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Annual Progress Report to

U. S. Atomic Energy Commission

for Contract AT(11-1) 3263

R. N. Zare

SEPARATION OF ISOTOPES

Technical Reports by

M. R. Ghate, C. H. Choi and T. I. Taylor

November 1, 1973

Department of Chemistry, Columbia University

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Technical Reports

Table of Contents

Chemistry Department, Columbia University, New York, New York
R. N. Zare, Principal Investigator, Nov. 1, 1973

A.E.C. Contract AT(11-1) 3263

SEPARATION OF ISOTOPES

Madhav R. Ghate, C. H. Choi and T. I. Taylor

Abstract

The chemical exchange reaction between carbon dioxide (CO_2) and carbamate of di-n-butyl amine ($R_2NCOO^{-+}HNR_2$) in triethyl amine as a solvent results in a concentrations of carbon-13 in the liquid phase and oxygen-18 in the gas phase. A solvent carrier system with thermal reflux has been investigated and the results are summarised. Based on these studies, a six section cascade was designed for the preparation of high concentrations of carbon-13. The cascade was successfully operated for 240 days to study various startup procedures and other characteristics. During the first 141 days, concentration of carbon-13 reached a value of 66.9% ^{13}C.

Measurements of single stage separation factors (α) for different amine-carbamate systems by batch and multistage

techniques is being continued. Preliminary results indicate that α is nearer 1.006 than 1.01 assumed previously. Correlations are being made between the effectiveness of amines for the separation of carbon-13 and their structure, reaction rates and thermodynamic properties as well as the physical characteristics of their solutions.

This report also includes a copy of the preprint of one article on the results of our previous research on the preparation of nitrogen-14 highly depleted of nitrogen-15.

SECTION I

SUMMARY OF TECHNICAL REPORTS

Madhav R. Ghate and R. N. Zare

Summary of Technical Reports:

The following is a brief summary of the principal reuslts of the technical papers of our Annual Progress Report on the "Separation of Isotopes" for 1973

Summary of Data and Experiments performed to obtain high concentration of carbon-13 by chemical exchange reaction between amine carbamate and carbon dioxide:

Most of the characteristics of the (DNBA-TEA) system

$$^{13}CO_2 + R_2N^{12}COO^- \rightleftarrows {}^{12}CO_2 + R_2N^{13}COO^- \quad ,$$

for the concentration of carbon-13 were summarised in detail in our previous reports. Section II of this report describes all those experiments in brief and their relation to the design of a six section tapered cascade. As mentioned in our last year's report, it was necessary to clean all the sections of the cascade and modify the boilers to avoid the formation of exchangeable decomposition products.

The whole system was reconditioned by cleaning the refluxers and packing. The packing in the refluxers was replaced with helicies. All the six columns were then connected using Teflon tubing and were tested for leaks by both evacuating and pressurizing with dry nitrogen.

Using feed CO_2 at the first column only, the cascade operated well for 30 days until the overall separation was 79.8 (47.7% ^{13}C). One of the Teflon tubes developed a crack, causing the cascade to return to the normal concentration. This was repaired and the cascade was operated without any breakdown for 141 days during which time overall separation in the sixth column was 177 (66.9% ^{13}C). Since the rate of build-up was rather slow, it was decided to add one more section to the cascade and it was done. With this added section, operation of the cascade was continued for another 80 days, thus bringing the total operation time to about 8 months. Addition of the seventh section did not improve the performance of the cascade.

Single Stage Separation Factors and the Properties of Amines. As mentioned in the report for last year, an isotope ratio mass spectrometer with a double collector was reconditioned for more precise determinations of single stage separation factors, α_{13} and α_{18}. This is important, not only for the operation and evaluation of the present system for concentrating carbon-13, but also for comparison of different amine-solvent systems. The overall separation of carbon-13 for over fifteen amines in methanol have been determined. Attempts were made to correlate the overall separations with structure, basicity, rate of reaction, and physical properties. For further progress it was evident that it would be necessary to have more precise values for C_{13}.

Several single stage equilibrations were made to test the reproducibility and reliability of both the procedures and the analyses with the mass spectrometer. After some preliminary experiments, CO_2 was equilibrated with 100 ml of 2M DNBA in TEA in a 325 ml vessel with magnetic stirring bars. At equilibrium there was 149.6 m moles of carbamate and 9.16 m moles of CO_2 or a ratio of 16.3. A total of 44 determinations for six different gas phase samples gave a value of 1.0060 ± 0.0012 (S.D.) for α. The rather wide spread of the results from 1.0045 to 1.0092 indicated that further work on the equilibration sampling, purification of the mass spectrometric determination of isotope ratios was needed.

Further tests were made using 30.8 ml of 2M DNBA in a 1157 ml flask so that the m moles of carbamate and CO_2 were about equal at equilibrium. Mass spectrometric measurements were made on the CO_2 from both the gas and the liquid phase. The average of 12 analyses gave $\alpha = 1.0060 \pm 0.0008$ (S.D.) with a spread from 1.0049 to 1.0073. A similar run with 2M monomethanolamine in methanol gave an average value of 1.0059 ± 0.0006 (S.D.) for 13 measurements. The spread was from 1.0050 to 1.0070. Although the reproducibility for both these runs was significantly better than the first ones, it was evident that the resolution, sensitivity and noise of the mass spectrometer should be improved to determine differences for amine solvent systems. To this effect, a more sensitive recorder was added to the mass spectrometer.

The values obtained for α_{13} are somewhat lower than the approximate value of 1.01 arrived at earlier from a determination of α_{18} with a single collector mass spectrometer and the relative separations of carbon-13 and oxygen-18 at the same time in the same column. In preparation for determination of α_{18} using the double collector mass spectrometer, water was prepared by catalytic reduction of CO_2 to H_2O and CH_4. Carbon dioxide equilibrated with this water gave $\alpha_{18} = 1.040 \pm 0.002$ (S.D.) with a spread of 1.037 to 1.043 during adjustments of the mass spectrometer. This may be compared to the reported value of 1.038 so that further refinement of the measurements with the double collector mass spectrometer is needed. Once a reliable value of α_{18} for the CO_2 - carbamate system is obtained, it will be possible to recalculate α_{13} from previous reults of the relative separations of oxygen-18 and carbon-13 in the exchange columns.

Multistage System for the Relative Values of α_{13}. Because of the importance of α_{13} in correlating the properties of amine-solvent system with their performance in separation columns, a multistage method was devised to minimize the effect of reaction rate, etc. This is essentially five horizontally arranged cells with magnetic stirrers for mixing the liquid and gas phases. The 250 ml cells are interconnected for counter flow of liquid and gas with low opportunity of mixing between cells or stages. A saturator, refluxer and pump are provided as in the case of exchange columns. The residence time for the gas and liquid phases as they flow through the cells can be controlled by the flow rate of the carbamate. Samples of CO_2 for analyses were withdrawn with an hypodermic syringe through septums in the top os each cell.

In one run with 2 M monoethanolamine in methanol, the flow rate was reduced from 4 ml/min to 0.5 ml/min over a period of eleven days. Although the curves showed that the system was not quite at equilibrium, it was stopped to improve the pumping system. The overall separations relative to tank carbon dioxide used for the feed were: stage 1, $S_1 = 1.0051$; stage 3, $S_3 = 1.0144$; stage 5, $S_5 = 1.0238$; and for the reflux system $S_r = 1.0282$.

Using the relation $\ln S_3 - \ln S_1 = (\alpha-1) - (s_3-s_1)$, we obtained a value of $(\alpha-1) = 0.0046$ for stages (s_3-s_1). Similar calculations gave $(\alpha-1) = 0.0046$ also for (s_5-s_3), (s_5-s_1), and for the overall separation from feed to the reflux. The value for $(\alpha-1)$ is expected to agree with $(\alpha-1) = 0.0059$ for the static system only if the following assumptions apply: complete equilibrium, 100% stage efficiency, no mixing between cells, no leaks, and no loss of exchangeable carbon in the refluxer. Based on the above comparison, the effective stage efficiency is only $(0.0046/0.0059) \times 100 = 78\%$. Improvements are being made in the pumping, stirring, and refluxing in an effort to obtain greater efficiency and reproducible reuslts for the relative values of $(\alpha-1)$ for different amine-solvent systems.

Preprint of the article "NO-HNO_3 Exchange System for Production of Nitrogen-14 Highly Depleted of Nitrogen-15" Madhav R. Ghate and T. I. Taylor. Separation Science, 9, No. 2 (1973).

II. PREPARATION OF HIGH CONCENTRATION OF CARBON-13 BY SOLVENT CARRIER CHEMICAL EXCHANGE REACTION BETWEEN AMINE CARBAMATE AND CARBON DIOXIDE IN A MULTI STAGE CASCADE.

Madhav R. Ghate and T. I. Taylor

INTRODUCTION

Isotope effects for carbon, oxygen, nitrogen and deuterium in the exchange distillation of several low boiling amine carbamates have been studied by Holmberg.[1,2] Yealts[3] and Brown[4] have investigated these systems further and have determined the effect of temperature on the separation factors.

Most of the current production of carbon-13 is carried out either by distillation of carbon monoxide or by thermal diffusion method. Low temperature distillation of carbon

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[1] K. E. Holmberg, "Proceedings of International Symposium on Isotope Separation," North Holland Publishing Co., Amsterdam, 1958, p. 201.

[2] K. E. Holmberg, Acta Chem. Scand., 16, 2117 (1962).

[3] L. B. Yealts, Jr., Annual Progress Report ORNL 2782 (1959), p. 22.

[4] L. L. Brown, Annual Progress Report ORNL 2983 (1960), p. 19.

monoxide can produce large quantities of carbon-13, but it requires rather sophisticated equipment and substantial capital investment.[5,6] The thermal diffusion method is capable of producing only small quantities of enriched material. Another class of separation process is the chemical exchange method. Chemical exchange method such as exchange of carbon-13 between HCN and CN$^-$ developed by Urey and his co-workers[7] was used a number of years by Eastman Kodak Company.[8] The taxicity of the chemicals and their tendency to polymerize required special precautions in using the system. Chemical reflux also required large quantities of chemicals.

Among the chemical exchange methods, solvent carrier systems with thermal reflux are rather attractive for both laboratory and large scale operations. Studies on the ex-

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5. R. A. Schwind, Chem. Progress Eng. 50, 75 (1969).
6. D. E. Armstrong, A. C. Briemeister, B. B. McInteer, and R. M. Potter, Los Alamos Scientific Laboratory Report LA-4391 (1970).
7. C. A. Hutchinson, D. N. Steward and H. C. Urey, J. Chem. Phys., 8, 532 (1940).
8. D. W. Stewart, Nucleonics, 1, 18 (1947).

change of carbon dioxide with a variety of amine carbamates in different solvents,[9,10,11] such as

$$R_2N^{12}COO^- + {}^{13}CO_2 \rightleftharpoons R_2N^{13}COO^- + {}^{12}CO_2 \qquad \alpha \approx 1.0065$$

methanol indicated either a greater exchange rate, or a larger value for the separation factor (α) was required for practical use of the system. During further investigations of solvent carrier systems to concentrate carbon-13, it was found that the exchange between CO_2 and amine carbamate of di-n-butylamine (DNBA) dissolved in triethylamine (TEA) was promising[13,14] even though single stage separation factor (α) is rather low. This system allowed significantly higher through put rates and gave substantially higher overall separations of carbon-13 in the same columns.[13]

In order to design a cascade of exchange columns for the concentration of carbon-13, studies were made[13] on such variables as: type of solvent, concentration of amine (DNBA),

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9. A. R. Gubta and T. I. Taylor, Annual Progress Report to U.S.A.E.C., Contract AT (30-1) 755, Section IV (1962).
10. J. P. Agrawal and T. I. Taylor, Ibid., Section IIA (1967).
11. J. P. Agrawal, Separation Science, 6 (6), 819 (1971).
12. J. P. Agrawal, Ibid., 6 (6), 831 (1971).

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13. Madhav R. Ghate and T. I. Taylor, Annual Progress Report to U.S.A.E.C., Contract AT (30-1) 755, Section II (1969).
14. Madhav R. Ghate and T. I. Taylor, Ibid., Section II (1970).

effect of catalyst, flow rate, diameter of the column, etc. on the performance of the column. Based on these preliminary studies, a multistage cascade was designed and tested.[14,15,16] The results of some of the above studies and the data on the performance of the six-section cascade which was operated without any stop for eight months are described in this report.

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[15] Madhav R. Ghate and T. I. Taylor, Annual Progress Report to U.S.A.E.C., Contract AT (11-1) 3263, Cu-3263, Section II (1971).

[16] Madhav R. Ghate and T. I. Taylor, Ibid., COO-3263 (1972).

EXPERIMENTAL

The exchange system consists of an exchange column packed with HeliPak packing, a reboiler with a stripping section, and an amine saturator. The dimensions of each of these components depend upon the flow rates of gas and liquid that are to be used. A typical reboiler with a stripping section is shown in Fig. I. It consists of a boiler B, a stripping section S, a drip-tip T, and a cooling condenser C. The cooling condenser is fitted with a nichrome wire coil in order to conduct the liquid in a stream around the surface of the condenser. This feature aids in the prevention of any solid deposit that may form due to a drop in temperature of cooling water. The liquid that leaves the boiler goes through a small bend with a stopcock. This small bend collects the small amount of heavy decomposition products that forms after a long period of operation and thus prevents them from entering the exchange column. A typical complete exchange system with its associated equipment is shown in Fig. 2.

Level Controller. It was observed that the drop in liquid level in the boiler is mainly due to the loss of solvent vapors in the exit stream of waste CO_2. As a result it was necessary to control the liquid level in the boiler to maintain the concentration of (DNBA) at a constant value. In the past we have successfully used a level controller consisting of an inverted container of TEA which allowed air to enter when the level was low. In the present investigations, various level

Figure 1. A typical boiler used for a 25 mm i.d. exchange column in the cascade for the concentration of carbon-13. B, boiler; C, condenser; S, stripping section; T, drip-tip.

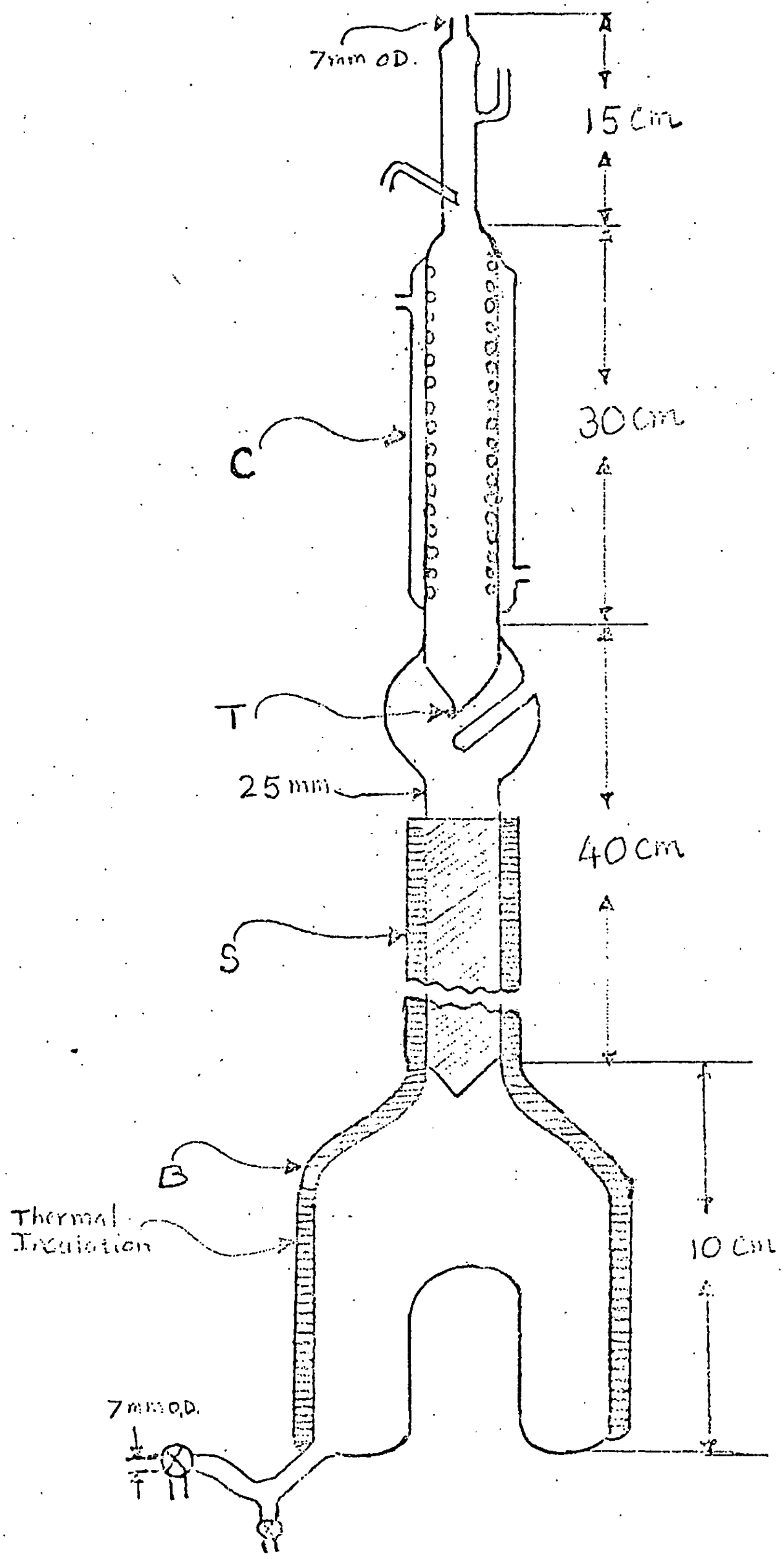
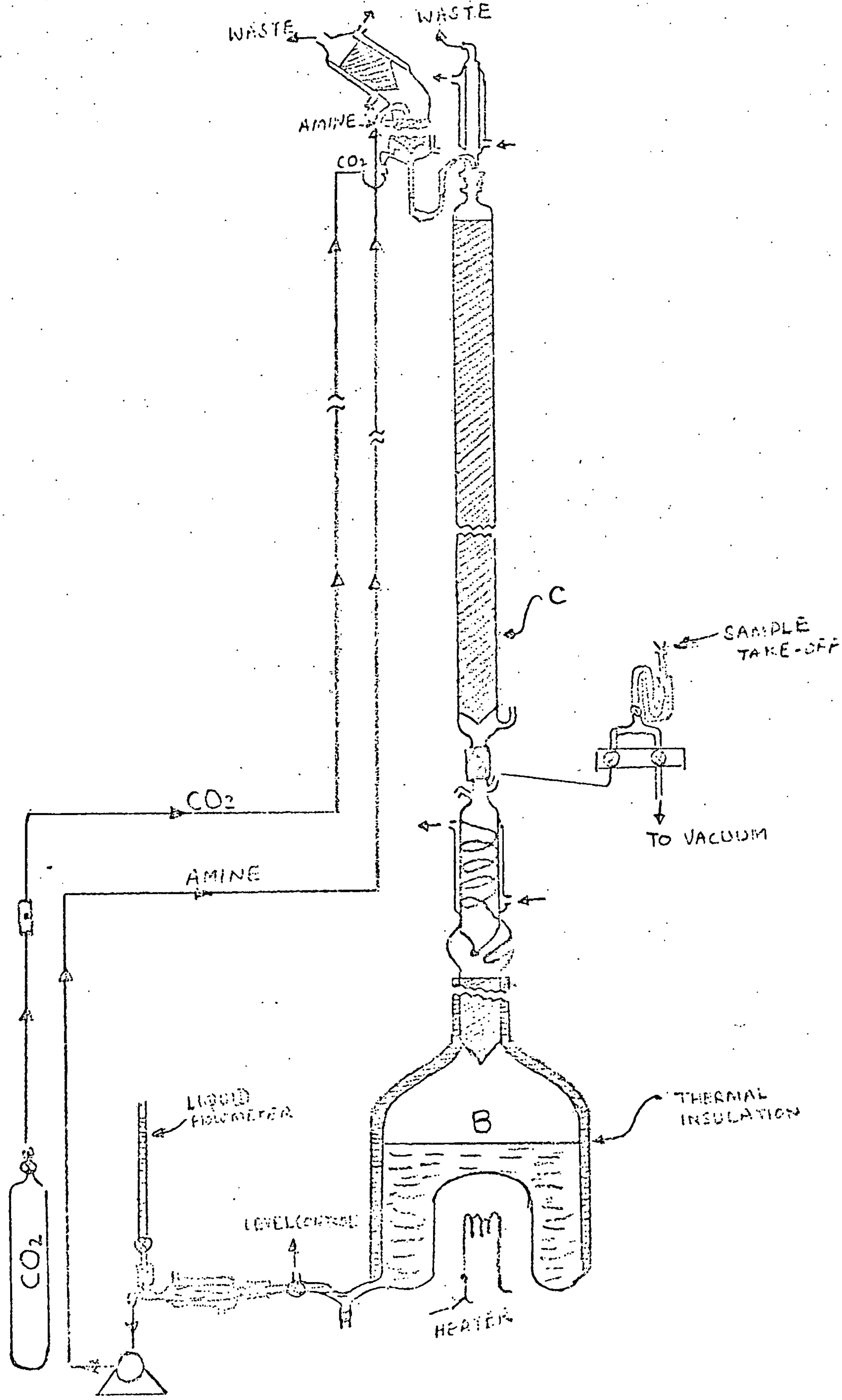

7mm O.D.
15 cm
30 cm
C
T
25 mm
40 cm
S
B
Thermal Insulation
10 cm
7mm O.D.

Figure 2. Schematic diagram of a single column exchange system: C, exchange column; B, boiler; P, pump.

