# REPORT:

# CARBON DIOXIDE ABSORBENTS.

Contract No. NObs-50023

For
The Navy Department
Bureau of Ships
Washington 25, D.C.
(Code 649P)

By
The Girdler Corporation
Research and Development Laboratory
Gas Processes Division
Louisville, Kentucky

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Report No. T2.20-2-3

THE GIRDLER CORPORATION
GAS PROCESSES DIVISION
PROCESS DEVELOPMENT AND RESEARCH LABORATORIES
LOUISVILLE, KENTUCKY

# GENERAL INTRODUCTION TO AMINE STUDIES FOR THE NAVY.

May 17, 1950

Report by:

R. E. Reitmeier

## Sentence Summary

A program for the selection of an amine solution for the removal of carbon dioxide from submarine atmospheres is outlined.

This report describes the general scope of an investigation which has for its purpose the selection of the most desirable material for the removal of carbon dioxide from submarine atmospheres. The problem involves the removal of approximately 3 percent carbon dioxide from air and, although complete removal of the carbon dioxide is not required it is desirable to reduce it to less than 1.5 percent. Any process selected for the removal of carbon dioxide should preferably have the following characteristics.

1. It should give reasonably complete removal of the carbon dioxide with a minimum contamination of the atmosphere with materials not normally present in air and should not introduce toxic materials into the atmosphere.

2. The power requirements for the operation of the process should be at a minimum.

3. The materials used for absorption or adsorption of the carbon dioxide should have sufficient stability toward oxygen that the degradation over a period of sixty days does not influence the operation of the process within the limits of the design.

4. The physical size and weight of the equipment should be as small as feasible.

5. The process should operate using utilities normally available in a submarine.

6. The process should be operable with a minimum of attention by the submarine personnel.

7. The quantity and cost of the material used for absorption or adsorption should be reasonable.

Considerable previous work has been done by the University of Pennsylvania (1) and Northwestern University (2) to select and evaluate the materials that could be used for the removal of carbon dioxide. Before this investigation was started it was decided at a joint meeting of representatives of the Girdler Corporation and the Navy Department to limit this investigation to the study of those materials which were believed to show the greatest immediate promise for the solution of the problem, namely, water soluble amines and alkali salts of amino acids. It was decided to further limit the investigation to those amines and alkali salts or amino acids which were either commercially available and those which would be commercially available within approximately two years. It was agreed that the process would involve the circulation of an aqueous solution of the amine or the alkali salt of the amino acid with the carbon dioxide being absorbed in one part of the cycle and removed or regenerated from the solution by heat in another part of the cycle. The solution essentially free of carbon dioxide would then be cooled and returned to the first part of the cycle for the absorption of more carbon dioxide.

In general, there are three commercially available amino alcohols used for the removal of acid gases such as carbon dioxide from gas streams. These amines are: monoethanolamine, a primary amine; diethanolamine, a secondary amine; and triethanolamine, a tertiary amine. These amines in aqueous solution have found wide application for the removal of carbon dioxide from gas streams essentially free of oxygen. Although other amines could, no doubt, be used the above three amines are readily available, reasonably inexpensive, and exhibit many of the desired properties for the removal of carbon dioxide from gas streams essentially free of oxygen. However, there are serious objections to the use of these amines for the removal of carbon dioxide from gas streams containing appreciable quantities of oxygen.

Monoethanolamine, although not so susceptable to oxidation as diethanolamine, undergoes appreciable oxidation resulting in the formation of non-alkaline materials which are corrosive to carbon steel and in volatile materials which will contaminate the submarine atmosphere. Although of the three amines, monoethanolamine has the highest capacity per unit weight of material and the greatest reaction rate with carbon dioxide, it has the highest vapor pressure and frequently exhibits a phenomenon referred to as "fogging" when used to remove carbon dioxide so that much larger quantities of the amine are thus introduced into the atmosphere than are introduced as a result of vaporization. The relatively high vapor pressure and the phenomenon of "fogging" would probably result in an undesirable degree of contamination of the submarine atmosphere, and although the contaminating materials could be removed, extra equipment and utilities would be involved. Even though materials such as the iodides may be used to inhibit the oxidation of monoethanolamine in aqueous solutions, the rate of oxidation would probably still be too great for satisfactory operation. Nevertheless, the use of this amine should not be eliminated from further consideration since its high capacity for carbon dioxide absorption, its high reaction rate and its relatively low energy requirement for removal of the carbon dioxide may make it superior to most other amines.

Diethanolamine has a capacity per unit weight and a reaction rate with carbon dioxide appreciably less than that of monoethanolamine. In addition, it is considerably more susceptible to oxidation than either monoethanolamine or triethanolamine. It has in its favor a very low vapor pressure and exhibits no tendency towards "fogging". Although its lower capacity for the absorption of carbon dioxide per unit volume of solution can be partially overcome by increasing the molal concentration of diethanolamine over that of monoethanolamine, the lower reaction rate cannot be appreciably improved. Moreover, the energy requirement for removal of the carbon dioxide from the solution of the amine is greater than that for monoethanolamine.

Triethanolamine has the lowest capacity and reaction rate of the three amines. The energy requirement for removal of the carbon dioxide is greater than that for either monoethanolamine or diethanolamine. On the other hand, triethanolamine is less susceptible to oxidation than any of the other amines and from this standpoint it is the most desirable of the three amines for the removal of carbon dioxide from submarine atmospheres.

Although the alkali salts of several amino acids have been used commercially on the Continent, they have not been used in the United States and information is not available to fully evaluate them in comparison with the three amines previously discussed.

Since a commercial process for the removal of carbon dioxide from air has not previously been required, the Girdler Corporation has never made extensive studies to determine which of the various amines would be most suitable where resistance to oxidation is of primary importance. However, extensive investigations have been conducted to reduce or eliminate the oxidation of the three amines, monoethanolamine, diethanolamine, and triethanolamine when contacted with gas streams containing relatively small quantities of oxygen.

The properties of an amine or an alkali salt of an amino acid which should be studied in order to evaluate the various materials and permit the selection of the most desirable for the removal of carbon dioxide from air are:

1. Resistance to oxidation.
2. Vapor pressure.
3. Capacity for the absorption of carbon dioxide.
4. Reaction rate with carbon dioxide.
5. Energy requirements for reactivation.
6. Cost per equivalent unit of active material.
7. Toxicity of vapors.
8. Degree of "fogging".
9. Solubility of amine and its corresponding carbonate in water.
10. Thermostability.
11. Corrosiveness toward materials of fabrication.

In order to evaluate each of the above points the investigation was divided into several different studies, namely

1. Literature Survey.
2. A preliminary study of the susceptability of each material to oxidation by an accelerated oxidation test.
3. A study of the alkalinity of each of the materials at 25°C. and 90°C. by the determination of the pH of aqueous solutions at each of these temperatures.
4. A study of the susceptability of each material to oxidation by a prolonged oxidation test.
5. The determination of the capacity of each material for the absorption of carbon dioxide.

6. A study of the reaction rates of each material with carbon dioxide.
7. A study of the relative energy requirements for reactivation.

Included in the literature survey (Girdler Report No. T2.20-2-2) was a tabulation of all the representative types of known amines as well as their structures and physical properties. Their availability, suppliers, and approximate price was also listed. Through the literature survey, it was possible to eliminate 68 materials from further consideration on the basis of their vapor pressure, solubility in water, toxicity, and thermostability. Approximately 39 materials remained to be evaluated.

These materials were evaluated on the basis of the pH of their aqueous solution (Girdler Report No. T2.28-1-1) and an accelerated oxidation test (Girdler Report No. T2.15-1-3). The accelerated oxidation test permitted the elimination of another 25 materials due to their extreme unstability toward oxidation. The remaining 14 materials were subjected to the prolonged oxidation test (Girdler Report No. T2.15-1-3). These materials were further studied by the determination of the pH of their aqueous solutions at 90°C. (Girdler

Report No. T2.28-1-1). They were evaluated for their capacity to absorb carbon dioxide (Girdler Report No. T2.11-3-2) and their reaction rate with carbon dioxide (Girdler Report No. T2.11-3-1). The relative energy requirements for reactivation were studied and results tabulated in Girdler Report No. T2.12-1-1.

Girdler Report No. T2.20-2-4 summarizes all pertinent observations and on the basis of these observations, those amines best suited for the application in question are indicated.

## Literature Cited.

1. Gaff, John A., and Banwell, Roy W., Final Report of the Central Engineering Laboratory, Report OSRD No. 5482, University of Pennsylvania, June 30, 1945.
2. Stutman, L. F., Trimonthly Reports, Chemical Engineering Department, Northwestern University, Jan. 1-March 31, April 1-June 31, and July 1-Sept. 30, 1949, NR 261-018.

REPORT BY: ______________________ DATE: ____________

READ AND UNDERSTOOD BY: ______________________ DATE: ____________

Distribution: T.F., P.F., P.D.F., U.O.F., R.E.R., M.R.A.

jc

Report No. T2.20-2-2

THE GIRDLER CORPORATION
GAS PROCESSES DIVISION
PROCESS DEVELOPMENT AND RESEARCH LABORATORIES
LOUISVILLE, KENTUCKY

# AMINES FOR THE REMOVAL OF CARBON DIOXIDE FROM GAS STREAMS: SUPPLIERS AND PHYSICAL PROPERTIES

March 3, 1950

Report by:

Kenton Atwood

## Sentence Summary

Fifty-three amines which might be used in removing carbon dioxide from gas streams have been selected for laboratory investigation.

## I. INTRODUCTION:

The object of this report is to select a number of amines which might be used for removing carbon dioxide from submarine atmospheres by a cyclic process similar to the Girbotol process. From these amines the one best suited for the purpose will be selected by investigation in our laboratory.

An ideal amine for use in a submarine should have a low vapor pressure and a low equivalent weight, and should be very resistant to oxidation or any other reaction which would reduce the carbon dioxide absorbing capacity. The rate of carbon dioxide removal by the amine solution should be rapid, and regeneration should require a low power consumption.

## II. SUMMARY AND CONCLUSIONS:

Fifty-three amines, or mixtures of amines, which might be used in removing carbon dioxide from submarine atmospheres are listed in this report (Table III). All but a few of them will be subjected to laboratory screening tests in order to determine which amines will be investigated more intensively. These amines were selected after examination of the literature on the physical properties of various types of amines and a survey of a large number of suppliers.

## III. DISCUSSION:

### A. Properties of Amines

The total number of amines which might theoretically be synthesized and used in removing carbon dioxide from gas streams is very large, and inspection of Beilstein's Handbuch indicates that several thousand amines have already been prepared. It would, therefore, be impractical to list all known amines in any report not of encyclopedie proportions. In Table I, therefore, only examples of various types of amines are listed.

Most of the information given in Table I is from Heilborn's "Dictionary of Organic Compounds," New York: Oxford University Press, 1943, although some information is from "Beilstein's Handbuch der Organischen Chemie," or the data sheets prepared by the various suppliers of amines. Molecular weights and boiling points (at atmospheric pressure unless otherwise specified) are given to the nearest unit.

Each amine listed in Table I has a classification number which is used throughout this report. Groups of amines with similar structure are given consecutive numbers, and blanks are left between the various classes for the inclusion of new compounds. In the preparation of Table I compounds with both an amino and a hydroxyl group, or two amino groups on the same carbon atom have been omitted, as have azo-compounds and unsaturated amines with the exception of ring compounds. These amines would probably be unstable and, therefore, unsuitable for prolonged use. Only a few compounds with strongly acidic groups are listed in Table I. A later section of this report considers briefly the possible application of amino acids.

## B. Suppliers of Amines

Possible suppliers of amines were located in "Thomas' Register of American Manufacturers," 37th Ed. (1947), the "Green Book" (1949-50) of the Oil, Paint and Drug Reporter, Chemical Industries' "Buyers Guidebook," 24th Annual Revision (1948), and our Catalog File. The letter reproduced in the Appendix of this report was sent to these suppliers. Table II indicates whether or not a reply was received between January 1 and March 1, 1950, and gives the classification numbers (Table I) of the amines that the various companies have available. In the case of the few companies which offer a great number of amines, however, only those which are thought to have possible application in the removal of carbon dioxide from submarine atmospheres are listed in the "Amines Available" column.

For the purpose of this discussion any interest expressed by a company in an amine is considered indicative of some degree of commercial availability. The letter C indicates that carload lots of the material may be obtained at the present time; R indicates that a company has produced the compound on a small scale and would like to develop a market; RN indicates that a company is considering the production of the amine but has not yet prepared enough material to send out for testing; CL indicates that material is available in limited quantities, generally drum lots; CD indicates that large scale production of an amine has been discontinued, probably for lack of a market.

## C. Selection of Amines for Laboratory Study

Although insoluble amines might be used in removing carbon dioxide from gas streams, a process using dry amines would be quite different from the Girbotol process and would probably involve several new engineering problems. Therefore amines which are not soluble to the extent of at least 10 or 15% in water have been considered unsuitable for laboratory study.

It is thought that air saturated with amine vapor from a monoethanolamine solution might be injurious to personnel compelled to breathe it for a long period of time. The amine could probably be removed rather readily by charcoal, but it would be undesirable to require the extra equipment. Therefore, most of the compounds with a boiling point under 160°C. are not considered for laboratory investigation. In a few cases compounds with slightly lower boiling points should be investigated to determine the effect of certain structures on the behavior of amines.

Only amines which are commercially available or which might be available if a market developed are considered for laboratory study. It is possible, however, that the laboratory study of the amines now available would suggest the desirability of manufacturing some other amine to the specifications indicated by the laboratory work.

All of the alkyl primary amines listed in Table I (Nos. 1 to 6) have low boiling points. It appears probable that the solubility in water would be low if the molecular weight of an amine were sufficiently high to allow a high boiling point. The same considerations eliminate alkyl secondary (11-13) and tertiary (21-23) amines.

Of the alkyl di- and polyamines with all primary amine groups (31-37), ethylene diamine (31), propylenediamine (32), and 1-3 diaminobutane (37) have low boiling points. In this group hexamethylenediamine (35) is the only commercially available compound with a high boiling point. Among the other alkyl di- and polyamines (51-101), only Nos. 52, 53, 54, 55, 62, and 63 are commercially available.

Most of the alkanol aliphatic amines (Nos. 111-167) listed in Table I are commercially available. Exceptions are Nos. 112, 113, 114, 115, and 134. Among the available compounds, only dimethylaminoethyl alcohol (141) is known to have a low boiling point.

In the group of amines containing isocyclic rings (Nos. 171-214) aniline (171), dimethylaniline (191), and m-phenylenediamine (211) are probably not basic enough to react with carbon dioxide. Phenylethylamine (174), methylaniline (181), diphenylamine (182), and dimethylaminomethylphenol (192) are not very soluble in water. Cyclohexylamine (172) and methyl-cyclohexylamine (183) have low boiling points. Most of the other compounds in the group (Nos. 175, 176, 201, 202, 212, and 214) are not commercially available. This leaves only two compounds, benzylamine (173) and 2,4,6-tri(dimethylaminomethyl)phenol (213), which are not eliminated without laboratory tests.

Among the heterocyclic amines given in Table I (221-248) piperidine (221), piperazine (222), pyridine (233), picoline (234), morpholine (238), and methyl piperidine (248) have low boiling points. Several other compounds (Nos. 235, 236, 237, and 244) are not known to be commercially available.

All of the compounds and mixtures of Table I which are not eliminated by unfavorable physical properties or unavailability are listed in Table III. The suppliers are given, along with the degree of commercial availability of their amines. Prices, usually in drum lots, are listed when they are known.

A few of the amines given in Table III probably will not be tested in the laboratory, at least in the near future. Samples of isopropylaminopropylamine (55), polyethylene glycolamine 175 (3M), and diethylamino-2,3-propanediol (149) may not be available for several months. Previous laboratory experience has indicated that solutions of the diamines are exceedingly corrosive, and unless the diamines which will be tested (52, 53, 54, 63, 161) prove to be promising several others with similar structures (37, 55, 62, 165, 166, 167, 1M) probably will not be studied. Since the data sheet on hexamethylene diamine (35) states that the compound is exceedingly toxic and that the water solutions are rather unstable, this diamine may not be considered further. Acetyl ethanolamine (136), acetyl morpholine (242), and 2,6-dimethyl morpholine (243) are probably such weak bases that their solutions will not absorb carbon dioxide to any significant extent. Since furfuryl amine (246) is probably more unstable and in addition has a lower boiling point than tetrahydrofurfuryl amine (247), it may be necessary to make tests on the saturated compound only.

### D. The Alkazid Reagents

In Europe the Alkazid reagents, which are sodium or potassium salts of amino acids, have been widely used for removing carbon dioxide from gas streams (H. Baehr, Refiner and Natural Gasoline Manufacturer 17, No. 6, 237-244 (June, 1938), and PB Report No. 1110, June, 1945 (R8.20-1-3)). Small samples of dimethyl glycine $((CH_3)_2NCH_2COOH)$, whose potassium salt is alkazid "DIK", one of the two main alkazid reagents, may be obtained from DuPont. This basic salt will probably be subjected to the same laboratory tests as the amines listed in Table III, and if a sample of alkazid "M", the potassium salt of methyl alanine $(CH_3CH(NHCH_3)COOH)$ can be obtained it will also be tested. The latter base is said to be superior to alkazid "DIK" as a carbon dioxide absorber, but the material may not be available in this country.

**REPORT BY:** ______________________ **DATE:** ____________

**READ AND UNDERSTOOD BY:** ______________________ **DATE:** ____________

Distribution: **T.F., P.F., P.D.F., U.O.F., R.E.R., K.A.**

## IV. APPENDIX:

Gentlemen:

We wish to obtain information on the price and availability of any water-soluble organic bases which you can supply in drum lots. These compounds, of which examples are piperidine, ethylene diamine, and diethanolamine, should be soluble to the extent of at least 10 or 15% in water at room temperature, and preferably miscible in all proportions. Organic bases boiling under 70°C. probably would be of no interest to us.

If you expect to offer any new organic bases for sale within the next one or two years, we would like to have quotations on them also. We would also appreciate any information you could furnish on the chemical and physical properties of these compounds.

Very truly yours,

THE GIRDLER CORPORATION

R. E. Reitmeier, Director
of Research and Development

## TABLE

## PROPERTIES

| No. | Name | Formula |
|---|---|---|
| ALIPHATIC AMINES | | |
| Alkyl Primary Amines | | |
| 1 | Methylamine | $CH_3NH_2$ |
| 2 | Ethylamine | $C_2H_5NH_2$ |
| 3 | n-Propylamine | $C_3H_7NH_2$ |
| 4 | n-Butylamine | $C_4H_9NH_2$ |
| 5 | n-Amylamine | $C_5H_{11}NH_2$ |
| 6 | n-Hexylamine | $C_6H_{13}NH_2$ |
| Alkyl Secondary Amines | | |
| 11 | Dimethylamine | $(CH_3)_2NH$ |
| 12 | Diethylamine | $(C_2H_5)_2NH$ |
| 13 | Di-n-propylamine | $(C_3H_7)_2NH$ |
| Alkyl Tertiary Amines | | |
| 21 | Trimethylamine | $(CH_3)_3N$ |
| 22 | Triethylamine | $(C_2H_5)_3N$ |
| 23 | Tri-n-propylamine | $(C_3H_7)_3N$ |
| Alkyl Di- and Poly-Amines, All Primary Amino Groups | | |
| 31 | Ethylenediamine | $NH_2C_2H_4NH_2$ |
| 32 | Propylenediamine | $CH_3CH(NH_2)CH_2NH_2$ |
| 33 | Tetramethylenediamine | $NH_2C_4H_8NH_2$ |
| 34 | Pentamethylenediamine | $NH_2C_5H_{10}NH_2$ |
| 35 | Hexamethylenediamine | $NH_2C_6H_{12}NH_2$ |
| 36 | Triamino Propane | $NH_2CH_2CH(NH_2)CH_2NH_2$ |
| 37 | 1-3-Diaminobutane | $NH_2CH_2CH_2CH(NH_2)CH_3$ |
| Alkyl Di- and Poly-amines, Primary and Secondary Amino Groups | | |
| 51 | Methyl Ethylenetriamine | $CH_3NHC_2H_4NH_2$ |
| 52 | Diethylenetriamine | $NH_2C_2H_4NHC_2H_4NH_2$ |
| 53 | Triethylenetetramine | $NH_2(C_2H_4NH)_2C_2H_4NH_2$ |
| 54 | Tetraethylenepentamine | $NH_2(C_2H_4NH)_3C_2H_4NH_2$ |
| 55 | Isopropylaminopropylamine | $(CH_3)_2CHNHC_3H_6NH_2$ |
| Alkyl Di- and Poly-Amines, Primary and Tertiary Amino Groups | | |
| 61 | $\beta$-amino-$\alpha\gamma$-bis-(dimethylamino)propane | $(CH_3)_2NCH_2CH(NH_2)CH_2N(CH_3)_2$ |
| 62 | Dimethylaminopropylamine | $(CH_3)_2NC_3H_6NH_2$ |
| 63 | Diethylaminopropylamine | $(C_2H_5)_2NC_3H_6NH_2$ |

I

OF AMINES

| Molecular Weight | Boiling Point, °C. | Solubility in Water, % by Weight | Remarks |
|---|---|---|---|
| 31 | -7 | V.S. | |
| 45 | 17 | Com. | |
| 59 | 49 | Com. | |
| 73 | 78 | Com. | |
| 87 | 104 | Com. | |
| 101 | 130 | S. | |
| 45 | 7 | V.S. | |
| 73 | 56 | V.S. | |
| 101 | 110 | S.S. | |
| 59 | 4 | Com. | |
| 101 | 89 | V.S. | |
| 143 | 157 | S.S. | |
| 60 | 117 | V.S. | |
| 74 | 121 | V.S. | |
| 88 | 159 | V.S. | Bad odor, putrescein. |
| 102 | 179 | V.S. | Bad odor, cadaverine. |
| 116 | 205 | V.S. | Bad odor, unstable compound. |
| 130 | 190 | V.S. | |
| 88 | 147 | V.S. | |
| 74 | | | Hydrochloride known. |
| 103 | 207 | Com. | |
| 146 | 278 | Com. | |
| 189 | 333 | Com. | |
| 116 | | V.S. | |
| 145 | 175 | | |
| 102 | 69°/72mm. | V.S. | |
| 130 | 168 | V.S. | |

Key

| | |
|---|---|
| Com. | - miscible in all proportions. |
| V.S. | - very soluble. |
| S. | - soluble. |
| S.S. | - slightly soluble. |
| i. | - insoluble. |
| d | - decomposes. |

## TABLE I

## PROPERTIES

| No. | Name | Formula |
|---|---|---|
| **ALIPHATIC AMINES** (Contd.) | | |
| Alkyl Di- and Poly-Amines, Secondary Amino Groups Only | | |
| 81 | N,N'Dimethyl Ethylenediamine | $CH_3NHC_2H_4NHCH_3$ |
| 82 | N,N'Diethyl Ethylenediamine | $C_2H_5NHC_2H_4NHC_2H_5$ |
| Alkyl Di- and Poly-Amines, Secondary and Tertiary Amino Groups | | |
| 91 | N,N,N'Trimethyl Ethylenediamine | $(CH_3)_2NC_2H_4NHCH_3$ |
| Alkyl Di- and Poly-Amines, Tertiary Amino Groups Only | | |
| 101 | Tetramethyl Ethylenediamine | $(CH_3)_2NC_2H_4N(CH_3)_2$ |
| **ALKANOL ALIPHATIC AMINES** | | |
| Alkanol Primary Amines | | |
| 111 | Monoethanolamine | $NH_2C_2H_4OH$ |
| 112 | 3-Aminopropyl Alcohol | $NH_2C_3H_6OH$ |
| 113 | 2-Aminopropyl Alcohol | $CH_3CH(NH_2)CH_2OH$ |
| 114 | 4-Amino-1-butanol | $NH_2C_4H_8OH$ |
| 115 | 3-Aminopropylene Glycol | $NH_2CH_2CH(OH)CH_2OH$ |
| 117 | Monoisopropanolamine | $CH_3CH(OH)CH_2NH_2$ |
| 118 | 2-Amino-1-butanol | $HOCH_2CH(NH_2)C_2H_5$ |
| 119 | 4-Amino-2-butanol | $CH_3CH(OH)CH_2CH_2NH_2$ |
| 120 | 1-Amino-2-methyl-2-propanol | $NH_2CH_2C(OH)(CH_3)_2$ |
| 121 | 2-Amino-2-methyl-1,3-propanediol | $HOCH_2C(NH_2)(CH_3)CH_2OH$ |
| 122 | 2-(2-Aminoethoxy)ethanol (Diethyleneglycolamine) | $NH_2C_2H_4OC_2H_4OH$ |
| 123 | Tris(hydroxymethyl)aminomethane | $C(NH_2)(CH_2OH)_3$ |
| 124 | 2-Amino-2-methyl-1-propanol | $HOCH_2C(NH_2)(CH_3)_2$ |
| 125 | 4-Amino-4-methyl-2-pentanol (Hexanolamine) | $CH_3C(NH_2)(CH_3)CH_2CH(OH)CH_3$ |
| Alkanol Secondary Amines | | |
| 131 | N-Methyl Ethanolamine | $CH_3NHC_2H_4OH$ |
| 132 | N-Ethyl Ethanolamine | $C_2H_5NHC_2H_4OH$ |
| 133 | Diethanolamine | $NH(C_2H_4OH)_2$ |
| 134 | Methylaminopropanol | $CH_3NHC_3H_6OH$ |
| 135 | N-Butyl Monoethanolamine | $C_4H_9NHC_2H_4OH$ |
| 136 | N-Acetyl Ethanolamine | $CH_3CONHC_2H_4OH$ |
| 137 | Diisopropanolamine | $(CH_3CH(OH)CH_2)_2NH$ |

(Contd.)

