBON ISOTOPE BY A CHEMICAL METHOD

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Summary

The isotope exchange reaction between CO_2 and an aqueous solution of monoethanolamine bicarbonate has been used for the enrichment of the rare carbon isotope. The radioactive isotope C^{14} was used as indicator. Monoethanolamine bicarbonate was decomposed by simply boiling in a boiler. Activated carbon and silica gel were employed in the exchange column as fillers.

The effect of the monoethanolamine bicarbonate concentration and of the temperature in the exchange column on the separation factor was established. Maximum separation of the carbon isotope was attained at a temperature in the exchange column of 20° with a 0.9 - 1.0 M. solution of the bicarbonate.

Carbonic anhydrase was used to increase the exchange reaction, its addition to the bicarbonate solution increasing the separation factor of the column and lowering the time required to attain equilibrium in the column at equal concentrations of the products.

The addition of carbonic anhydrase to the solution in operation lowers the CO_2 solubility in the boiling monoethanolamine, making for complete return of the CO_2 to the column.

A similar effect is observed on adding ethyl alcohol to the solution.

END

FOR REASONS OF SPEED AND ECONOMY
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