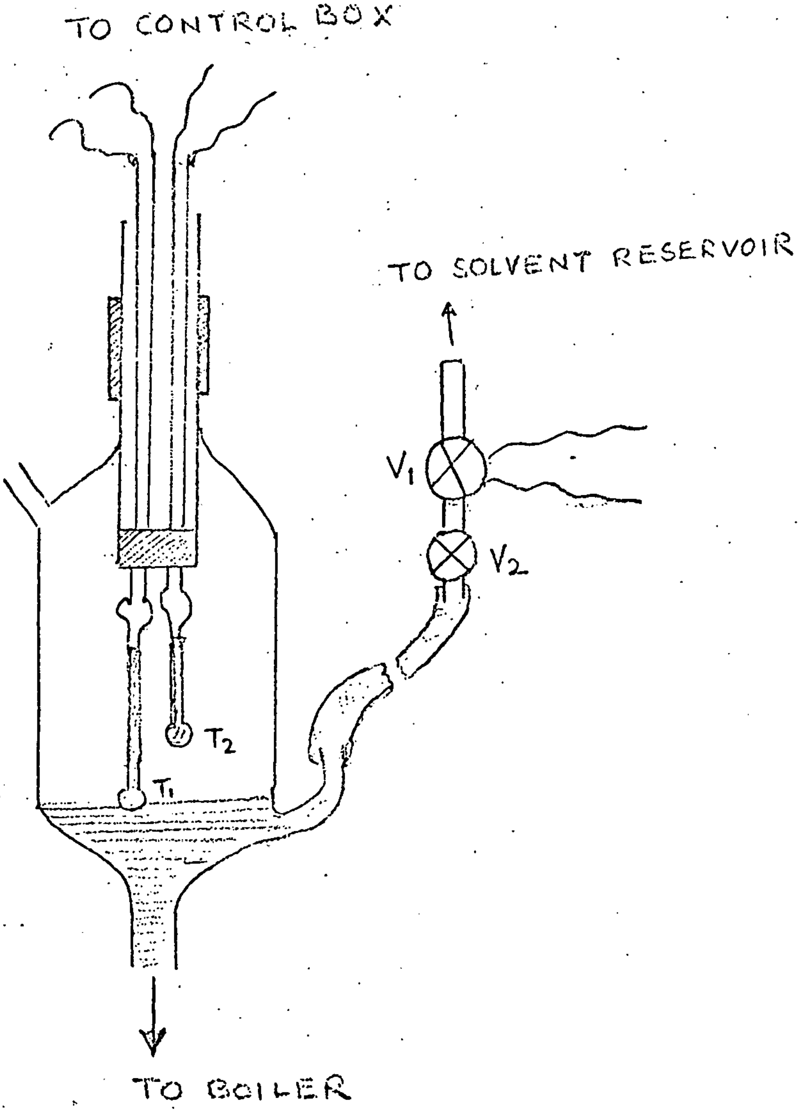

WASTE
WASTE
AMINE
CO2
C
SAMPLE TAKE-OFF
TO VACUUM
CO2
AMINE
THERMAL INSULATION
B
LIQUID FLOWMETER
LEVEL CONTROL
HEATER
CO2

controlling devices were tried. The one described below is versatile, simple and reliable. It makes use of thermistors as the sensing elements. Thermistors are semiconductors having large negative temperature coefficients of resistance. If a constant voltage is applied to the thermistor, its temperature will be lower and its resistance higher in the liquid than in air due to better heat transfer in the liquid. This property of thermistors was utilized to control the liquid level using two thermistors in a standard bridge circuit with some modifications. In Fig. 3 the level controller is shown schematically. When the level of the liquid is below T_1, the balance of the bridge is set so that solenoid valve V_1 is open and solvent flows into the boiler. The flow of solvent through V_1 is controlled by a throttle valve V_2. When the level of the liquid rises to T_1, the balance of the bridge is changed and this closes the solenoid valve V_1. The function of thermistor T_2 is to compensate for changes in room temperature.

Another level controller that uses a float to interrupt a light beam has also operated satisfactorily.

<u>Procedure for a run</u>. Before starting a run the column is flooded with DNBA solution in various solvents to ensure proper wetting of the packing. Then the column is allowed to drain slowly while the feed of amine solution is being pumped into the amine saturator. After draining the excess fluid from the column, the liquid flow is adjusted to the operating value. The column is allowed to operate under this condition

Figure 3. Level controller. T_1 and T_2, thermistors; V_1, solenoid valve (normally closed); V_2, throttle valve.


TO CONTROL BOX
TO SOLVENT RESERVOIR
V_1
V_2
T_2
T_1
TO BOILER

to obtain steady flow of liquid through the packing and to adjust the liquid level in the boiler. Then the feed of CO_2 is started to the amine saturator. After a predetermined time the boiler heater is turned on. This time depends upon the hold-up in the column and the flow rate at which amine solution is pumped into the amine saturator. The voltage of the boiler heater is so adjusted that the temperature near the drip-tip T is about 70°C. Then the level controller is connected to the boiler. Attainment of a constant temperature and boiling rate is necessary since fluctuations result in erratic changes of the liquid level in the controller. The progress of separation is followed by withdrawing small gas samples at different time intervals and analyzing them mass spectrometrically.

Mass Spectrometric Analysis. The gas sample collected in the sample bulb is first frozen with liquid nitrogen and then opened to the vacuum system to pump out noncondensible impurities. Then liquid nitrogen is replaced by dry ice to keep the water and solvent vapors condensed. The gas sample is then introduced into the mass spectrometer and a scan of the mass spectrum is taken from mass 12 to 46. From the peak heights at mass 44 and 45, the separation S_{13} is calculated as follows:

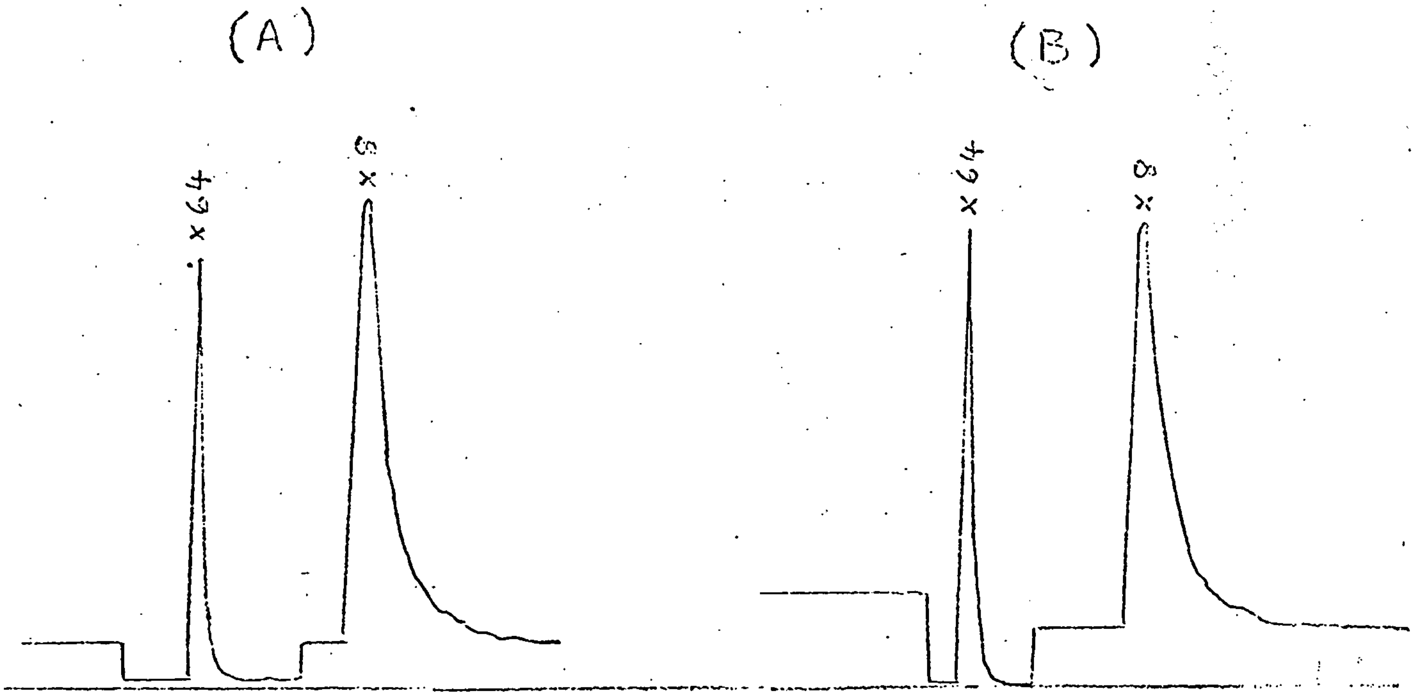
$$S_{13} = \frac{\text{R tank } CO_2}{\text{R Sample}}$$

$$\text{where } R = \frac{\text{peak height of mass 44}}{\text{peak height of mass 45}}$$

Determination of the Composition of the Amine Solution. As mentioned earlier the overall separations are influenced by the concentration of DNBA. Since this may vary because of loss or an addition of solvent, it is essential that the composition of liquid in the boiler be monitored. Various volumetric methods were tried but none was satisfactory. Consequently it was decided that a gas chromatographic method should be investigated. Different types of columns under various conditions were tested and the one which was reasonably satisfactory consisted of Gas-chrom-Q as a column support and silicone QF1 as a stationary phase. A typical gas chromatogram of a 2M DNBA in TEA is given in Fig. 4. For day to day analysis, a calibration curve for standard solutions of DNBA is obtained first, then a sample from the boiler is analyzed. Over long periods of time it was found that concentration of DNBA in the boiler remained within the range of 1.9M to 2M. Larger variations in concentration were corrected by addition of DNBA or solvent TEA as needed.

22

Figure 4. Gas chromatogram of (A) 2M DNBA in TEA and (B) a sample from the boiler after three days of operation.


(A)
×64
×8
(B)
×64
×8

RESULTS AND DISCUSSION

The chemical reaction between an amine and carbon dioxide to form a carbamate can be represented as follows:

$$2R_2NH + CO_2 \rightarrow R_2NCOO^- {-}{-}{-} {}^+H_2NR_2 \qquad (1)$$

where R is an alkyl group. The isotopic equilibrium between the carbamate and carbon dioxide is

$$R_2N^{12}COO^- + {}^{13}CO_2 \rightleftharpoons R_2N^{13}COO^- + {}^{12}CO_2, \qquad (2)$$

$$\alpha \approx 1.01$$

Thus, carbon-13 concentrates in the carbamate at the lower end of the exchange column. Oxygen-18 concentrates in the carbon dioxide with $\alpha \approx 1.013$.

In the exchange system shown in Fig. 1, the isotopic exchange reaction (2) is utilized as follows. The amine carbamate solution from the saturator A flows down the exchange column C_2 through the stripping section C_1 to reboiler B. The hot vapors of the solvent decompose the carbamate to amine and carbon dioxide in the stripping section. Carbon dioxide rises countercurrently in the exchange column where it is contacted with the carbamate and the amine solution is pumped back to the saturator at the upper end of the exchange column. The effectiveness of the system in concentrating carbon-13 depends upon a number of factors which require investigation to select the optimum operating conditions. These include such factors as α, the nature of the amine, the solvent, the concentration of the amine, the flow rate, etc.

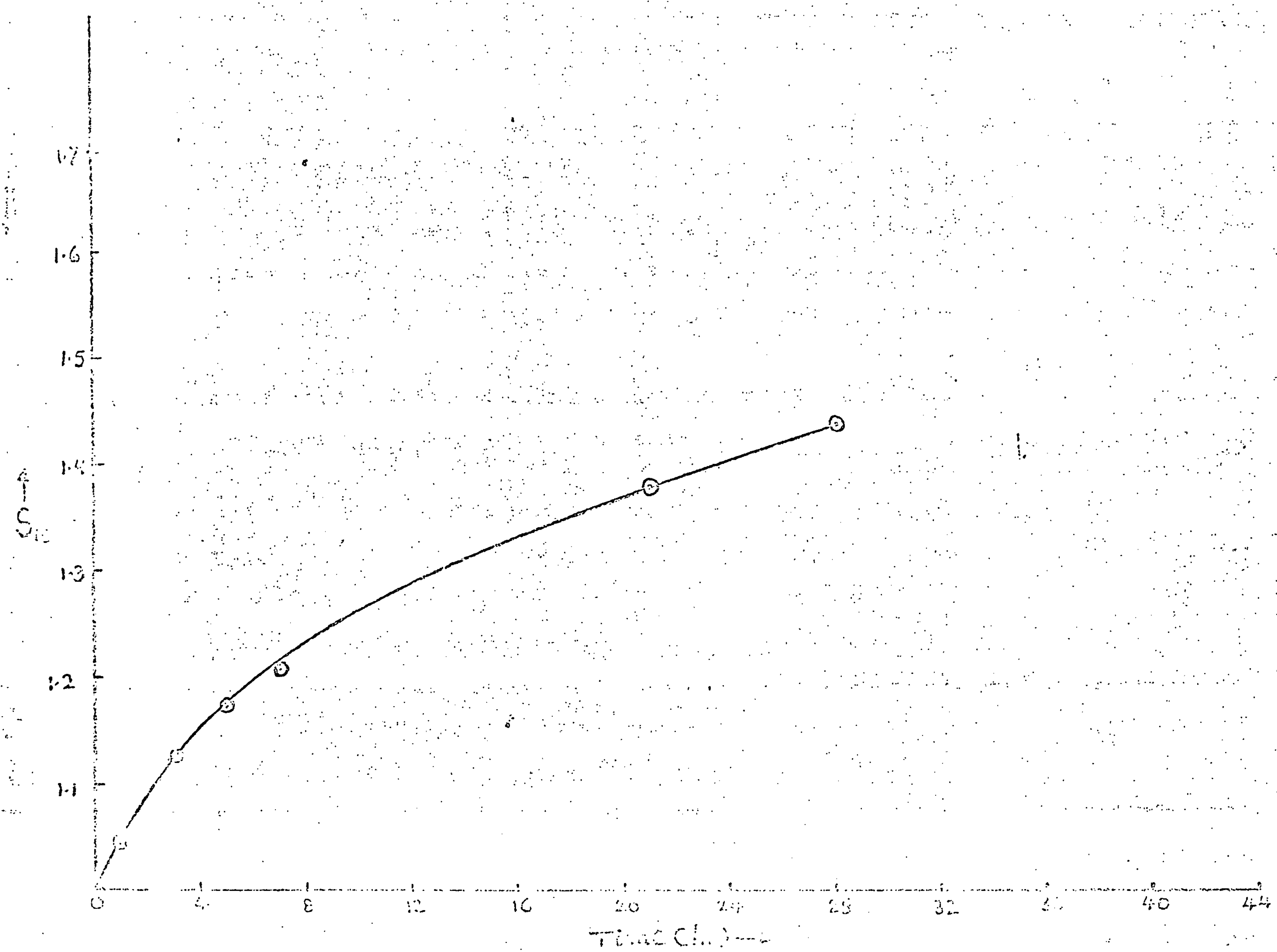
Although previous investigations[18-20] had shown some significant differences among the amines in the same solvent, the choice of the amine is in part dependent upon the solvent selected. For proper operation of the stripping section it is desirable, for example, that the boiling point of the amine be somewhat higher than that of the solvent. The solubility of its carbamate in the solvent, the viscosity of the solution and the absorption of carbon dioxide are also of importance. Since the differences among solvents had been found to be greater than the differences among most amines, consideration was given first to the effect of different types of solvent.

1. Effect of Solvent

Since methanol had been used as a solvent in many of the previous experiments[18-20] it was selected as a reference solvent. Besides the boiling point, the solubility of the amine and the carbamate, the viscosity, etc., two other properties were given consideration in selecting a solvent. These were the basicity and the solubility of carbon dioxide in the solvent. Triethylamine (TEA) and pyridine have significantly different basicities and were found to have suitable solvent properties otherwise. The results of the progress of overall separation with time using these solvents and methanol are plotted in Fig. 5 - 11 and summarized in Table I.

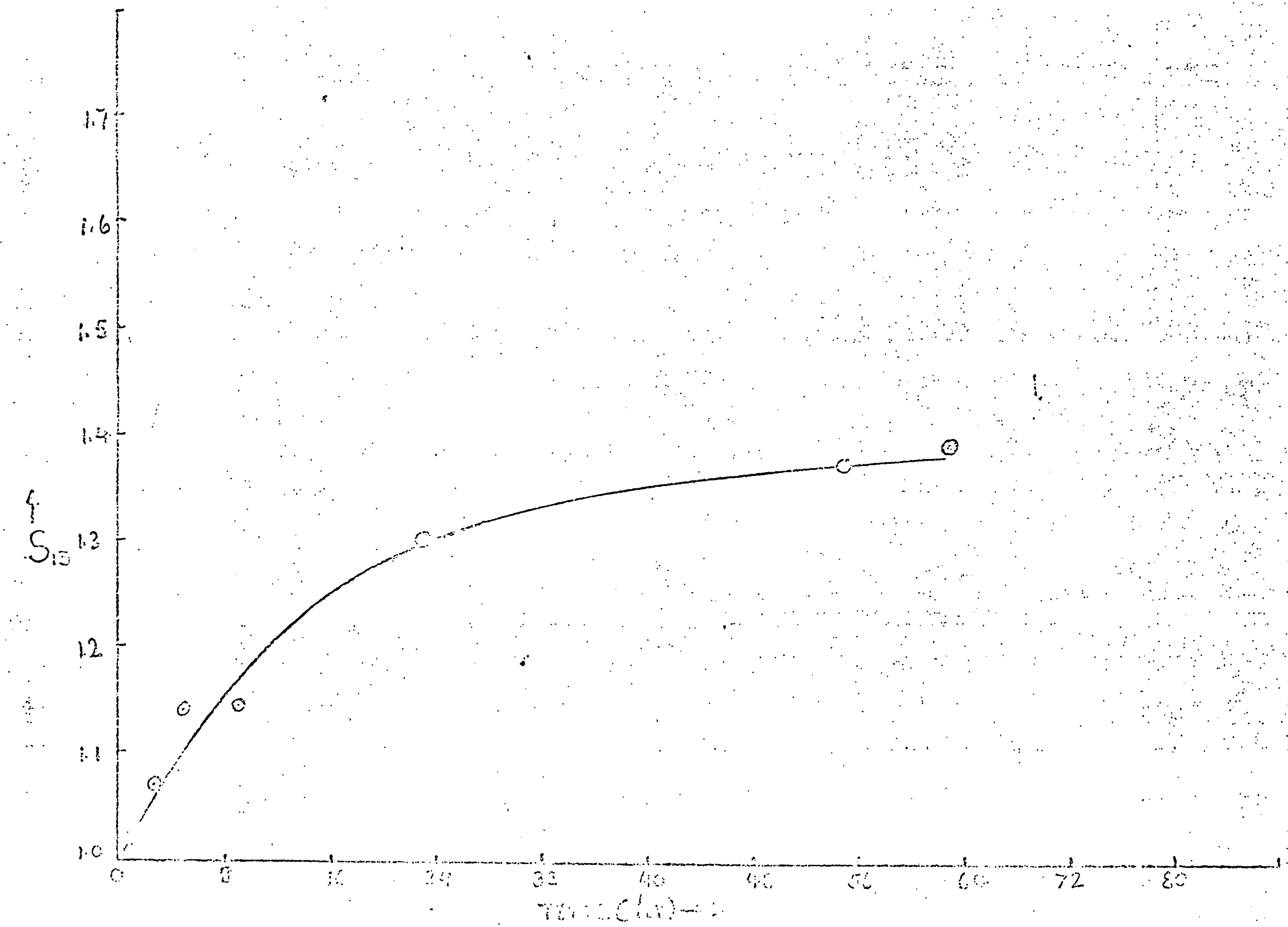
It can be seen from these results that di-n-butylamine (DNBA) in triethylamine ($S_{13} = 2.05$) is considerably more

Fig. 5. Run 5. Overall separation for 1M ISOBA in methanol as a function of time. Flow rate: 4ml/min. Column: 25 mm i.d. x 100 cm packed with "HeliPak" 3013.


1·7
1·6
1·5
1·4
1·3
1·2
1·1
S_{10}
0
4
8
12
16
20
24
28
32
36
40
44
Time (h.) →

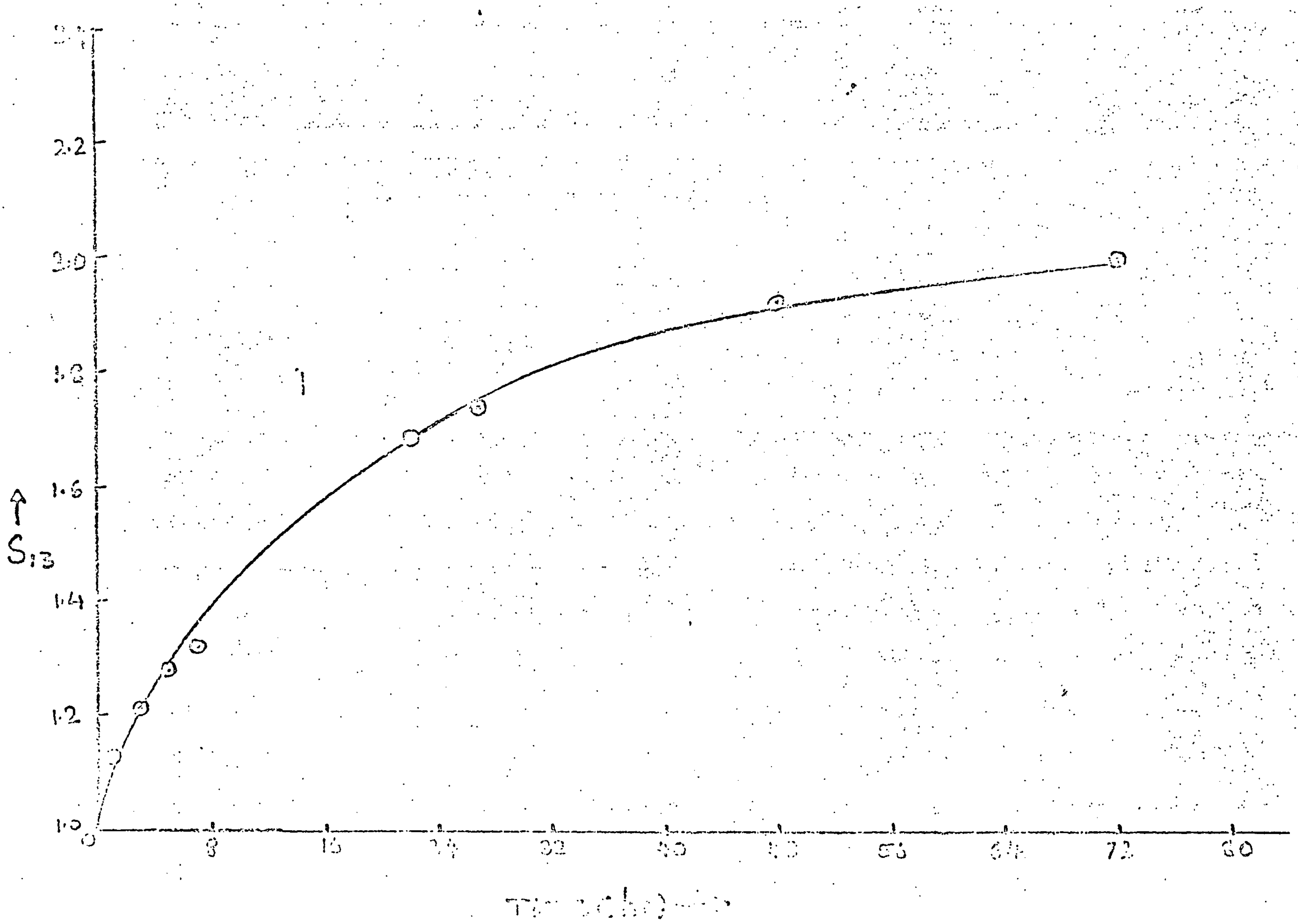
[illegible]

Fig 6. Run 19. Overall separation for 1M MEA in methanol as a function of time. Flow rate: 4 ml/min. Column: 25 mm i.d. x 100 cm packed with "HeliPak" 3013.



↑
S_{15}
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0
8
16
24
32
40
48
56
64
72
80
TIME (hr) →

Fig. 7. Run 15. Overall separation of 1M DNBA in TEA as a function of time. Flow rate: 4 ml/min. Column: 25 mm i.d. x 100 cm packed with "HeliPak" 3013.



2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
↑
S_{13}
1
0
8
16
24
32
40
48
56
64
72
80
TIME (hr) →

Fig. 8. Run 25A. Overall separation of 1 M DNBA in TEA as a function of time and addition of methanol to system. Flow rate: 4ml/min. Column: 25 mm i.d. x 100 cm packed with "HeliPak" 3013.