## OF AMINES

| Molecular Weight | Boiling Point, °C. | Solubility in Water, % by Weight | Remarks |
|---|---|---|---|
| 88 | 119 | V.S. | |
| 116 | 150 | S. | |
| 102 | 140 | V.S. | |
| 116 | 121 | | |
| 61 | 171 | Com. | |
| 75 | 188 | V.S. | |
| 75 | 175 | V.S. | |
| 89 | 205 | S. | |
| 91 | 265(d) | V.S. | Absorbs $CO_2$ |
| 75 | 160 | Com. | |
| 89 | 178 | V.S. | |
| 89 | 180 | V.S. | |
| 89 | 151 | V.S. | |
| 105 | 152/10 mm. | V.S. | |
| 105 | 215/500 mm. | V.S. | |
| 121 | Melts 168 | V.S. | |
| 89 | 165 | V.S. | |
| 117 | 179 | Com. | $k = 2.2 \times 10^{-4}$ |
| 75 | 160 | Com. | |
| 89 | 167 | Com. | |
| 105 | 269 | Com. | |
| 89 | 74-7/2.5 mm. | V.S. | |
| 117 | 198 | V.S. | |
| 103 | Melts 64 | V.S. | |
| 133 | 249 | 87% | |

Key

Com. - miscible in all proportions.
V.S. - very soluble.
S. - soluble.
S.S. - slightly soluble.
i. - insoluble.
d. - decomposes.

## TABLE I

## PROPERTIES

| No. | Name | Formula |
|---|---|---|
| **ALKANOL ALIPHATIC AMINES (Contd.)** | | |
| Alkanol Tertiary Amines | | |
| 141 | 2-Dimethylethanolamine | $(CH_3)_2NC_2H_4OH$ |
| 142 | 2-Diethylethanolamine | $(C_2H_5)_2NC_2H_4OH$ |
| 143 | Triethanolamine | $N(C_2H_4OH)_3$ |
| 144 | Ethyl Diethanolamine | $C_2H_5N(C_2H_4OH)_2$ |
| 145 | Methyl Diethanolamine | $CH_3N(C_2H_4OH)_2$ |
| 146 | N-Butyl Diethanolamine | $C_4H_9N(C_2H_4OH)_2$ |
| 147 | Triisopropanolamine | $(CH_3CH(OH)CH_2)_3N$ |
| 148 | 2-(2-Dimethylaminoethoxy)ethanol | $(CH_3)_2NC_2H_4OC_2H_4OH$ |
| 149 | Diethylamino-2,3-propanediol | $(C_2H_5)_2NCH_2CH(OH)CH_2OH$ |
| Alkanol Di- and Poly-Amines, Primary Amino Groups Only | | |
| 151 | Diamino-isopropyl Alcohol (Dapol) | $NH_2CH_2CH(OH)CH_2NH_2$ |
| Alkanol Di- and Poly-Amines, All Other Types | | |
| 161 | 2-Aminoethylethanolamine | $NH_2C_2H_4NHC_2H_4OH$ |
| 162 | 5-Amino-2,2,5-trimethyl-3-aza-1-hexanol | $CH_3C(NH_2)(CH_3)CH_2NHC(CH_3)_2CH_2OH$ |
| 163 | N-Hydroxyethyl Propylenediamine | $CH_3CH(NHC_2H_4OH)CH_2NH_2$ |
| 164 | N-N'-Dihydroxyethyl Ethylenediamine | $(CH_2NHC_2H_4OH)_2$ |
| 165 | Aminoisopropylethanolamine | $NH_2CH_2CH(CH_3)NHC_2H_4OH$ |
| 166 | Aminoethylisopropanolamine | $NH_2C_2H_4NHCH_2CH(OH)CH_3$ |
| 167 | Aminoisopropylisopropanolamine | $NH_2CH_2CH(CH_3)NHCH_2CH(OH)CH_3$ |
| **AMINES CONTAINING ISOCYCLIC RINGS** | | |
| Isocyclic Primary Amines | | |
| 171 | Aniline | $C_6H_5NH_2$ |
| 172 | Cyclohexylamine | $\underline{CH_2CH_2CH_2CH_2CH_2C}HNH_2$ |
| 173 | Benzylamine | $C_6H_5CH_2NH_2$ |
| 174 | β-Phenylethylamine | $C_6H_5C_2H_4NH_2$ |
| 175 | α-Camphylamine | $H_2NCH_2CH_2\underline{CHC(CH_3)_2C(CH_3)=CH}CH_2$ |
| 176 | 1,2,3,4-Tetrahydro-1-naphthylamine | $\underline{C_6H_4CH(NH_2)CH_2CH_2C}H_2$ |
| Isocyclic Secondary Amines | | |
| 181 | Methylaniline | $C_6H_5NHCH_3$ |
| 182 | Diphenylamine | $(C_6H_5)_2NH$ |
| 183 | Methylcyclohexylamine | $\underline{CH_2C_4H_8C}HNHCH_3$ |

(Contd.)

OF AMINES

| Molecular Weight | Boiling Point, °C. | Solubility in Water, % by Weight | Remarks |
|---|---|---|---|
| 89 | 135 | Com. | Supplied by Sharples. |
| 117 | 162 | Com. | |
| 149 | 360 | Com. | |
| 133 | 249 | Com. | |
| 119 | 247 | Com. | |
| 161 | 272 | V.S. | |
| 191 | 305 | V.S. | |
| 133 | | V.S. | |
| 147 | | V.S. | Supplied by Sharples. |
| 90 | 185 | Com. | |
| 104 | 244 | Com. | |
| 160 | | V.S. | |
| 118 | 240 | Com. | |
| 148 | Melts 98 | V.S. | |
| 118 | | V.S. | |
| 118 | | V.S. | |
| 132 | | V.S. | |
| 93 | 184 | S.S. | Very weak base. |
| 99 | 134 | V.S. | Supplied by Monsanto. |
| 107 | 185 | Com. | k = $2.4 \times 10^{-5}$ at 25°C. |
| 121 | 198 | 3% | Absorbs $CO_2$; Monsanto. |
| 153 | 195 | | |
| 147 | 247/714 mm. | S. | Strong base. |
| 107 | 196 | i. | |
| 169 | 302 | i. | |
| 113 | 145 | V.S. | |

Key

Com. - miscible in all proportions.
V.S. - very soluble.
S. - soluble.
S.S. - slightly soluble.
i. - insoluble.
d. - decomposes.

TABLE I

PROPERTIES

| No. | Name | Formula |
|---|---|---|
| **AMINES CONTAINING ISOCYCLIC RINGS** (Contd.) | | |
| Isocyclic Tertiary Amines | | |
| 191 | Dimethylaniline | $C_6H_5N(CH_3)_2$ |
| 192 | o- and p-Dimethylaminomethylphenol | $HOC_6H_4CH_2N(CH_3)_2$ |
| Isocyclic Alkanol Amines, All Types | | |
| 201 | o-Aminobenzyl Alcohol | $NH_2C_6H_4CH_2OH$ |
| 202 | β-Amino β-phenyl Ethyl Alcohol | $C_6H_5CH(NH_2)CH_2OH$ |
| Isocyclic Di- and Poly-Amines, All Types | | |
| 211 | m-Phenylenediamine | $C_6H_4(NH_2)_2$ |
| 212 | p-Aminobenzylamine | $C_6H_4(NH_2)CH_2NH_2$ |
| 213 | 2,4,6-Tri(dimethylaminomethyl)phenol | $HOC_6H_2(CH_2N(CH_3)_2)_3$ |
| 214 | 1,2,3-Triaminobenzene | $C_6H_3(NH_2)_3$ |
| **HETEROCYCLIC AMINES, ALL TYPES** | | |
| 221 | Piperidine | $CH_2C_3H_6CH_2NH$ |
| 222 | Piperazine | $C_2H_4NHC_2H_4NH$ |
| 233 | Pyridine | $C_5H_5N$ |
| 234 | α-Picoline(2-methylpyridine) | $C_5H_4N(CH_3)$ |
| 235 | ω-Amino-α-picoline or α-picolylamine | $C_5H_4N(CH_2NH_2)$ |
| 236 | ω-Amino-β-picoline or β-picolylamine | $C_5H_4N(CH_2NH_2)$ |
| 237 | 2,3'Dipiperidyl | $CH_2(CH_2)_3NHCHCH(CH_2)_3NHCH_2$ |
| 238 | Morpholine | $C_2H_4NHC_2H_4O$ |
| 239 | N-Ethyl Morpholine | $OC_2H_4N(C_2H_5)CH_2CH_2$ |
| 240 | N-Aminoethyl Morpholine | $OC_2H_4N(C_2H_4NH_2)CH_2CH_2$ |
| 241 | N-Hydroxyethyl Morpholine | $C_2H_4OC_2H_4NC_2H_4OH$ |
| 242 | N-Acetyl Morpholine | $CH_3CONC_2H_4OCH_2CH_2$ |
| 243 | 2,6-Dimethyl Morpholine | $OCH(CH_3)CH_2NHCH_2CH(CH_3)$ |
| 244 | Tetramethyl Morpholine | $OCH(CH_3)CH(CH_3)NHCH(CH_3)CH(CH_3)$ |
| 245 | 2,5-Dimethyl Piperazine | $HNCH_2CH(CH_3)NHCH_2CH(CH_3)$ |
| 246 | Furfurylamine | $CH=CHCH=C(CH_2NH_2)O$ |
| 247 | Tetrahydrofurfurylamine | $CH_2CH_2CH_2CH(CH_2NH_2)O$ |
| 248 | 4-Methyl Piperidine | $CH_3CHC_2H_4NHCH_2CH_2$ |
| **MIXTURES** | | |
| 1M | Tetramine C-10 | Mixture of 52, 53, 54 |
| 2M | Mixed Ethyl Ethanolamines | Mixture of 132, 144 |
| 3M | Polyethyleneglycolamine 175 | $H(OC_2H_4)_nNH_2$ (n = 3 to 5) |

## OF AMINES

| Molecular Weight | Boiling Point, °C. | Solubility in Water, % by Weight | Remarks |
|---|---|---|---|
| 121 | 193 | i. | |
| 151 | 80-130/2 mm. | S.S. | DMP 10, Rohm & Haas |
| | | | |
| 123 | 270-80 (d) | S. | Probably not very basic. |
| 137 | 261 | | Probably soluble in water. |
| | | | |
| 108 | 283 | V.S. | Not very basic. |
| 122 | 269 | S. | Absorbs $CO_2$. |
| 265 | 143-149/3 mm. | S.(cold)<br>S.S.(hot) | DMP 30, Rohm & Haas. |
| 123 | 336 | S. | Strong base. |
| | | | |
| 85 | 106 | Com. | $k = 1.58\times10^{-3}$ at 25°C. |
| 86 | 140 | V.S. | $k = 6.4\times10^{-5}$; Chemo Puro |
| 79 | 116 | Com. | $k = 2.4\times10^{-9}$; Koppers |
| 93 | 129 | V.S. | $k = 3.2\times10^{-8}$; Koppers |
| 108 | 91/15 mm. | V.S. | Basic, $k = 1\times10^{-6}$ |
| 108 | 102-3/14 mm. | Com. | Basic, $k = 1.1\times10^{-6}$ |
| 168 | 270 | S. | Robinson Bros. |
| 87 | 129 | | |
| 115 | 138 | Com. | |
| 130 | 202 | Com. | |
| 131 | 226 | Com. | |
| 129 | d | Com. | |
| 115 | 147 | Com. | |
| 143 | | V.S. | |
| 114 | 162 | V.S. | |
| 97 | 146 | Com. | |
| 101 | 152/735 mm. | V.S. | |
| 99 | 128 | V.S. | |
| | | | |
| | | Com. | |
| | | Com. | |
| 175 | | V.S. | |

Key

Com. - miscible in all proportions.
V.S. - very soluble.
S. - soluble.
S.S. - slightly soluble.
i. - insoluble.
d. - decomposes.

## TABLE

## Suppliers

| Name of Company | Address of Company |
|---|---|
| American Cyanamid Company | New Products Development Department<br>30 Rockefeller Plaza<br>New York 20, N. Y.<br>V. V. Lindgren |
| American Roland Corporation | 16 Hudson Street<br>New York 13, N. Y. |
| Armour and Company | Chemical Division<br>1355 West 31st Street<br>Chicago 9, Illinois<br>K. E. Johnson |
| Philipp Bauer Company, Ind. | 19 East 41st Street<br>New York 17, N. Y. |
| Carbide and Carbon Chemicals Division | 30 East 42nd Street<br>New York 17, N. Y.<br>John Conway |
| Carwin Company | Stiles Lane,<br>North Haven, Connecticut |
| Chemo Puro Manufacturing Corp. | 26-32 Skillman Avenue<br>Long Island City 1, New York<br>P. C. Hereld |
| Ciba Company, Inc. | 627 Greenwich Street<br>New York 14, N. Y.<br>Frank B. Gill |
| Commercial Solvents Corporation | Terre Haute, Indiana<br>Louis L. Hallock |
| Consolidated Midland Corporation | Katonah, New York<br>J. S. Kilheffer |
| The Dow Chemical Company | Technical Service & Development Div.<br>Midland, Michigan<br>John C. Van Horn |
| E. I. du Pont de Nemours & Company | Polychemicals Department<br>Wilmington 98, Delaware<br>H. M. Cadot |
| Eastman Kodak Company | Distillation Products Industries Div.<br>Rochester 3, New York<br>W. J. Simcox |
| Edcan Laboratories | 10-20 Pine Street<br>South Norwalk, Connecticut |
| Eimer and Amend | Greenwich and Morton Streets<br>New York 14, New York |
| Evans Chemetics, Inc. | 250 East 43rd Street<br>New York 17, N. Y.<br>H. Roger Coleman |
| Enco Chemical Corporation | 441 Lexington Avenue<br>New York 17, N. Y. |
| B. F. Goodrich Chemical Company | Rose Building<br>Cleveland 15, Ohio |
| R. W. Greeff & Company, Inc. | 10 Rockefeller Plaza<br>New York 20, N. Y.<br>C. E. Griffith |

## II

## of Amines

| Reply | Amines Available | Samples Obtained |
|---|---|---|
| Yes | 55, 62, - RN | |
| No | | |
| Yes | | |
| No | | |
| Yes | 52, 53, 54, 111, 117, 133, 136, 137, 142, 143, 145, 147, 161, 242, - C; 1M, - CD; 131, 132, 146, 163, 164, 240, 241, 243, 245, - R; 3M, - RN | All listed except 117, 146, and 3M. |
| No | | |
| Yes | 222 | |
| Yes | Weakly basic aromatic amines. | |
| Yes | 121, 124, - C; 123, - CL; 118, 162, - R | All listed. |
| Yes | Pharmaceutical trade only. | |
| Yes | 111, 117, 133, 143, - C; 122, 148, 161, 165, 166, 167, - R | 117, 122, 148 |
| Yes | 35, - C; 62, - R | 35 |
| Yes | Research quantities only | |
| No | | |
| Yes | Research quantities only | |
| Yes | N-alkyl substituted ethylene diamines have been made. | |
| No | | |
| Yes | | |
| Yes | | |

## TABLE II

## Suppliers

| Name of Company | Address of Company |
|---|---|
| Heyden Chemical Corporation | Garfield, New Jersey<br>T. R. Aalto |
| Hoffman-LaRoche, Inc. | Roche Park<br>Nutley 10, New Jersey<br>J. A. Aeschlimann |
| Hooker Electrochemical Company | 4715 Buffalo Avenue<br>Niagara Falls, New York<br>L. S. Bovier |
| Jefferson Chemical Company, Inc. | 711 Fifth Avenue<br>New York 22, N. Y.<br>E. H. Bohle |
| Koppers Company, Inc. | Tar Products Division<br>Koppers Building<br>Pittsburgh 19, Pennsylvania |
| B. L. Lemke & Company, Inc. | General Office<br>Lodi, New Jersey |
| The Matheson Company, Inc. | East Rutherford, New Jersey<br>H. R. Pearce |
| Mann Fine Chemicals, Inc. | 136 Liberty Street<br>New York, N. Y. |
| Monsanto Chemical Company | Organic Chemicals Division<br>St. Louis 4, Missouri<br>A. G. Rossow |
| National Aniline Division<br>Allied Chemical & Dye Corporation | 40 Rector Street<br>New York, N. Y. |
| Naugatuck Chemical Division of<br>United States Rubber Company | 1232 6th Avenue<br>New York, N. Y. |
| William D. Neuberg Company, Inc. | 420 Lexington Avenue<br>New York 17, N. Y.<br>E. W. Phillips |
| Niacet Chemicals Division<br>United States Vanadium Corporation | P. O. Box 380<br>Niagara Falls, New York<br>John Galaba |
| Nopco Chemical Company (formerly<br>National Oil Products) | Logan and Davis Streets<br>Harrison, New Jersey<br>Logan Grupelli |
| Pittsburgh Plate Glass Company | Columbia Chemical Division<br>Fifth Avenue at Bellefield<br>Pittsburgh 13, Pennsylvania<br>J. A. Neubauer |
| The Polychemical Company | 494 Hunts Point Avenue<br>New York 59, N. Y.<br>Dr. G. Schorsch |
| The Quaker Oats Company | Chemicals Department<br>Board of Trade Building<br>141 W. Jackson Blvd.<br>Chicago 4, Illinois<br>R. H. Wittekindt |
| Reilley Tar and Chemical Corp. | 1615 Merchants Bank Building<br>Indianapolis, Indiana |
| The Retort Pharmaceutical Company | 37th Avenue and 23rd Street<br>Long Island City 1, New York |

(Contd.)

of Amines

| Reply | Amines Available | Samples Obtained |
|---|---|---|
| Yes | 173, - R | 173 |
| Yes | Pharmaceutical trade only | |
| Yes | 246, 247, - R | 246, 247 |
| Yes | 111, - RN | |
| Yes | 233, 234, - C | |
| Yes | Pharmaceutical trade only | |
| Yes | Mostly fine chemicals | |
| No | | |
| Yes | 172, 174, - C; 173, - RN | 172, 174 |
| No | | |
| No | | |
| Yes | 133, - C | |
| Yes | | |
| Yes | Weakly basic fatty amines | |
| Yes | | |
| Yes | 31, 52, 111 | |
| Yes | 246, - R; 247, - RN | 246 |
| No | | |
| No | | |

## TABLE II

## Suppliers

| Name of Company | Address of Company |
|---|---|
| Riverdale Chemical Company | 324 East 147th Street<br>Harvey, Illinois<br>J. F. Breen |
| Robinson Brothers, Ltd. | West Bromwich, England |
| Rohm and Haas Company | Washington Square<br>Philadelphia 5, Pennsylvania<br>E. H. Riddle |
| R. S. A. Corporation | 690 Sawmill River Road<br>Ardsley, New York<br>G. E. Anthony |
| Scher Brothers | 519 Getty Avenue<br>Clifton, New Jersey |
| Sharples Chemicals, Inc. | 123 South Broad Street<br>Philadelphia 9, Pennsylvania<br>P. G. Smith |
| Shell Development Company | 50 West 50th Street<br>New York 20, New York<br>George K. Nelson |
| Shepard Chemical Corporation | 33 West 42nd Street<br>New York 18, N. Y. |
| The Sherwin-Williams Company | 1800 Guild Hall Building<br>Cleveland 1, Ohio |
| The Treemond Company | 153 Waverly Place<br>New York 14, N. Y. |
| Union Oil Company of California | Wilmington, California<br>Dr. T. F. Doumani |
| Wyandotte Chemicals Corporation | Wyandotte, Michigan<br>J. L. Craig |

(Contd.)

of Amines

| Reply | Amines Available | Samples Obtained |
|---|---|---|
| Yes | | |
| Yes | Dipiperidyls, as 237 | |
| Yes | 192, - C; 213, - R | 192, 213 |
| Yes | | |
| No | | |
| Yes | 141, 142, 2M, - C; 119, 132, 135, 144, 146, - CD; 37, 63, - R; 149, - RN | 37, 63, 119, 132, 135, 142, 144, 146, 2M |
| Yes | 120, 125, - R | 120, 125 |
| No | | |
| Yes | | |
| Yes | | |
| Yes | | |
| Yes | 111, - RN | |

Key

C - Commercially available
CD - Once commercially available but discontinued
CL - Commercially available in limited quantities
R - Available in research quantities
RN - Research quantities not now available

TABLE

## High Boiling, Water-Soluble Amines Which Are

| No. | Name | Structural Formula |
|---|---|---|
| 35 | Hexamethylene Diamine | $NH_2CH_2CH_2CH_2CH_2CH_2CH_2NH_2$ |
| 37 | 1-3-Diaminobutane | $NH_2CH_2CH_2CH(NH_2)CH_3$ |
| 52 | Diethylenetriamine | $NH_2CH_2CH_2NHCH_2CH_2NH_2$ |
| 53 | Triethylenetetramine | $NH_2C_2H_4NHC_2H_4NHC_2H_4NH_2$ |
| 54 | Tetraethylenepentamine | $NH_2C_2H_4NHC_2H_4NHC_2H_4NHC_2H_4NH_2$ |
| 62 | Dimethylaminopropylamine | $(CH_3)_2NCH_2CH_2CH_2NH_2$ |
| 55 | Isopropylaminopropylamine | $(CH_3)_2CHNHCH_2CH_2CH_2NH_2$ |
| 63 | Diethylaminopropylamine | $(C_2H_5)_2NCH_2CH_2CH_2NH_2$ |
| 125 | 4-Amino-4-methyl-2-pentanol (hexanolamine) | $CH_3C(NH_2)(CH_3)CH_2CH(OH)CH_3$ |
| 148 | 2-(2-Dimethylaminoethoxy)ethanol | $(CH_3)_2NC_2H_4OC_2H_4OH$ |
| 111 | Monoethanolamine | $HOCH_2CH_2NH_2$ |
| 117 | Monoisopropanolamine | $CH_3CH(OH)CH_2NH_2$ |
| 118 | 2-Amino-1-butanol | $HOCH_2CH(NH_2)CH_2CH_3$ |
| 124 | 2-Amino-2-methyl-1-propanol | $HOCH_2C(NH_2)(CH_3)_2$ |
| 119 | 4-Amino-2-butanol | $CH_3CH(OH)CH_2CH_2NH_2$ |
| 120 | 1-Amino-2-methyl-2-propanol (isobutanolamine) | $NH_2CH_2C(OH)(CH_3)_2$ |
| 121 | 2-Amino-2-methyl-1,3-propanediol | $HOCH_2C(NH_2)(CH_3)CH_2OH$ |
| 122 | 2-(2-Aminoethoxy)ethanol (Diethyleneglycolamine) | $NH_2C_2H_4OC_2H_4OH$ |
| 123 | Tris(hydroxymethyl)aminomethane | $NH_2C(CH_2OH)_3$ |
| 131 | N-Methyl Ethanolamine | $CH_3NHC_2H_4OH$ |
| 132 | N-Ethyl Ethanolamine | $C_2H_5NHC_2H_4OH$ |
| 133 | Diethanolamine | $(C_2H_4OH)_2NH$ |
| 135 | N-Butyl Monoethanolamine | $HOC_2H_4NHC_4H_9$ |
| 136 | N-Acetyl Ethanolamine | $CH_3CONHC_2H_4OH$ |
| 137 | Diisopropanolamine | $(CH_3CH(OH)CH_2)_2NH$ |
| 142 | Diethylethanolamine | $(C_2H_5)_2NC_2H_4OH$ |
| 143 | Triethanolamine | $(C_2H_4OH)_3N$ |
| 144 | Ethyl Diethanolamine | $C_2H_5N(C_2H_4OH)_2$ |
| 145 | Methyl Diethanolamine | $CH_3N(C_2H_4OH)_2$ |
| 146 | N-Butyl Diethanolamine | $C_4H_9N(C_2H_4OH)_2$ |
| 147 | Triisopropanolamine | $(CH_3CH(OH)CH_2)_3N$ |
| 151 | 1-3-Diamino-2-propanol (Diamino isopropyl alcohol or Dapol) | $NH_2CH_2CH(OH)CH_2NH_2$ |

### Key

i. - insoluble.
S. - soluble.
V.S. - very soluble.
Com. - miscible in all proportions.
C - commercially available.
CD - once commercially available but discontinued.
CL - commercially available in limited quantities.
R - available in research quantities.
RN - research quantities not now available.

III

## Commercially Available or May Be in the Near Future

| Mol. Wt. | Equiv. Weight | Boiling Point, °C. | Soly. in Water | Suppliers | Price per Lb., $ |
|---|---|---|---|---|---|
| 116 | 58 | 205 | V.S. | DuP, CL | 1.30 |
| 88 | 44 | 147 | V.S. | Sh, R | |
| 103 | 34 | 207 | Com. | Carb, C | 0.50 (1947) |
| 146 | 37 | 278 | Com. | Carb, C | 0.50 (1947) |
| 189 | 38 | 333 | Com. | Carb, C | 0.50 (1947) |
| 102 | 51 | 69/72mm. | V.S. | Cyan, RN, DuP, R | |
| 116 | 58 | | V.S. | Cyan, RN | |
| 130 | 65 | 168 | V.S. | Sh, R | |
| 117 | 117 | 179 | Com. | S.Dev, R | 0.35-0.50 |
| 133 | 133 | | V.S. | Dow, R | |
| 61 | 61 | 171 | Com. | Carb, C, Dow, C | 0.24 (Dow) |
| 75 | 75 | 160 | Com. | Carb, C, Dow, C | 0.24 (Dow) |
| 89 | 89 | 178 | V.S. | Comm, R | |
| 89 | 89 | 165 | V.S. | Comm, C | |
| 89 | 89 | 180 | V.S. | Sh, R | |
| 89 | 89 | 151 | V.S. | S.Dev, R | 0.50-0.75 |
| 105 | 105 | 152/10mm. | V.S. | Comm, C | |
| 105 | 105 | | V.S. | Dow, R, Carb, CL | 0.60 (Carb) |
| 121 | 121 | Melts 168 | V.S. | Comm, CL | 0.75-1.20 |
| 75 | 75 | 160 | Com. | Carb, R | 0.75 |
| 89 | 89 | 167 | Com. | Carb, R, Sh, CD | |
| 105 | 105 | 269 | Com. | Carb, C, Dow, Neu | 0.25(Dow);0.27(Neu) |
| 117 | 117 | 198 | V.S. | Sh, CD | |
| 103 | 103 | Melts 64 | V.S. | Carb, C | 0.35 |
| 133 | 133 | 249 | 87% | Carb, C | 0.27 |
| 117 | 117 | 162 | Com. | Carb, C, Sh, C | 0.62 (Sh Tech.) |
| 149 | 149 | 360 | Com. | Carb, C, Dow, C | 0.23 (Dow) |
| 133 | 133 | 249 | Com. | Sh, CD | |
| 119 | 119 | 247 | Com. | Carb, C | 0.75 |
| 161 | 161 | 272 | V.S. | Carb, C, Sh, CD | |
| 191 | 191 | 305 | V.S. | Carb, C | 0.32 |
| 90 | 45 | 185 | Com. | S.Dev, RN | 1.00(S.Dev est.) |

Key

Carb - Carbide & Carbon
Sh - Sharples
DuP - DuPont
Cyan - American Cyanamid
S.Dev - Shell Development
Comm - Commercial Solvents
Neu - William D. Neuberg
Heyd - Heyden
Mons - Monsanto
Hook - Hooker
Q.O. - Quaker Oats
Rohm - Rohm & Haas
Rob - Robinson Bros.

TABLE III

## High Boiling, Water-Soluble Amines Which Are

| No. | Name | Structural Formula |
|---|---|---|
| 161 | 2-Aminoethylethanolamine | $NH_2C_2H_4NHC_2H_4OH$ |
| 162 | 5-Amino-2,2,5-trimethyl-3-aza-1-hexanol | $CH_3C(NH_2)(CH_3)CH_2NHC(CH_3)_2CH_2OH$ |
| 163 | N-Hydroxyethyl Propylenediamine | $CH_3CH(NHC_2H_4OH)CH_2NH_2$ |
| 164 | N,N'-Dihydroxyethyl Ethylenediamine | $(CH_2NHC_2H_4OH)_2$ |
| 149 | Diethylamino-2-,3-propanediol | $(C_2H_5)_2NCH_2CH(OH)CH_2OH$ |
| 165 | Aminoisopropylethanolamine | $NH_2CH_2CH(CH_3)NHC_2H_4OH$ |
| 166 | Aminoethylisopropanolamine | $NH_2C_2H_4NHCH_2CH(OH)CH_3$ |
| 167 | Aminoisopropylisopropanolamine | $NH_2CH_2CH(CH_3)NHCH_2CH(OH)CH_3$ |
| 173 | Benzylamine | $C_6H_5CH_2NH_2$ |
| 239 | N-Ethyl Morpholine | $C_2H_4OC_2H_4NC_2H_5$ |
| 240 | N-Aminoethyl Morpholine | $C_2H_4OC_2H_4NC_2H_4NH_2$ |
| 241 | N-Hydroxyethyl Morpholine | $C_2H_4OC_2H_4NC_2H_4OH$ |
| 242 | N-Acetyl Morpholine | $CH_3CONCH_2CH_2OCH_2CH_2$ |
| 243 | 2,6-Dimethyl Morpholine | $OCH(CH_3)CH_2NHCH_2CH(CH_3)$ |
| 245 | 2,5-Dimethyl Piperazine | $HNCH_2CH(CH_3)NHCH_2CH(CH_3)$ |
| 246 | Furfurylamine | $CH=CHCH=C(CH_2NH_2)O$ |
| 247 | Tetrahydrofurfurylamine | $CH_2CH_2CH_2CH(CH_2NH_2)O$ |
| 213 | 2,4,6-Tri(dimethylaminomethyl)phenol | $HOC_6H_2(CH_2N(CH_3)_2)_3$ |
| 237 | 2,3'Dipiperidyl | $CH_2(CH_2)_3NHCHCH(CH_2)_3NHCH_2$ |
| 1M | Tetramine C-10 | Mixture of 52, 53, 54 |
| 2M | Mixed Ethyl Ethanolamines | Mixture of 132, 144 |
| 3M | Polyethyleneglycolamine 175 | $H(OC_2H_4)_nNH_2$ ($n = 3$ to 5) |

### Key

i. - insoluble.
S. - soluble.
V.S. - very soluble.
Com. - miscible in all proportions.
C - commercially available.
CD - once commercially available but discontinued.
CL - commercially available in limited quantities.
R - available in research quantities.
RN - research quantities not now available.

(Contd.)

Commercially Available or May Be in the Near Future

| Mol. Wt. | Equiv. Weight | Boiling Point, °C. | Soly. in Water | Suppliers | Price per Lb., $ |
|---|---|---|---|---|---|
| 104 | 52 | 244 | Com. | Carb, C | 0.43 |
| 160 | 80 | | V.S. | Comm, R | |
| 118 | 59 | 240 | Com. | Carb, R | |
| 148 | 74 | Melts 98 | V.S. | Carb, R | 0.52 |
| 147 | 147 | | V.S. | Sh, RN | |
| 118 | 118 | | V.S. | Dow, R | |
| 118 | 118 | | V.S. | Dow, R | |
| 132 | 132 | | V.S. | Dow, R | |
| 107 | 107 | 185 | Com. | Heyd, R, Mons, RN | 2.50-3.00(Mons est) |
| 115 | 115 | 138 | Com. | Carb, R | |
| 130 | 65 | 202 | Com. | Carb, R | |
| 131 | 131 | 226 | Com. | Carb, R | |
| 129 | 129 | d | Com. | Carb, C | |
| 115 | 115 | 147 | Com. | Carb, R | |
| 114 | 57 | 162 | V.S. | Carb, R | |
| 97 | 97 | 146 | V.S. | Hook, R, Q.O., R | 0.45-0.50(Hook) |
| 101 | 101 | 152/735mm. | V.S. | Hook, R, Q.O., R | 0.80-0.90(Hook) |
| 265 | 88 | 146/3 mm. | S.(cold)<br>i.(hot) | Rohm, R | |
| 168 | 84 | 270 | S. | Rob, CL | 3.50 |
| | | | Com. | Carb, CD | 0.50 (1947) |
| | | | Com. | Sh, C | 0.33 |
| 175 | 175 | | V.S. | Carb, RN | 0.60 |

Key

Carb - Carbide & Carbon
Sh - Sharples
DuP - DuPont
Cyan - American Cyanamid
S.Dev - Shell Development
Comm - Commercial Solvents
Neu - William D. Neuberg
Heyd - Heyden
Mons - Monsanto
Hook - Hooker
Q.O. - Quaker Oats
Rohm - Rohm & Haas
Rob - Robinson Bros.

Report No. T2.15-1-30

THE GIRDLER CORPORATION
GAS PROCESSES DIVISION
PROCESS DEVELOPMENT AND RESEARCH LABORATORIES
LOUISVILLE, KENTUCKY

# THE RELATIVE RESISTANCE TO OXIDATION OF COMMERCIALLY AVAILABLE AMINES.

May 19, 1950

| Work by: | Report by: |
|---|---|
| R. C. Kindrick | R. C. Kindrick |
| Kenton Atwood | Kenton Atwood |
| M. R. Arnold | M. R. Arnold |

## Sentence Summary

Thirty-nine amines and four mixtures of amines have been tested for relative resistance to oxidation in an accelerated oxidation test.

## I. INTRODUCTION:

Through an evaluation of the information tabulated in the literature survey, Girdler Report No. T2.20-2-2, many materials listed were eliminated from further consideration as acceptable absorbents for carbon dioxide in the presence of oxygen. Approximately forty compounds and mixtures were not eliminated. The purpose of this report is to describe the results of accelerated oxidation tests made on these materials in order to establish the relative resistance to oxidation of each. Since the resistance to oxidation is an extremely important characteristic for carbon dioxide absorbents which are to be used in the presence of oxygen, the results of the accelerated oxidation test permitted the elimination of several of the compounds from further study and thus simplified the remainder of the investigation.

When substances containing amino groups are employed as absorbents for carbon dioxide in the presence of oxygen, oxidation of the material usually occurs, resulting in serious losses in alkalinity and the formation of corrosive products. The loss in alkalinity resulting from oxidation is especially serious since it not only influences the capacity of the solution for the absorption of carbon dioxide, but it also introduces undesirable products into the atmosphere. Although generally the formation of corrosive materials is especially undesirable, it is of secondary importance in this application since the materials of construction will be alloys which will withstand attack from these products of oxidation.

## II. SUMMARY AND CONCLUSIONS:

(1) Thirty-nine amines and eleven mixtures of amines have been tested for relative resistance to oxidation.

(2) The following amines showed sufficient resistance to oxidation that they have been selected for further study:

Isobutanolamine
2-methyl-2-amino-1-propanol
N-ethyl diethanolamine
N-methyl diethanolamine
N-butyl diethanolamine
2(2-dimethyl amino ethoxy) ethanol
Diethyl amino ethanol
Triethanolamine
Triisopropanolamine
Diethyl amino propylamine
Aminoethyl morpholine
NN' dimethyl glycine
α-alanine

The following mixtures of amines showed sufficient resistance to oxidation that they have been selected for further study:

50% methyl diethanolamine: 50% diethanolamine
50% methyl diethanolamine: 50% diethyleneglycolamine
25% methyl diethanolamine: 75% diethyleneglycolamine
Sharples Mixed Ethyl ethanolamine #161

On the basis of additional data to be obtained on the properties of these carbon dioxide absorbents one or more of these amines or mixtures will be recommended for the removal of carbon dioxide from submarine atmospheres.

(3) Tertiary amines, as a group, are the most resistant to oxidation. Secondary amines are the least resistant to oxidation. The resistance of primary amines depends largely upon the structure of the individual compound.

(4) Certain of the tertiary amines appear to act as anti-oxidants, protecting primary and secondary amines from oxidation.

## III. INVESTIGATIONAL PROCEDURE AND EXPERIMENTAL DATA:

### A. Source of Reagents.

The sources of most of the amines used in this investigation are given in Report No. T2.20-2-2. The only exceptions to this rule were the amino acids which were obtained from the following suppliers:

| | |
|---|---|
| α-alanine | Eastman Kodak, Rochester, New York |
| NN' dimethyl glycine | Du Pont de Nemours, Wilmington, Delaware |

More than one source is listed for the following amines in Report No. T2.20-2-2. Samples of the amines from the suppliers indicated were employed in this investigation.

| | |
|---|---|
| Monoethanolamine | Carbide and Carbon |
| Monoisopropanolamine | Dow |
| N-ethyl ethanolamine | Sharples |
| Diethanolamine | Carbide and Carbon |
| Triethanolamine | Carbide and Carbon |
| Butyl diethanolamine | Sharples |
| Benzyl amine | Heyden |
| 2,5-Dimethylpiperazine | Hooker |

Samples of diethyleneglycolamine from both Dow, and Carbide and Carbon were employed. The source of this material is indicated in the experimental data embodied in this report.

The carbon dioxide employed was obtained in high pressure cylinders from Pure Carbonic, Inc., New York.

The oxygen used was supplied in high pressure cylinders by Air Reduction, Louisville, Kentucky.

### B. Apparatus and Procedure.

The accelerated oxidation test used in this investigation involved contacting 1000 liters of a gas mixture consisting of 50% carbon dioxide and 50% oxygen at a rate of 100 cc. per minute with 100 ml. of 2.5 N amine solution at 80°C. The solutions were analyzed before and after this treatment.

A weighed sample of each of the amines to be tested was titrated with N/10 sulfuric acid using methyl red as the indicator. From this result the alkalinity of the compound was calculated and the weight of amine necessary for a 2.5 N solution was obtained. Thus, all of the solutions tested were made up 2.5 N with respect to the equivalent weight as determined by titrating with a strong acid using methyl red indicator.

A photograph of the apparatus employed is shown in Figure 1. The same apparatus is shown in diagram form in Figure 2. Exactly 100 ml. of the solutions to be tested were added to each of the six test tubes designated as H in Figure 2. Six coils of 39 B & S gauge stainless steel wire, Type 304, approximately 15 feet in length, were weighed on an analytical balance. One of each of these coils of wire was added to the solutions in tubes H. The purpose of the stainless steel was to at least partially reproduce the conditions found in actual plant operation and include in the results of the tests the influence of stainless steel.

Each of the scrubbers labeled J, Figure 2, contained exactly 50 ml. of N/2 sulfuric acid diluted to the desired volume with distilled water for the absorption of ammonia, an oxidation product of the amines. The apparatus was assembled as shown in Figure 1 and 2. A gas mixture consisting of 50% oxygen and 50% carbon dioxide (by volume) was passed through the apparatus at a controlled rate. This mixture was obtained by metering the respective gases directly from the high pressure cylinders by means of flowmeters A and B.

The oxygen and carbon dioxide flowed through 1/4" rubber tubing to a gas mixing chamber C where they were combined into a homogeneous gas which then passed to water saturator D. Here the gas was saturated with water at room temperature. At E samples of the gas were withdrawn periodically for Orsat analysis. The carbon dioxide concentration of the gas mix was held at 50 ± 4% throughout the test. The gas mixture then flowed by way of manifold F into tubes H. Here the gas was contacted with the amine solution at 80 ± 0.5°C. at a rate of 100 ± 10 cc. per minute. This rate was obtained by adjusting the screw clamps at G until each meter labeled K showed the required rate of flow. A coarse fritted dispersion tube (Harshaw Catalogue No. H27020 - coarse) was used for contacting the gas with the solution. The gas emerged from tubes H by way of condensers I where water and amine vapors were condensed and returned to tubes H. Since the gas was saturated with water at room temperature and the condensers operated at approximately 15°C., the amine was diluted by excess water vapor. Therefore, in order to maintain the solutions at constant volume, it was necessary periodically to bypass water saturator D. Thus, the concentration of the amine was approximately constant throughout the test. Any volatile alkaline products, notably ammonia, not refluxing into the amine solution tubes were removed from the gas by acid scrubbers J. The outlet gas was measured by wet test meters K.

Samples of the original amine solutions were analyzed for free amine concentration, total organic nitrogen concentration, primary amine concentration, iron content and iron capacity. One thousand liters of gas were contacted with each solution which required approximately seven days. The solutions were then removed from the tubes and together with washings from the tubes and condensers, were weighed to within 0.1 gm. From this weight and the specific gravity the volume was calculated. These solutions were analyzed for the components given above. The analytical results were corrected to the same basis as the original amine concentration by multiplying the results by final volume/original volume, (100 ml.).

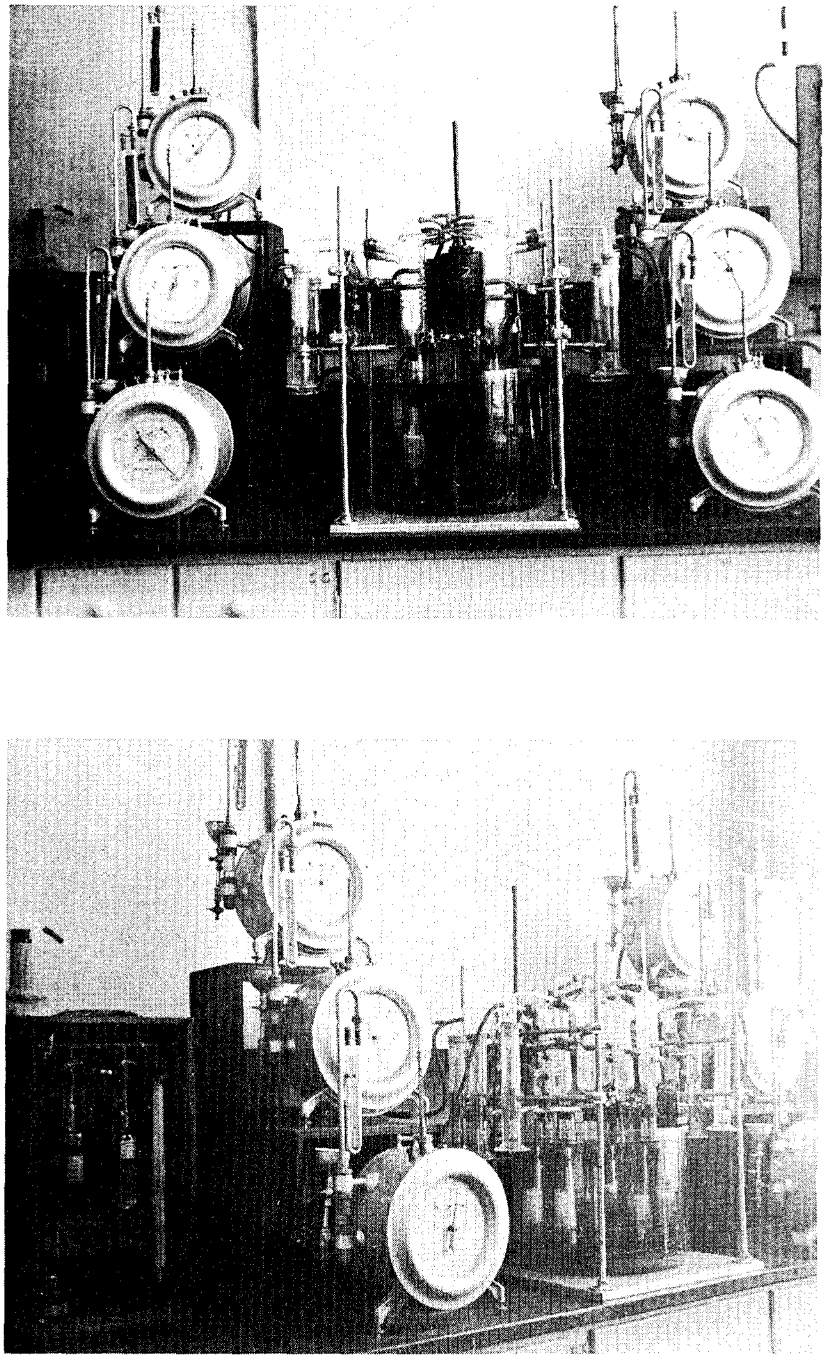


FIGURE 1

## LEGEND

A. Flow meter for measuring the rate of oxygen flow.

B. Flow meter for measuring the rate of carbon dioxide flow.

C. Gas mixing chamber constructed of iron pipe having a volume of approximately 2-1/2 liters packed with Raschig rings.

D. Water saturator.

E. Glass "T" outlet for sampling gas.

F. A gas manifold constructed of 1/4" copper tubing.

G. Rubber tubing connections from manifold equipped with screw clamps for adjusting rate through each manifold outlet.

H. Pyrex test tubes of 200 ml. capacity equipped with coarse fritted gas dispersion tubes.

I. Friedricks condensers.

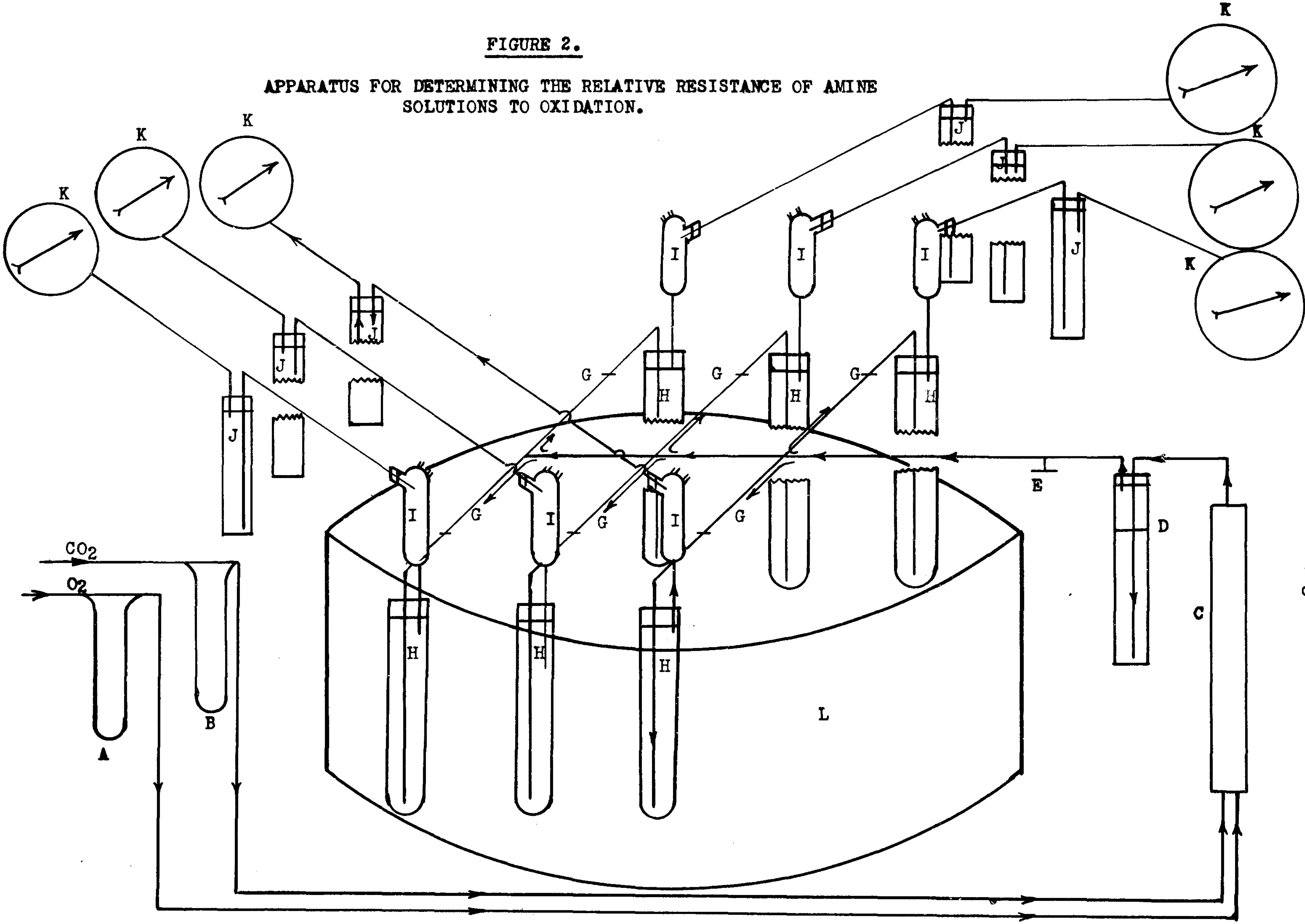
J. Gas scrubbers equipped with Folin bell dispersion tubes.