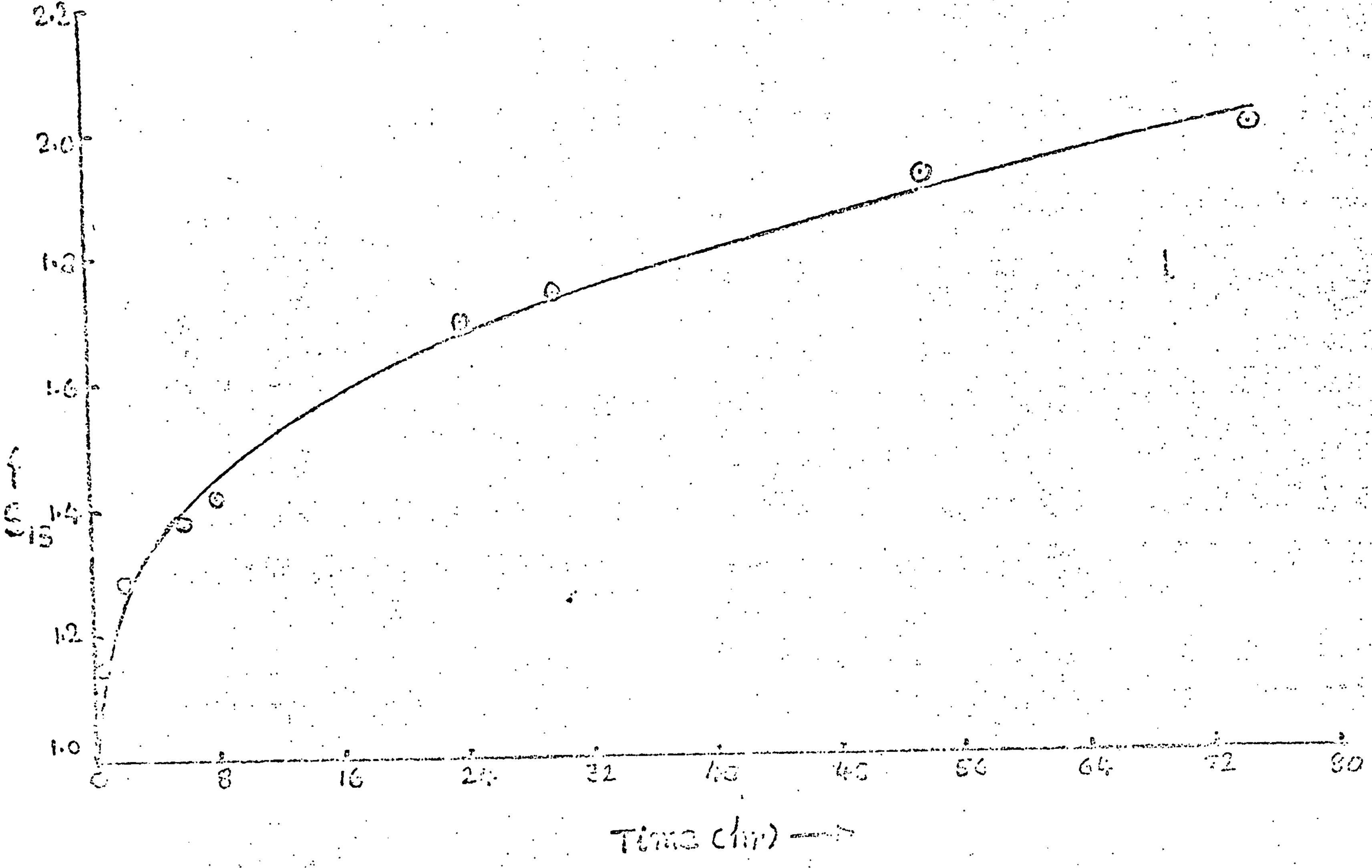


Fig. 8

Fig. 9. Run 17. Overall separation of 1 M DNBA in pyridine as a function of time. Flow rate: 4ml/min. Column: 25 mm i.d. x 100 cm packed with "HeliPak" 3013.

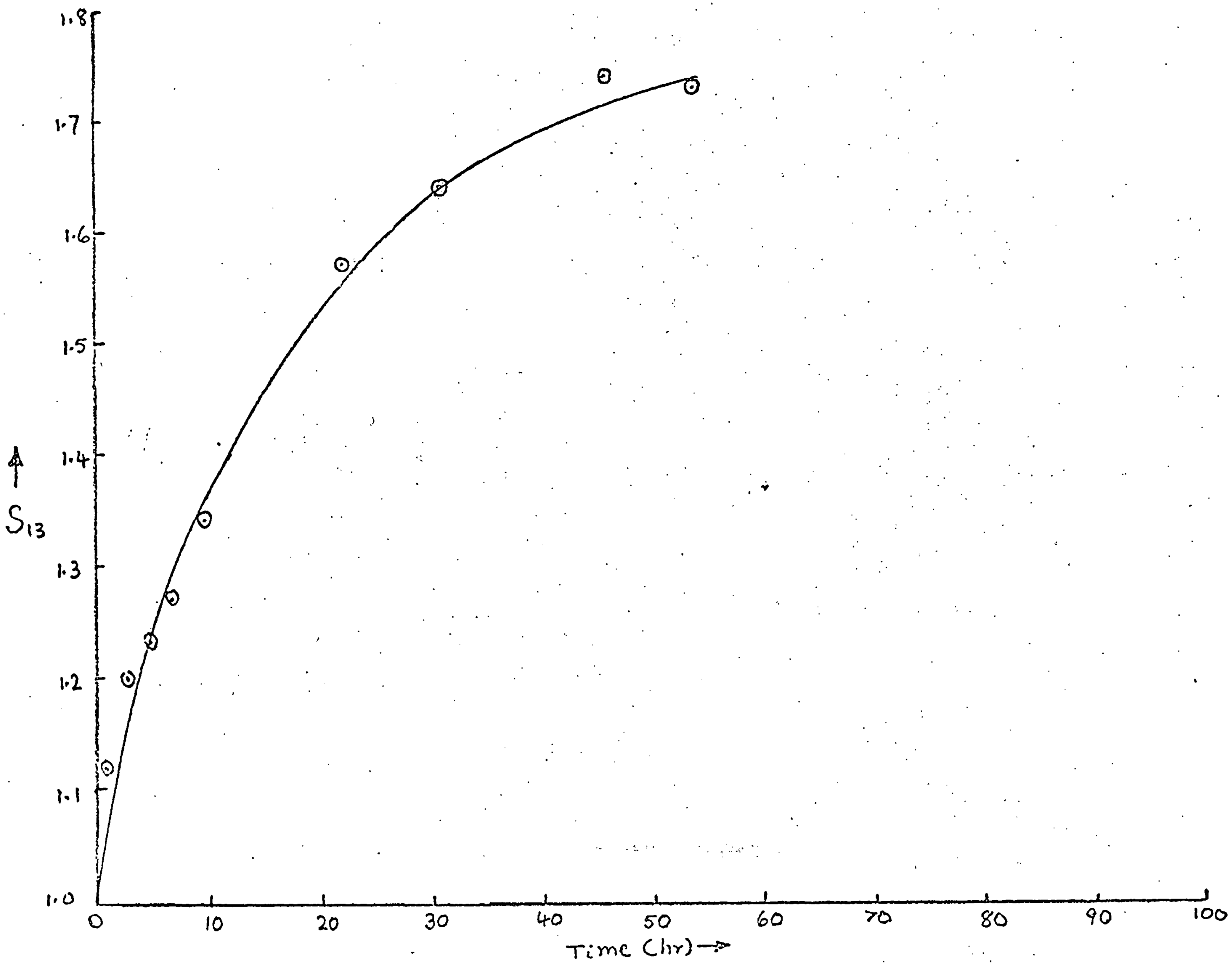

1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
S_{13}
0
10
20
30
40
50
60
70
80
90
100
Time (hr)

Fig. 10. Run 21. Overall separation of 1 M DNBA in 50:50 (v/v) TEA and methanol as a function of time and flow rate. Flow rate: 4ml/min. and 8ml/min. Column: 25 mm i.d. x 100 cm packed with "HeliPak" 3013.

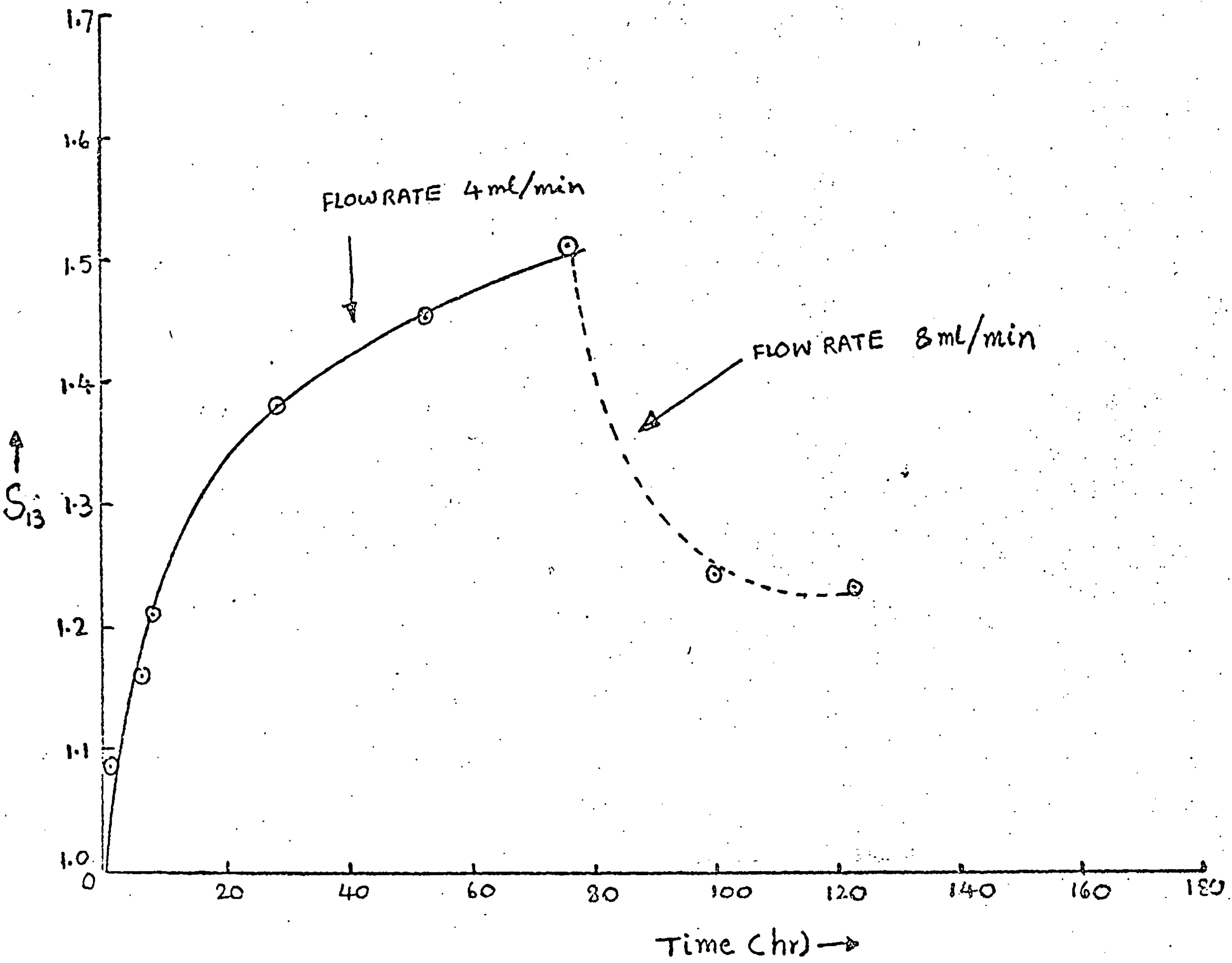
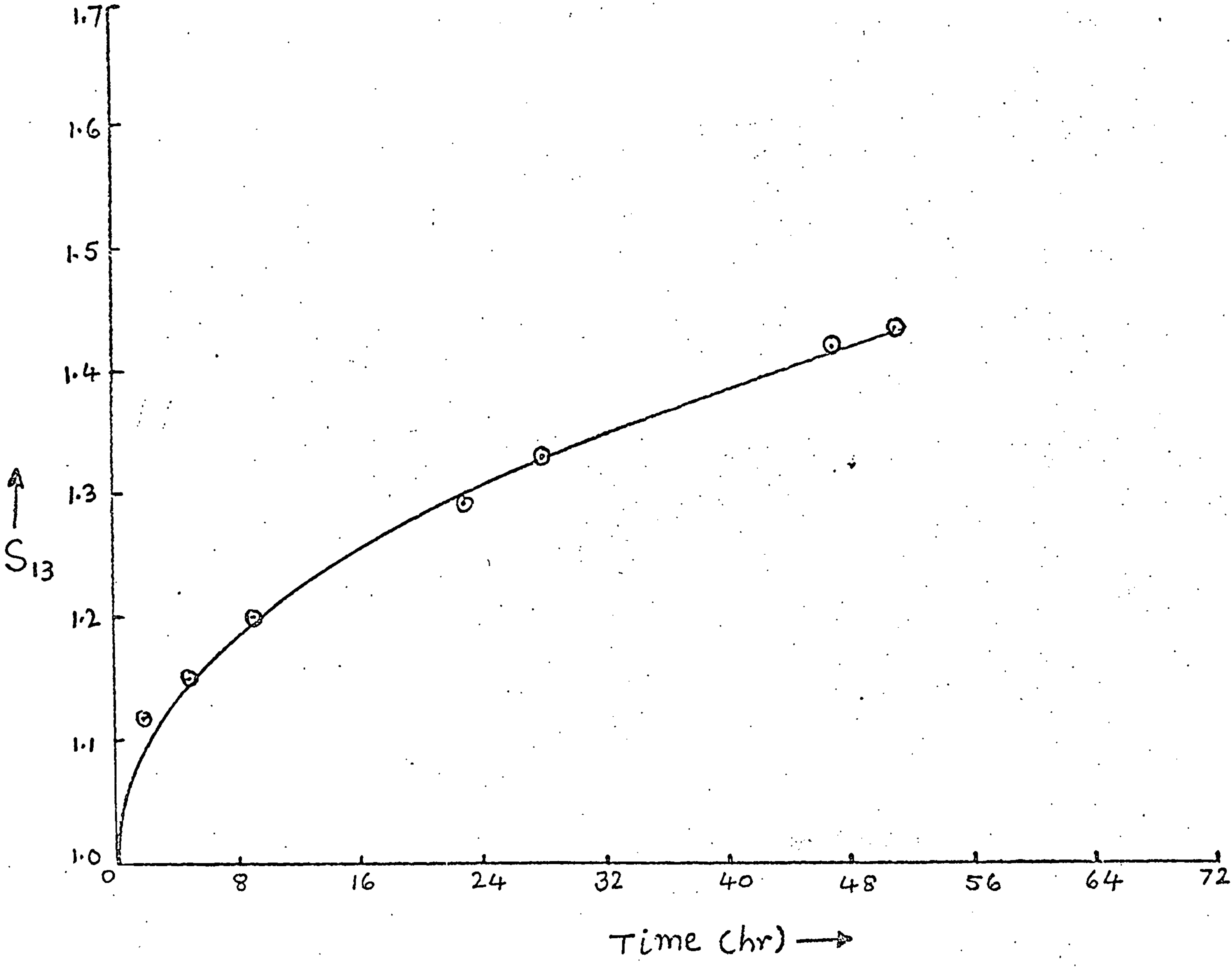

1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0
S_{13}
FLOWRATE 4 ml/min
FLOW RATE 8 ml/min
20
40
60
80
100
120
140
160
180
Time (hr)

Fig. 11. Run 18. Overall separation of DNBA in methanol as a function of time. Flow rate: 4ml/min. Column: 25 mm i.d. x 100 cm packed with "HeliPak" 3013.


1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
S_{13}
0
8
16
24
32
40
48
56
64
72
Time (hr)

(8)

effective than DNBA in methanol ($S_{13} = 1.43$), DNBA in pyridine ($S_{13} = 1.74$), or MEA in methanol ($S_{13} = 1.39$). That is, with 1M DNBA, the concentration of carbon-13 was increased by 105% with TEA as solvent compared to 74% for pyridine and 43% for methanol. A small amount of methanol mixed with TEA did not affect the overall separation ($S_{13} = 1.99$) but when the solvent was 50% by volume methanol, the overal separation dropped to $S_{13} = 1.52$.

A measure of the total volume of CO_2 absorbed per ml of solution could be obtained by measuring the ml/min of amine solution pumped to the saturator. This assumes that the amine solution was completely saturated with CO_2 in the saturator. From the CO_2 feed required by the saturator, saturation appeared to be complete for 1M solutions but not for the 2M solution of DNBA. Because of some fluctuations due to the boiling, the ml/min of CO_2 in the exit stream could not be measured too precisely. Some static measurements of the solubilities of CO_2 in the solutions are given in another section of the report.

Except for the mixed TEA-methanol solvent, there are no large differences in the CO_2 absorbed per ml. of solution.

41

Table I. Effect of solvent on overall separation in a 2.5 cm i.d.X 100 cm column with 1M DNBA.

Solvent	Flow Rate			S	lnS	HETP cm
	$\frac{ml}{min}$	$\frac{ml}{cm^2 - min}$	L* $\frac{m\ moles\ CO_2}{cm^2 - min}$			
Methanol	4.00	0.800	0.640	1.43	0.358	2.77
TEA	4.17	0.835	0.668	2.05	0.718	1.38
Pyridine	4.15	0.830	0.664	1.74	0.554	1.78
1M Methanol in TEA	4.15	0.830	0.664	1.99	0.688	1.44
50:50 (v/v) Methanol + TEA	4.15	0.830	0.664	1.52	0.419	2.56

* Moles of CO_2 absorbed per mole of DNBA is taken as 0.80 and α = 1.01.

2. Effect of Amine Concentration on Separation

Because of the small single stage separation factor ($\alpha = 1.01$), it is desirable to use high concentration of DNBA, large diameter columns, or fast flow rates to increase the interstage flow for large isotope transport. At higher concentrations, due to increased viscosity of carbamate, the advantage gained by higher throughput is reduced by the loss in overall separation. The results obtained in 2.5 cm i.d.X 100 cm exchange column for DNBA - TEA system are given in Table II. The concentration of di-n-butylamine (DNBA) was varied from 1M to 2.84M. It can be seen that overall separation S_{13} is not greatly affected in the concentration range of 1M to 2M. At concentrations higher than 2M DNBA, the overall separation is affected significantly as seen from the drop in overall separation from 1.94 at 2M to 1.69 at 2.84M. Use of concentrations higher than 2M DNBA not only results in loss of separation but also creates other problems such as deposition of solid carbamate on colder parts of the exchange system. From the practical point of view it was felt that 2M DNBA would be the optimum concentration to be used in the preparation of enriched carbon-13.

3. Effect of Catalyst

Because of the relatively slow exchange rate of amine carbamate-CO_2 system, attempts were made to catalyze the exchange reaction between carbamate of monoethanol amine in

Table II. Effect of amine concentration on overall separation in a 2.5 cm i.d. x 100 cm column with DNBA in TEA.

DNBA conc. M	Flow rate			S	lnS	HETP cm	$\frac{HETP}{L}$
	$\frac{ml}{min}$	$\frac{ml}{cm^2 - min}$	L* $\frac{m\ moles\ CO_2}{cm^2 - min}$				
1.00	4.17	0.835	0.668	2.05	0.718	1.38	2.07
1.40	4.00	0.800	0.905	2.02	0.703	1.40	1.55
2.00	4.17	0.835	1.338	1.94	0.663	1.50	1.12
2.84	4.00	0.800	1.820	1.69	0.525	1.89	1.04

*Moles of CO_2 absorbed per mole of DNBA is taken as 0.80 and $\alpha = 1.01$.

Table III. Effect of catalyst on overall separation in a 5.2 cm i.d. X 90 cm column using 2M DNBA in TEA.

Flow rate $\frac{\text{m mole } CO_2}{cm^2 - min}$	Catalyst	S	HETP cm
1.15	-	1.61	1.87
1.28	Zn-acetylacetonate	1.55	2.04
1.21	0.02M Cu - acetate	1.56	2.00

methanol and carbon dioxide using transition metal ions such as Cu^{++}, Co^{++}, and Zn^{++}.(9) With other amines and solvents they were not very effective as catalysts. Most salts of these elements are not very soluble in DNBA - TEA solutions. However, it was found that anhydrous cupric acetate and zinc acetylacetonate were sufficiently soluble to determine their effect on overall separation. The results obtained in a 5.2 cm i.d. X 90 cm exchange column are summarized in Table III. It can be seen from these results that neither 0.02M cupric acetate nor 0.05M zinc acetylacetonate made a marked improvement in the overall separation.

4. Effect of Flow Rate on Separation

The interstage flow can be increased by increasing the flow rate or concentration of the feed material. In order to determine the optimum flow rate at which various sections in the cascade can be operated, experiments using different diameter columns were carried out. These columns were packed with Heli-Pak #3013 packing and were operated at various flow rates. Typical results obtained in a 5.2 cm i.d. X 90 cm and in a 2.5 cm i.d. X 100 cm exchange column are summarized in Tables IV and V.

The effect of flow rate L on overall separation S can be expressed by the equation developed by Cohen(17) and applied by Jeevanandam and Taylor(18) in this laboratory.

According to this equation the variation of overall separation S with flow rate is expressed as follows:

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(17) K. Cohen, "Theory of Isotope Separations", McGraw Hill Book Co., New York (1951).

(18) M. Jeevanandam and T. I. Taylor, Adv. in chem.

Table IV. Effect of flow rate on the performance of a 5.2 cm i.d. x 90 cm column with 1M and 2M DNBA in TEA.

Flow rate		L						$k_Ta \times 10^5$
$\frac{ml}{min}$	$\frac{ml}{cm^2 - min}$	$\frac{m\ moles\ CO_2}{cm^2 - min}$	S	lnS	HETP cm	$\frac{1}{L}$	$\frac{HETP}{L}$	$\frac{moles\ CO_2}{cm^3 - sec}$
1M DNBA								
16.0	0.75	0.60	1.70	0.531	1.69	1.67	2.78	0.60
24.0	1.13	0.90	1.49	0.399	2.24	1.11	2.49	0.67
30.0	1.41	1.13	1.41	0.344	2.60	0.88	2.30	0.72
39.2	1.85	1.48	1.35	0.300	2.99	0.68	2.02	0.83
2M DNBA								
16.0	0.75	1.20	1.63	0.489	1.83	0.83	1.53	1.09
23.5	1.11	1.78	1.45	0.372	2.41	0.56	1.35	1.23
29.4	1.38	2.21	1.37	0.315	2.84	0.45	1.29	1.30
39.2	1.85	2.96	1.25	0.223	4.01	0.34	1.35	1.23

For this table the moles of CO_2 absorbed per mole of DNBA is taken as 0.80 and α as 1.01.

Table V. Effect of flow rate on the performance of a 2.5 cm i.d. x 100 cm column with 2M DNBA in TEA

Flow rate L			S	lnS	$\frac{1}{L}$	$\frac{HETP}{cm}$	$\frac{HETP}{L}$	k_T x 10^5
$\frac{ml}{min}$	$\frac{ml}{cm^2 - min}$	$\frac{m\ moles\ CO_2}{cm^2 - min}$						$\frac{mole\ CO_2}{cm^3 - sec}$
4.2	0.85	1.3	1.94	0.663	0.77	1.49	1.15	1.43
8.4	1.7	2.7	1.54	0.432	0.37	2.30	0.85	1.85
14.5	2.9	4.6	1.31	0.270	0.22	3.68	0.81	1.98

$$\ln S_\infty = \frac{(k_T a)\ Z\ (\alpha - 1)}{L} \qquad (3)$$

where Z is the length of the column and L is the interstage flow expressed as m moles CO_2/cm^2-min. The specific transfer rate k_T (moles CO_2/cm^2-sec), when multiplied by interfacial area (a) in a one centimeter length of column per cm^2 of cross sectional area, gives an interphase transfer rate $k_T a$ per cm^3 of the column.

At the steady state with no product withdrawal, equation (3) indicates that $\ln S_\infty$ should vary linearly with $\frac{1}{L}$ provided the quantities $(\alpha - 1)$ and $k_T a$ remain constant. Alternatively the equation (3) can be put in the form:

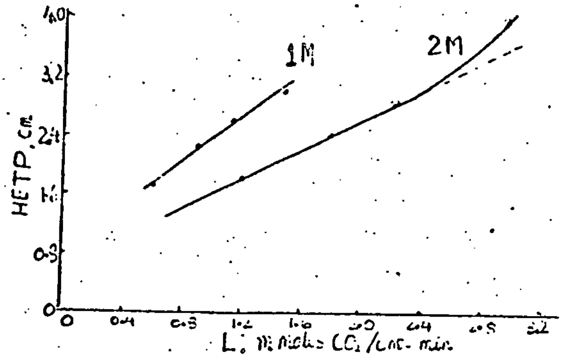
$$\frac{L}{k_T a} = \frac{Z\ (\alpha - 1)}{\ln S_\infty} = \text{HETP} \qquad (4)$$

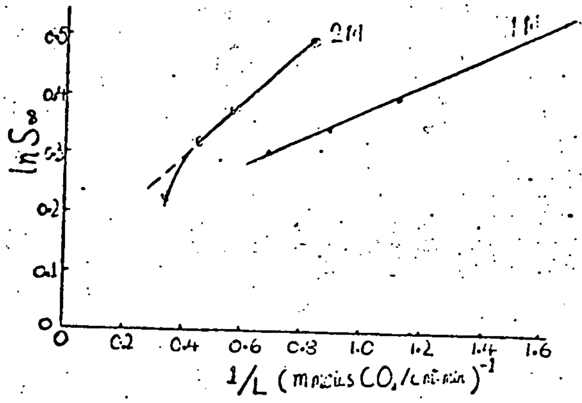
so that HETP should vary linearly with flowrate L. In Fig. 12 plots of HETP vs L, $\ln S_\infty$ vs. $\frac{1}{L}$, and interphase transfer rate $k_T a$ vs flowrate L are shown. It can be seen from these plots that, at lower flowrates, HETP varies linearly with L and $\ln S_\infty$ varies linearly as $\frac{1}{L}$, but at higher flow rates there is a significant deviation from the linear relationships. The rather rapid increase in HETP with flowrate probably results from a decrease in interfacial area with a corresponding decrease in interphase transfer rate $k_T a$. This is not unreasonable since the viscosity of 2M DNBA in TEA saturated with carbon dioxide is rather high (1.10 cp) as compared to (0.59 cp) for 1M DNBA.[23]

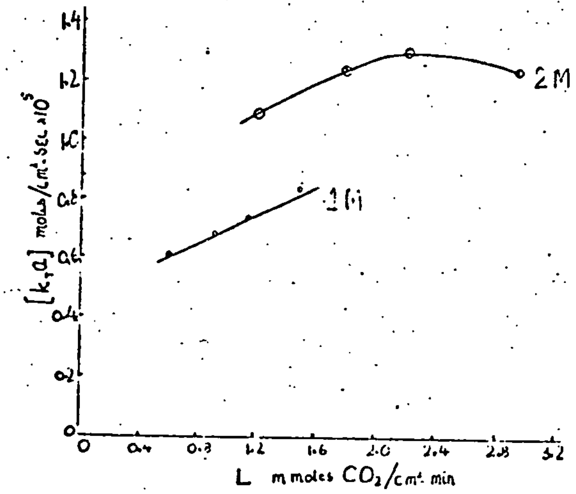
Another measure of the optimum concentration and flow rate is the relative volumes of the single column required

49

Figure 12. Effect of interstage flow rate and concentration of DNBA in TEA on HETP, ln S_∞ and interphase transfer rate k_Ta in a 5.2 cm i.d. x 90 cm column packed with Heli-Pak 3013.


HETP, cm
4.0
3.2
2.4
1.6
0.8
0
1M
2M
0
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
L, m moles CO2/cm²·min


ln S∞
0.5
0.4
0.3
0.2
0.1
0
2M
1M
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1/L (m moles CO2/cm²·min)^-1


[k_L a] moles/cm³·sec×10^5
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
2M
1M
0
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
L m moles CO2/cm² min

for a given overall separation S_∞ and the initial transport T, for a feed containing atom fraction N_o of the desired isotope. The volume required is:

$$V \sim \frac{T \ln S_\infty}{(N_o)(1-N_o)} \times \frac{HETP}{L\ (\alpha - 1)^2} \qquad (5)$$

or

$$V \sim (\text{CONSTANT}) \times \frac{HETP}{L(\alpha - 1)^2}$$

If $(\alpha - 1)$ is constant, the volume required is proportional to the ratio of HETP/L. On this basis, the values of HETP/L tabulated in Table IV, show that the values are significantly smaller for 2M DNBA than for 1M DNBA. Also, the minimum volume for 2M DNBA would be obtained for a flow of 2.4 m mole/cm^2 - min, which corresponds to the maximum for the interphase transfer rate $k_T a$. However, this concentration is too high because of the practical consideration of deposition of solid in the cooler parts of the system.

5. Calculation for a Cascade to Enrich Carbon-13

With the information gathered from the preliminary studies and using known equations, calculations for a multistage exchange system were carried out. The overall separation needed to obtain the desired enrichment in such a system is given by the equation

$$S = \frac{N_p}{1 - N_p} \Bigg/ \frac{N_f}{1 - N_f} = \alpha^n \qquad (6)$$

58

where S is the overall separation; N_p and N_f are the mole fractions of the desired component in the enriched material and feed material respectively; α is the single stage separation factor; and N is the total number of theoretical plates. This equation is for operation at equilibrium with no production.

In the present case, the single stage separation factor α for the chemical exchange

$$R_2N^{12}COO^- + {}^{13}CO_2 \rightleftharpoons R_2N^{13}COO^- + {}^{12}CO_2 \qquad (7)$$

is approximately 1.01. If 90 mole percent carbon-13 ($N_p = 0.90$) is to be obtained from natural feed material with a concentration of 1.13 mole percent carbon-13 ($N_f = 0.0113$), an overall separation S of 786 would be required. According to Eq. (6), this corresponds to 672 theoretical plates for equilibrium operation. For a practical system with production about 1.5 times the theoretical plates for equilibrium operations are usually provided, which would be about 1000 plates for this system.

When a large number of plates is required, a tapered cascade of several columns is used to reduce the hold-up of the system and thus the time required for steady state. Such an arrangement is particularly important for this system because the transport of isotope is low as a result of the small α and the slow rate of exchange. Due to the physical limitations of the laboratory, the packed length of the columns was limited to 250 cm. Six columns would provide total length of 1500 cm.

A column 6.4 cm i.d. x 250 cm long filled with Heli-Pak 3013 was selected for column 1 of the cascade. The area is 32.2 cm^2 so that a liquid flow rate of 1.24 ml/cm^2 - min of 2M DNBA gives a total flow of 40.0 ml/min or an interstage flow L_f of (40 ml/min) (2M) (0.8 mole CO_2/ml) = 64 m moles CO_2. This flow rate is somewhat greater than the optimum of 0.8 to 0.9 ml/cm^2 - min, but the higher flow rate in the initial column increases the transport of isotope into the system and consequently the rate of production of the isotope.

From material balance considerations, the maximum production PN_p or the transport of carbon-13 is given by

$$PN_p = T = \frac{[L_f N_f (\alpha-1)(1-N_f) + PN_f]}{1 + (\alpha-1)(1-N_f)} \tag{8}$$

or for the low concentrations of carbon-13 at the feed end of the first column,

$$\begin{aligned} PN_p = T &\approx L_f\ N_f\ (\alpha-1)\ (1-N_f) \\ &\approx (64)\ (0.0113)\ (0.01)\ (0.9887) \\ &\approx 7.1 \times 10^{-3} \text{ m moles } {}^{13}C/\text{min} \\ &\approx (7.1 \times 10^{-3})\ (1440)\ (13) = 131 \text{ mg. } {}^{13}C/\text{day}. \end{aligned}$$

In the above equations, T = transport rate in m moles of carbon-13; L_f = flow in m moles of CO_2 as carbamate and dissolved CO_2; α = single stage separation factor; N_f = mole fraction of carbon-13 in the product; and P = m moles of "carbon dioxide" withdrawn as product. A constant transport of 7.1×10^{-3} m moles of ^{13}C/min as calculated above was used

30
54

in determining the size and operating conditions for the other five columns of the cascade. Because of fluctuations, losses, etc., only a fraction of the above maximum transport is usually withdrawn as product. It is hoped that at about 75 percent or 100 mg of carbon-13 per day can be withdrawn from the system.

One of the advantages of the solvent carrier system is that the concentration of the active solute (DNBA) can be varied and this allows independent changes in the liquid flow rate and the interstage flow L. Thus, adjustments for the diameters of the columns used for the cascade can be made by changing the flow rate of 2M DNBA or by changing the concentration of DNBA. This makes it possible to use some columns already available in the laboratory. Others can be made on the basis of approximate calculations for constant transport. The diameters of the six columns used for the cascade are given in Table VI. Columns 1 through 4 were packed with Heli-Pak 3013 and the two smaller columns were packed with Heli-Pak 3012.

Preliminary experiments on the operation of individual columns to near equilibrium indicated that the HETP for the 6.4 cm column at the relatively high flow rate of 1.24 ml/cm^2-min of 2M DNBA would be about 2.3 cm. The approximate values of HETP for the other columns when operated to near their equilibrium separations are 2.0 cm for column 2 and 1.5 cm for columns 3, 4, 5 and 6. These values for HETP correspond to the following numbers of theoretical plates for equilibrium

Table VI. Diameters of columns, flows and estimated concentration of Carbon-13, based upon steady state operation in the tapered cascade of six columns using 2M DNBA in TEA. Each column is 250 cm long.

Column Number	Diameter i.d. cm	Cross section cm^2	HETP cm	Mole fraction ^{13}C	L_f $\frac{\text{m moles}}{\text{min}}$	F liquid flow ml/min	F $\frac{\text{ml}}{cm^2\text{-min}}$
1	6.4	32.2	3.1	0.025	64.0	40.0	1.24
2	5.2	21.2	2.7	0.061	28.6	18.7	0.87
3	3.4	9.1	2.0	0.18	11.7	7.3	0.81
4	2.5	4.9	2.0	0.43	3.8	2.4	0.49*
5	1.5	1.77	2.0	0.73	1.5	0.95	0.54*
6	1.18	1.09	2.0	0.90	0.61	0.38	0.37*

* These flows can be increased, if necessary, for proper wetting of the packing by decreasing the DNBA concentration.

for column 2 and 1.5 cm for columns 3, 4, 5 and 6. These values for HETP correspond to the following numbers of theoretical plates for equilibrium operation with no production: column 1 = 109; column 2 = 125; and columns 3, 4, 5 and 6 = 167. This is a total of 902 instead of 1000 plates calculated previously. The cascade of six columns provides 902/672 = 1.34 times the minimum number of theoretical plates so that the values for HETP for production will be (1.34) x (2.3) = 3.1 cm for column 1; 2.7 cm for column 2; and 2.0 cm for columns 3, 4, 5 and 6 as summarized in Table VI.

An HETP of 3.1 cm for column 1 would result in 250/3.1 = 81 plates or an overall separation ($S = \alpha^n$) of 2.23. The mole fraction N_p of carbon-13 at the product end of this column would be $N_p = SR_f / (1 + SR_f) = (2.23)(0.0114) / (1.025) = 0.025$ where R_f for the feed material with mole fraction N_f of carbon-13 is $R_f = N_f \ (1-N_f) = (0.0113) / (0.9887) = 0.0114$. As calculated previously, a total flow of 40 ml/min (1.24 ml/cm^2-min) of 2M DNBA results in a maximum transport of 7.1×10^{-3} m moles ^{13}C per min or a maximum production rate $P = T/N_p = 7.1 \times 10^{-3} / 0.90 = 7.9 \times 10^{-3}$ m moles of "carbon dioxide" per min at 90% carbon-13.

The product material from column 1 with mole fraction 0.025 for carbon-13 enters the feed end of column 2. With an HETP of 2.7 cm, there will be 93 plates in the 250 cm column and the separation in this column will be 2.5. The total separation at the bottom of column 2 will then be (2.23)(2.5) = 5.6 or a carbon-13 concentration of 0.061. In order to maintain a constant transport T of carbon-13, the flow L_f required can be obtained as follows from a rearranged form of Eq. 6:

$$L_f = \frac{T[1 + (\alpha-1)(1-N_f)] - PN_f}{(N_f)\ (1-N_f)\ (\alpha-1)} \qquad (9)$$

$$= \frac{(7.1 \times 10^{-3})[1 + (0.01)(0.975)] - (7.9 \times 10^{-3})(0.025)}{(0.025)(0.975)(0.01)}$$

$$= \frac{7.17 \times 10^{-3} - 0.197 \times 10^{-3}}{2.47 \times 10^{-4}} = \frac{6.97 \times 10^{-3}}{2.47 \times 10^{-4}}$$

$$= 28.6 \text{ m moles/min}$$

Since one ml of 2M DNBA in TEA absorbs 1.6 m moles of CO_2, a liquid flow rate of $F = L_f/1.6 = 28.6/1.6 =$ 18.7 ml/min.

The diameter of column 2 is 5.2 (area = 21.2 cm^2) so that the flow of 2M DNBA in ml/cm^2-min is 18.7/21.2 = 0.87. This is near the optimum flow rate of 2M DNBA in this column as determined in the preliminary experiments.

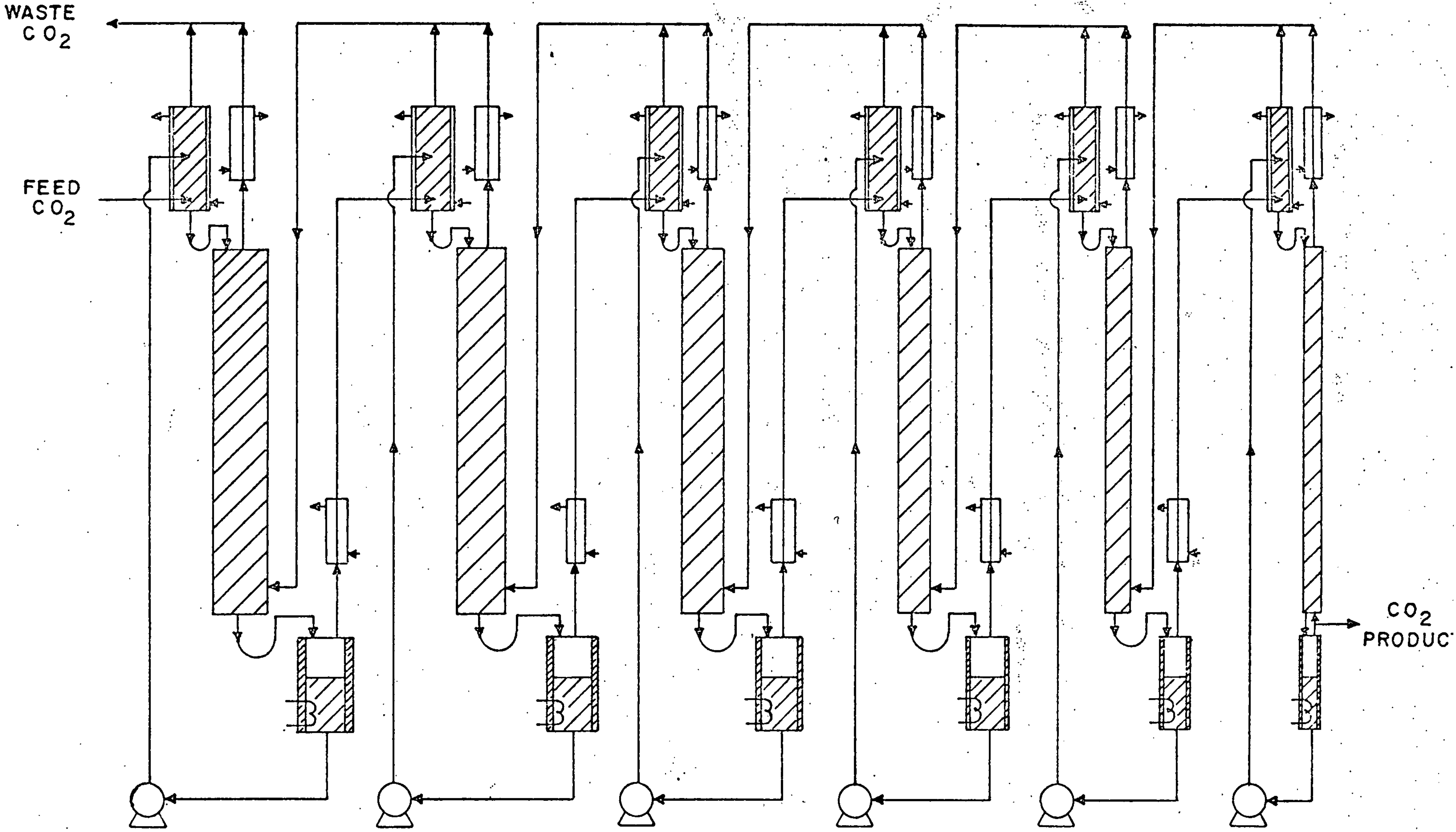
37
VS

Similar calculations were made for the four remaining columns and the results are summarized in Table Vi. For optimum flow of 0.8 to 0.9 ml/cm^2-min in column 4, it would be desirable to use a smaller diameter column but a column 2.5 cm i.d. was already available. If the 0.50 ml/min is too low for proper wetting of the packing (Heli-Pak 3013) in column 4, the concentration of DNBA can be decreased to 1 to 1.5M DNBA with a corresponding increase in the flow rate to give the required interstage flow for constant transport T of carbon-13. Columns 5 and 6 with the smaller size packing (Heli-Pak 3012) may operate properly at the lower flow rates and give even shorter values for HETP. If they do not, as will be shown by the data for the start up of the system, the concentrations of DNBA and the flow rates can be changed.

6. Schematic Arrangement and Operation of the Cascade

A flowsheet showing the general arrangement of each section of the cascade is shown in Fig. 13 Each section contains a saturator at the top; an exchange column; and a reboiler with a stripping section at the bottom. The dimensions of each of these components of the section were chosen so that the system could be operated under a variety of conditions. These sections were then intercoupled in such a manner that each of them could be isolated from the rest of the system in the event

Fig. 13. Flow diagram for a tapered cascade of six sections for the concentration of carbon-13. All exchange columns are 250 cm long and their diameters are respectively: (1) 6.4 cm, (2) 5.2 cm, (3) 3,4 cm, (4) 2.5 cm, (5) 1.5 cm, (6) 1.18 cm. The first four columns are packed with Heli-Pak 3013 (0.050 x 0.100 x 0.100 in.) rectangular spirals of stainless steel wire and the last two columns are packed with Heli-Pak 3012 (0.030 x 0.070 x 0.070 in).


WASTE
CO2
FEED
CO2
CO2
PRODUCT

of a breakdown. A typical coupling of two sections is shown in Fig. 14.

The tapered design of the cascade of columns necessitates a progressive decrease in the amine flow rate from section 1 through section 6 (see Table VI). A solution of 2M DNBA in TEA is pumped at the predetermined flow rate from the boiler B_1 into amine saturator S_1 (Fig. $\overset{14}{13}$) where it reacts with a feed of natural CO_2 to form amine carbamate. Excess CO_2 from the saturator passes through the amine trap and is discarded as waste. The amine carbamate solution flows into the exchange column and then to boiler B_1 where it is decomposed completely into amine solution and carbon dioxide.

The whole amount of carbon dioxide is then allowed to enter amine saturator S_2 to form carbamate. Since the flow of amine is less, part of this CO_2 is used and the rest is returned to the bottom of column C_1. The carbamate that flows through column C_2 enters boiler B_2 and is decomposed there into amine and CO_2. The amount of CO_2 formed in B_2 is fed to the saturator S_3 and excess is returned to the bottom of column C_2. Similarly all the sections are interconnected. The gas that leaves the top of each column is mixed with the excess gas leaving the saturator of that column. Due to

Figure 14. Schematic diagrams showing a typical interstage coupling for two sections of the cascade. $P_{1,2}$ are pumps; $B_{1,2}$ are boilers; $C_{1,2}$ are the exchange columns; and $S_{1,2}$ are amine saturators. Samples for analysis are withdrawn at $T_{1,2}$.