K. Wet test meter.

L. Water bath.

FIGURE 2.

APPARATUS FOR DETERMINING THE RELATIVE RESISTANCE OF AMINE SOLUTIONS TO OXIDATION.



The excess acid in scrubbers J was back titrated with standard sodium hydroxide using methyl orange as the indicator. From these results the volatile alkaline material was calculated. Since at 15°C., the temperature of condensers I, the vapor pressure of the amines was considered negligible, the alkaline products were calculated as ammonia.

Frequently during the oxidation test copious quantities of crystalline material were deposited in the condensers. When this occurred, this material, which proved to be predominantly ammonium carbonate, was not readded to the amine solution as described above, but analyzed separately as described below under Analytical Methods, Section 4.

## C. Analytical Methods.

### (1) Free Amine Concentration.

The term "free amine concentration" is employed to express that amine which is available to react with carbon dioxide. Specifically, it is that amine which is titratable with a strong acid using methyl red as an indicator. With this limitation the term is interchangeable with basicity or alkalinity.

The determination of free amine concentration was made by titrating exactly 1.00 ml. of amine solution with standard N/10 sulfuric acid. When the apparent end-point was reached, the solution was boiled to expel carbon dioxide. The titration was then continued until the final end point was reached.

Calculation:

Equivalents of amine/liter = ml. of acid x normality of acid

### (2) Primary Amine Concentration.

The primary amine concentration was determined according to Standard Method SM-17 (See Appendix). This method essentially entails reacting the solution with nitrous acid and measuring the nitrogen evolved in the reaction by means of a gas burette. The calculation shown in this method applies only to monoethanolamine. Therefore, the calculation was modified to the following formula:

Total amine equivalents/liter = V x W x 35.6 = Equivalents of primary amine/liter

V = volume of nitrogen observed at the atmospheric temperature and barometric pressure read at the time of the determination.

W = weight of nitrogen in 1 cc. of moist gas under the conditions of the determination, grams.

### (3) Total Organic Nitrogen Concentration.

This determination was run by a modification of the Micro Kjeldahl Method described in Standard Method SM-33. (See Appendix.) The catalyst described in this procedure is not sufficient to permit reduction of all organic nitrogen to ammonia. Therefore, it was necessary to substitute the following catalyst mixture in these determinations.

Metallic copper, .03 gm.
Ranker's Solution, 1 ml. (prepared by dissolving 1.6 gm. salicylic acid in 200 ml. concentrated sulfuric acid)
Potassium acid sulfate, .03 gm.
Metallic mercury, 1 drop

The distillation and titration were carried out as described in Standard Method SM-3. In order to obtain a value directly comparable to the free amine concentration the calculations were modified to the following formula:

Gm. atomic weights of total organic nitrogen/liter =

$$\left[(\text{ml. of acid} \times \text{N or acid}) - (\text{ml. of base} \times \text{N of base})\right] \quad 10{,}000$$

(4) Analysis of Crystalline Condenser Material.

The crystalline material was transferred quantitatively from the condenser to a 100 ml. volumetric flask and diluted to volume. The total alkalinity of the material was determined by titrating 10 ml. aliquots of the resulting solution with N/10 sulfuric acid, according to the "free amine" determination (See Analytical Methods, section above.) Next, the ammonium carbonate present in the material was determined in the following manner. A 25 ml. aliquot of the solution was transferred to a 50 ml. three-necked flask, and approximately 100 ml. of water were added after 20 ml. of 40% sodium hydroxide solution were added to the flask by means of a separatory funnel. Nitrogen was passed through the mixture at room temperature and thence through 50 ml. of N/10 sulfuric acid for 4 hours. The excess acid was back-titrated using methyl orange as the indicator.

Calculations:

$$\text{Total equivalents of alkaline material} = \text{ml. acid} \times \text{N acid} \times \frac{1}{100}$$

$$\text{Equivalents of } NH_3 = \left[(\text{ml. of acid} \times \text{N of acid}) - (\text{ml. of base} \times \text{N base})\right] \times \frac{1}{250}$$

Equivalents of amine = Total equivalents of alkaline material - equivalents of ammonia

The result obtained for the ammonia fraction which in most cases amounted to 95% of the total alkalinity, was added to the previous result obtained for ammonia (See Apparatus and Procedure). The amine fraction was added to the result previously obtained for free amine concentration (See Apparatus and Procedure).

(5) Iron Content.

This determination was carried out according to Standard Method SM-25 (See Appendix).

(6) Iron Capacity.

The iron capacities of the solutions were determined according to Standard Method SM-27. This is a standard laboratory method for determining the capacity of the solution to dissolve iron from an extended surface and in turn is a measure of the relative resistance of low carbon steel to corrosion by amine solutions.

D. Experimental Data.

Table I shows the data obtained in this investigation on the relative effect of oxidation on the 2.5 N solutions of single amines. The formula for each compound is given together with its identification number from Report No. T2.20-2-2 which gives the physical properties of each amine. The primary amine concentration before and after each test is presented in equivalents per liter. The free amine lost during the oxidation test is expressed in percent of the original concentration and was calculated as follows:

$$\frac{(\text{Free amine before test - free amine after test}) \times 100}{\text{Free amine before test}}$$

The primary amine concentrations before and after the test are also expressed in equivalents per liter. Whenever possible the primary amine loss is given in percent. Most of the secondary and tertiary amines originally contained no primary amine as impurities. Therefore, this percent loss of primary amine could not be calculated. The total organic nitrogen is also shown in equivalents of nitrogen as amine per liter before and after the test and the resulting loss is given in percent. The ammonia evolved during the test is given in equivalents (moles) per liter of amine solution. Finally the nitrogen material balance is given showing the percent of the original organic nitrogen concentration accounted for during the test. This value was calculated in the following manner:

Percent total nitrogen recovered =

$$\frac{(\text{Gm. atomic wts. total N/liter + equivalents of } NH_3 \text{ evolved/liter amine soln.})}{\text{Gm. atomic wts. of total N/liter before test}} \, 100$$

Table II shows the results of this investigation for the relative resistance of various mixtures of amines to oxidation. The composition of the amine mixture is given in percent by weight. The identification number of each of the components is also shown and from reference to these in Report No. T2.20-2-2 the physical properties of the components may be found. The free amine concentrations before and after the oxidation test are expressed in equivalents per liter and the loss incurred in percent. Primary amine concentrations are expressed in a similar manner whenever any such amines are present. The total organic nitrogen concentrations are presented in equivalents of nitrogen as amine before and after oxidation, and the resulting loss is expressed in percent. The ammonia evolved during the test is given in equivalents (moles) of ammonia per liter of amine solution. The nitrogen material balance is expressed in percent of the original nitrogen accounted for.

## TABLE

## The Relative Effect of Oxidation

| Amine | Formula | No. |
|---|---|---|
| Primary Alkanol Monoamines | | |
| Isobutanolamine | $CH_3C(CH_3)(OH)CH_2NH_2$ | 120 |
| Hexanolamine | $CH_3CH(OH)CH_2C(NH_2)(CH_3)CH_3$ | 125 |
| 2-Amino 2-methyl 1-propanol | $(CH_3)_2C(NH_2)CH_2OH$ | 124 |
| 4-Amino-2-butanol | $CH_3CH(OH)CH_2CH_2NH_2$ | 119 |
| 2-Amino 2-methyl 1,3-propanediol | $HOCH_2C(NH_2)(CH_3)CH_2OH$ | 121 |
| Tris(hydroxymethyl)amino methane | $(CH_2OH)_3CNH_2$ | 123 |
| Monoisopropanolamine | $CH_3CH(OH)CH_2NH_2$ | 117 |
| 2(2-Aminoethoxy)ethanol+<br>(Diethyleneglycolamine) | $NH_2C_2H_4OC_2H_4OH$ | 122 |
| 2-Amino 1-butanol | $HOCH_2CH(NH_2)CH_2CH_3$ | 118 |
| Monoethanolamine | $NH_2CH_2CH_2OH$ | 111 |
| Heterocyclic Primary Amines | | |
| Tetrahydrofurfurylamine | $\underline{CH_2CH_2CH_2CH(CH_2NH_2)O}$ | 247 |
| Primary Amines Containing Isocyclic Rings | | |
| Benzyl Amine | $C_6H_5CH_2NH_2$ | 173 |
| Alkaline Salts of Primary Amino Acids | | |
| $\alpha$-Alanine (K Salt) | $NH_2CH(CH_3)COOK$ | |
| Secondary Alkanol Monoamines | | |
| Diethanolamine | $(HOCH_2CH_2)_2NH$ | 133 |
| N-Ethyl Ethanolamine | $CH_3CH_2NHCH_2CH_2OH$ | 132 |
| N-Methyl Ethanolamine | $CH_3NHCH_2CH_2OH$ | 145 |
| N-Butyl Ethanolamine | $HOC_2H_2NHC_4H_9$ | 135 |
| Diisopropanolamine | $(CH_3CH(OH)CH_2)_2NH$ | 129 |
| Tertiary Alkanol Monoamines | | |
| N-Ethyl diethanolamine | $C_2H_5N(C_2H_4OH)_2$ | 144 |
| N-Methyl diethanolamine | $CH_3N(C_2H_4OH)_2$ | 145 |
| N-Butyl diethanolamine | $C_4H_9N(C_2H_4OH)_2$ | 146 |
| 2(2-dimethylaminoethoxy)ethanol | $(CH_3)_2NC_2H_4OC_2H_4OH$ | 148 |
| Diethylaminoethanol<br>(diethyl monoethanolamine) | $(C_2H_5)_2NC_2H_4OH$ | 142 |
| Triethanolamine | $(C_2H_4OH)_3N$ | 143 |
| Triisopropanolamine | $(CH_3CH(OH)CH_2)_3N$ | 147 |

* Equivalents per liter
** Percent loss of amine, by wt.
*** Gram atomic weights per liter
\+ Dow sample

I

on 2.5N Solutions of Single Amines

| Free Amine |  |  | Primary Amine |  |  | Total Organic Nitrogen |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|
| Before, E/L* | After, E/L* | Loss, %** | Before, E/L* | After, E/L* | Loss, %** | Before, GA/L*** | After, GA/L*** | Loss, %** | $NH_3$ Lost | $N_2$ Mat'l. Bal. |
| 2.56 | 2.52 | 1.56 | 2.56 | 2.62 | -2.34 | 2.56 | 2.62 | -2.34 | .03 | 103.5 |
| 2.52 | 2.45 | 2.78 | 2.65 | 3.13 | -18.1 | 2.65 | 2.70 | -1.89 | .01 | 102.2 |
| 2.43 | 2.33 | 4.11 | 2.58 | 2.24 | 13.2 | 2.59 | 2.48 | 4.25 | .17 | 103.0 |
| 2.50 | 2.10 | 16.0 | 2.49 | 2.19 | 12.0 | 2.59 | 2.37 | 8.49 | .13 | 97.3 |
| 2.47 | 1.91 | 2.27 | 2.68 | 2.25 | 16.0 | 2.62 | 2.31 | 11.8 | .14 | 93.5 |
| 2.49 | 1.89 | 24.1 | 2.70 | 2.20 | 18.5 | 2.61 | 2.40 | 8.04 | .12 | 96.6 |
| 2.44 | 1.65 | 32.4 | 2.44 | 1.72 | 29.5 | 2.44 | 2.13 | 12.7 | .22 | 96.3 |
| 2.50 | 1.67 | 33.2 | 2.51 | 1.91 | 23.9 | 2.47 | 2.22 | 10.1 | .12 | 94.7 |
| 2.55 | 1.49 | 41.6 | 2.55 | 1.66 | 34.9 | 2.60 | 2.24 | 13.8 | .10 | 90.0 |
| 2.47 | 1.33 | 46.2 | 2.55 | 1.47 | 42.4 | 2.50 | 2.27 | 9.2 | .06 | 93.2 |
| 2.47 | 1.34 | 45.7 | 2.55 | 1.44 | 43.5 | 2.50 | 2.22 | 11.2 | .06 | 91.2 |
| 2.54 | 1.69 | 33.5 | 2.58 | 1.91 | 26.0 | 2.65 | 2.47 | 6.8 | .05 | 95.1 |
| So extensively decomposed that analysis was impossible. |  |  |  |  |  |  |  |  |  |  |
| 2.50 | 2.56 | -2.4 | 2.43 | 2.49 | -2.47 | 2.48 | 2.53 | -2.01 | .03 | 103.2 |
| 2.54 | 0.981 | 61.4 | nil | 0.39 | - | 2.49 | 2.08 | 16.5 | .17 | 90.4 |
| 2.51 | 0.51 | 79.7 | nil | 0.27 | - | 2.61 | 2.19 | 16.1 | .11 | 88.1 |
| 2.49 | 0.51 | 79.5 | .015 | nil | 100 | 2.51 | 2.23 | 11.2 | .19 | 96.4 |
| 2.48 | 0.32 | 87.1 | nil | nil | - | 2.50 | 0.188 | 24.8 | .29 | 86.8 |
| 2.45 | 0.18 | 92.7 | .03 | .02 | 33.3 | 2.54 | 2.42 | 4.8 | .04 | 96.8 |
| 2.50 | 2.46 | 1.60 | nil | nil | - | 2.56 | 2.52 | 1.56 | .01 | 98.8 |
| 2.46 | 2.42 | 1.63 | nil | nil | - | 2.54 | 2.52 | 0.79 | .01 | 99.6 |
| 2.50 | 2.42 | 3.2 | nil | nil | - | 2.50 | 2.52 | -0.79 | .000 | 100.8 |
| 2.49 | 2.36 | 5.22 | nil | nil | - | 2.55 | 2.51 | 1.57 | .02 | 99.2 |
| 2.51 | 2.35 | 6.4 | nil | nil | - | 2.47 | 2.46 | 0.40 | .03 | 100.8 |
| 2.52 | 2.36 | 6.4 | nil | nil | - | 2.48 | 2.60 | -4.8 | .003 | 105. |
| 2.50 | 2.23 | 10.8 | nil | nil | - | 2.49 | 2.43 | 2.41 | .008 | 98.0 |

## TABLE I

## The Relative Effect of Oxidation

| Amine | Formula | No. |
|---|---|---|
| **Alkaline Salts of Tertiary Amino Acids** | | |
| K salt of N'N Dimethyl Glycine | $(CH_3)_2NCH_2COOK$ | |
| **Aliphatic Polyamines** | | |
| Diethylenetriamine | $NH_2C_2H_4NHC_2H_4NH_2$ | 52 |
| Triethylenetetramine | $NH_2(C_2H_4NH)_2C_2H_4NH_2$ | 53 |
| Tetraethylenepentamine | $NH_2(C_2H_4NH)_3C_2H_4NH_2$ | 54 |
| Diethylaminopropylamine | $(C_2H_5)_2NC_3H_6NH_2$ | 63 |
| **Alkanol Polyamines** | | |
| Diaminoisopropanol | $NH_2CH_2CH(OH)CH_2NH_2$ | 151 |
| N-Hydroxyethylpropylene diamine | $CH_3CH(NHC_2H_4OH)CH_2NH_2$ | 163 |
| 5-Amino-2,2,5-trimethyl-3-aza-1-hexanol | $CH_3C(NH_2)(CH_3)CH_2NHC(CH_3)_2CH_2OH$ | 162 |
| Hydroxyethyl ethylene diamine | $NH_2C_2H_4NHC_2H_4OH$ | 161 |
| N'N'Dihydroxyethyl ethylene diamine | $(CH_2NHC_2H_4OH)_2$ | 164 |
| Aminoethyl morpholine | $\underline{OC_2H_4N(C_2H_4NH_2)CH_2C}H_2$ | 240 |
| 2,5-Dimethyl piperazine | $H\underline{NCH_2CH(CH_3)NHCH_2C}HCH_3$ | 245 |
| 2,4,6-Tri(dimethylaminomethyl) phenol | $HOC_6H_2(CH_2N(CH_3)_2)_3$ | 213 |
| 2,4,6-Tri(dimethylaminomethyl) phenol (K salt) | $KOC_6H_2(CH_2N(CH_3)_2)_3$ | 213 |

* Equivalents per liter

** Percent loss of amine, by wt.

*** Gram atomic weights per liter

(Contd.)

on 2.5N Solutions of Single Amines

| Free Amine | | | Primary Amine | | | Total Organic Nitrogen | | | | $N_2$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Before, E/L* | After, E/L* | Loss, %** | Before, E/L* | After, E/L* | Loss, %** | Before, GA/L*** | After, GA/L*** | Loss, %** | $NH_3$ Lost | Mat'l. Bal. |
| 2.47 | 2.32 | 6.07 | nil | nil | - | 2.44 | 2.31 | 5.33 | .02 | 95.5 |
| 2.42 | 1.85 | 23.6 | 1.56 | 1.20 | 23.0 | 2.97 | 2.76 | 7.1 | .15 | 97.9 |
| 2.52 | 1.96 | 22.2 | 2.02 | 1.80 | 6.93 | 3.68 | 3.24 | 11.9 | .20 | 92.4 |
| 2.60 | 1.60 | 38.5 | 1.70 | 1.36 | 20.0 | 3.85 | 3.35 | 14.3 | .32 | 94.8 |
| 2.46 | 2.44 | 0.81 | 1.26 | 1.18 | 6.35 | 2.50 | 2.52 | -0.80 | .02 | 101.6 |
| 2.42 | 0.60 | 75.2 | 2.56 | 1.62 | 36.7 | 2.50 | 1.78 | 28.8 | .63 | 96.0 |
| 2.48 | 1.14 | 54 | 1.61 | 0.82 | 49.1 | 2.68 | 2.34 | 12.7 | .13 | 91.8 |
| 2.58 | 0.84 | 67.4 | 1.46 | 0.90 | 38.4 | 2.90 | 1.92 | 33.8 | .49 | 82.8 |
| 2.36 | 1.30 | 56.1 | 1.33 | 0.89 | 33.1 | 2.56 | 2.42 | 5.5 | .12 | 99.2 |
| 2.90 | 0.66 | 72.5 | nil | 0.57 | - | 2.62 | 2.48 | 7.63 | .06 | 94.7 |
| 2.54 | 2.28 | 10.2 | 2.06 | 0.201 | 2.4 | 4.02 | 4.02 | 0.00 | .02 | 100.5 |
| 2.24 | 0.26 | 88.4 | nil | nil | - | 2.80 | 2.38 | 15.0 | .11 | 88.6 |

Not analyzed, evidence of extensive decomposition

Not analyzed, evidence of extensive decomposition

## TABLE

## The Relative Effect of Oxidation on 2.5N

| Composition of Amine Mixture (% by wt.) | Identification No. | Free Amine<br>Before, E/L* | <br>After, E/L* | <br>Loss, %** |
|---|---|---|---|---|
| **Mixtures of Tertiary and Secondary Amines** | | | | |
| Sharples Mixed Ethyl Ethanol Amines #161+ | 2M | 2.50 | 2.35 | 6.00 |
| 50% Ethyl diethanolamine | 144 | | | |
| 50% Ethyl monoethanolamine | 132 | 2.67 | 2.37 | 11.2 |
| 50% Ethyl diethanolamine | 144 | | | |
| 50% Diethanolamine | 133 | 2.39 | 2.20 | 7.9 |
| 50% Methyl diethanolamine | 145 | 2.47 | 2.35 | 4.8 |
| 50% Diethanolamine | 133 | 2.55 | 2.36 | 7.4 |
| 25% Methyl diethanolamine | 145 | 2.46 | 1.82 | 26.0 |
| 75% Diethanolamine | 133 | | | |
| 10% Methyl diethanolamine | 145 | 2.50 | 1.33 | 46.8 |
| 90% Diethanolamine | 133 | | | |
| 50% Triethanolamine | 143 | 2.58 | 1.40 | 45.7 |
| 50% Diethanolamine | 133 | | | |
| **Mixtures of Tertiary and Primary Amines** | | | | |
| 50% Methyl diethanolamine | 145 | 2.49 | 2.40 | 3.6 |
| 50% Monoethanolamine | 111 | | | |
| 50% Methyl diethanolamine | 145 | | | |
| 50% Diethyleneglycolamine++ | 122 | 2.52 | 2.48 | 1.6 |
| 25% Methyl diethanolamine | 145 | | | |
| 75% Diethyleneglycolamine++ | 122 | 2.47 | 2.43 | 1.62 |
| 10% Methyl diethanolamine | 145 | 2.52 | 2.32 | 7.94 |
| 90% Diethyleneglycolamine++ | 122 | | | |

* Equivalents per liter

** Percent loss of amine, by wt.

*** Gram atomic weights per liter

\+ Sharples assay: 41% ethyl diethanolamines; 52% ethyl diethanolamine, 7% high and low boiling fractions.

++ Carbide and Carbon Sample.