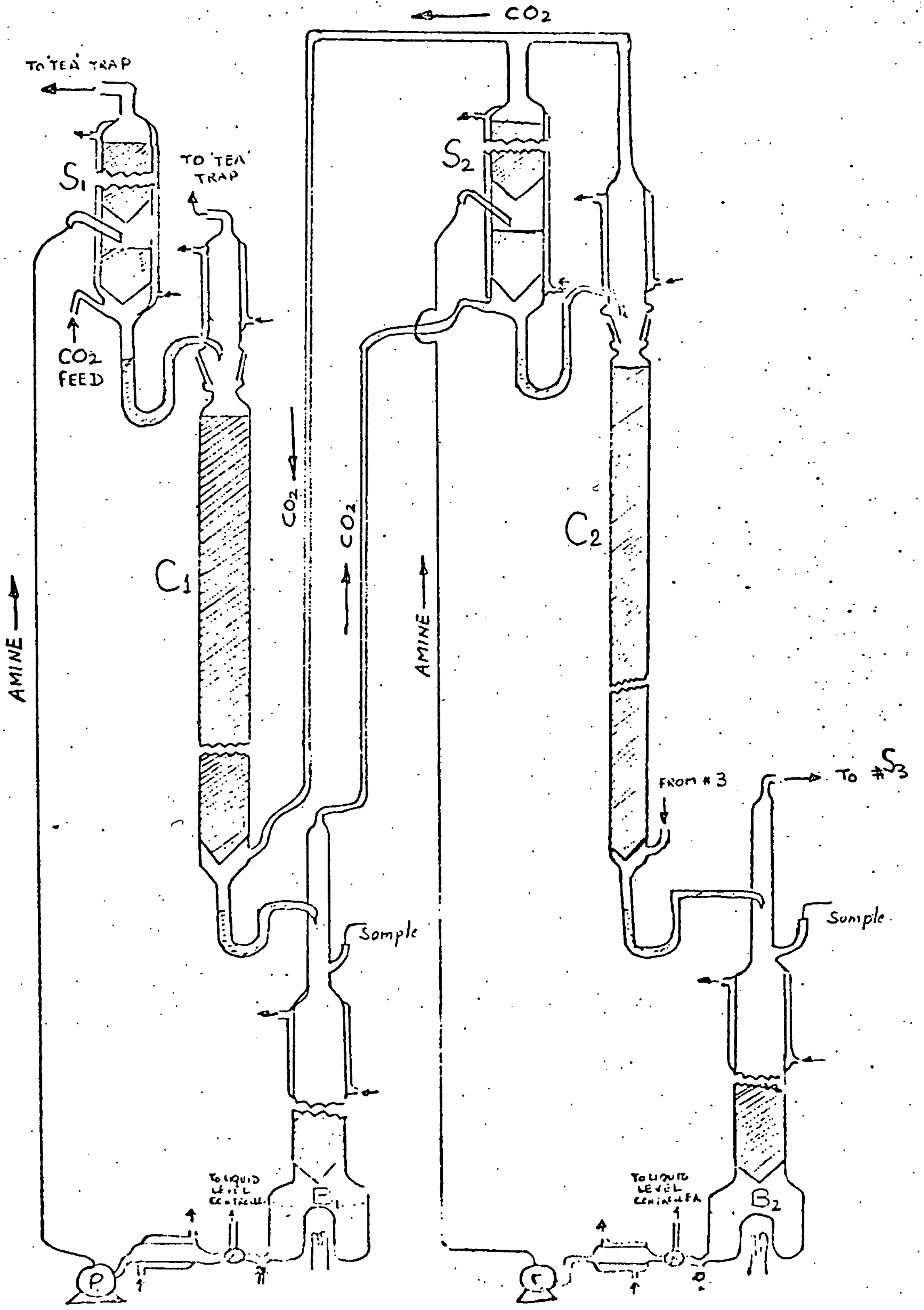

CO2
TO TEA TRAP
TO TEA TRAP
S1
S2
CO2 FEED
C1
C2
CO2
CO2
AMINE
AMINE
FROM #3
To #S3
Sample
Sample
TO LIQUID LEVEL CONTROLLER
TO LIQUID LEVEL CONTROLLER
B1
B2
P
P

Fig. 3

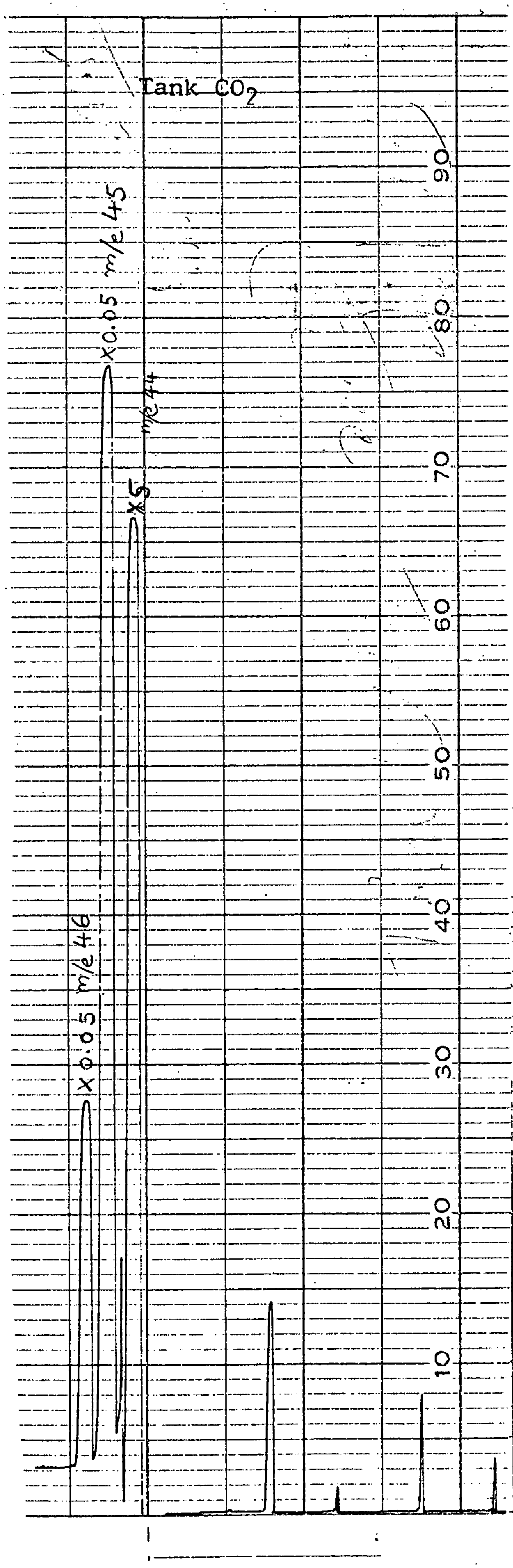
this type of coupling, the amount of gas that is entering at the bottom of any column is equivalent to the amount of gas that is leaving the boiler associated with that column.

The advantage of the above type of intercoupling of sections lies in the fact that one does not need additional pumps to transport enriched material in the forward directions. It is necessary to balance the flow of solvent vapors forward and backward direction by cooling the gases at the proper places. Failure to obtain solvent balance results in changes of the DNBA concentration. Gas chromatographic analysis was used to detect any changes in concentration that occurred so that corrections could be made.

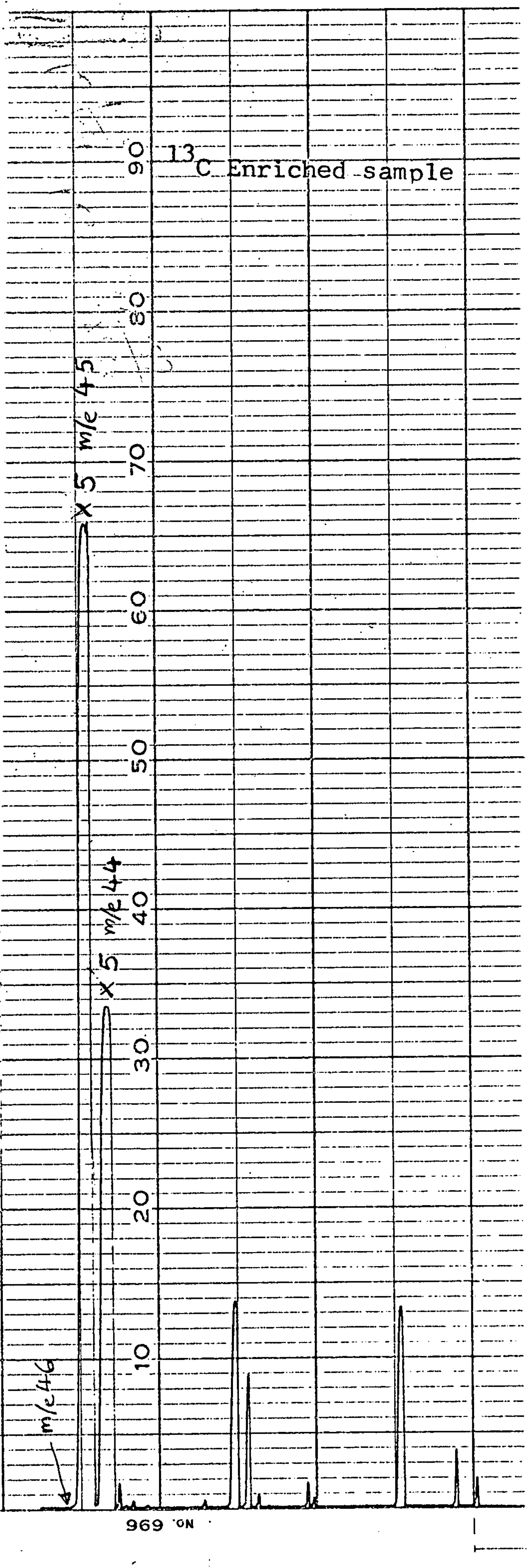
It was convenient to condense the solvent vapors in the waste gases from section 1 and return the required amount of solvent to the system. Instead, the gases from saturator S_1 and the exchange column C_1 were passed through a cooled amine trap to recover the solvent. The liquid level in boiler B_1 was maintained at a predetermined mark with a thermistor controller as described in chapter two.

Operation of the six section cascade: As mentioned in our last report, all the boilers were opened and the original stainless steel Pro-Pak packing was removed. The boilers then cleaned with 5% solution of HF to remove a black deposit that was formed during the prolonged operation. The stripping sections of the refluxers were repacked with Raschig rings and glass helicies. All the columns were thoroughly cleaned and dried. After connecting all of the columns together, the whole cascade system was tested for leaks by evacuating and observing the leak rate, and by pressurising with dry nitrogen. It was decided to start the cascade by admitting the CO_2 feed at column 1 only. Accordingly all columns were flooded with 2 M DNBA solution in TEA. The solution was then drained slowly while pumping 2M solution of DNBA in TEA to the saturators. When excess solution from all the columns was removed and all of them were operating at their predetermined flow rates, CO_2 feed to column was started. After about 30 minutes when the carbamate started flowing from the bottom of the column, the heater to the boiler 1 was turned on. The carbon dioxide thus produced in the boiler 1 was then fed to the saturator 2. When the carbamate started flowing from the bottom of column 2, the heater to the boiler 2 was turned. This procedure was continued until all the columns were operating properly. At first the cascade operated very well for 30 days bringing the concentration of carbon-13 in the sixth column to 47.7 %. Then one of the Teflon connections between column 3 and column 4 developed a crack thus causing the cascade to return to normal concentration of carbon-13. This was repaired and the cascade was then operated without any breakdown for 141 days. During this period the overall separation in the sixth column reached to a value of 177 (66.9 % ^{13}C). A typical mass spectra of this sample is shown in Fig. 15. Since the rate of build up was rather slow, it was decided to add one more section to the cascade. While the work on this section was in progress, the operation of the cascade was continued. The seventh section was independently tested, and then it was connected to the section 6. The cascade was then operated for another 80 days, thus bringing the total operation period to eight months. This added section did not improve the performance of the cascade significantly. The cascade was then shut down, during this operation it was observed that there was considerable channeling in the first three sections of the cascade.

Fig.15 A typical mass spectra of a carbon-13 enriched sample



Tank CO_2



^{13}C Enriched sample

III. EXPERIMENTS ON THE SINGLE STAGE SEPARATION FACTORS FOR CARBON-13 BETWEEN CARBON DIOXIDE AND AMINE CARBAMATE.

Madhav R. Ghate, (Late) T. I. Taylor, and C. H. Choi

INTRODUCTION

Carbon dioxide reacts with primary and secondary amines in non-aqueous solvents to form carbamates according to the following reaction:

$$2R_2NH + CO_2 \rightleftharpoons R_2NCOO^- + {}^+H_2NR_2 \qquad (1)$$

Equilibrium between carbon dioxide in the gase phase with carbamate in solution results in an increased concentration of carbon-13 in the solution phase or alternatively an increase of carbon-12 in the carbon dioxide of the gas phase:

$$^{13}CO_2 + R_2N\,^{12}COO^- \rightleftharpoons {}^{12}CO_2 + R_2N\,^{13}COO^- \qquad (2)$$

The single stage separation factor (α) for the enrichment of carbon-13 in the carbamate solution is given by

$$\alpha_{13} = \frac{(N_{13})\Big/(1-N_{13})}{(n_{13})\Big/(1-n_{13})} = \frac{(N_{13})(1-n_{13})}{(n_{13})(1-N_{13})} \qquad (3)$$

where N_{13} and n_{13} refer to the mole fractions of carbon-13 in the exchangeable carbon of the species in the liquid (l) and the gas phase (g) respectively. Simultaneously equilibrium between carbon dioxide in the gas phase with the carbamate in the solution results in the concentration of oxygen-18 in the gas phase as follows:

$$C\,{}^{16}O_2 + R_2NC\,{}^{16}O{}^{18}O^- \rightleftharpoons C\,{}^{16}O{}^{18}O + R_2NC\,{}^{16}O{}^{16}O^- \qquad (4)$$

The single stage separation factor (α) for the enrichment of oxygen-18 is given by

$$\alpha_{18} = \frac{(n_{18})\big/(1-n_{18})}{(N_{18})\ (1-N_{18})} = \frac{(n_{18})(1-N_{18})}{(N_{18})(1-n_{18})} \qquad (5)$$

Thus, α_{13} and α_{18} can be obtained from the same experiment in which CO_2 is equilibrated with a carbamate solution.

Previous measurements of the single stage effects indicated that α_{13} was too small for precise determination with a single collector mass spectrometer. Although α_{18} was also small, the average of a number of measurements by Gupta and Taylor[1] resulted in a value of 1.013 for CO_2 equilibrated with the carbamate of monoethanolamine in methanol. For other amine-solvent combinations the value of α_{18} varied from 1.010 to 1.013.

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[1] A. R. Gupta and T. I. Taylor, Annual Progress Report to U.S.A.E.C., Contract AT (30-1) 755, (1962), (1963).

A value for α_{13} was calculated from the simultaneous separations of the carbon and oxygen isotopes in exchange columns. When CO_2 is refluxed by reaction of an amine solution at the upper end of an exchange column, oxygen-18 is enriched and carbon-13 is depleted. At equilibrium and total reflux the overall separations for oxygen-18 and carbon-13 are given by:

$$S_{18} = \alpha_{18}^{s} \quad \text{or} \quad \ln S_{18} = s \ln \alpha_{18}$$

$$\approx s(\alpha_{18} - 1) \qquad (6)$$

$$\text{and} \quad S_{13} = \alpha_{13}^{s}$$

$$\text{or} \quad \ln S_{13} = s \ln \alpha_{13}$$

$$\approx s(\alpha_{13} - 1) \qquad (7)$$

Since the number of plates s in the column are the same for the isotopes

$$\frac{\ln S_{18}}{\ln S_{13}} = \frac{(\alpha_{18} - 1)}{(\alpha_{13} - 1)}$$

$$\text{or} \quad (\alpha_{13} - 1) = \frac{\ln S_{13}}{\ln S_{18}}(\alpha_{18} - 1)$$

$$= \frac{\ln S_{13}}{\ln S_{18}}(\alpha_{18} - 1) \qquad (8)$$

Unfortunately the overall separation S_{18} for oxygen-18 is reduced by formation and subsequent recirculation of small amounts of water and decomposition products with exchangeable oxygen. This effect is variable so that the most reliable values for α_{13} will be obtained from those experiments in which S_{18}/S_{13} is the greatest. In one typical experiment Gupta and Taylor[1] obtained a value of 1.009 for α_{13}. In addition to the formation of water and decomposition products, uncertainties in the wetting of packing and dynamic hold-up of the column would influence the overall separation and equilibrium. Thus it is rather impossible to obtain reliable and reproducible values of separation factors from the exchange column experiments. In order to overcome this difficulty several single stage and multi stage equilibrations were made to test the reproducibility and the reliability of both the procedures and the analyses with the mass spectrometer.

EXPERIMENTAL

SINGLE STAGE EQUILIBRATIONS: These equilibrations were carried out in two different equilibration flasks. One of them has a capacity of 1157 ml and the other has 325 ml. The use of these two flasks permitted us to obtain a very high and about equal ratio of carbamate i.e. carbon in liquid phase and carbon dioxide i.e. carbon in gas phase. The flasks are shown schematically in Fig. 1 and Fig. 2. Before starting the equilibration flask was thoroughly dried and weighed with and without air. Then a predetermined volume of amine solution was poured into the flask. The solution was frozen with liquid nitrogen and the flask was evacuated. After obtaining sufficiently high vacuum, the flask was isolated from the pump and the solution was warmed up to release the trapped air. Again the solution was frozen with liquid nitrogen and the flask was evacuated. This procedure of degassing the solution was continued until all the trapped air was removed from the amine solution. Then the flask was carefully weighed to obtain the weight of the amine solution. After this it was again connected to the vacuum line to pump out air between the stopcock on the flask and the vacuum line. The flask was isolated from the pump and was connected to the CO_2 line. The flow of CO_2 was so adjusted that a small quantity of it was drawn into

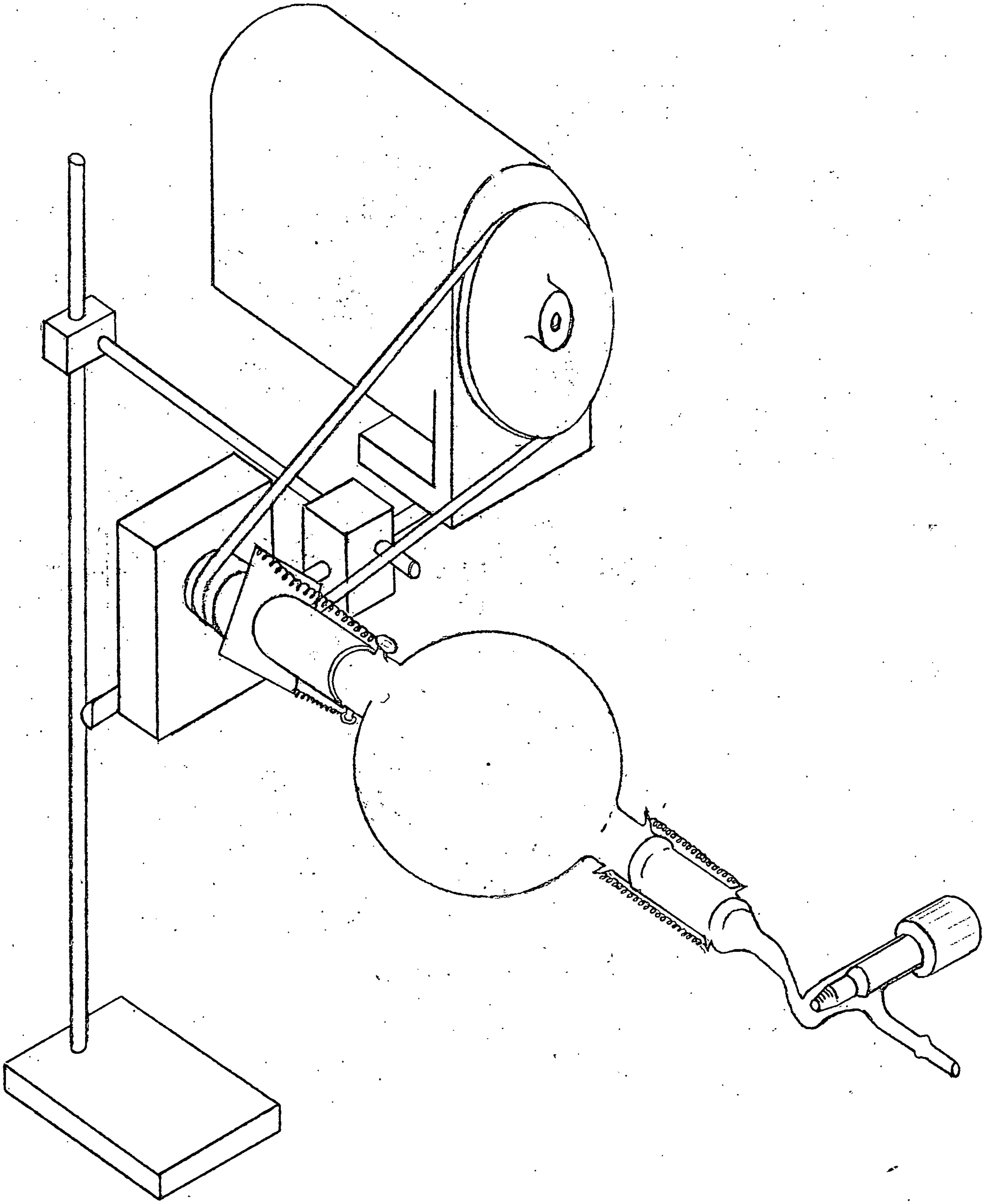
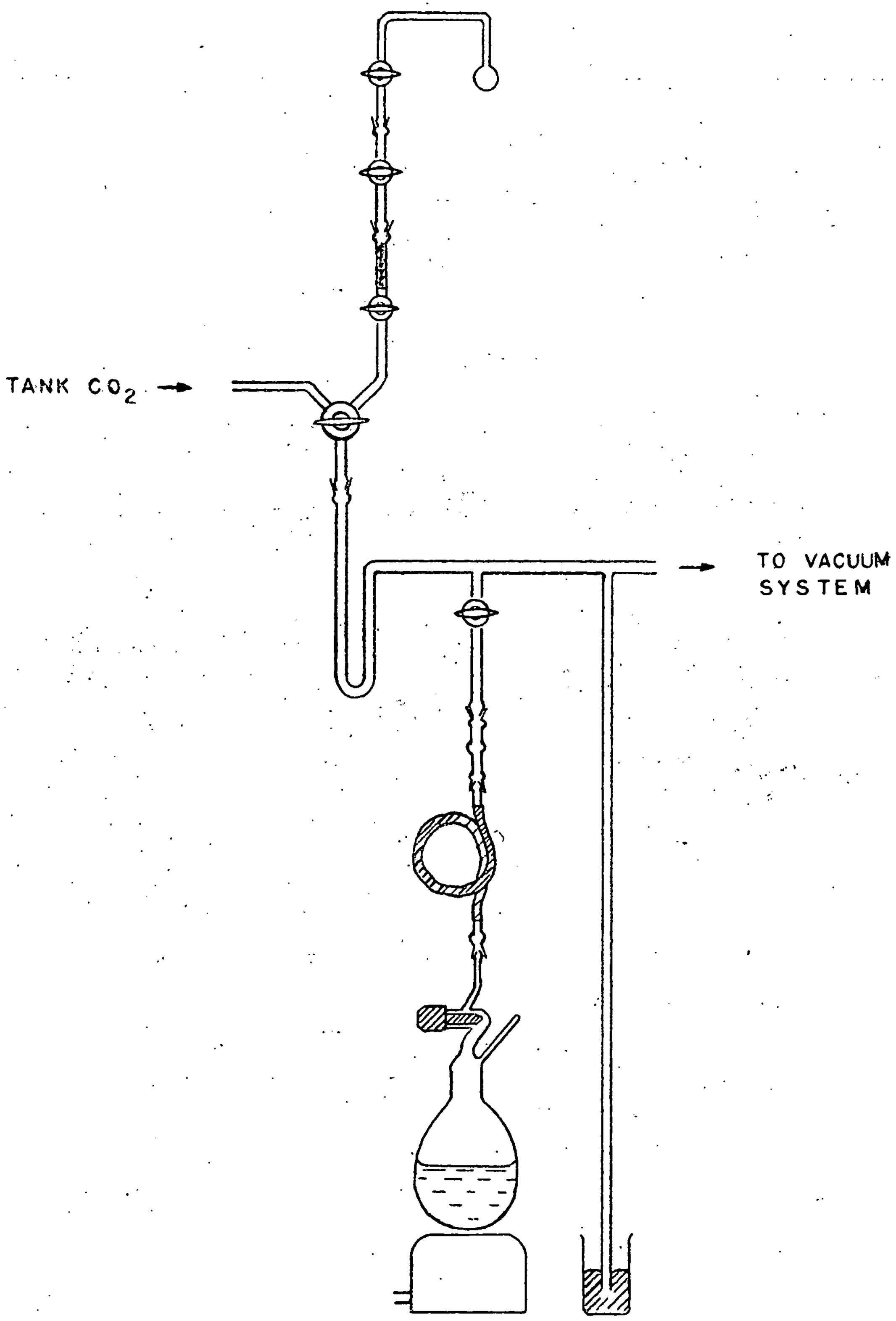