## II

## Solutions of Mixed Aliphatic Alkanol Amines

| Primary Amine | | | Total Organic Nitrogen | | | Ammonia Evolved, E/L* | Nitrogen Material Balance, % |
|---|---|---|---|---|---|---|---|
| Before, E/L* | After, E/L* | Loss, %** | Before, GA/L*** | After, GA/L*** | Loss, %** | | |
| nil | nil | - | 2.59 | 2.50 | 3.4 | .01 | 96.9 |
| nil | nil | - | 2.68 | 2.38 | 11.2 | .004 | 90.0 |
| nil | nil | - | 2.46 | 2.32 | 5.7 | .01 | 94.7 |
| nil | nil | - | 2.60 | 2.66 | -2.3 | .001 | 102.3 |
| nil | nil | - | 2.56 | 2.50 | 2.34 | 0.000 | 97.6 |
| nil | nil | - | 2.52 | 2.50 | 0.8 | .02 | 100.0 |
| nil | nil | - | 2.60 | 2.43 | 2.7 | .13 | 98.4 |
| nil | nil | - | 2.62 | 2.42 | 7.6 | .05 | 94.2 |
| 1.76 | 1.73 | 1.73 | 2.53 | 2.45 | 3.16 | 0.000 | 96.8 |
| 1.48 | 1.43 | 3.4 | 2.66 | 2.76 | -3.8 | .001 | 104.0 |
| 2.03 | 1.96 | 3.4 | 2.49 | 2.62 | -5.2 | .001 | 105.6 |
| 2.34 | 2.23 | 4.7 | 2.52 | 2.50 | 0.8 | .001 | 99.6 |

Data obtained on the relative corrosive properties of the solutions are presented in Table III. The iron contents of the solutions are given in parts per million before and after the test. These values show the concentrations of iron dissolved in the solutions. The iron capacities are also expressed in parts per million. These data show the relative corrosive properties of the solutions toward low carbon steel. The loss in weight of the stainless steel wire is expressed in inches of penetration per year. This value was calculated from the following formula which is valid since the weight loss of specimen was negligible in all cases:

$$IPY = \frac{Q \times 365}{D \times A}$$

Q = milligrams lost per day per gram of wire
A = area of 1 gm. of wire in sq. inches.
D = density of wire in milligrams per cu. inch
365 = days per year

## TABLE III.

## THE RELATIVE CORROSIVE PROPERTIES OF AMINE SOLUTIONS.

| | Iron Content | | Iron Capacity | | |
|---|---|---|---|---|---|
| Amine | Before Test (p.p.m.) | After Test (p.p.m.) | Before Test (p.p.m.) | After Test (p.p.m.) | Corrosion Rate of Stainless Steel (IPY) |
| Isobutanolamine | 40 | 40 | 50 | 350 | $4.3 \times 10^{-5}$ |
| Hexanolamine | 20 | 25 | 60 | 50 | $3.3 \times 10^{-5}$ |
| 2-amino 2-methyl 1-propanol | 25 | 20 | 30 | 40 | $3.3 \times 10^{-5}$ |
| 4-amino 2-butanol | 50 | 40 | 55 | 1000 | $4.3 \times 10^{-5}$ |
| 2-amino 2-methyl 1,3 propandiol | 35 | 70 | 40 | 110 | $3.3 \times 10^{-5}$ |
| Tris(hydroxy methyl) amino methane | 20 | 20 | 30 | 100 | $2.1 \times 10^{-5}$ |
| Monoisopropanolamine | 40 | 60 | 60 | 110 | NL |
| Diethyleneglycolamine | 50 | 60 | 55 | 120 | NL |
| 2-amino 1-butanol | 50 | 40 | 80 | 40 | $1.6 \times 10^{-4}$ |
| Monoethanolamine | 60 | 25 | 70 | 40 | $8.3 \times 10^{-5}$ |
| | 60 | 25 | 70 | 45 | $1.3 \times 10^{-5}$ |
| Tetrahydrofurfurylamine | 20 | 25 | 45 | 30 | $2.6 \times 10^{-5}$ |
| Benzyl amine | | Not Analyzed | | | NL |
| $\alpha$-alanine | 25 | 30 | 5000 | ND | $1.4 \times 10^{-4}$ |
| Diethanolamine | 30 | 100 | 50 | 7000 | NL |
| Ethyl monoethanolamine | 20 | 20 | 25 | 1500 | NL |
| Methyl monoethanolamine | 20 | 25 | 30 | 1050 | $7.7 \times 10^{-5}$ |
| Butyl monoethanolamine | 40 | 80 | 50 | 1500 | NL |
| Diisopropanolamine | 50 | 50 | 70 | 4000 | $1.2 \times 10^{-4}$ |
| Ethyl diethanolamine | 25 | 30 | 30 | 50 | NL |
| Methyl diethanolamine | 25 | 30 | 30 | 50 | $3.2 \times 10^{-5}$ |
| Butyl diethanolamine | 25 | 20 | 30 | 50 | NL |
| 2(2-dimethyl amino) ethanol | 20 | 20 | 40 | 70 | NL |

## TABLE III. (Continued)

## THE RELATIVE CORROSIVE PROPERTIES OF AMINE SOLUTIONS.

| | Iron Content | | Iron Capacity | | |
|---|---|---|---|---|---|
| **Amine** | Before Test (p.p.m.) | After Test (p.p.m.) | Before Test (p.p.m.) | After Test (p.p.m.) | Corrosion Rate of Stainless Steel (IPY) |
| Diethylamino ethanol | 20 | 25 | 30 | 70 | NL |
| Triethanolamine | 40 | 60 | 60 | 110 | NL |
| Triisopropanolamine | 50 | 30 | 90 | 80 | $8.0 \times 10^{-5}$ |
| K salt of NN' dimethyl glycine | 20 | 20 | 16,000 | 5000 | $8.0 \times 10^{-5}$ |
| Diethylenetriamine | 40 | 50 | 80 | 70 | $8.9 \times 10^{-5}$ |
| Triethylenetetramine | 30 | 20 | 9000 | 900 | $1.5 \times 10^{-4}$ |
| Tetraethylene pentamine | 30 | 20 | 9000 | 1200 | NL |
| Diethyl amino propylamine | 20 | 25 | 25 | 50 | $1.4 \times 10^{-4}$ |
| Diaminoisopropanol | 50 | 50 | 80 | 2500 | NL |
| N-Hydroxyethyl propylene diamine | 0.0 | 30 | 4000 | 524 | $1.8 \times 10^{-4}$ |
| 5-Amino 2,2,5-trimethyl 3-aza 1-hexanol | 20 | 25 | 35 | 656 | NL |
| Hydroxyethyl ethylene diamine | 50 | 30 | 90 | 80 | $1.3 \times 10^{-4}$ |
| NN'-Hydroxyethyl ethylene diamine | 40 | 35 | 2000 | 650 | $1.4 \times 10^{-4}$ |
| Amino ethyl morpholine | 50 | 40 | 80 | 750 | $4.3 \times 10^{-5}$ |
| 2,5-Dimethyl piperazine | 20 | 30 | 50 | 1500 | NL |
| 2,4,6-Tri(dimethyl amino methyl) phenol | ND | ND | ND | ND | ND |
| **Mixed Amines** | | | | | |
| Sharples Mixed Ethyl Ethanolamines #161 | 25 | 30 | 30 | 30 | NL |
| 50% Ethyl monoethanolamine<br>50% Ethyl diethanolamine | 30 | 30 | 40 | 40 | $1.7 \times 10^{-4}$ |
| 50% Ethyl diethanolamine<br>50% Diethanolamine | 30 | 30 | 30 | 30 | NL |
| 50% Methyl diethanolamine | 30 | 30 | 30 | 40 | $2.5 \times 10^{-5}$ |
| 50% Diethanolamine | 30 | 40 | 30 | 40 | NL |
| 50% Triethanolamine<br>50% Diethanolamine | 30 | 30 | 40 | 525 | $8.9 \times 10^{-5}$ |
| 25% Methyl diethanolamine<br>75% Diethanolamine | 30 | 40 | 30 | 40 | NL |
| 10% Methyl diethanolamine<br>90% Diethanolamine | 30 | 40 | 30 | 4000 | NL |
| 50% Ethyl diethanolamine<br>50% Monoethanolamine | 30 | 30 | 30 | 40 | $9.0 \times 10^{-5}$ |
| 50% Methyl diethanolamine<br>50% Diethyleneglycolamine | 30 | 40 | 30 | 40 | NL |
| 25% Methyl diethanolamine<br>75% Diethyleneglycolamine | 30 | 40 | 40 | 40 | NL |
| 10% Methyl diethanolamine<br>90% Diethyleneglycolamine | 40 | 40 | 40 | 40 | NL |

ND - Not Determined NL - No Loss in Weight

## IV. DISCUSSION:

### A. Evaluation of the Method.

The primary purpose of this investigation was to classify various amines with respect to their relative resistance to oxidation. Every effort was made to subject each amine to the same conditions, but the very nature of the test made exact control difficult. The following data taken from Table I shows duplicate results obtained from two independent oxidation tests.

| Free Amine Loss (%) | Primary Amine Loss (%) | Organic Nitrogen Loss (%) | Ammonia Evolved Equivalents per Liter of Amine Solution | Nitrogen Material Balance |
|---|---|---|---|---|
| 46.2 | 42.4 | 9.2 | .06 | 93.2 |
| 45.7 | 43.5 | 11.2 | .06 | 91.2 |

Results obtained in a previous investigation in which 3.0 N monoethanolamine solution was studied show the following values.

| Free Amine Loss (%) | Primary Amine Loss (%) | Organic Nitrogen Loss (%) | Ammonia Evolved Equivalents per Liter of Amine Solution | Nitrogen Material Balance |
|---|---|---|---|---|
| 41.7 | - | 18.3 | 0.24 | 90 |

These results for a compound which is subject to a relatively high oxidation rate indicate that the method is reproducible within the limits necessary to classify an amine with reference to degradation incurred through oxidation.

Since alkalinity losses were of primary interest in this investigation, the values given for percent loss in free amine concentration are the most significant data given in Table I and II. These results are based on a direct titration of the amine (See Analytical Methods, Section 1). In most cases this method gives values reproducible to within 2 parts per thousand.

The original solutions were prepared on the basis of a free amine determination on a weighed sample of the material. Most of these compounds are extremely hydroscopic and, therefore, it was simpler in many cases to prepare 2.5 N solutions of these amines on the basis of alkalinity values obtained experimentally than on the basis of their theoretical equivalent weights. From Table I it may be seen that in some cases the free amine concentration is much lower than the total nitrogen. Not all of the amine titrated with methyl red indicator. However, any amine titrating below the methyl red end point is considered unreactive toward carbon dioxide. Therefore, all solutions were prepared to titrate 2.5 N when methyl red was used as the indicator.

The primary amine concentration was determined by the Van Slyke reaction (See Analytical Methods, Section 2). For simple primary amines like monoethanolamine, this reaction proceeds rapidly and quantitatively. However, when the compound contains groups which offer steric hindrance, the reaction goes slowly. In such cases precise results do not necessarily indicate accuracy. In some cases it was necessary to allow the reaction to continue overnight. The results obtained in these cases were usually higher than that obtained for the total nitrogen content. Usually the amount of salt formation in an amine solution may be estimated by subtracting the "free amine concentration" from the "primary amine concentration". Such a correlation of the data presented in Tables I and II would probably result in erroneous conclusions because of the analytical errors just described.

The accuracy of the total organic nitrogen analysis may be reflected in the nitrogen material balance. Where decomposition was excessive, frequently a relatively high percentage of total organic nitrogen was unaccounted for.

The micro Kjeldahl Method (See Analytical Methods, Section 3) by which these results were obtained depends on complete reduction of the organic nitrogen to ammonia. Where extensive oxidation occurs, compounds are formed which are difficult to decompose to ammonia. The addition of metallic copper and Ranker's solution reduces only 90% of the nitrates and nitrites present. Also there are forms of organic nitrogen for which no efficient catalyst has been discovered. This may account for the low material balances obtained when decomposition was excessive. There is also the possibility, of course, that nitrogen was given off as a decomposition product which could not be detected by the analytical methods employed.

The iron content test is based on a colorimetric determination which is considered to yield very precise results. However, the organic matter must first be oxidized completely so that no trace of the original color remains; otherwise the color of the thiocyanate is obscured. In some cases the solutions were quite difficult to decompose completely, and the iron content could be estimated only to within ± 10%. However, a difference of this magnitude in the iron content of a solution is not usually considered as significant in routine Girbotol work.

The iron capacity test is carefully controlled, but the accuracy of this test is limited by the precision obtained for the iron content of the solution as well as control of the conditions under which the solution is contacted with iron filings. The data given for this characteristic of the solutions in Table III should, therefore, be accepted only as indicative of the range of the corrosive properties of the solution.

### B. The Relative Effect of Oxidation on Various Types of Amines.

From Table I it may be readily observed that among the aliphatic alkanol monoamines the tertiary amines as a group showed the least loss of free amine as a result of oxidation. The secondary amines as a group showed the greatest loss. The primary compounds are not so clearly classified, their relative free amine loss depending largely upon the structure of the individual compound.

According to Sidgwick[1], amines are oxidized by two general types of mechanisms:

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[1] Sidgwick, N. V., The Organic Chemistry of Nitrogen, Oxford University Press, 1942, p. 26.

(1) One mechanism which is illustrated by the reaction of peroxides which oxidize tertiary amines to the amine oxide ( $R_3N \rightarrow O$ )

(2) Another mechanism is typified by the reaction of reagents such as permanganate which will not oxidize tertiary amines.

The oxides of tertiary amines are very weak bases, much less basic than the amine from which they are derived. Their ionization constants are of the order $10^{-10}$ and they do not react basic to phenolphthalein.[1] The results given in Table II were obtained from titrations with methyl red as the indicator. It was, therefore, possible that these oxides may have been formed and were titrated as free amine. Therefore, methyl diethanolamine solutions before and after oxidation were titrated using both indicators. The results are shown below:

| | Before Oxidation Equivalents/liter | After Oxidation Equivalents/liter |
|---|---|---|
| Methyl red | 2.46 | 2.42 |
| Phenolphthalein | 2.25 | 2.13 |
| Difference | .21 | .29 |

The differences between these two results are relatively insignificant and it was concluded that little or no amine oxides had been formed. Therefore, it is indicated that amines in general do not react with oxygen in a manner similar to the peroxide reaction.

Primary amines are reported in the literature[2] to oxidize by the permanganate type of mechanism according to the following equations.

$$(1)\quad RCH_2NH_2 \xrightarrow{O} RCH_2N{:} \longrightarrow RCH{:}NH \xrightarrow{H_2O} RCHO + NH_3$$

$$(2)\quad R_2CHNH_2 \xrightarrow{O} R_2CHN{:} \longrightarrow R_2C{:}NH$$

$$\xrightarrow{H_2O} R_2C{=}O + NH_3$$

Thus a free radical is formed which rearranges to an imine. This intermediate rearranges to an aldehyde or ketone depending on whether the amino group is attached to a primary or secondary carbon atom. When the adjacent carbon is tertiary no free radical is formed since free radical formation is actuated by the presence of hydrogen on the carbon atom adjacent to the active group.

Secondary amines react according to the following permanganate type mechanism[3].

$$R_2NH \xrightarrow{O} R_2N\cdot \longrightarrow R_2N{:}NR_2$$

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[1] Stewart, T. D. and Maeser, S., "The Strength of Trimethylamine Oxide and Trimethyl Alkoxyl Ammonium Hydroxides as Bases. The Structure of Ammonium Compounds", Journal of the American Chemical Society 46, pp. 2585 and 2590, (1924).

[2] Sidgwick, op. cit., p. 26.

[3] Sidgwick, op. cit., p. 26.

The tetrasubstituted hydrazine formed may then undergo further complicated reactions. Since free radical formation is actuated by the presence of hydrogen on the adjacent carbon atom it is of interest that secondary amines may have two methylene groups adjoining the amino groups and would, therefore, be expected to be particularly subject to oxidation.

Of the primary alkanol amines tested the loss in alkalinity is apparently influenced by two factors. The first of these is the type of carbon atom adjacent to the amino group. When the amino group is attached to a tertiary carbon atom, as in 2-methyl-2-amino-1-propanol, as a general rule the oxidation rate is markedly reduced. This bears out the theory discussed previously. The second factor is the type of hydroxyl group present, i.e., whether the alcohol is primary, secondary or tertiary. The tertiary type of alcohol, such as that in isobutanolamine, apparently resists oxidation. The secondary alcohol, illustrated by 4-amino-2-butanol is more resistant than the primary type illustrated by monoethanolamine. The data showing this trend are supported by facts concerning the relative oxidation rates of alcohols in general. It is known that tertiary alcohols are especially resistant to oxidation, secondary alcohols may be oxidized to ketones at which point the reaction usually ceases, while primary alcohols go readily to the aldehyde and then to the acid.

The data at hand indicate that a primary hydroxyl group is more readily oxidized than a primary amino group attached to a primary carbon atom. This is illustrated by the results for isobutanol amine and 2-amino-2-methyl-1-propanol. When more primary hydroxyl groups are added to 2-amino-2-methyl-1-propanol as in 2-amino-2-methyl-1, 3-propanediol and in tris(hydroxyl methyl) amino methane, each additional hydroxyl group increases the oxidation rate.

In view of the above considerations it is believed that the more easily oxidized groups contained in the alkanol amines investigated can be arranged in the following order of least resistance to oxidation. (1) secondary amino groups, (2) primary alcohol groups and (3) primary amino groups attached to a primary carbon atom. The failure of tertiary alkanol amines containing primary hydroxyl groups to undergo appreciable oxidation is unexpected and contrary to the above predictions. Therefore, it appears that the tertiary amino group has the unexpected property of retarding the oxidation of primary alcohol groups. Further experimental evidence to substantiate this viewpoint may be found in Table II wherein the oxidation results are given for mixtures of tertiary amines with primary and secondary amines. These results demonstrate that the rates of oxidation of the primary and secondary amines are markedly reduced in the presence of tertiary amines, such as methyl diethanolamine and ethyl diethanolamine. For example, in a 2.5 N solution of diethanolamine and methyl diethanolamine where the amines are present in equal quantities, the alkalinity loss would be predicted to be about 30% on the basis of the results obtained from diethanolamine solutions alone. However, the alkalinity loss from duplicate runs of the above mixture averaged only 6%. Therefore the presence of the methyl diethanolamine retarded the oxidation rate of diethanolamine several fold. It should be pointed out that triethanolamine (Table II) in a 50:50 mixture did not protect diethanolamine from oxidation. Since the secondary amino group is more easily oxidized than a primary alcohol group, it is possible that triethanolamine protects its own primary alcohol groups from oxidation, but is unable to protect additional groups like secondary amines. It is also of interest that as the ratio of methyl diethanolamine to diethanolamine was decreased the solutions evidenced greater oxidation.

It may be observed from the data contained in Table I that the polyamines as a class showed very low resistance to oxidation. Solutions of diethylaminopropylamine and aminoethyl morpholine are notable exceptions to this rule. These compounds, however, contain tertiary amino groups. Therefore, the low alkalinity losses in these solutions lends credence to the theory that the presence of a tertiary amino group retards oxidation of other groups. However, with the exception of these two compounds, the oxidation rate of polyamines was high. It is interesting to note that the polyamines containing hydroxy groups oxidized more readily than the purely aliphatic amines. This indicates that the hydroxyl group enters into the oxidation mechanism. It may be oxidized independently or enter into an intramolecular reaction of the oxidized groups. This latter hypothesis is supported by the trend wherein a reduction in alkalinity loss occurred by separation of the hydroxyl and amino groups in the molecule. For example, diaminoisopropanol, in which two primary amino groups are on carbon atoms adjacent to that containing the hydroxyl group, showed a higher alkalinity loss than N-hydroxyethylpropylenediamine, 5-amino-2,2,5-trimethyl-3-aza-1-hexanol, or NN' dihydroxyethyl ethylenediamine. These latter three compounds all contain secondary amino groups, and would, therefore, be expected to oxidize more rapidly than diaminoisopropanol. The same effect may be noted in the relative oxidation rates for the alkanol primary monoamines. For example, 2-amino-4-butanol and monoisopropanolamine both have the same structure except in the case of the first compound the hydroxyl and nitrogen groups are separated by a methylene group. The former amine showed an alkalinity loss of 16% while the latter showed a loss of 32.4%. A similar case is illustrated by the comparative alkalinity losses of hexanolamine and 2-amino-2-methyl-1-propanol. The fact that in these compounds the hydroxyl and amino groups are separated by one or more methylene groups seems, therefore, to indicate the influence of this type of structure on the oxidation rate of these compounds.

The heterocyclic ring compounds, with the exception of aminoethyl morpholine, show low resistance to oxidation. This probably indicates a rupture of the ring and complete disruption of the heterocyclic molecule. The same may be said for the isocyclic ring compounds. Benzyl amine and 2,4,6-tri(dimethylamino methyl)phenol were so extensively decomposed that it was impossible to take a homogeneous sample of the residue.

The alkalinity losses incurred by the amino acids tested were very low. The NN' dimethyl glycine which is a tertiary amine and α-alanine which is a primary amine would be expected, in view of the previous discussion, to be resistant to oxidation.

## C. Corrosive Properties.

The relative corrosive properties of the various amine solutions tested are shown in Table III. It is obvious from the data given that the stainless steel employed in this investigation underwent negligible corrosion and the iron contents of the solutions showed relatively little change as a result of being contacted with this metal during the test.

On the other hand, the iron capacities which measure the corrosive properties of amine solutions toward low carbon steel varied with the type of compound as well as the type of oxidation products which are formed.

As seen from Table II the oxidation products of the secondary alkanolamines are particularly corrosive to low carbon steel. The alkaline salts of the amino acids were very corrosive as were many of the diamines before and after oxidation. In general the primary and tertiary alkanol monoamines had low iron capacities both before and after oxidation. The mixtures of tertiary and secondary amines, with the exception of those mixtures in which oxidation was excessive, showed little corrosive action on low carbon steel. Before it can definitely be stated that any amine solution may be safely employed in a plant of low carbon steel construction, prolonged corrosion tests simulating plant conditions would be required.

## D. Selection of Amines for Further Study.

As has been emplasized before, alkalinity loss in these tests was taken as the primary indication of oxidation rate. As may be observed from Table I the amines may be divided roughly into two classes, those which lost roughly 11% or less in alkalinity and those which lost 20% or more. The one exception, 4-amino-2-butanol, which lost 16% in alkalinity has a strong butyric like odor, which would be undesirable if it were used in the purification of air for breathing purposes. Since time does not permit an intensive study of other comparative properties of a large number of these amines, it was decided to limit the selection to the group which showed 11% or less in alkalinity loss. Of this group the following compounds were selected from Table I.

1. Isobutanolamine
2. 2-amino-2-methyl-1-propanol
3. α-alanine (K salt)
4. N-ethyl diethanolamine
5. N-methyl diethanolamine
6. N-butyl diethanolamine
7. 2(2-dimethyl amino ethoxy) ethanol
8. Diethyl amino ethanol (diethyl monoethanolamine)
9. Triethanolamine
10. Triisopropanolamine
11. NN' dimethyl glycine
12. Amino ethyl morpholine
13. Diethyl amino propylamine

Hexanolamine was eliminated from further consideration, since the carbonate is insoluble at room temperature and it is described by the manufacturers as very toxic.

The fact that certain of the tertiary amines act as anti-oxidants protecting primary and secondary amines led to further study of these mixtures.

Most of the tertiary amines have high boiling points and are resistant to oxidation. However, as a group they have been found to have relatively low carbon dioxide capacities and slow absorption rates. On the other hand, the primary amines which contain amino groups attached to a primary carbon atom have high carbon dioxide capacities and absorption rates. Diethanolamine, a secondary amine, has an intermediate capacity and absorption rate. Nevertheless, applicable primary and secondary amines are highly susceptible to oxidation and in addition most of the primary amines have relatively high vapor pressures. Therefore, when it was discovered that the tertiary amines have the property of retarding the oxidation of other amines, it was decided to combine several of these tertiary amines with primary or secondary amines so that the resulting mixture, if resistant to oxidation, would possess the added desirable properties of high carbon dioxide capacity, fast absorption rates and relatively low vapor pressure.

The results of the oxidation test on these mixtures are shown in Table II. Ethyl diethanolamine, when present as 50% by weight of the total amine protected diethanolamine, ethyl ethanolamine, and monoethanolamine. Methyl diethanolamine also protected diethanolamine, when present as 50% by weight of the total amine, as well as diethylene glycol amine. Methyl diethanolamine also afforded excellent protection for diethylene glycolamine when present in ratio of 25:75 respectively. On reducing the ratio to 10:90 the alkalinity loss rose to 7.9% and there was evidence of polymer formation.

At the time this data was obtained in order that contract obligations might be fulfilled, it was necessary to limit the additional time to be spent on these mixtures. Therefore, only those mixtures which promise the greatest degree of adaptability to the use intended were selected for detailed study. The combinations chosen were based on the following considerations:

(1) Boiling Point.
(2) Carbon dioxide absorption rate and capacity.
(3) Commercial availability.

Methyl diethanolamine is available commercially at the present time, while ethyl diethanolamine is not. They have similar boiling points (See Report T2.20-2-2). Methyl diethanolamine has a slightly higher carbon dioxide absorption rate. Therefore methyl diethanolamine mixtures will be used in further studies.

Of the primary amines studied in combination with tertiary amines, diethyleneglycolamine has by far the highest boiling point. Whereas monoethanolamine boils at 171°C; diethyleneglycolamine boils at above 225°C. Both are available commercially and have similar carbon dioxide capacities and absorption rates (See Report No. T2.20-2-2). Therefore, diethyleneglycolamine was chosen for further study in combination with methyl diethanolamine.

Of the secondary amines studied diethanolamine has by far the highest boiling point and is available commercially. Therefore, it was selected for further study.

On the basis of these considerations, the following mixtures from Table II were selected for detailed study.