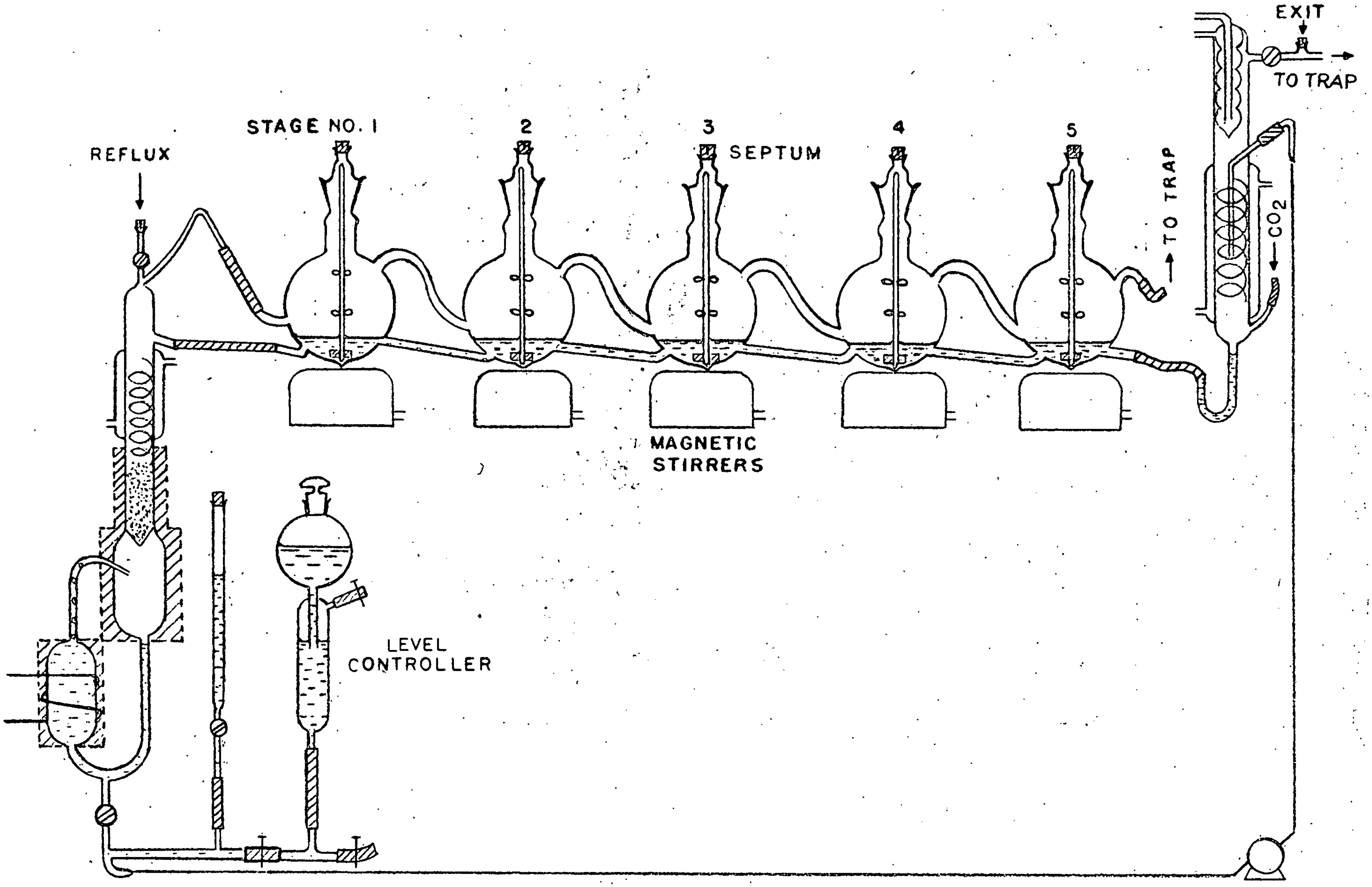
Fig 1



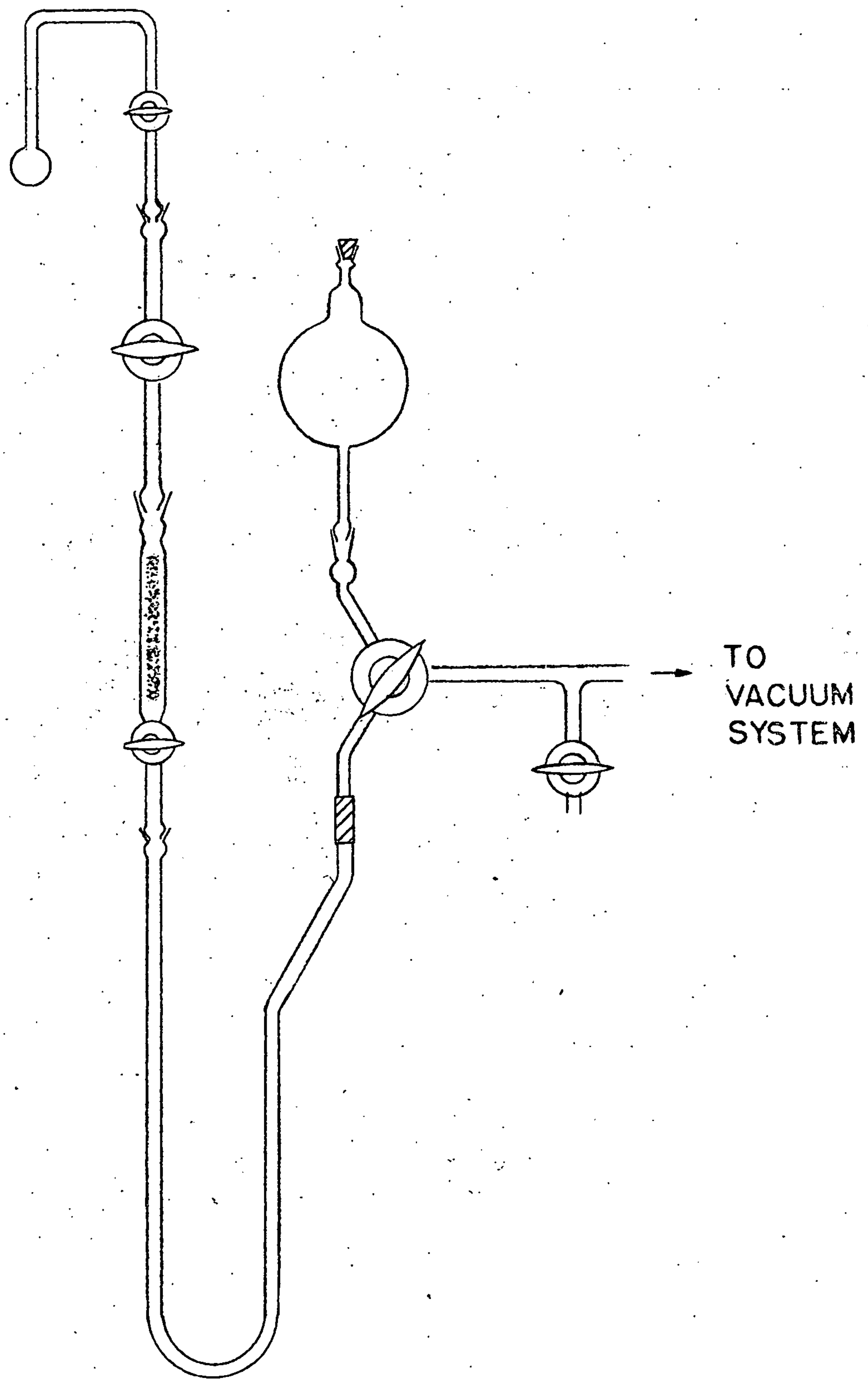
Fi 2

the flask. Intermittently the flask was shaken to facilitate the reaction. When the pressure inside the flask reached 1 atm the stopcock on the flask was closed. The flask was again weighed to obtain the weight of total CO_2 added to the flask. Knowing the temperature, volume of the solution and the v.p. of amine, the amount of CO_2 in the gas phase and in the liquid phase was calculated. The flask was rotated for about 72 hours before any sample was removed from the system. After a predetermined time, the flask was connected to the vacuum line and the air between the stopcock on the flask and the vacuum line was pumped out. Then the flask was connected to the pre-evacuated sample bulb. The stopcock on the flask was opened very slowly to allow the gas to enter into the sample bulb through the dry ice trap and over P_2O_5. The dry ice trap and P_2O_5 prevented any amine vapors to enter into the gas sample. When the pressure inside the sample bulb reached about 70 cm Hg, stopcocks on the sample bulb and the flask were closed. Similarly, gas samples from the liquid phase were collected by reacting a small amount of liquid with 6M H_3PO_4 in a Y-tube. The gas samples thus collected were analyzed on the double collector Nier-type mass spectrometer.

MULTISTAGE EQUILIBRATION SYSTEM: It is essentially five horizontally arranged cells with magnetic stirrers for mixing gas and liquid phases. It is schematically shown in Fig. 3. Each cell is ~ 250 ml large and these cells are inter-


EXIT
TO TRAP
STAGE NO. 1
2
3
SEPTUM
4
5
REFLUX
TO TRAP
CO_2
MAGNETIC STIRRERS
LEVEL CONTROLLER

(3)


TO
VACUUM
SYSTEM

connected for counter flow of liquid and gas with low possibility of mixing between the cells. It also has saturator, refluxer, pump and liquid level controller similar to that in the case of an exchange column.

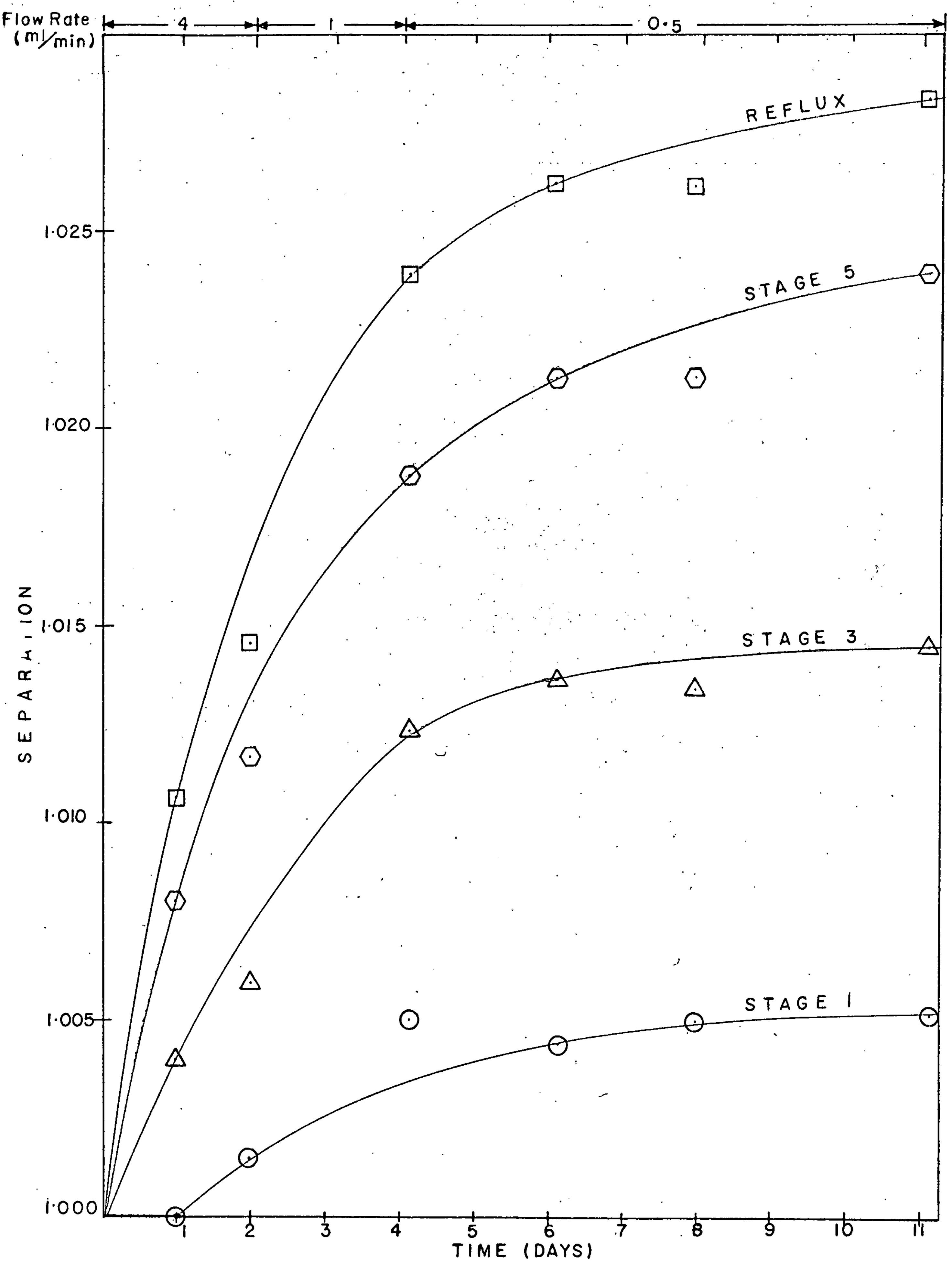
PROCEDURE FOR A RUN: Before starting the run, amine solution was pumped into the cell 5, and was allowed to flow from cell 5 to cell 4, and so on until it started flowing into the refluxer. Then the flowrate was adjusted to the predetermined value and CO_2 flow was started into the saturator. After about 15 minutes the boiler heater was turned on. The change in the isotopic composition in each of the cells was followed by withdrawing small gas samples through the septum by means of a hypodermic syringe. This entire gas sample was allowed to pass through a dry ice trap and over P_2O_5 into the pre-evacuated sample bulb. The arrangement for collecting these samples is shown in Fig. 4.

RESULTS AND DISCUSSION

Precise determination of the single stage separation factor (α) is important not only for the operation and evaluation of the present exchange system but also for comparison of different amine-solvent systems. Several single stage equilibrations were made to test reproducibility and reliability of both the procedures and the analyses with the mass spectrometer. In order to account for the day to day variations in the mass spectrometer characteristics, a "standard CO_2" sample was analyzed before and after each sample. This "standard CO_2" was prepared by isotopic dilution method, and its isotopic composition was about 1.01 times that of normal carbon dioxide. In the preliminary experiments several measurements were done. The value of single stage separation factor (α) for 2M DNBA in TEA was 1.0060 ± 0.0012 (S.D.). In the initial measurements the spread of the results was rather wide ranging, from 1.0045 to 1.0092. This was reduced by using a more sensitive recorder, thus increasing the measurement accuracy. A total of 168 measurements were done on four different amine-solvent systems. The results of these measurements are summarized in Table 1. It can be seen from these results that the value of 1.0056 ± 0.0014 (S. D.) for α is obtained. The spread of results is from 1.0048 to 1.0063, which is quite to the expectation. Attempts will be made in future studies to improve experimental techniques to confirm this value.

MULTI STAGE EQUILIBRATION SYSTEM: Since a lot more information is available through column experiments on methanol as solvent, it was decided to study monoethanol amine carbamate in methanol-carbon dioxide exchange system in this set up. In one run with 2M MEA in methanol, change in isotopic composition was measured as various flow rates ranging from 4 ml/min to 0.5 ml/min. This is shown in Fig. 5. Although the curves show that the system was not quite at equilibrium, the overall separation values relative to the tank carbon dioxide used for the feed were: stage 1, $S_1 = 1.0051$; stage 3, $S_3 = 1.0144$; stage 5, $S_5 = 1.0238$; and for the reflux system, $S_r = 1.0282$. In order to calculate single stage separation factor (α) material balance calculations were carried out for carbon-13, and the following relation was obtained:

$\ln S_3 - \ln S_1 = (\alpha - 1)(S_3 - S_1)$ where S_1, S_3 represent the overall separation in cell 1 and cell 3 and S_1 and S_3 represent the cell number. Using the above relation a value of $(\alpha - 1) = 0.0046$ for stages $(S_3 - S_1)$ was obtained. Similar calculations gave $(\alpha - 1) = 0.0046$


Flow Rate (ml/min)
4
1
0·5
REFLUX
STAGE 5
STAGE 3
STAGE 1
SEPARATION
1·025
1·020
1·015
1·010
1·005
1·000
1
2
3
4
5
6
7
8
9
10
11
TIME (DAYS)

for $(S_5 - S_3)$, $(S_5 - S_1)$, and for the overall separation from feed to reflux. The value for $(\alpha - 1)$ is fairly in agreement with $(\alpha - 1) = 0.0056$ obtained from the single stage equilibration studies, only if the following assumptions apply: the system was at complete equilibrium, stage efficiency was 100%, there was no mixing between the cells, there were no leaks and no loss of exchangeable carbon from the refluxer. Improvements are being made to improve the stirring and refluxing in an effort to obtain higher efficiency and reproduceable results for the relative values of $(\alpha - 1)$ for different amine solvent systems.

Table 1. Single stage separation factor (α) values obtained from single stage equilibration

System	m/M	α_{13}
1M DNBA in TEA	1.01	1.0048 ± 0.0014
1M DNBA in Methanol	0.75	1.0054 ± 0.0016
2M DNBA in TEA	1.01	1.0061 ± 0.0011
2M MEA in Methanol	1.01	1.0063 ± 0.0010

Average 1.0056 ± 0.0014

$NO-HNO_3$ Exchange System for Production of Nitrogen-14 Highly Depleted of Nitrogen-15.*

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Summary

The isotopic exchange reaction between NO and HNO_3 was used to prepare nitrogen-14 highly depleted nitrogen-15. This required an efficient reflux system of low hold-up to convert oxides of nitrogen to nitric acid by reaction with oxygen and water. A study of the characteristics of the one constructed showed that less than 1 part in 32,000 of the nitric acid was lost from the refluxer as oxides of nitrogen. Nitrogen-14 with an atom fraction of less than 0.00004 of nitrogen-15 was prepared at the rate of 46.0g/day. The application of the refluxer to a system for producing nitrogen-15 is discussed.

[+] Deceased (July 1973)

* This investigation was supported in part by a grant from the U. S. Atomic Energy Commission.

INTRODUCTION

Nitrogen-14 highly depleted of nitrogen-15 has several applications in nuclear physics, chemical and industrial research (1-3). A relatively pure nitrogen-14 could be prepared by a chemical exchange method, that has been successfully used to concentrate nitrogen-15 having isotopic concentration over 99.5%. The chemical exchange method involves the exchange reactions between nitric acid and nitric oxide. The major reactions are as follows: (4-7)

Exchange

$$^{15}NO + H^{14}NO_3 \rightleftharpoons {}^{14}NO + H^{15}NO_3 \qquad \alpha=1.055 \tag{1}$$

Product reflux

$$3SO_2 + 2HNO_3 + 2H_2O \rightleftharpoons 3H_2SO_4 + 2NO \tag{2}$$

$$SO_2 + 2HNO_3 \rightleftharpoons H_2SO_4 + 2NO_2 \tag{3}$$

Waste reflux

$$2NO + O_2 \rightleftharpoons 2NO_2 \tag{4}$$

$$3NO_2 + H_2O \rightleftharpoons 2HNO_3 + NO \tag{5}$$

As seen from the above reactions, in the preparation of nitrogen-15 reactions (1) through (3) are of prime importance, while (4) and (5) of secondary. Since nitrogen-14 gets concentrated in the gas phase, contrary to earlier case reactions (1), (3) and (4) are of great importance. In the present investigation attempts are made to develop refluxers to obtain quantitative conversion of oxides of nitrogen to nitric acid and obtain nitrogen-14 isotope highly depleted of nitrogen-15 isotope.

Figure 1. Exchange system with a short column to test designs for the upper refluxer.

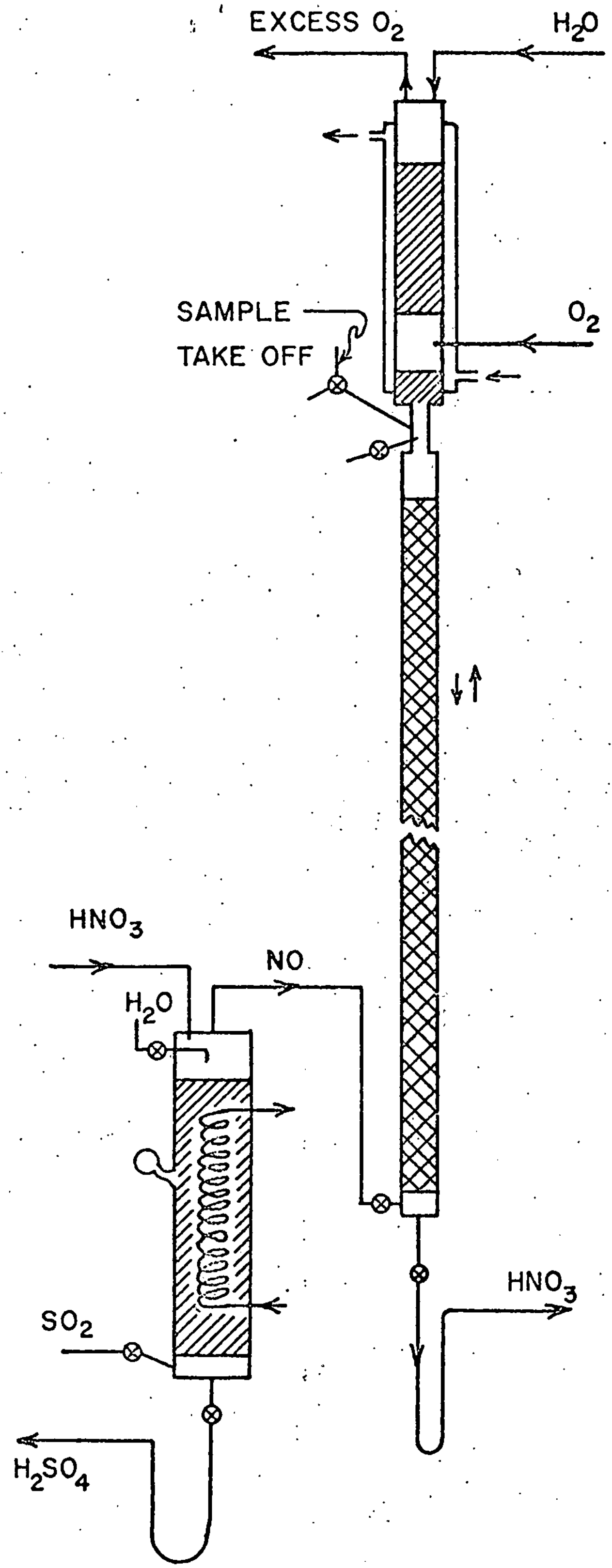
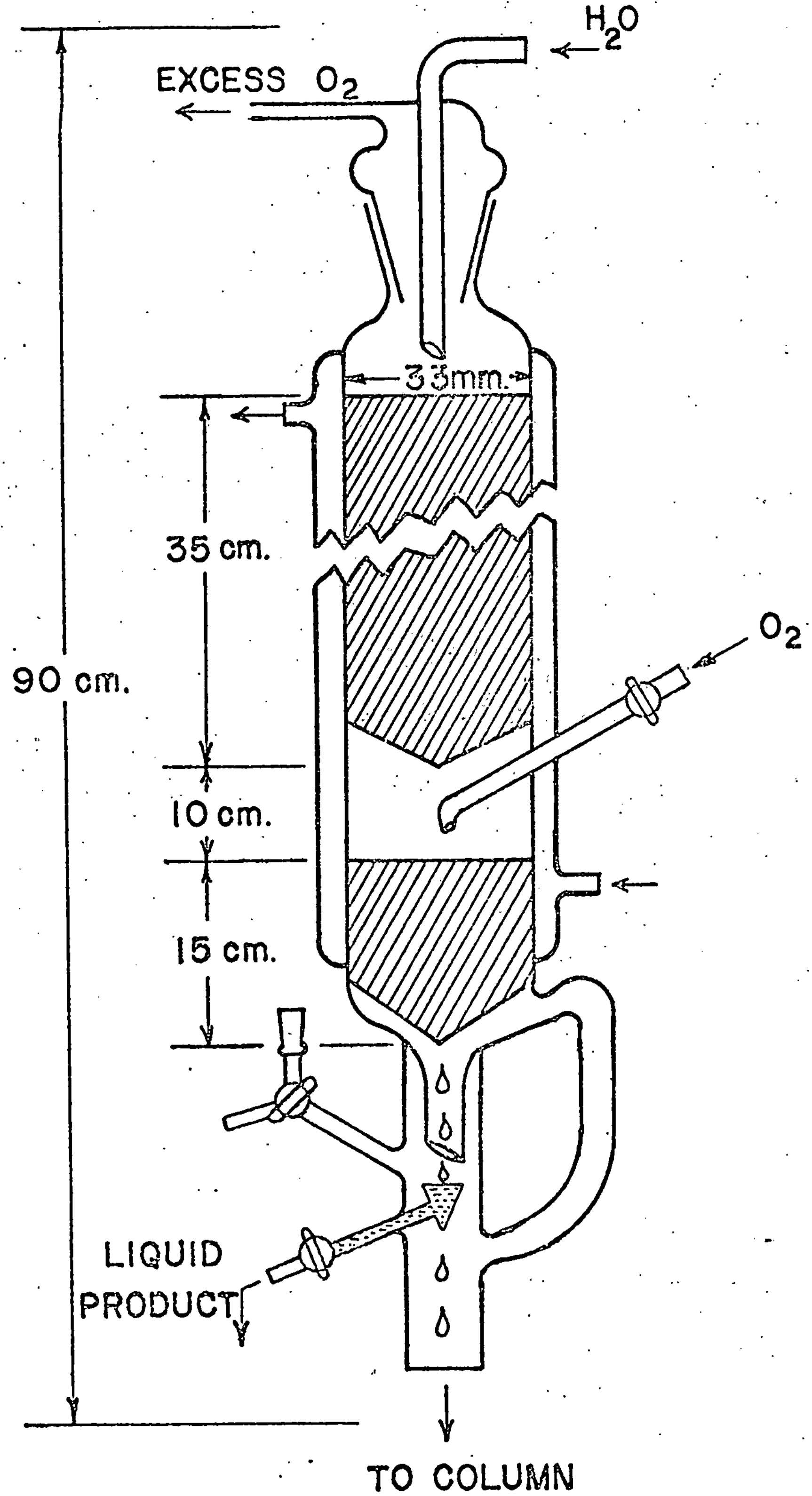

EXCESS O_2
H_2O
SAMPLE
TAKE OFF
O_2
HNO_3
NO
H_2O
SO_2
H_2SO_4
HNO_3

Figure 2. Details of the design of the upper refluxer for converting oxides of nitrogen to nitrogen to nitric acid.