1. 50% diethyleneglycolamine and 50% methyl diethanolamine
2. 75% diethyleneglycolamine and 25% methyl diethanolamine
3. 50% diethanolamine and 50% methyl diethanolamine
4. Sharples Mixed Ethyl Ethanolamines #161 will also be studied since it is a commercially available mixture.

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Report No. T2.11-3-2

THE GIRDLER CORPORATION
GAS PROCESSES DIVISION
PROCESS DEVELOPMENT AND RESEARCH LABORATORIES
LOUISVILLE, KENTUCKY

# THE CARBON DIOXIDE CAPACITIES OF SOLUTIONS OF VARIOUS AMINES RESISTANT TO OXIDATION.

May 18, 1950

| Work by: | Report by: |
|---|---|
| R. C. Kindrick | R. C. Kindrick |
| Kenton Atwood | Kenton Atwood |
| M. R. Arnold | M. R. Arnold |

## Sentence Summary

The carbon dioxide capacities of 2.5 N solutions of sixteen amines and four mixtures of amines have been determined at 85°F. and at a carbon dioxide partial pressure of 19 mm. of Hg. (approximately 2.6% carbon dioxide by volume).

## I. INTRODUCTION:

From the data contained in Girdler Report No. T2.15-1-30, thirteen amines and four mixtures of amines were selected from fifty amines and mixtures as being relatively resistant to oxidation. From this selected group of compounds one or more will be recommended for the removal of carbon dioxide from air on the basis of comparative data pertaining to additional properties of their solutions.

The first of these properties to be determined was the capacity of 2.5 N solutions of the amines for carbon dioxide under the conditions to be employed in plant operation. The term carbon dioxide capacity is used to designate the concentration of carbon dioxide in an amine solution in equilibrium with a gas possessing a given partial pressure of carbon dioxide at a specified temperature. In other words, the solution is saturated with carbon dioxide under the specified conditions, temperature and carbon dioxide pressure, when its capacity is reached. It follows that an amine solution having a low carbon dioxide capacity under specified conditions would be less desirable than a solution having a high capacity, since less solution would be needed in the latter case to remove a given amount of carbon dioxide from a gas. This holds provided, of course, that the rates at which carbon dioxide is absorbed from the gas are comparable. (See Girdler Report No. T2.11-3-2).

Therefore, the purpose of the present investigation was to determine the carbon dioxide capacities of the amine solutions selected from the data in Girdler Report No. T2.15-1-30 under conditions similar to those which will be employed in the removal of carbon dioxide from submarine atmospheres. Since the design data in our files pertain largely to monoethanolamine, diethanolamine, and triethanolamine, the capacities of mono- and di- ethanolamine solutions will be determined for comparison purposes in addition to the seventeen solutions previously selected. Diethyleneglycolamine was also included since it is a component of mixtures which promise to be applicable to the problem at hand.

## II. SUMMARY AND CONCLUSIONS:

(1) The carbon dioxide capacities of sixteen 2.5 N amine solutions and four 2.5 N solutions of amine mixtures have been determined at 85°F. and at a carbon dioxide partial pressure of 19 mm. of Hg. (approximately 2.6% carbon dioxide by volume).

(2) The type of amine, i.e., primary, secondary, or tertiary together with the pH of the solution largely determines the carbon dioxide capacity under the conditions of this investigation.

(3) The following amines have been selected for further study:

isobutanol amine
2-amino-2-methyl-1-propanol
diethyleneglycolamine
$\alpha$-alanine
methyl diethanolamine
ethyl diethanolamine
2(2-dimethyl amino ethoxy) ethanol

diethyl amino ethanol
NN' dimethyl glycine
diethylamino propylamine
aminoethyl morpholine
Sharples Mixed ethylethanolamines # 161
50% methyl diethanolamine: 50% diethanolamine
50% methyl diethanolamine: 50% diethyleneglycolamine
25% methyl diethanolamine: 75% diethyleneglycolamine

(4) The following amines have been eliminated on the basis of low carbon dioxide capacities:

triisopropanolamine
butyl diethanolamine

## III. INVESTIGATIONAL PROCEDURE AND EXPERIMENTAL DATA:

### A. Source of Reagents (See Girdler Report No. T2.20-2-2)

### B. Apparatus and Procedure

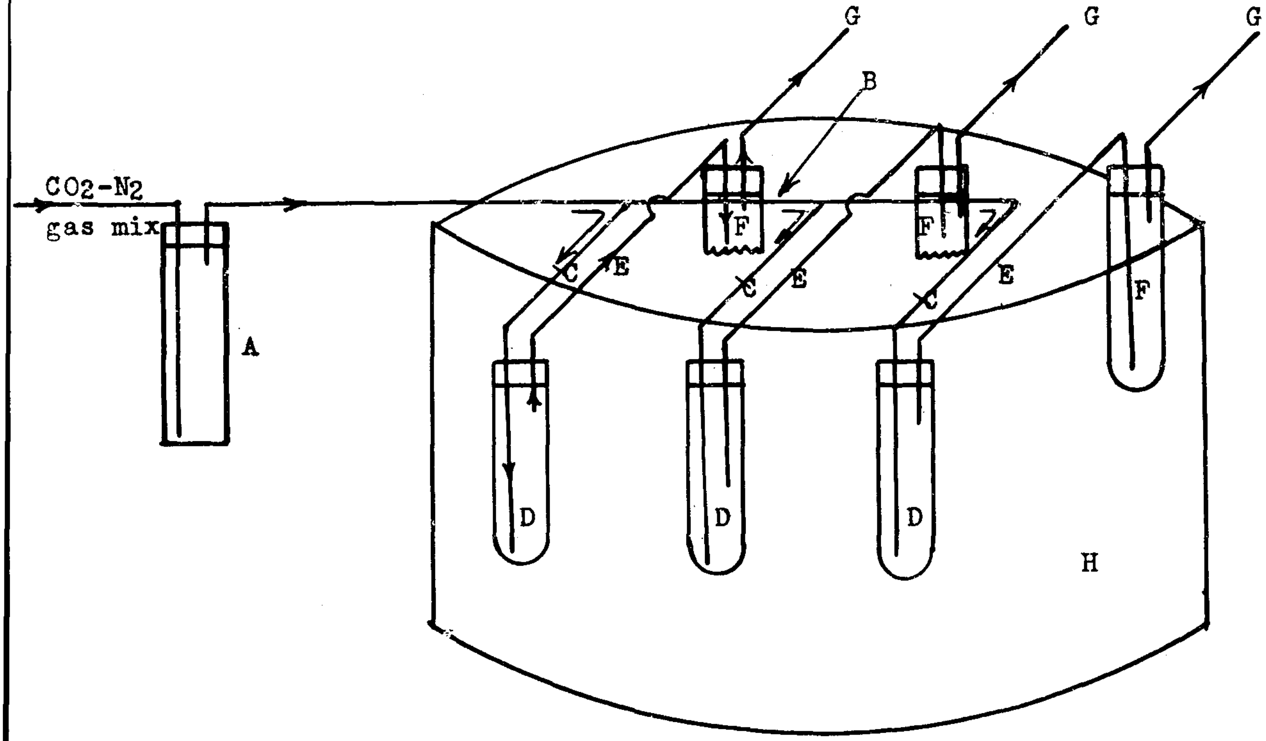
Essentially, the method used for the determination of the carbon dioxide capacities of a given amine solution consisted in passing a gas composed of 2.6% carbon dioxide and 97.4% nitrogen through a 2.5 N solution held at 85°F. in a water bath until analyses of the outlet and inlet gases were identical showing that no more carbon dioxide was being absorbed from the gas. The carbon dioxide content of the solution was then determined.

A gas mixture containing 2.6% carbon dioxide and 97.4% nitrogen was prepared in the following manner. A high pressure gas cylinder (1.5 cubic feet in volume) was evacuated by means of a water aspirator. Sufficient nitrogen was then added to the cylinder to give a pressure gauge reading of 20 lbs. Next approximately 14 lbs. of carbon dioxide were added and then nitrogen until the gauge reading was 500 lbs. The solution was throughly mixed by simultaneous heating one end of the cylinder and cooling the other for four hours. The gas was analyzed for carbon dioxide. From this analysis the balance of nitrogen necessary to give a 2.6% carbon dioxide mixture was calculated. After this addition of nitrogen the gas was mixed as before and analyzed. Since the concentration of carbon dioxide in the mixture was specified to be 2.60 ± .05%, it was necessary always to add a slight excess of this gas to the original mixture and then adjust the concentration upon the basis of analysis because mechanical gauges do not permit this degree of accuracy.

The apparatus employed for determining the capacities of the amine solutions is shown in Figure 1. The gas mixture consisting of 2.6% carbon dioxide in nitrogen flowed through 1/4 inch rubber tubing to saturator A which contained 2.5 M diethyleneglycol solution. Here the gas was saturated with water vapor at room temperature over a solution containing approximately the same mole fraction of water as the amine solutions. Since the amines in scrubbers D were held at 85°F., approximately room temperature, dilution or concentration of the amine was avoided by this means. From scrubber A the gas passed by way of manifold B into tubes D, each containing 75 ml. of the 2.5 N amine solution to be tested. The rate at which the gas passed through each solution was adjusted to approximately 300 cc. per minute by adjusting the screw clamps

FIGURE 1.

APPARATUS FOR DETERMINING THE CARBON DIOXIDE CAPACITIES OF AMINE SOLUTIONS.



A. Water saturator consisting of a 300 ml. container equipped with a fritted dispersion tube.
B. Gas manifold constructed of 1/4" copper tubing.
C. Rubber tubing connections fitted with screw clamps.
D. Scrubbers consisting of 150 ml. test tubes equipped with fritted gas dispersion tubes.
E. Carry over tubes constructed of 1/4" glass tubing.
F. Vapor traps.
G. Gas outlet points.
H. Water Bath held at 85° ± 0.5°F.

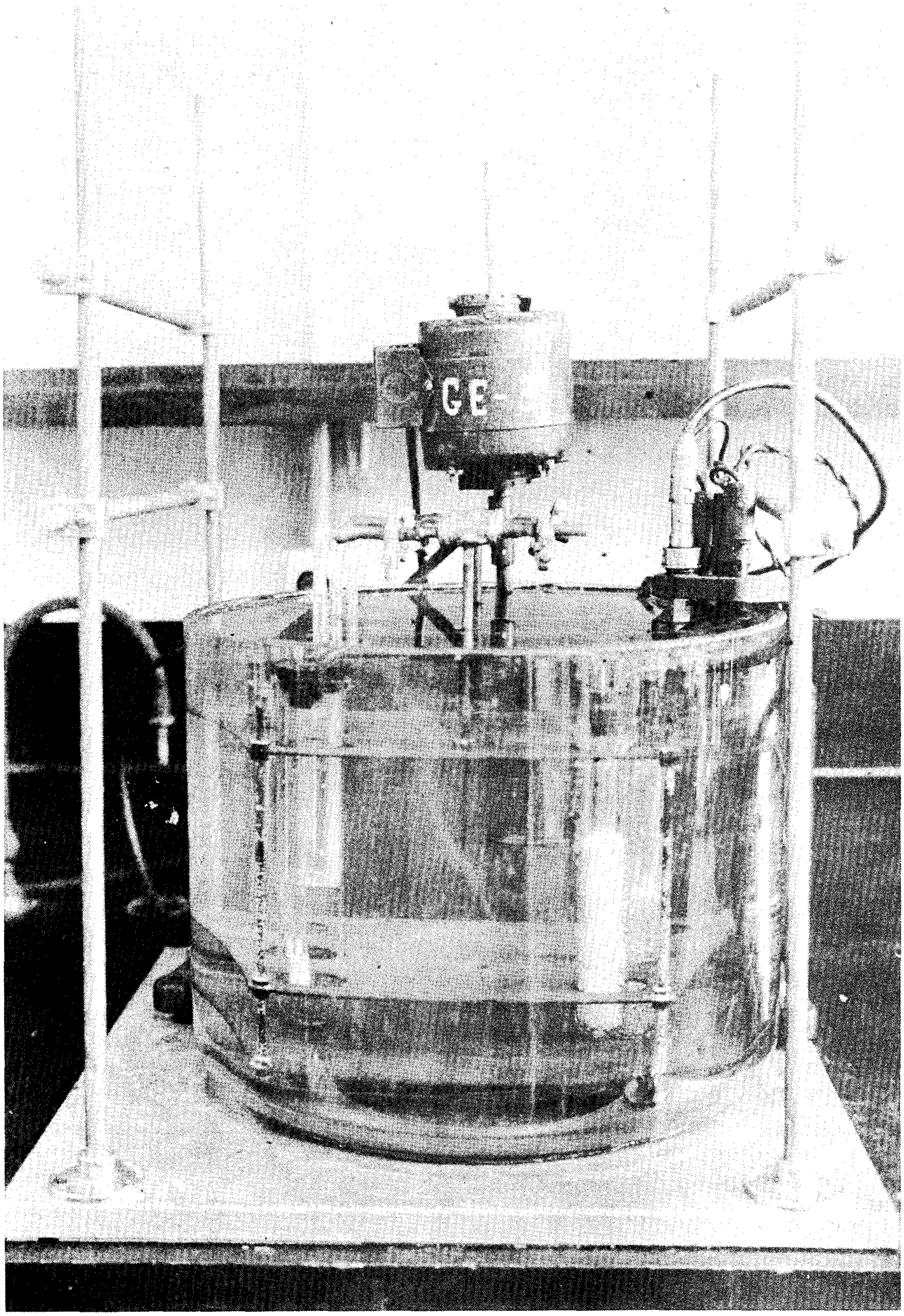


FIGURE 2

at C. The gas and solution were contacted by means of coarse fritted gas dispersion tubes . Upon leaving the amine solution tubes the gas passed by way of tubes E to traps F. All tubes and traps were below the liquid level in bath H. This was to prevent any water which might condense from the gas from refluxing into the tubes and was an added precaution against dilution of the amine solution.

Periodically the gas at the outlets G was analyzed for carbon dioxide. While the gas was being sampled at the outlet, its rate through the amine solution was reduced to 100 cc. per minute to prolong contact time between the solution and the gas. When the outlet and inlet gas compositions were identical, the solution was removed from the tubes and submitted for analysis for carbon dioxide concentration. The alkalinity of the solutions was determined before and after saturation to insure a constant alkalinity.

## C. Analytical Methods

### (1) Analysis of the gas mixture for carbon dioxide concentration.

The gas mixture was passed at a rate of approximately 100 cc. per minute through a train arranged in the following order.

a. A 50 ml. bulb containing anhydrous magnesium perchlorate for the removal of water vapor.
b. A weighed 50 ml. bulb containing ascarite, which removes carbon dioxide from gases.
c. A wet test meter.

When approximately 6 liters of nitrogen had passed, as observed from the wet test meter reading, the ascarite bulb was reweighed on an analytical balance. The percent of carbon dioxide present in the gas was calculated in the following manner:

$$\% \, CO_2 = \frac{\text{Volume of } CO_2 \text{ in liters at S.C. x 100}}{\text{Volume of nitrogen in liters (corrected)} + \text{volume of } CO_2 \text{ in liters at S.C.}}$$

S.C. = 0°C. and 760 mm. of Hg.

$$\text{Volume in liters of } CO_2 = \frac{\text{gain in weight of ascarite x 22.4}}{44}$$

### (2) Analysis of the amine solution for carbon dioxide concentration.

This analysis was carried out by Standard Method SM-5 (See Appendix). Essentially, this procedure consists of acidifying a one ml. sample of the solution being tested with phosphoric acid, which liberates carbon dioxide from the amine solution. The evolved carbon dioxide is measured in a burette and this volume corrected to standard conditions.

### (3) Analysis of the amine solutions for alkalinity.

This determination was carried out by the "Free Amine Analysis" which is described in detail in Girdler Report No. T2.15-1-30 under "Analytical

Methods", Section 1. It consists of titrating 1 ml. of the amine solution with standard N/10 sulfuric acid using methyl red as the indicator.

D. Experimental Data

Table I presents the results obtained for the carbon dioxide capacities of the amines investigated at 85°F. and at a $CO_2$ partial pressure of 19 mm. of Hg (equivalent to 2.6% carbon dioxide at one atmosphere). The carbon dioxide capacities are expressed in volumes of carbon dioxide at standard conditions (0°C. and 760 mm. of Hg) per volume of solution at room temperature. The identification numbers of the amines are also given. These numbers correspond to those assigned each compound in Girdler Report No. T2.20-2-2 from which the physical properties of the amines may be obtained. The pH of the 2.5 N amine solution is at 25°C. These values were taken from Girdler Report No. T2.28-1-1.

TABLE I.

| Amine | Identification No. | pH of pure solution(25°C.) | Carbon Dioxide Capacity at 85°C. and 19 mm. $CO_2$ pressure (V at S.C./V) |
|---|---|---|---|
| 1. Monoethanolamine | 111 | 12.1 | 30.0 |
| 2. Diethanolamine | 133 | 11.6 | 24.8 |
| 3. Triethanolamine | 143 | 11.2 | 3.7 |
| 4. Isobutanolamine | 120 | 11.8 | 26.2*<br>26.4 |
| 5. 2-amino 2-methyl 1-propanol | 124 | 12.2 | 33.1 |
| 6. Diethyleneglycolamine[2] | 122 | 11.9 | 29.7 |
| 7. dlαAlanine (K salt) | | 13+ | 29.3 |
| 8. Methyl diethanolamine | 145 | 11.7 | 12.9<br>13.1* |
| 9. Ethyl diethanolamine | 144 | 11.8 | 14.7 |
| 10. Butyl diethanolamine | 146 | 11.2 | 6.8 |
| 11. 2(2-dimethyl amino) ethoxy ethanol | 148 | 11.8 | 15.4 |
| 12. Diethyl amino ethanol | 142 | 12.1 | 34.0 |
| 13. Triisopropanolamine | 147 | 10.5 | 1.6 |
| 14. NN' dimethyl glycine (K salt) | | 13+ | 37.9 |
| 15. Diethyl amino propylamine | 63 | 12.6 | 29.1 |
| 16. Amino ethyl morpholine | 240 | 11.8 | 28.3 |
| 17. Sharples Mixed Ethyl Ethanolamines #161 | 2M | 11.8 | 23.3 |
| 18. 50% (by wt.) methyldiethanolamine - 50% diethanolamine | 145<br>133 | 11.8 | 19.1 |
| 19. 50% methyl diethanolamine<br>50% diethyleneglycolamine[1] | 145<br>122 | 11.9 | 22.0 |
| 20. 25% methyl diethanolamine<br>75% diethyleneglycolamine[1] | 145<br>122 | 12.0 | 26.0 |

* Approached from the supersaturated side.

[1] Carbide and Carbon Sample.

[2] Dow Sample.

## IV. DISCUSSION:

### A. Evaluation of Results

The analytical method employed for determining the carbon dioxide concentration in the gas mixtures gives precision of the order of 2 parts per thousand.

The method used for determining the carbon dioxide concentration in the solution is probably accurate only to within five percent, since the instrument employed may be read only to within 0.5 V/V. However, such results are well within the degree of accuracy necessary to evaluate any amine with respect to capacity.

Table I shows duplicate results for isobutanolamine and methyl diethanolamine. The values indicated by asterisks were determined by approaching equilibrium from the supersaturated side, a standard technique for determining the accuracy of capacity determination. This entails saturating the solution first with pure carbon dioxide. Thus, at the beginning of the test the solution contains a higher concentration of carbon dioxide than its capacity under the conditions of the investigation. The capacity is then determined in the usual manner. Equilibrium is approached when the concentration of carbon dioxide in the outlet gas no longer exceeds that of the inlet gas. The results shown in Table I obtained by the supersaturated method check within analytical error with these obtained by approaching equilibrium from the undersaturated side. This demonstrates that equilibrium was approached in both determinations. This evidence strongly supports the accuracy of the data given in Table I.

### B. Influence of pH on Carbon Dioxide Capacity

It may be seen from Table I that among the primary amines, with the exception of the alkaline salt of $\alpha$-alanine the pH strongly influences the carbon dioxide capacity. Monoethanolamine which has the highest pH also has the highest capacity. Isobutanolamine which has the lowest pH also has the lowest capacity. The tertiary amines as a group have lower capacities than the primary or secondary amines in the same pH range. For example, ethyl diethanolamine (tertiary) with a pH of 11.8 has a carbon dioxide capacity of 14.7 while isobutanolamine (primary) with the same pH value shows a capacity of 26.2. Diethyl amino ethanol is an exception to this rule. This tertiary amine with a pH of 12.1 has a capacity exceeding that of monoethanolamine which showed the same pH value.

It may be seen from the data for tertiary amines that within this group the pH of the solution greatly influences the carbon dioxide capacity of the solution. Diethylamino ethanol which shows the highest pH value also shows the highest capacity. Triisopropanolamine with the lowest pH value has the lowest capacity. Diethanolamine was the only secondary amine investigated. Therefore, no definite statement may be made as to the relationship of pH and capacity on this group of compounds. However, diethanolamine seems to compare favorably with the primary amines of similar pH.

The only polyamines tested were diethyl amino propylamine and amino ethyl morpholine. These compounds both contain a primary and a tertiary amino group. Although 2.5 N solutions of these compounds contain only 1.25

equivalents of primary amine, they have capacities in the range of the primary amines. The effect of the tertiary group is apparent in the case of diethyl amino propylamine which has a pH of 12.6 and would, therefore, be expected to have a capacity of 35 V/V at S.C. or more if all the amine present were primary.

The mixtures do not fall into any definite pattern relating carbon dioxide capacity and pH. The capacity of each of these mixtures is largely dependent upon the capacities of their components and their ratio present.

### C. Selection of Amines for Further Study

It may be readily observed from the data presented in Table I that triethanolamine, butyl diethanolamine, and triisopropanolamine have capacities which compare very unfavorably with any of the other amines studied. Triethanolamine, however, will be studied in detail because of the design data which is available on this amine. Butyl diethanolamine has a strong butyric-like odor in addition to a low capacity. These two properties render this compound undesirable for the purpose intended. Therefore, it will be eliminated from further studies. Triisopropanolamine possesses an extremely low capacity of 1.6 V/V at S.C. Such a capacity would render the use of this amine entirely uneconomical. Therefore, other properties of this compound will not be investigated. Further studies will be carried out on the remaining amines and mixtures of amines.

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jc

Report No. T2.11-3-1

THE GIRDLER CORPORATION
GAS PROCESSES DIVISION
PROCESS DEVELOPMENT AND RESEARCH LABORATORIES
LOUISVILLE, KENTUCKY

# THE RELATIVE CARBON DIOXIDE ABSORPTION RATES OF AMINES RESISTANT TO OXIDATION.

May 22, 1950

Work by:

R. C. Kindrick
Kenton Atwood
M. R. Arnold

Report by:

R. C. Kindrick

## Sentence Summary

The relative carbon dioxide absorption rates of 14 amines and 4 mixtures of amines have been determined.

## I. INTRODUCTION:

The purpose of the present series of investigations is the selection of an amine to be employed in a cyclic process for the removal of carbon dioxide from submarine atmospheres. In Girdler Report Nos. T2.15-1-30 and T2.11-3-2 ten amines and four mixtures of amines were selected as being relatively resistant to oxidation and having carbon dioxide capacities suitable for this purpose. Other properties of these solutions will be compared with monoethanolamine, diethanolamine, and triethanolamine. On the basis of these studies one or more will be recommended for the removal of carbon dioxide from submarine atmospheres.

The purpose of the present investigation is to compare the rates at which carbon dioxide is absorbed by these amine solutions from a gas stream containing a concentration of carbon dioxide similar to that found in submarine atmospheres and at the temperature which would probably be employed in the absorber.

## II. SUMMARY AND CONCLUSIONS:

(1) The relative carbon dioxide absorption rates of 14 amines and 4 mixtures of amines have been determined and compared to monoethanolamine, diethanolamine, and triethanolamine.

(2) Tertiary amines, regardless of the pH of their aqueous solutions, absorb carbon dioxide at a relatively slower rate than do primary and secondary amines. A reaction mechanism has been proposed to explain this phenomenon.

(3) Straight-chain primary amines as a general rule have a greater carbon dioxide absorption rate than highly branched compounds.