H_2O
EXCESS O_2
33mm.
35 cm.
90 cm.
O_2
10 cm.
15 cm.
LIQUID PRODUCT
TO COLUMN

packed column with excess of oxygen and no other inert gas, a part of the nitric oxide may also be oxidised in the solution phase. Although the absorption of NO_2 and N_2O_4 in water to form nitric acid has been investigated extensively (10-15), but there is no general agreement on the details of the mechanism of the reaction. However, it is significantly influenced by the concentration of nitric acid and the composition of the gas phase. In the present case situation it is more complicated due to the concentration gradient present along the refluxer. For the preparation of either nitrogen-15 or nitrogen-14 exchange system is to be operated at 10M HNO_3 concentration. In order to obtain this concentration of HNO_3, precalculated water was supplied from the top of the refluxer. For approximately 10M HNO_3 which is in equilibrium with the oxides of nitrogen, the mole fractions of the gas phase components are: 0.81 NO; 0.083 NO_2; 0.051 N_2O_4; 0.041 N_2O_3 and 0.15 H_2O (16,17). Using these values, for a flow of 10 ml HNO_3/min of 10M HNO_3 corresponding to 100 m moles Nitrogen/min, the flow of each species in m moles/min is NO=75.2; NO_2=7.7; N_2O_4=4.75; and N_2O_3=3.8. By combining the reactions proposed by Verhoek and Daniels (18) with those in literature (19,20), the overall reactions and the oxygen requirement can be calculated. The following are the reactions:

$$2NO_2 \rightleftharpoons N_2O_4 \tag{7}$$

$$NO + NO_2 \rightleftharpoons N_2O_3 \tag{8}$$

$$NO + 3/4\ O_2 + 1/2\ H_2O \rightleftharpoons HNO_3 \tag{9}$$

$$NO_2 + 1/4\ O_2 + 1/2\ H_2) \rightleftharpoons HNO_3 \tag{10}$$

$$N_2O_4 + 1/2\ O_2 + H_2O \rightleftharpoons 2HNO_3 \qquad (11)$$

$$N_2O_3 + O_2 + H_2O \rightleftharpoons 2HNO_3 \qquad (12)$$

The oxygen requirement thus calculated turns out to be 64.5 m moles/min for a flow of 10 ml HNO_3/min. The water requirement for the refluxer to form nitric acid is 50 m mol/min, plus the amount that is required to make 10 ml/min of 10 M HNO_3. Since 10 M HNO_3 is 48.6% by weight HNO_3 and its density is 1.259g/cc at 25°C, 6.6g of water will be needed.

Exchange System for Nitrogen-14. After preliminary experiments had shown that the product refluxer operated satisfactorily, sufficient data was obtained with a 157 cm long X 2.2 cm i.d. column to design an exchange system to obtain relatively pure nitrogen-14. In this column the steady state overall separation of 9.4 was attained in about 13-14 hours. Using a value of 1.055 for the single stage separation factor (α), H.E.T.P. of 3.8 was obtained this value was in approximate agreement with the values obtained by Taylor and Spindel (5) for the concentration of nitrogen-15. Due to greater values of overall separations and the uncertainty about the hold-up in the product refluxer, it was not possible to estimate the rate of approach to steady state using equations proposed by Cohen (21). However, it was evident from the relatively short time required to attain steady state overall separation, that the hold-up in the product refluxer would not in any way affect the operation of the larger system.

A reduction of the nitrogen-15 content of normal nitrogen by a factor of 100 was considered adequate for most of the applications of Nitrogen-14. The minimum number of theoretical plates required for this separation is 86, as calculated from the relation n = log S/log α, α = 1.055. Using the value of 3.8 cm for H.E.T.P. as measured earlier by Ghate and Taylor (22), the minimum length of the packed column would be 327 cm. Usually, for production, one provides 1.5 to 2 times the minimum number of theoretical plates so that an exchange column of 500 to 650 cm long would be suitable.

Since about 100 g of Nitrogen-14 depleted of Nitrogen-15 was desired, the size of the exchange system to obtain this quantity in a reasonable time was arrived at as follows: The maximum m mole HNO_3/min of product P with a mole fraction N_p of Nitrogen-14 that can be withdrawn for a given interstage flow, L, in m mole HNO_3/min is (5)

$$P = \frac{L\ No\ (1-No)(\alpha-1)}{N_p[1+(\alpha-1)(1-No)]-No} \qquad (13)$$

The mole fraction (1-No) of nitrogen-15 in the feed material is 0.00365 so that No is 0.99635, and since the desired concentration of nitrogen-15 in the product is 0.0000365, the mole fraction N_p of nitrogen-14 is 0.9999635. For α=1.055 and interstage flow L = 100 m mole/min, the maximum withdrawal rate P is calculated to be 5.24 m mole HNO_3/min or 106 g/day of nitrogen at the specified concentration. This would correspond to the maximum P/L ratio 70.052. This maximum withdrawal rate applies only to a column with an infinite number of stages. In order to account for the losses and fluctuations, the practical withdrawal rate is usually 30 to 40% lower than the minimum.

Figure 3. Exchange system for the preparation of nitrogen-14 highly depleted of nitrogen-15.

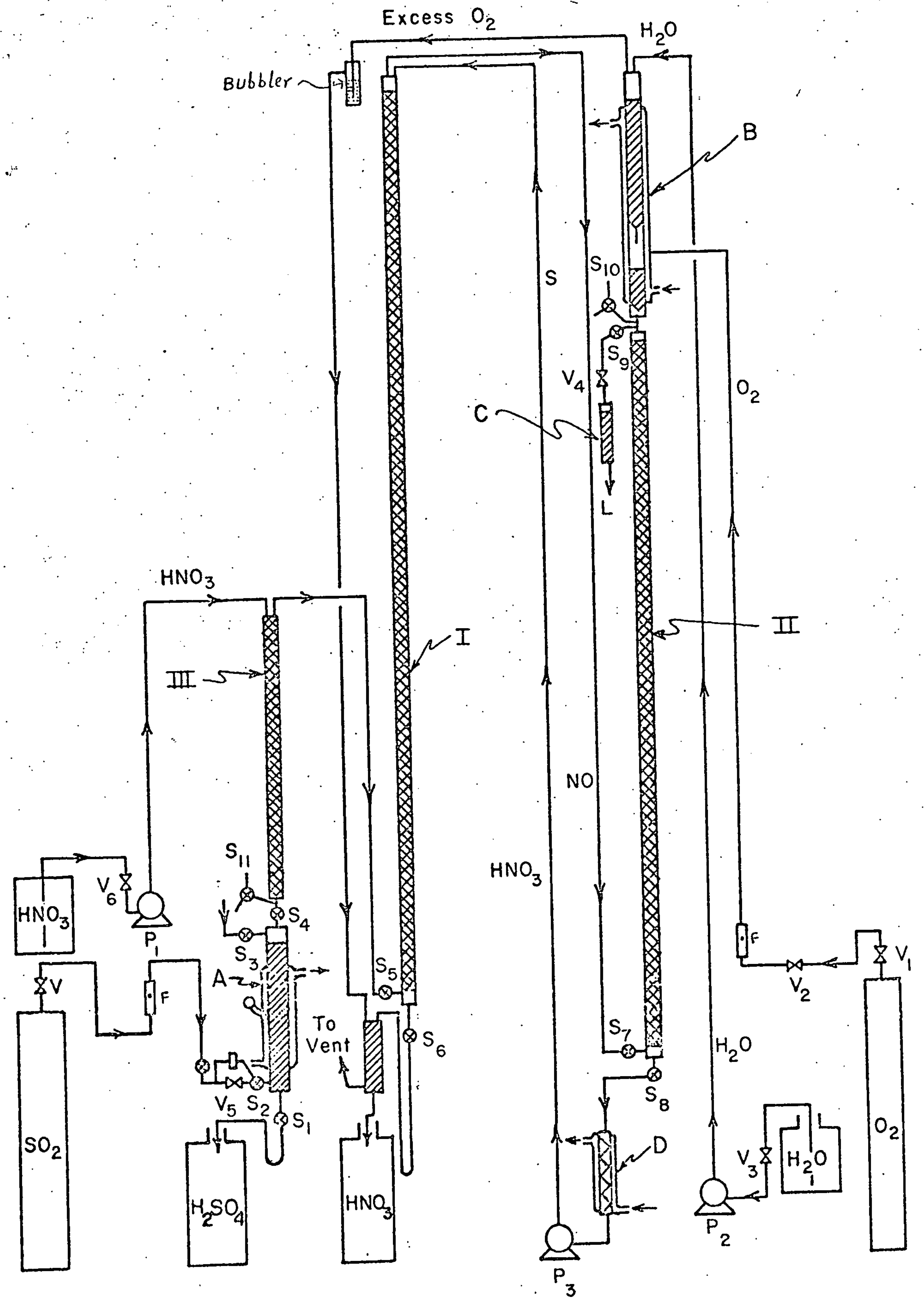
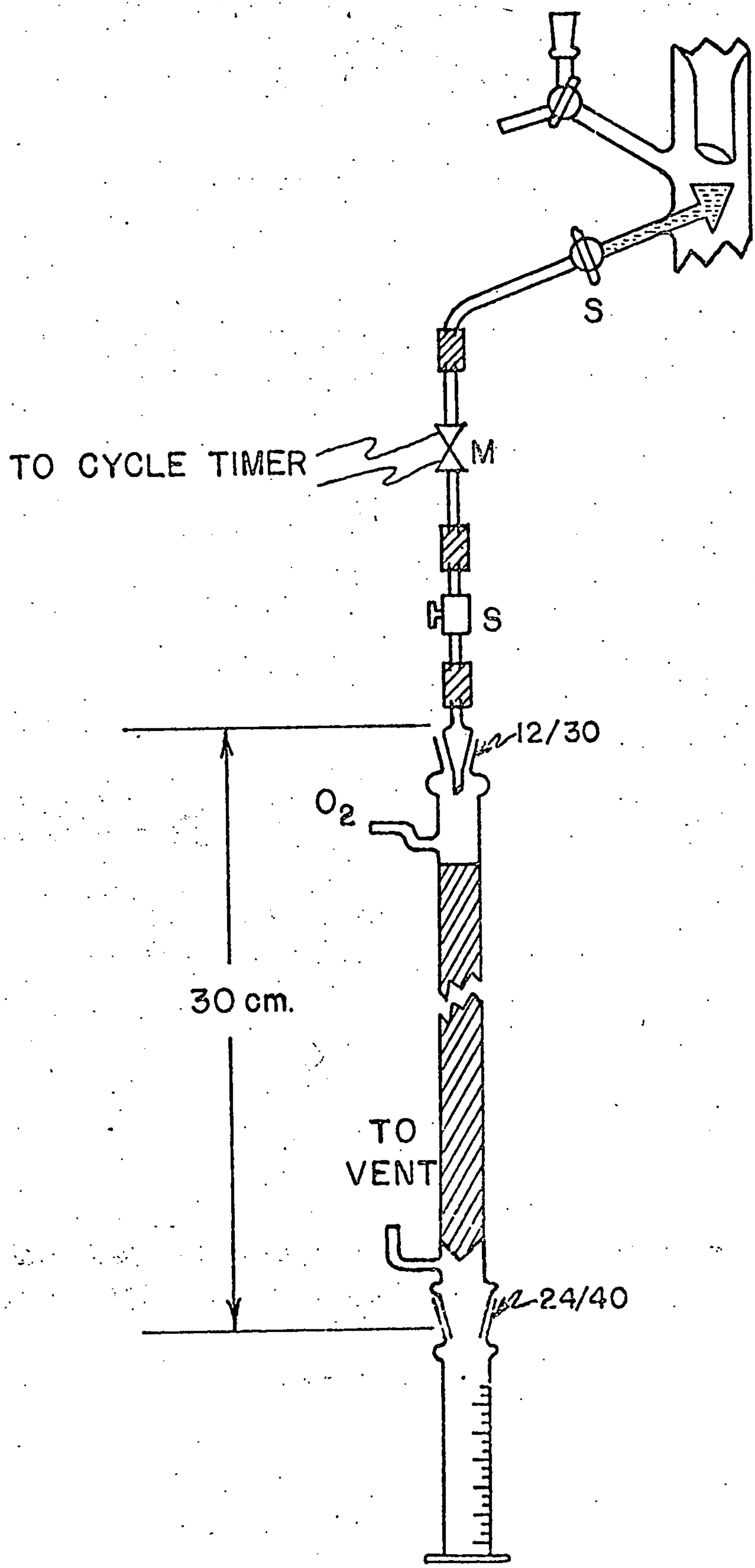

Excess O_2
H_2O
Bubbler
B
S
S_{10}
S_9
V_4
C
L
O_2
I
II
III
HNO_3
S_{11}
V_6
HNO_3
P_1
S_4
S_3
A
S_5
V
F
To Vent
S_6
S_7
S_8
V_5
S_2
S_1
SO_2
H_2SO_4
HNO_3
NO
HNO_3
D
P_3
H_2O
P_2
V_3
H_2O
O_2
F
V_1
V_2

Figure 4. Details of product withdrawal system.


S
TO CYCLE TIMER
M
S
12/30
O_2
30 cm.
TO VENT
24/40

That is, it should be possible to withdraw 64 g of nitrogen per day at an overall separation of about 100.

Based on the above estimates, the exchange system shown diagrammatically in Fig. 3 was constructed. Because of the limited height of the room, it was necessary to make the exchange column in two sections. The two sections I and II were intercoupled through a bellows pump (P_3). Both these sections provided a total of 525 cm of packed length, packed with HeliPak 3013. The product reflexer (B) at the top of column II is supplied with a precalculated amount of oxygen and water to obtain 10 M HNO_3 at the rate of 10 ml/min. At the bottom of this refluxer product, a withdrawal system was connected, details of which are shown in Fig. 4. To withdraw the liquid product (HNO_3) at the desired rate, a solenoid valve (M) was connected to the cycle timer which controlled the percentage of time the valve was open. The liquid product is than passed counter currently with the small stream of oxygen over a section packed with glass helicies. In this manner dissolved oxides of nitrogen were oxidised and a clear product was obtained.

Start up procedure. Before starting operation of the exchange system, columns were flooded with 10 M HNO_3 to ensure proper wetting of the packing. Then columns were drained slowly with a flow of 10 ml 10 M HNO_3/min to column III and 7.5 ml H_2O/min to the product refluxer. When the columns were free from excess liquid, SO_2 was passed through the bottom refluxer (A) to generate oxides of nitrogen according to reactions (2) and (3). These oxides then rise counter currently through columns III, I and II, and finally enter into the product refluxer where they are mixed with oxygen and absorbed into water to produce nitric acid.

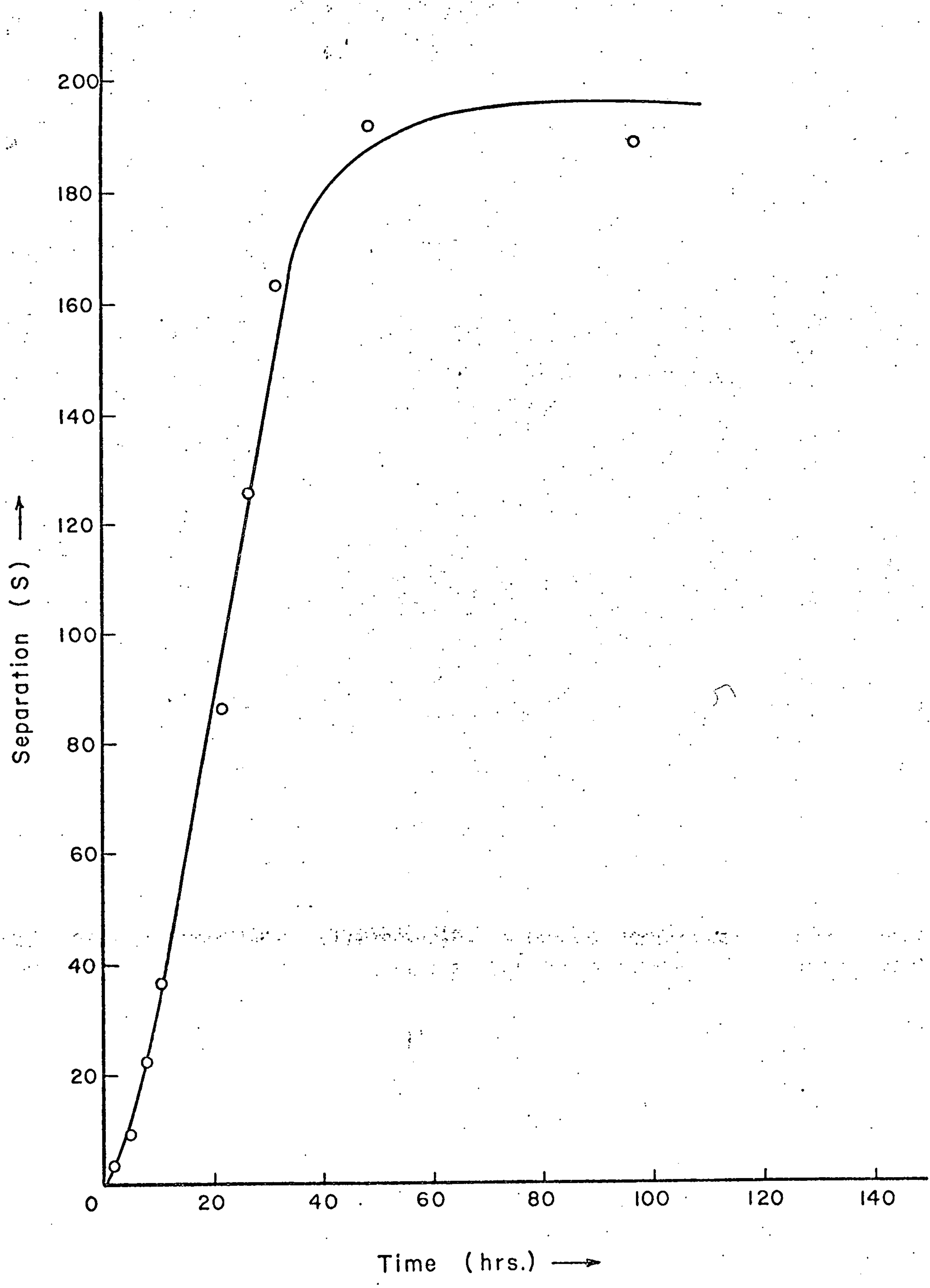
The progress of the separation was followed by isotopic analyses of gas and liquid samples withdrawn from the top of column II, Fig. 3. Since direct introduction of oxides of nitrogen into the mass-spectrometer is unsatisfactory because of their reaction, decomposition and adsorption in the ion source (23-25), it was necessary to convert them to nitrogen (26). The conversion to nitrogen was accomplished by passing the oxides of nitrogen through Cu/CuO furnace maintained at 750°C (5). In the case of liquid samples, the nitric acid was first converted to nitric oxide by reaction with Hg and H_2SO_4 (27) and then it was converted to nitrogen as described above.

The isotopic analyses of the nitrogen samples were made with a single collector Nier-type mass spectrometer (28).