## III. INVESTIGATIONAL PROCEDURE AND EXPERIMENTAL DATA:

### A. Source of Reagents.

See Report No. T2.20-2-2.

### B. Procedure.

Essentially, the procedure followed consisted in passing a gas mixture containing 2.6% carbon dioxide and 97.4% nitrogen through 50 ml. of a 2.5 N amine solution at a rate of 500 cc./min. for specified lengths of time at 85°F. The solution was then analyzed for carbon dioxide concentration.

A diagram of the apparatus employed is shown in Figure 1. A gas mixture containing 2.60 ± .05% carbon dioxide was prepared in high pressure cylinders according to the directions found in Girdler Report No. T2.11-3-2. Tube E contained exactly 50 ml. of the 2.5 N amine solution to be investigated. This container consisted of a test tube 2.89 cm. in diameter and 20 cm. in height. It was fitted with a 2-hole rubber stopper equipped with gas inlet tube F. This inlet tube was constructed of capillary tubing the outer diameter of which measured 7.11 mm. and the inner diameter 1.58 mm. The tip of the tube was ground so that the surface was at right angles to the walls of the tube. The stopper was fitted into tube E so that inlet tube F extended parallel to the walls of the test tube to an immersion depth of 6.66 cm. in the solution. Tube C contained 50 ml. of water. This tube was approximately of the same design

## LEGEND

A. Flow meter.

B. Pinch clamp.

C. By pass.

D. Pinch clamp.

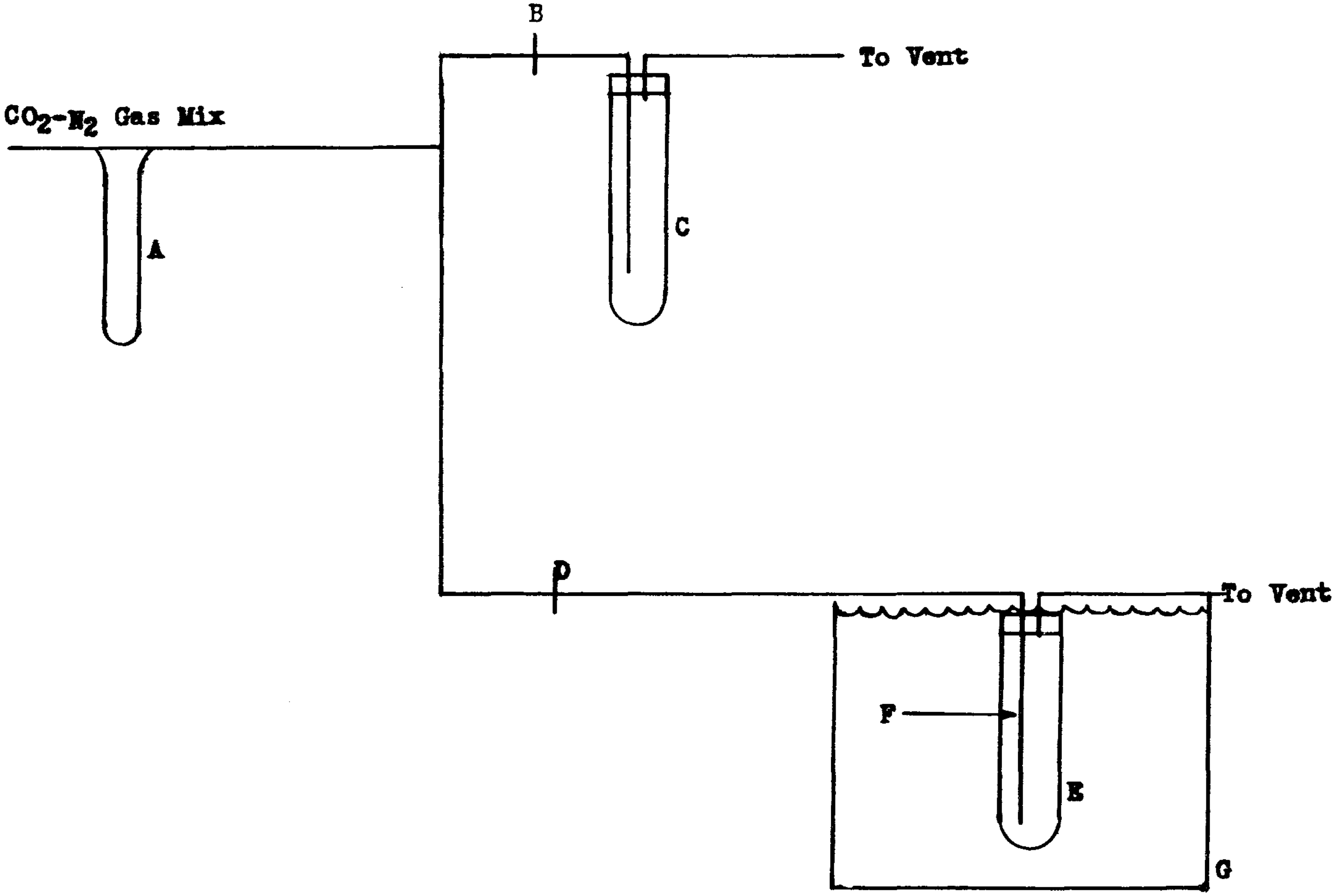
E. Test tube 2.89 cm. in diameter and 20 cm. in height.

F. Gas inlet tube of outer diameter 7.11 mm. and inner diameter 1.58 mm. immersed in solution to a depth of 6.66 cm.

G. Water bath.

FIGURE 1.

APPARATUS FOR DETERMINING THE RELATIVE $CO_2$ ABSORPTION RATES OF AMINE SOLUTIONS.



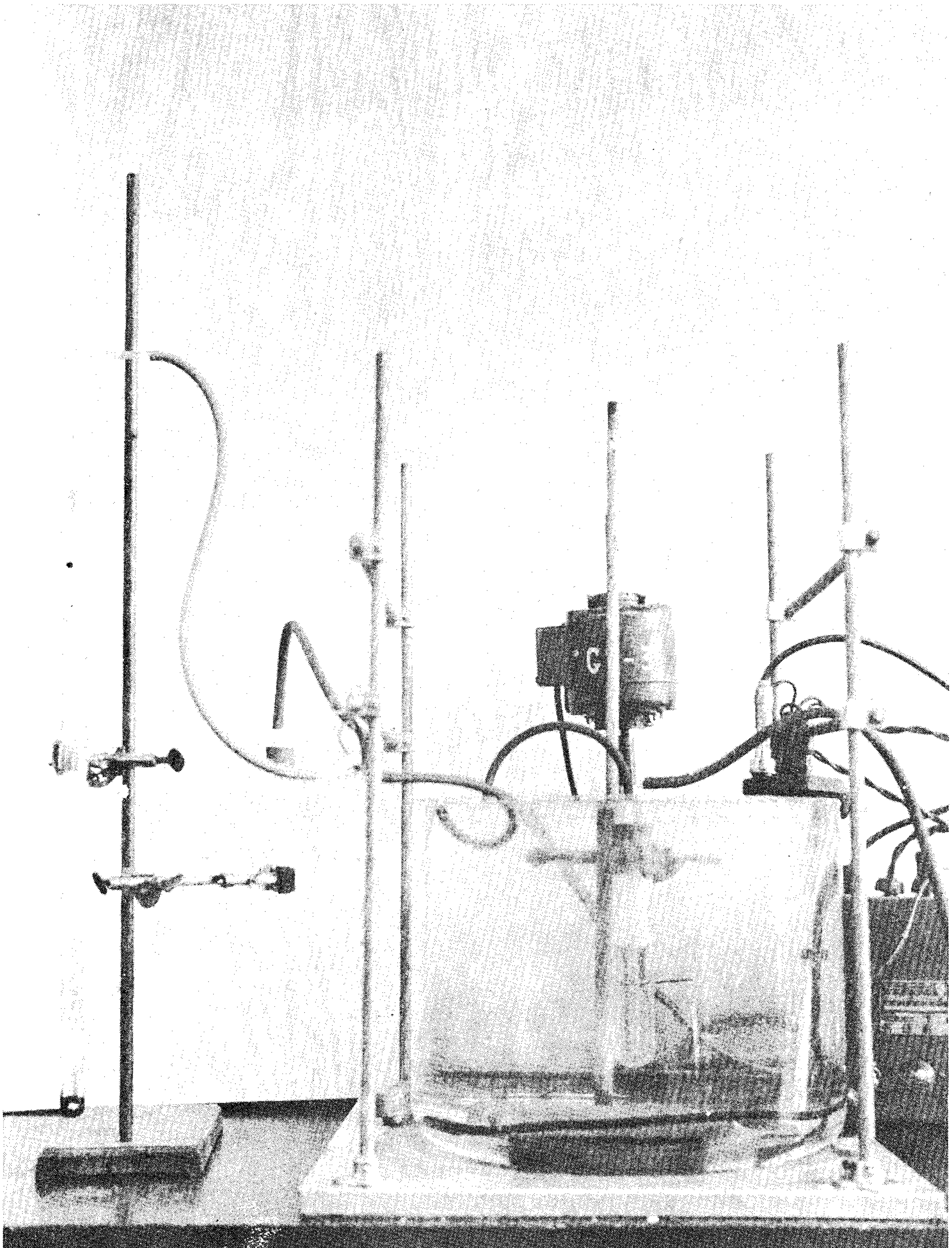


FIGURE 2

as tube E and served as a by-pass for the adjustment of the gas rate. The gas rate was measured by flowmeter A. The apparatus was assembled as shown in Figures 1 and 2.

While the gas rate was being adjusted to 500 cc./min., clamp D was closed and clamp B opened. Next, clamp B was closed and clamp D opened allowing the gas mixture to flow into tube E containing the amine solution. The gas rate was maintained at 500 ± 10 cc./min. throughout the test. After twenty minutes the amine solution was removed from the tube and submitted for analysis for carbon dioxide concentration.

A fresh charge of 50 ml. of amine was then added to tube E and the above procedure repeated allowing the gas to contact the amine solution for 40 minutes. This same procedure was repeated allowing contact for 60, 90, 120, and 180 minutes.

## C. Analytical Methods.

### (1) Analysis of the gas mixture for carbon dioxide.

This analytical method used in this determination is described in detail in Girdler Report No. T2.11-3-2. Essentially, this procedure consisted of passing the gas through a train composed of a bulb containing magnesium perchlorate for the removal of moisture, a weighed ascarite bulb for the absorption of carbon dioxide and a wet test meter for measuring nitrogen. From the gain in weight of the ascarite bulb and the volume of nitrogen the concentration of carbon dioxide was calculated.

### (2) Analysis of the solution for carbon dioxide concentration.

The method employed in this determination is described in detail in Standard Method, SM-5 (See Appendix). Essentially it consisted in acidifying 1 ml. of the amine solution with phosphoric acid and measuring the liberated carbon dioxide by means of a gas burette.

## D. Experimental Data.

Table I gives the results obtained for the relative absorption rates of the 2.5 N solutions of the primary and secondary amines tested. The identification number is taken from Report No. T2.20-2-2 which gives the physical properties of the compounds. The pH of the solutions at 25°C. is taken from Report No. T2.28-1-1. The concentration of carbon dioxide in the solutions is given in volumes of carbon dioxide at standard conditions (0°C. and 760 mm. of Hg.) per volume of solution at room temperature (V/V at S.C.). Solutions were contacted with 2.6% carbon dioxide in the standard apparatus described above for 20, 40, 60, 90, 120, and 180 minutes. Curves plotted from these data are shown in Graph I.

## TABLE I.

## THE RELATIVE CARBON DIOXIDE ABSORPTION RATES OF AMINE SOLUTIONS.

| Amine | Identification No. | pH of 2.5N Solution | Concentration of $CO_2$ in Soln. V/V at S.C. 20 min. | 40 min. | 60 min. | 90 min. | 120 min. | 180 min. |
|---|---|---|---|---|---|---|---|---|
| Monoethanolamine | 111 | 12.1 | 4.0 | 7.3 | 11.4 | 17.2 | 21.9 | - |
| | | | 3.5 | 7.0 | 12.1 | 17.1 | 22.0 | - |
| Diethyleneglycolamine | 122 | 12.0 | 2.9[1] | 6.5 | 10.9 | 16.0 | 21.0 | - |
| | | | 2.3[2] | 5.3 | 8.5 | 12.5 | 15.5 | 22.5 |
| Diethylaminopropylamine | 63 | 12.1 | 2.7 | 6.2 | 9.9 | 15.0 | 19.1 | - |
| K salt of $\alpha$-alanine | | 13+ | 3.1 | 6.2 | 10.0 | 13.7 | 17.9 | - |
| Amino ethyl morpholine | 240 | 11.8 | 2.6 | 5.8 | 8.9 | 13.7 | 17.7 | 23.0 |
| Isobutanolamine | 120 | 11.8 | 2.6 | 5.6 | 8.2 | 12.1 | 15.8 | - |
| Diethanolamine | 133 | 11.6 | 2.9 | 6.2 | 8.4 | 12.4 | 15.4 | - |
| 2-amino-2-methyl-1-propanol | 124 | 12.2 | 2.4 | 4.4 | 6.2 | 9.7 | 12.8 | - |
| Methyl diethanolamine | 145 | 11.8 | 0.70 | 1.7 | 2.2 | 3.0 | 3.7 | - |
| Diethyl amino ethanol | 142 | 12.1 | 0.51 | 1.1 | 1.6 | 2.8 | 3.5 | - |
| 2(2-dimethyl amino ethoxy)ethanol | | 11.8 | 0.22 | 0.52 | 0.87 | 1.8 | 2.4 | - |
| Ethyl diethanolamine | 144 | 11.8 | 0.22 | 0.33 | 0.62 | 1.4 | 1.9 | - |
| NN'dimethyl glycine (K salt) | | 13+ | 0.30 | 0.60 | - | 1.4 | 1.9 | - |
| Triethanolamine | 143 | 11.2 | 0.17 | 0.25 | 0.31 | 0.64 | 1.2 | - |
| Sharples mixed ethyl ethanolamines #161 | 2M | 11.8 | 2.4 | 5.8 | 8.0 | 11.7 | 14.8 | 18.7 |
| 50% ethyl diethanolamine | 144 | 12.0 | 2.6[1] | 6.1 | 9.2 | - | 16.1 | 19.6 |
| 50% diethyleneglycolamine | 122 | | 1.4[2] | 4.1 | 6.3 | 9.2 | 11.8 | 15.2 |
| 25% methyl diethanolamine | 145 | 12.0 | 2.3[2] | 5.0 | 7.5 | 11.6 | 14.8 | 20.1 |
| 75% diethyleneglycolamine | 122 | | | | | | | |
| 50% methyl diethanolamine | 145 | 11.7 | 1.6 | 3.4 | 5.7 | 7.9 | 10.6 | 15.3 |
| 50% diethanolamine | 122 | | | | | | | |

(1) Dow sample of diethyleneglycolamine.
(2) Carbide and Carbon sample of diethyleneglycolamine.

## IV. DISCUSSION:

### A. Evaluation of Data.

Graph I shows curves drawn from the data contained in Table I. The concentrations of carbon dioxide in the solution in V/V at S.C. are presented versus contact time in minutes. The actual values from Table I from which these curves were plotted are not shown since several of the curves are very close together. All of these data are shown in the same graph to facilitate comparison.

The method employed in this investigation for the determination of the carbon dioxide concentration in the amine solution is accurate only to within 0.5 V/V at S.C. However, when the curves in Graph I are compared, it is obvious that errors of this magnitude are insignificant in evaluating an amine with respect to its relative absorption rate. In Table I duplicate results are given for the absorption rate of monoethanolamine. The averages of these two results in each case are within the range of analytical error. These two determinations were carried out on duplicate pieces of apparatus meeting the specifications described above. It is possible therefore, to duplicate these results if equipment of precisely this design is employed. Consequently, the method used is considered adequate for determining the relative absorption rates of amines. Duplicate results are also shown in Table I for diethyleneglycolamine and for a mixture of 50% methyl diethanolamine and 50% diethyleneglycolamine. The first determination shown was carried out on a sample from the Dow Chemical Company. This sample was probably partially decomposed, since it had been received several years ago. The higher rates indicate that this sample may have contained some monoethanolamine as a decomposition product. The second results were obtained on a fresh sample from Carbide and Carbon and are probably more reliable.

It should be emphasized that these rates are only relative. A slight difference in solution height, gas rate, or type of gas to solution contact will give different results. However, it is probable that under any other given set of conditions the rates at which carbon dioxide will be removed at 85°F. from a gas containing 2.5% carbon dioxide by the 2.5 N solutions will have a similar relationship. By comparing these relative rates of absorption in standard apparatus with those for monoethanolamine, diethanolamine, and triethanolamine for which design data are available, the type of absorber design best suited to these amines may be determined.

### B. Relative Absorption Rates of Amines.

It may be observed from the data contained in Table I and the graphical presentation of this data shown in Graph I that the tertiary amines have relatively slow carbon dioxide absorption rates. The rate of absorption of carbon dioxide by primary and secondary amines seems to depend largely on the structure of the individual compound. The rate at which all of these compounds absorb carbon dioxide is not markedly dependent on the pH of the solution. For example a 2.5 N solution of diethyl amino ethanol has a pH of 12.1, comparable with that of monoethanolamine. However, the reaction rate of carbon dioxide with the tertiary amine solution (See Graph I) is approximately 20% of that of the primary amine. It might be assumed that the high pH of the diethyl amino ethanol solution resulted from the presence of traces of impurities. However, this assumption was disproved by comparing the pH values of solutions of monoethanolamine and diethyl amino ethanol containing various amounts of carbon dioxide.

The results are shown in the following table:

| Contact Time in Minutes | Diethyl Amino Ethanol | | Monoethanolamine | |
|---|---|---|---|---|
| | $CO_2$, V/V at S.C. | pH (25°C.) | $CO_2$, V/V at S.C. | pH (25°C.) |
| 20 | .05 | 11.4 | 4.0 | 10.8 |
| 40 | 1.1 | 11.3 | 7.3 | 10.7 |
| 60 | 1.6 | 11.2 | 11.4 | 10.5 |
| 90 | 2.8 | 11.03 | 17.2 | 10.15 |
| 120 | 3.5 | 11.02 | 21.9 | 9.75 |

From these data it is obvious that impurities did not influence the pH of the original diethyl amino ethanol to any appreciable extent since had such been the case, after the first addition of carbon dioxide, the pH of the solution would have dropped sharply. Moreover, it demonstrates that the pH is not the controlling factor, since after 90 minutes monoethanolamine solution with a low pH of 10.15 was still absorbing carbon dioxide at approximately the same rate as the original solution with a pH of 12.1

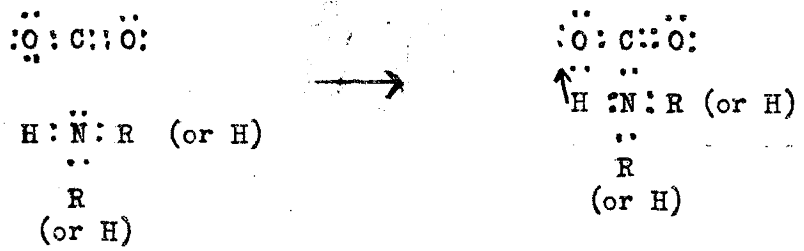
From these data it appears that the basicity of the solution does not alone determine its rate of carbon dioxide absorption. The great difference between the rates of absorption for the primary and secondary amines on the one hand, and tertiary amines on the other, therefore suggests that there may be a difference in the reaction mechanisms for these types of amines.

Anhydrous ammonia, for example, is known to react with carbon dioxide in the following manner:

$$CO_2 + NH_3 = CO(OH)NH_2 \quad \text{(Carbamic acid)}$$

$$CO(OH)NH_2 + NH_3 = CO(ONH_4)NH_2$$

This product, ammonium carbamate, reacts with water to form ammonium carbonate, and in aqueous solutions of carbon dioxide and ammonia an equilibrium between carbonate, bicarbonate, and carbonate exists. Anhydrous primary and secondary amines are known to undergo analogous reactions. The reaction between either ammonia, a primary amine, on a secondary amine and carbon dioxide could be quite rapid, as indicated by the following electronic structures:



After the nitrogen atom shares an electron pair with the carbon atom only a proton shift is required to form the indicated product. The electron structure for carbon dioxide is not the one normally given, $:\ddot{O}::C::\ddot{O}:$, but is thought to be one of the resonance forms. This reaction could not take place between carbon dioxide and tertiary amines, since these amines lack an active hydrogen.

From Table I and Table II it may be seen that the position of the amino groups influences the reaction rates of primary and secondary amines. Monoethanolamine and diethyleneglycolamine are straight chain compounds. The position of the amino group renders it relatively free to react rapidly. Likewise the primary amino group in diethyl amino propylamine is relatively uninhibited. The effect of steric hindrance becomes very marked in the case of 2-amino-2-methyl-1-propanol. Here, the amino group is attached to a tertiary carbon atom and the amino group is not free to react so readily as in the case of the straight chain compounds.

It should be observed that a mixture of 75% diethylenglycolamine and 25% methyl diethanolamine gave only a very slightly lower rate than diethyleneglycolamine alone when the Carbide and Carbon sample was used in both cases. Thus the pure diethyleneglycolamine has no great advantage over the 75-25 mixture as far as absorption rate is concerned until the solution approaches its capacity. However, there is a substantial drop in absorption rate when the diethyleneglycolamine concentration is reduced to 50% in the mixture.

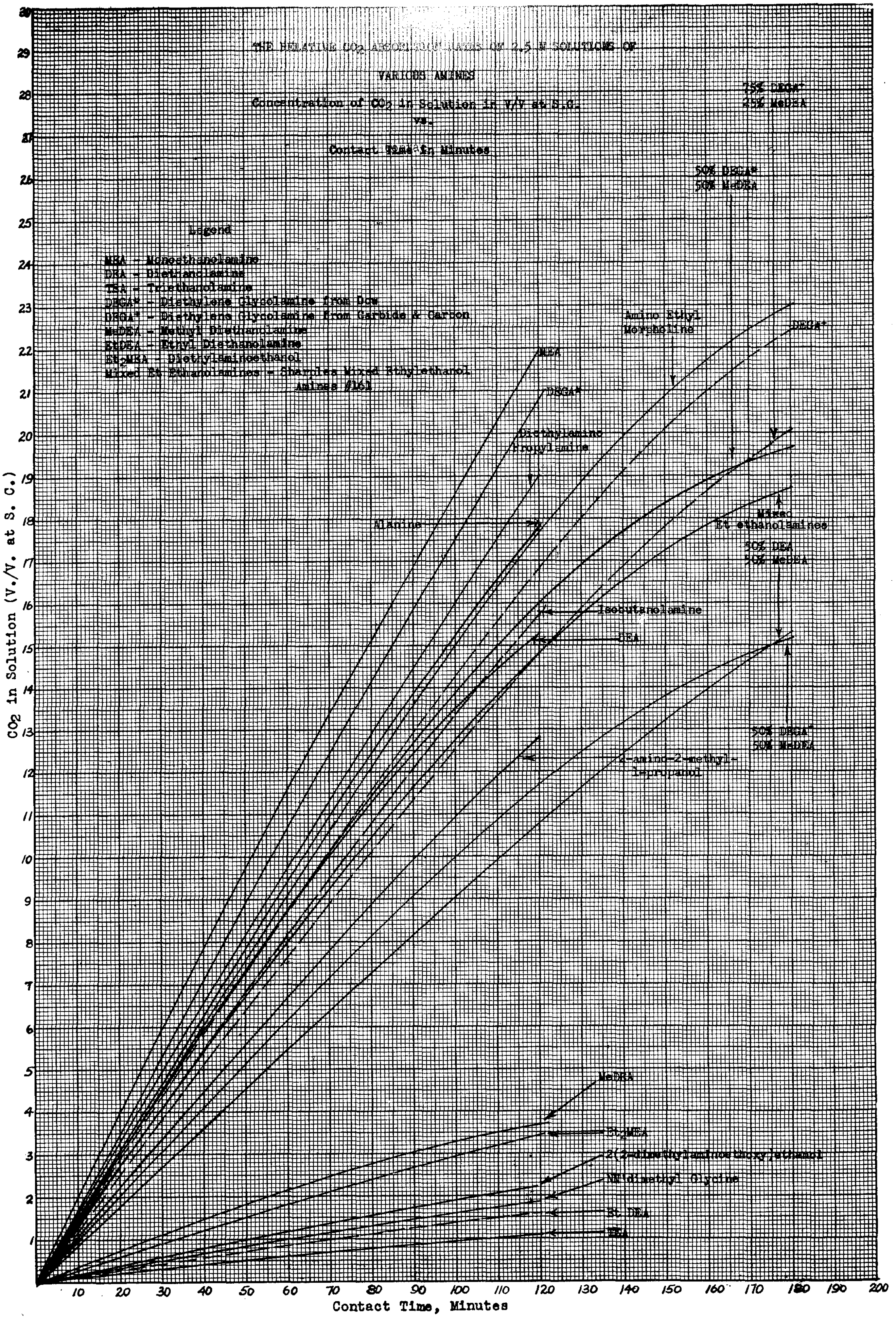
It may be observed from Graph I that the absorption rate of the alkaline salt of NN' dimethyl glycine is extremely low. This compound has been used for the selective removal of hydrogen sulfide from gas streams containing carbon dioxide. These results confirm the supposition that such a process was based on a low carbon dioxide absorption rate. All of the amines and mixtures other than this one will be subjected to further study.