RESULTS AND DISCUSSION

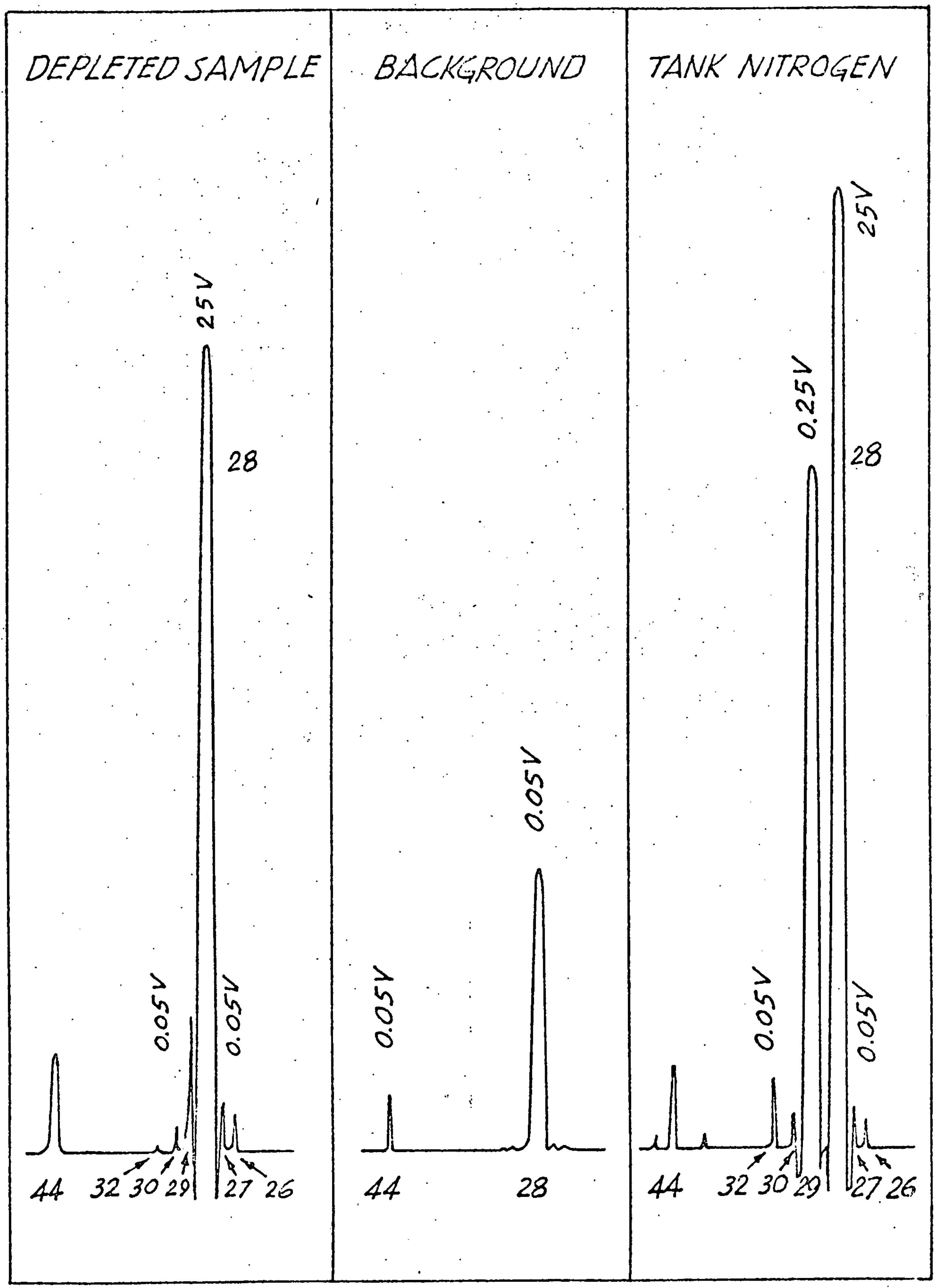
The progress of overall separation with time is shown in Fig. 5. After about 49 hours of operation under total reflux the overall separation of 192 was obtained. A typical spectra of nitrogen-14 highly depleted of nitrogen-15 is given in Fig. 6. In calculating the ratio of mass 28 to mass 29, a lot of difficulty was encountered due to uncertainty in the contribution of mass 29 background. However, attempts were made to estimate the mass 29 background contribution using gases other than nitrogen, but the results were not consistent. Using

Figure 5. Overall separation, S, as a function of time.



Separation (S) →
200
180
160
140
120
100
80
60
40
20
0
20
40
60
80
100
120
140
Time (hrs.) →

Figure 6. Mass spectrometer record showing the mass 29 peak in the product relative to that in tank nitrogen.


DEPLETED SAMPLE
BACKGROUND
TANK NITROGEN
25V
28
0.05V
0.05V
44
32
30
29
27
26
0.05V
0.05V
44
28
25V
0.25V
28
0.05V
0.05V
44
32
30
29
27
26

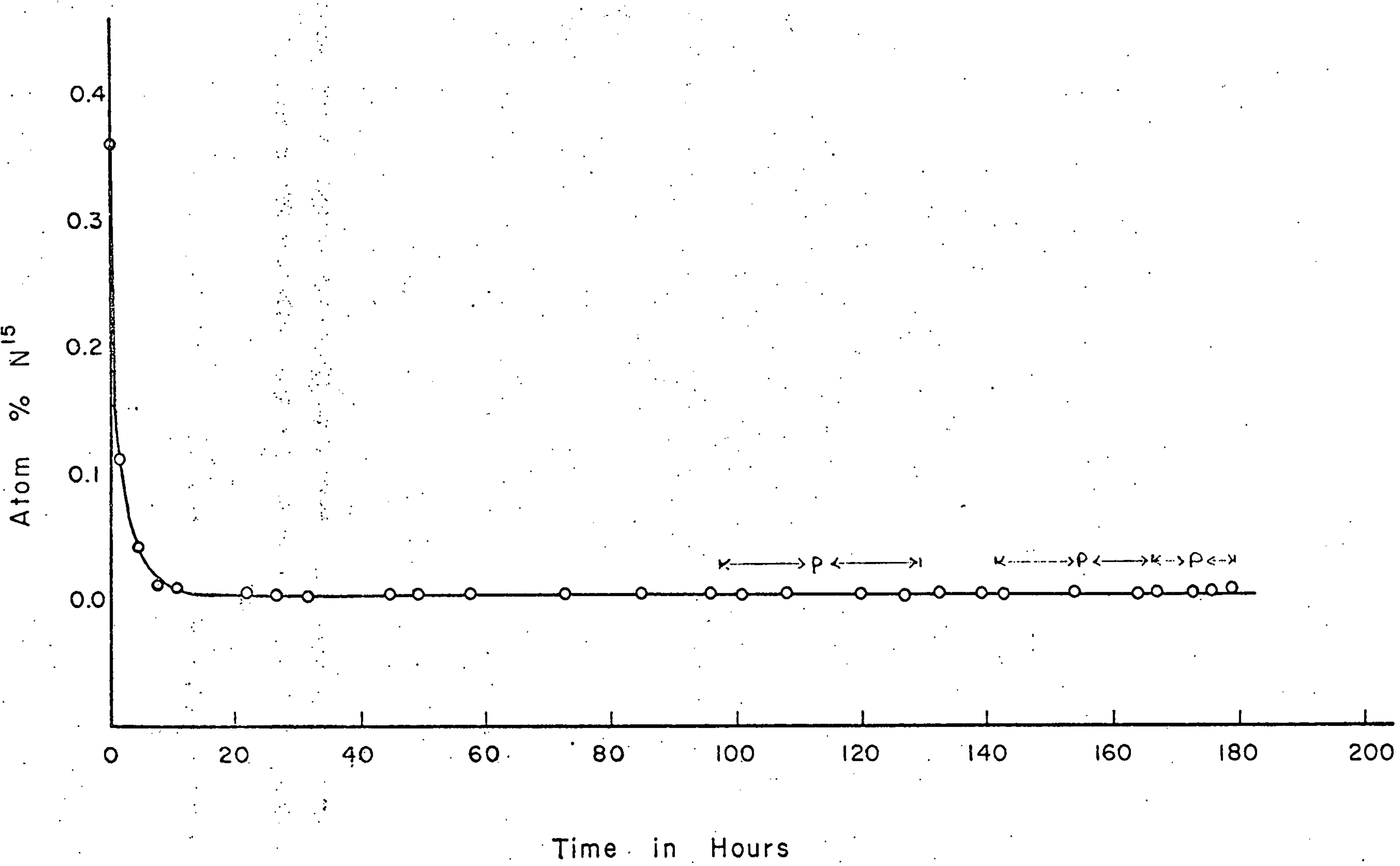
the approximate value of 2.5 divisions as the contribution of mass 29 background to the peak at mass 29 in the sample ratio R_p 24.800 of mass 28 to mass 29 was obtained. The average value of the similar ratio R_o for tank nitrogen with the particular settings of the ion source controls was 142. The overall separation is then S = 24,800/142 = 174.6. Since

$$S = \frac{R_p}{R_o} = \frac{N_p}{1-N_p} \Big/ \frac{N_o}{1-N_o} \qquad (14)$$

Where N_p = atom fraction of ^{14}N in product and N_o = atom fraction of ^{14}N in feed. Using the value of 0.99635 for N_o one obtains a value of 0.999979 for N_p when S = 174.6.

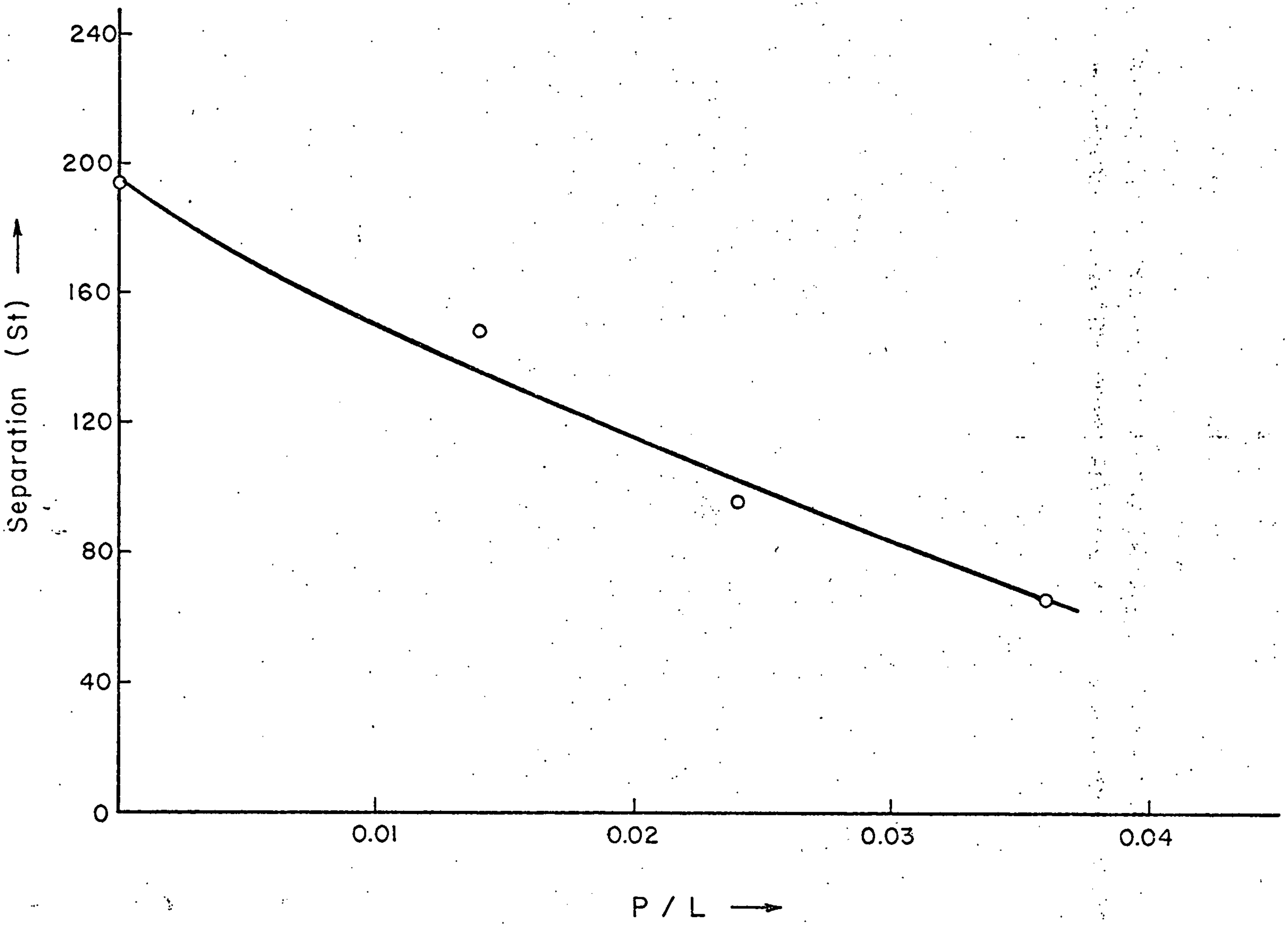
Effect of Product Withdrawal Rate: The exchange system was operated for about 96 hours and then the product was withdrawn at several different rates to determine the effect on the concentration of nitrogen-15 in the product. Figure 7 shows the change in the concentration of nitrogen-15 while the product was withdrawn at different rates. It is apparent from the plot that even the highest withdrawal rate has little or no effect on the concentration of nitrogen-15 in the product. However, a more sensitive measure of the effect of product withdrawal rate is obtained from the values of overall separations. Table 1 summarizes the results on this basis. In Fig. 8 overall separation S is plotted as a function of P/L, that is, the fraction of the interstate flow that is drawn off as a product. At a value of 0.023 for P/L, which corresponds to 2.3 m mole HNO_3 per min. or 46.0g nitrogen per day, the overall separation was reduced

Figure 7.. Atom fraction of nitrogen-15 during the operation of the system. P indicates the periods during which product was withdrawn.



Atom % N^{15}
0.4
0.3
0.2
0.1
0.0
P
P
P
0
20
40
60
80
100
120
140
160
180
200
Time in Hours

Figure 8. Overall separation as a function of the fraction of the interstage flow drawn off as product.


Separation (St) →
0
40
80
120
160
200
240
0.01
0.02
0.03
0.04
P / L →

to 100, which reduced the nitrogen-15 concentration by a factor of 100 from its natural abundance. The rate of 46.0 g/day at which the product was withdrawn was about 19% less than the 64.0 g/day arrived at in the design calculations. This indicates that the exchange column 2 to 2.5 times longer than the minimum length would probably have improved the agreement.

TABLE 1

Effect of product withdrawal rate on overall separation

Rate		$\frac{P}{L}$	R_p $\frac{\text{Mass 28}}{\text{Mass 29}}$	S $\frac{R_p}{R_o}$	Atom fraction ^{15}N
$\frac{\text{m mol HNO}_3}{\text{min.}}$	$\frac{\text{g Nitrogen}}{\text{day}}$				
0	0	0	27,300	192	0.000019
1.38	27.8	0.0138	21,300	150	0.000024
2.40	48.4	0.0240	13,700	96	0.000038
3.65	73.6	0.0365	10,800	76	0.000048

Performance of the Product Refluxer: A decrease in the production rate could result from the loss of oxides of nitrogen from the top of the refluxer. The extent of loss was measured by allowing the gases that leave the product refluxer to pass through 230 ml of water in a 250 ml graduated cylinder. After 10 to 40 hours, the solutions were titrated with standardized sodium hydroxide using chlorophenol red indicator. The ratio of losses to the interstage flow during the collection time was in the range of 1 part in 2,900 to 1 part in 33,000. This would be equivalent to a P/L ratio of 0.00034 to 0.00003 compared to a ratio of 0.0365 for the maximum product withdrawal. These observations indicate that the refluxer was quite efficient in converting the oxides of nitrogen into nitric acid.

Another indication of the reliable operation of the refluxer was the constancy of the concentration of the nitric acid produced. As shown in Table 2, the concentrations of various samples were in the range of 10.1 M to 10.8 M with an average of 10.45 M. This is slightly higher than 10.0 M because it includes the dissolved oxides of nitrogen withdrawn with nitric acid and oxidized by oxygen in the product withdrawal system.

TABLE 2

Concentration of nitric acid produced by product refluxer during initial part of the experiment.

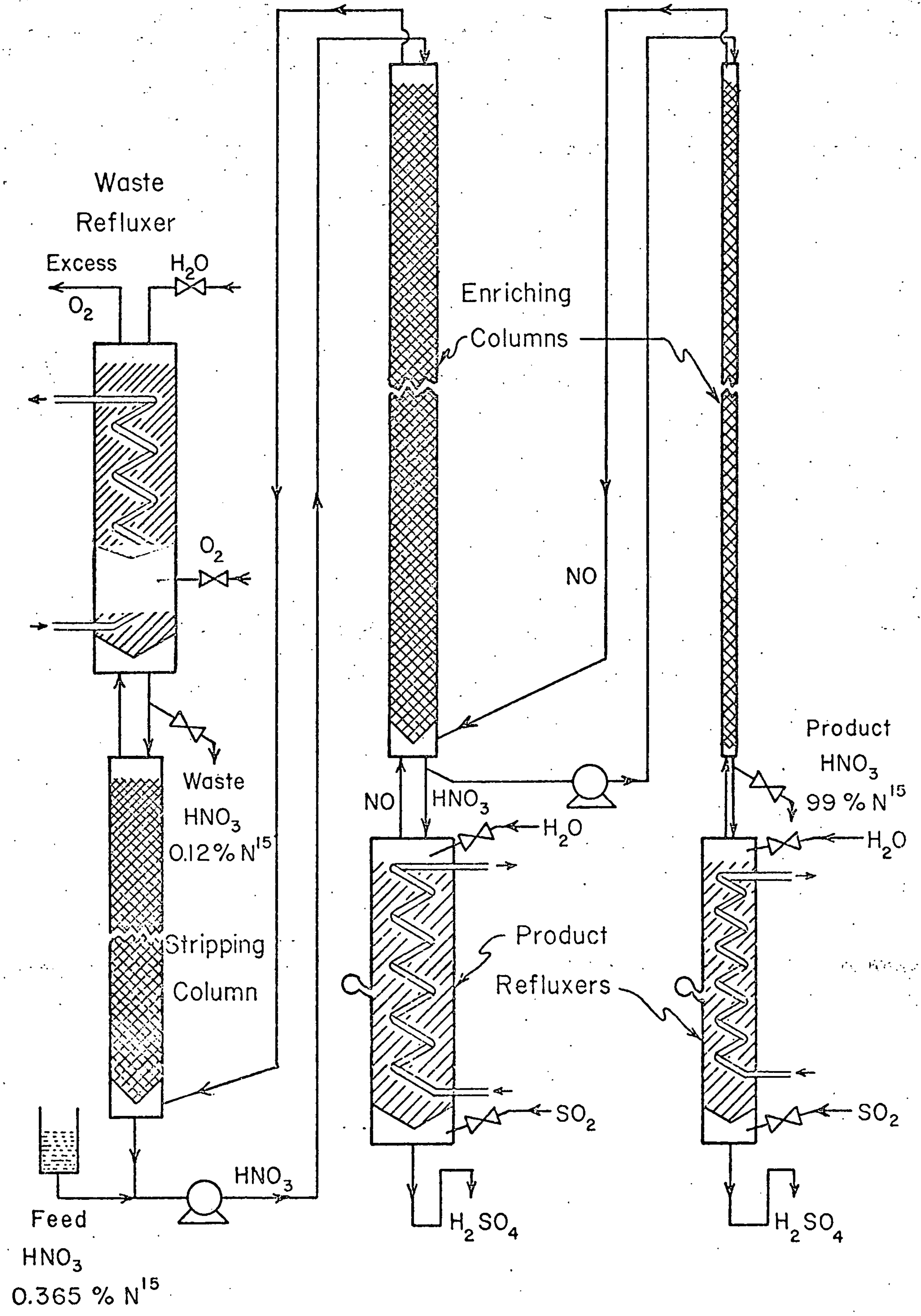
Product Number	Volume ml.	M moles/l	Product Number	Volume ml.	M moles/l
1	25.0	10.10	8	50.0	10.22
2	29.0	10.22	9	40.0	10.80
3	31.0	10.22	10	44.8	10.80
4	36.0	10.50	11	45.0	10.80
5	31.0	10.80	12	36.0	10.10
6	35.0	10.80	13	37.0	10.10
7	23.5	10.80	14	47.0	10.80
			Ave.	-	10.40±0.3

The rate of production of nitric acid by this refluxer is 281 moles HNO_3 per day per liter of volume. This is significantly greater than the 32 moles HNO_3 per day per liter of volume produced in commercial 60 ton/day high pressure nitric acid plants using air for oxidation (14). However, per unit cross sectional area, the refluxer used here produced only 17 moles HNO_3/day-cm^2 compared to 42 moles HNO_3/day-cm^2 for the commercial plants. Apparently the use of oxygen in the arrangement used as in the present work results in a much greater rate of oxidation and absorption of the oxides of nitrogen to form nitric acid.

APPLICATION TO PRODUCTION OF NITROGEN-15

The product refluxer discussed in the previous section has an important use in the production of nitrogen-15. As an example of the use of the refluxer for preparing 1 g per day of 99% nitrogen-15 is illustrated in Fig. 9. The minimum interstage flow rate L at the feed point where the atom fraction of nitrogen-15 is 0.00365, as calculated by equation 13 is 243 m mol/min. This is usually increased by 20 to 40% to take care of losses, fluctuations, etc., so that a flow of about 300 m mol/min would be used. Previous experience of Taylor and Spindel (5) and the present work show that H.E.T.P. values of about 4.0 cm can be obtained with HeliPak 3013 at flow rates as high as 3.0 ml/min-cm^2. On this basis the diameter and length of the first enriching column should be 3.5 cm and 550 cm respectively. The second enriching column which receives about 4% of the flow in the first column, is filled with

Figure 9. System for the production of 1g/day of 99% nitrogen-15 using a waste refluxer for recovery of 70% of the nitrogen-15 in the nitric acid.


Waste
Refluxer
Excess
O2
H2O
O2
Waste
HNO3
0.12% N15
Stripping
Column
Feed
HNO3
0.365 % N15
HNO3
Enriching
Columns
NO
NO
HNO3
H2O
Product
Refluxers
SO2
H2SO4
Product
HNO3
99 % N15
H2O
SO2
H2SO4

HeliPak 3012 and operates at about 1 ml/min-cm^2, so that its diameter should be 1.2 cm with a length of about 600 cm. The lengths indicated would provide 1.8 times the minimum number of stages required to produce 99% nitrogen-15. Similarly the diameter of the stripping section should be the same as the first enriching column since it has the same inter-stage flow. If it is desired to recover about 70% of the nitrogen-15 from the nitric acid, the atom fraction in the waste would be 0.0012, so that the stripping column should operate at an overall separation of 3.1 for nitrogen-14. With $\alpha = 1.055$ the minimum number of stages would be 21.0 and for the production twice of this should be provided. Using a value of 4.0 cm for H.E.T.P. the length of the stripping section should be 200.0 cm.

To convert the oxides of nitrogen to 10.0 M nitric acid the size of the refluxer can be calculated by using a proportional scaling factor. Since our present refluxer operated satisfactorily for the rate of 100 mg atom nitrogen/min, for the feed of 300 mg atom nitrogen/min the diameter of the refluxer would be about 5.8 cm i.d. and the total length of about 100-120 cm. The flows of water and oxygen would be 22.7 ml/min and 4.73 liters/min respectively. The heat generated would be about 9.47 kcal/min. Adequate cooling should be provided.

The rate of withdrawal W of waste nitric acid and the feed flow F can be arrived at by material balance calculations for nitric acid $P = F - W$, and a material balance on nitrogen-15, $PN_p = FN_o - WN_w$ where $N_p = 0.99$, $N_o = 0.00365$, and $N_w = 0.0012$.

Solving for F and W one obtains F = 18.87 m mol HNO_3/min and W = 18.82 m mol HNO_3/min, i.e. 1.88 ml 10 M HNO_3/min. Thus the feed and waste flows of nitric acid are essentially the same. This value of 1.88 ml 10 M HNO_3/min required when no stripping section and the refluxer to convert oxides of nitrogen to nitric acid are used. Such an arrangement would mean the requirement of 2.7 liters of HNO_3 per day as against 43.2 liters/day otherwise. Previous experience shows that use of the stripping section does not add any complications to the system. The savings in constructional costs since the nitric acid is produced at the atmospheric pressure, and the usage of nitric acid partially compensates for the cost of oxygen used. In addition, the removal of oxides of nitrogen from the waste gases would reduce pollution problems.

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