REPORT BY: ______________________ DATE: ____________

READ AND UNDERSTOOD BY: ______________________ DATE: ____________

Distribution:

T.F., P.F., P.D.F., U.O.F., R.E.R., M.R.A., R.C.K.


THE RELATIVE CO2 ABSORPTION RATES OF 2.5 N SOLUTIONS OF
VARIOUS AMINES
Concentration of CO2 in Solution in V/V at S.C.
vs.
Contact Time in Minutes
Legend
MEA - Monoethanolamine
DEA - Diethanolamine
TEA - Triethanolamine
DEGA* - Diethylene Glycolamine from Dow
DEGA+ - Diethylene Glycolamine from Carbide & Carbon
MeDEA - Methyl Diethanolamine
EtDEA - Ethyl Diethanolamine
Et2MEA - Diethylaminoethanol
Mixed Et Ethanolamines - Sharples Mixed Ethylethanol Amines #161
75% DEGA*
25% MeDEA
50% DEGA*
50% MeDEA
Amino Ethyl Morpholine
DEGA+
MEA
DEGA*
Diethylamino Propylamine
Alanine
Mixed Et ethanolamines
50% DEA
50% MeDEA
Isobutanolamine
DEA
50% DEGA+
50% MeDEA
2-amino-2-methyl-1-propanol
MeDEA
Et2MEA
2(2-dimethylaminoethoxy)ethanol
NN dimethyl Glycine
Et DEA
TEA
CO2 in Solution (V./V. at S. C.)
1
2
3
4
5
6
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110
120
130
140
150
160
170
180
190
200
Contact Time, Minutes

Report No. T2.28-1-1

THE GIRDLER CORPORATION
GAS PROCESSES DIVISION
PROCESS DEVELOPMENT AND RESEARCH LABORATORIES
LOUISVILLE, KENTUCKY

# THE pH OF AMINE SOLUTIONS AT 25°C. AND 90°C.

May 23, 1950

| Work by: | Report by: |
|---|---|
| R. C. Kindrick | R. C. Kindrick |
| Kenton Atwood | Kenton Atwood |
| M. R. Arnold | M. R. Arnold |

## Sentence Summary

The pH of forty-three 2.5 N solutions of amines at 25°C. and seventeen 2.5 N solutions at 90°C. has been determined.

## I. INTRODUCTION:

Approximately forty compounds which are commercially available were selected in the literature survey, Girdler Report No. T2.20-2-2, for possible use as absorbents for the removal of carbon dioxide from submarine atmospheres. In the present investigation the pH of 2.5 N solutions of these compounds and certain of their mixtures was determined at 25°C. In addition determinations of pH at 90°C. were made on some of the solutions which have been selected on the basis of other laboratory studies as being best qualified for the intended use. (See Girdler Report Nos. T2.15-1-30, T2.11-3-2 and T2.11-3-1).

Information on the pH of basic solutions is helpful in evaluating the application of the solutions for the removal of carbon dioxide. The pH of either a primary, secondary, or tertiary amine solution at 25°C. predicts within reasonable limits the relative capacity of that solution for the absorption of carbon dioxide under conditions approaching those employed in the absorber in plant operation. It was decided that any solutions having a pH of less than 10 at 25°C. were to be eliminated from further study since these solutions undoubtedly would have low carbon dioxide absorption capacities.

The pH of the solutions at 90°C. may aid in predicting within reasonable limits the relative energy or steam requirements for reactivation of the solution in plant operation in which step the carbon dioxide is desorbed from the solution at elevated temperatures.

## II. SUMMARY:

1. The pH at 25°C. has been determined for forty-three 2.5 N amine solutions. All these solutions show pH values above 10 and were, therefore, accepted as possible absorbents for carbon dioxide.

2. The pH at 90°C. has been determined for seventeen 2.5 N amine solutions.

3. These values will be employed in the correlation of other data.

## III. INVESTIGATIONAL PROCEDURE AND EXPERIMENTAL DATA:

### A. Procedure.

The 2.5 N solutions to be tested were prepared according to the procedure discussed in Girdler Report No. T2.15-1-30. All pH determinations were conducted using a Beckman pH meter. (Model G). Calomel Electrode 270 and Glass Electrode 290 E were employed in the pH determinations made at 25°C. This glass electrode is designed for pH measurements above 9 and sodium ion corrections are unnecessary. Five ml. samples were required. Eimer and Amend Standard Buffer Solution pH 10.00 ± .02 was employed as a standard for instrument adjustment. In the determination of the pH of solutions at 90°C. Beckman Glass Electrode No. 8990TA and Beckman Calomel Electrode No. 8970TA were employed. These electrodes are designed for pH measurements over a temperature range of 50-90°C. A buffer solution containing 12.49 gms. of boric acid per liter of exactly .1000 N sodium hydroxide solution (carbonate free) was used as a standard. By the extrapolation of data from The International Critical Tables (First Edition), Volume 1, p. 82, the pH of this solution was estimated to be 8.8 at 90°C. A sodium ion correction of +0.2 pH units was applied to this value using equations found in Dole, The Glass Electrode, New York, John Wiley and Sons, 1941, p. 158. A temperature correction of 0.4 pH units was also applied (See The National Technical Laboratories Bulletin, No. 58-B.) Thus the instrument setting at 90°C. for this standard was estimated to be 9.4 pH units.

One hundred ml. of the solutions to be investigated were employed. The temperature correction factors indicated in The National Technical Laboratories Bulletin No. 58-B were applied to the instrument reading obtained in each determination. Since none of the solutions tested contained appreciable concentrations of sodium ion this error was considered negligible. The temperature was controlled at 90 ± 0.5°C.

B. Experimental Data.

Table I shows the pH obtained at 25°C. for the 2.5 N amine solutions investigated. The identification number from Girdler Report No. T2.20-2-2 is given for each compound. From this report the physical properties of the amine may be obtained.

TABLE I.

| Amine | Identification Number | pH of 2.5 N Solution at 25°C. |
|---|---|---|
| Isobutanolamine | 120 | 11.8 |
| Hexanolamine | 125 | 13+ |
| 2-amino-2-methyl-1-propanol | 124 | 12.2 |
| 4-amino-2-butanol | 119 | 12.7 |
| 2-amino-2-methyl-1,3-propandiol | 121 | 11.0 |
| Tris(hydroxy methyl) amino methane | 123 | 12.4 |
| Diethyleneglycolamine | 122 | 11.9 |
| Monoisopropanolamine | 117 | 12.2 |
| 2-amino-1-butanol | 118 | 12.1 |
| Monoethanolamine | 111 | 12.1 |
| Tetrahydrofurfurylamine | 247 | 12.2 |
| Benzyl amine | 173 | 11.6 |
| Alkaline Salt of α-alanine | | 13+ |
| Diethanolamine | 133 | 11.6 |
| Ethyl ethanolamine | 132 | 12.5 |
| Methyl ethanolamine | 131 | 12.4 |
| Butyl ethanolamine | 135 | 11.8 |
| Diisopropanolamine | 137 | 11.0 |
| Ethyl diethanolamine | 144 | 11.8 |
| Methyl diethanolamine | 145 | 11.7 |
| Butyl diethanolamine | 136 | 11.2 |
| 2(2-dimethyl aminoethoxy) ethanol | 148 | 11.9 |
| Diethylamino ethanol | 142 | 12.1 |
| Triethanolamine | 143 | 11.2 |
| Triisopropanolamine | 147 | 10.5 |
| Alkaline salt of NN'dimethyl glycine | | 13+ |
| Diethylene triamine | 52 | 12.2 |
| Triethylenetetramine | 53 | 12.2 |
| Tetraethylenepentamine | 54 | 12.1 |
| Diethylaminopropylamine | 63 | 12.6 |
| Diaminoisopropanol | 15 | 11.9 |
| N-hydroxyethyl propylenediamine | 153 | 12.1 |

TABLE I. (Continued)

| Amine | Identification Number | pH of 2.5 N Solution at 25°C. |
|---|---|---|
| N-hydroxyethyl ethylene diamine | 161 | 11.6 |
| 5-amino 2,2,5-trimethyl 3-aza-1-hexanol | 162 | 11.7 |
| 2,5-dimethyl piperazine | 245 | 11.7 |
| NN'-dihydroxyethyl ethylene diamine | 164 | 11.6 |
| Aminoethyl morpholine | 240 | 11.8 |
| 2,4,6-tri(dimethylamino methyl) phenol | 213 | 11.6 |
| Alkaline salt of 2,4,6-tri(dimethylamino methyl) phenol | 213 | 13+ |
| Sharples Mixed ethyl ethanol amines #161 | 2M | 12.3 |
| 50% diethyleneglycolamine | 122 | 11.9 |
| 50% methyl diethanolamine | 145 | |
| 75% diethyleneglycolamine | 122 | 12.0 |
| 25% methyl diethanolamine | 145 | |
| 50% diethanolamine | 135 | |
| 50% methyl diethanolamine | 145 | 11.8 |

Table II presents the data obtained for the pH of 2.5 N amine solutions at 90°C. Also included are values for the pH at 25°C. taken from Table I. The difference between these two values is expressed as pH ($\mathrm{pH}_{25^\circ C} - \mathrm{pH}_{90^\circ C}$).

## TABLE II.

| Amine | pH of 2.5 N Solution at 25°C. | pH of 2.5 N Solution at 90°C. | pH ($pH_{25°C} - pH_{90°C}$) |
|---|---|---|---|
| Isobutanolamine | 11.8 | 10.5 | 1.3 |
| 2-amino-2-methyl-1-propanol | 12.2 | 10.7 | 1.5 |
| Monoethanolamine | 12.1 | 10.6 | 1.5 |
| Alkaline Salt of α-alanine | 13+ | 13+ | - |
| Diethanolamine | 11.6 | 10.2 | 1.4 |
| Methyl diethanolamine | 11.7 | 10.3 | 1.4 |
| Ethyl diethanolamine | 11.8 | 10.5 | 1.3 |
| 2(2-dimethyl aminoethoxy)ethanol | 11.9 | 10.6 | 1.3 |
| Diethylaminoethanol | 12.1 | 11.0 | 1.1 |
| Triethanolamine | 11.2 | 10.1 | 1.1 |
| Diethylaminopropylamine | 12.6 | 10.9 | 1.7 |
| Aminoethyl morpholine | 11.8 | 10.8 | 1.0 |
| Sharples Mixed Ethyl ethanol amines #161 | 12.3 | 10.8 | 1.5 |
| 50% methyl diethanolamine<br>50% diethanolamine | 11.8 | 10.3 | 1.5 |
| 50% Diethyleneglycolamine<br>50% Methyldiethanolamine | 11.9 | 10.6 | 1.3 |
| 75% Diethyleneglycolamine<br>25% Methyl diethanolamine | 12.0 | 10.7 | 1.3 |

## IV. DISCUSSION:

The data shown in Table I for the pH of solutions at 25°C. are probably accurate to within 0.1 pH units. The ionization constant for monoethanolamine is $3.2 \times 10^{-5}$ at 25°C. Assuming the activity coefficients to be unity a pH of 11.9 for a 2.5 N solution may be calculated from this constant. Table I shows a value of 12.1. Considering the fact that technical grade reagents were employed in this investigation, such a deviation of the experimental results from the theoretical value is not unexpected. Since none of the values obtained for the pH of these solutions at 25°C. were below 10 none of these compounds were eliminated from further consideration on this basis.

In determining the pH of solutions at 90°C. it was necessary to obtain the pH of the buffer employed as a standard by extrapolation. Then in order to convert this value to the instrument setting it was necessary to apply correction factors of appreciable magnitude. Therefore, the results given in Table II are probably not accurate to more than 0.5 of a pH unit. However, these results may be considered relative, since the errors involved are probably constant for all determinations.

For most of the solutions the decrease in alkalinity between 25°C. and 90°C. (Table II) was approximately the same. This decrease averaged 1.3 pH units. The change in the ionization constant of water between 25°C. and

90°C. accounts for approximately 0.83 pH unit. Thus, increasing the temperature of these amine solutions did not appear to change the ionization constants of the amines by more than a factor of three or four.

The full significance of the pH values obtained in this investigation will not be discussed in this report since the primary reason for their determination was to aid in the correlation of other data. For detailed correlation of these results with other solution properties the following reports should be consulted: Girdler Report Nos. T2.11-3-1, T2.11-3-2, and T2.12-1-1.

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READ AND UNDERSTOOD BY: ______________________ DATE: ____________

Distribution:

T.F., P.F., P.D.F., U.O.F., R.E.R., M.R.A., K.A., R.C.K.

jc

Report No. T2.12-1-1

THE GIRDLER CORPORATION
GAS PROCESSES DIVISION
PROCESS DEVELOPMENT AND RESEARCH LABORATORIES
LOUISVILLE, KENTUCKY

# THE RELATIVE STEAM REQUIREMENTS FOR REACTIVATION OF AMINES RESISTANT TO OXIDATION.

May 26, 1950

| Work by: | Report by: |
|---|---|
| R. C. Kindrick | R. C. Kindrick |
| Kenton Atwood | Kenton Atwood |
| M. R. Arnold | M. R. Arnold |

## Sentence Summary

The relative steam requirements for 13 amine solutions have been determined and compared to similar requirements for monoethanolamine, diethanolamine, and triethanolamine.

## I. INTRODUCTION:

In Girdler Report Nos. T2.20-2-2, T2.15-1-30, T2.11-2-2 and T2.11-2-1 all materials with the exception of 10 compounds and 4 amine mixtures were eliminated from further consideration as possible absorbents for the removal of carbon dioxide from submarine atmospheres.

The purpose of the present report is to describe the results obtained for the relative energy required for the reactivation of these solutions. As applied to a cyclic process in which carbon dioxide is removed by alkaline solutions, the term "reactivation" is indicative of that step in the process in which carbon dioxide is removed by heat. Since this step is usually carried out by "steam stripping", that is, contacting the solution at its boiling point with steam, the relative energy requirements were determined on the basis of the degree of reactivation or carbon dioxide removal achieved by contacting the solution with various amounts of steam. Since all available design data pertains to monoethanolamine, diethanolamine, and triethanolamine the relative steam requirements for the reactivation of monoethanolamine and diethanolamine were determined in addition to triethanolamine which was one of the materials selected for detailed study. The relative steam requirements for reactivation of the materials investigated were compared to the requirements of these three amines to aid in the design of equipment in which these new materials might be utilized.

## II. SUMMARY AND CONCLUSIONS:

(1) The amines found to be similar to monoethanolamine in steam requirements for reactivation were isobutanolamine, and a mixture composed of 75% diethyleneglycolamine and 25% methyl diethanolamine.

(2) The following amines were found to resemble diethanolamine in relative steam requirements for reactivation; a mixture composed of 50% diethyleneglycolamine and 50% methyldiethanolamine; diethylaminoethanol; 2-amino-2-methyl-1-propanol; Sharples Mixed Ethyl Ethanolamines #161; a mixture composed of 50% diethanolamine and 50% methyldiethanolamine; and aminoethyl morpholine.

(3) The following amines were found to resemble triethanolamine in relative steam requirements: 2(2-dimethylaminoethoxy) ethanol, ethyldiethanolamine, and methyldiethanolamine.

(4) In determining the total steam requirements for reactivation, the relative carbon dioxide absorption rates of the amines should be considered.

(5) The pH of the amine solution at 90°C. does not appear to influence the relative steam requirements for reactivation.

## III. INVESTIGATIONAL PROCEDURE AND EXPERIMENTAL DATA:

### A. Source of Reagents.

The sources of all reagents employed in this investigation are listed in Girdler Report No. T2.15-1-30.

## B. Apparatus and Procedure.

The procedure employed in studying the relative steam requirements for reactivation consisted essentially in boiling 1500 ml. of the 2.5 N solution to be reactivated in standardized equipment, sufficient heat being applied to yield 6 ml. of condensate per minute until 2000 ml. of condensate had been collected or until a maximum degree of reactivation had been achieved. Samples of the solution were taken after various volumes of condensate had been collected. The solution volume was held constant by the addition of water at the rate of 6 ml. per minute.

The 2.5 N solutions to be reactivated were prepared according to the procedure described in Girdler Report No. T2.15-1-30 and sufficient carbon dioxide added so that the concentration approximated the values obtained in Girdler Report No. T2.11-2-3 for the carbon dioxide capacity of the solution at 85°F. and a carbon dioxide partial pressure of 19 mm. of Hg.

The apparatus employed is shown in Figures 1 and 2. Flask **A** (see Figure 1), which contained 1500 ml. of the solution to be reactivated, consisted of a 2-liter 3-necked flask equipped with standard taper (20/30) ground glass joints. The maximum solution depth in this flask was 4 inches. Three "Hengar granules" were added to the contents of the flask to prevent superheating. This flask was entirely immersed in a metal cylindrical container B and the free space around the flask was packed with rock wool to prevent heat transfer to or from the solution. The flask was heated by Mekker Burner H through a circular opening 7 cm. in diameter cut in the bottom of container B. Since the remainder of the outside area of the flask was insulated, theoretically all heat transfer to the contents of the flask occurred through this opening. The free space in the top of the flask was maintained at 215°F. by control of a 500 watt auxiliary heater **I** which rested on the outside of the flask. The output of this heater was adjusted by manipulation of variac K in such a manner that thermometer S, which was in contact with the outside of the flask, always read 215°F. This added heat prevented steam from refluxing into the flask. The steam was conducted to the condenser through tube L which consisted of an angle bend equipped with 20/30 ground glass joints, and wrapped with sufficient nichrome ribbon so that 75 watts could be supplied through the control of variac N and ammeter M. This added heat was a further precaution against steam condensate returning to flask **A**.

Heat was applied to the contents of the flask by burner H until the first drop of condensate reached adapter **P**. Then stopcocks 1, 2, and 3 were closed and the pinch clamp at F was opened. The resulting steam pressure on the system forced solution from flask **A** through tube E (1/4" glass tubing) into graduate R. The 10 ml. sample thus obtained was cooled as it left the flask by means of micro condenser G. This prevented escape of carbon dioxide from the hot solution. The sample thus obtained was analyzed for carbon dioxide concentration. Stopcocks 1, 2, and 3 were reopened and the distillation continued at a rate of 6 ml. of condensate per minute. Water was added to the distilling flask from graduated funnel D by way of thistle tube C at the same rate as distillate was collected in graduate Q. Thus, the volume of the solution was approximately constant throughout the distillation.

After 50 ml. of condensate had been collected in graduate Q, pinch clamp F was again opened. Since liquid remained in tube E from the first

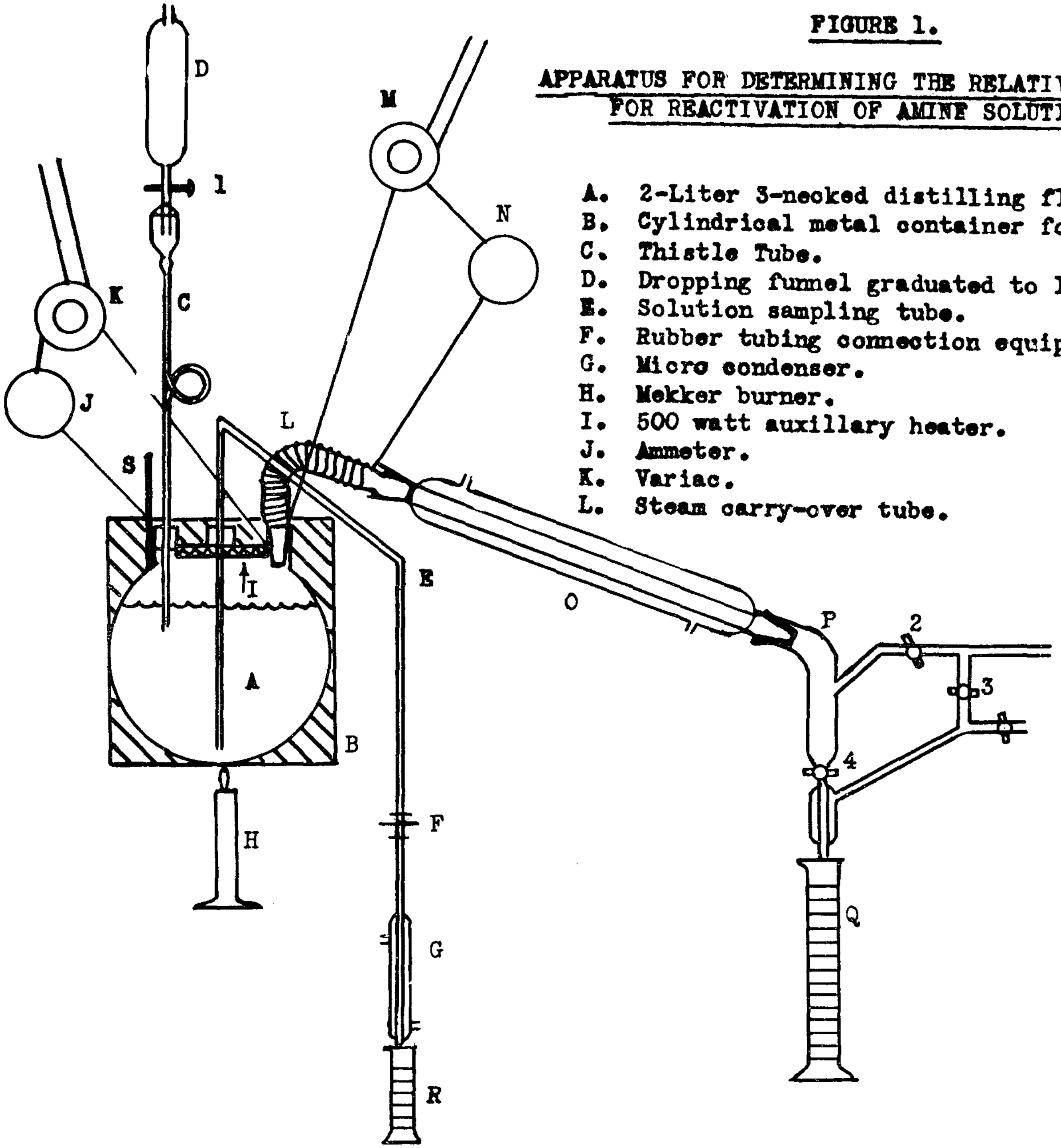

FIGURE 1.

APPARATUS FOR DETERMINING THE RELATIVE STEAM REQUIREMENTS FOR REACTIVATION OF AMINE SOLUTIONS.

A. 2-Liter 3-necked distilling flask.
B. Cylindrical metal container for holding insulation.
C. Thistle Tube.
D. Dropping funnel graduated to 1 ml.
E. Solution sampling tube.
F. Rubber tubing connection equipped with pinch clamp.
G. Micro condenser.
H. Mekker burner.
I. 500 watt auxillary heater.
J. Ammeter.
K. Variac.
L. Steam carry-over tube.
M. Variac
N. Ammeter.
O. Condenser
P. Adapter.
Q. 100 ml. graduated cylinder.
R. 25 ml. graduated cylinder.
S. Thermometer.
1,2,3,4. Stopcocks

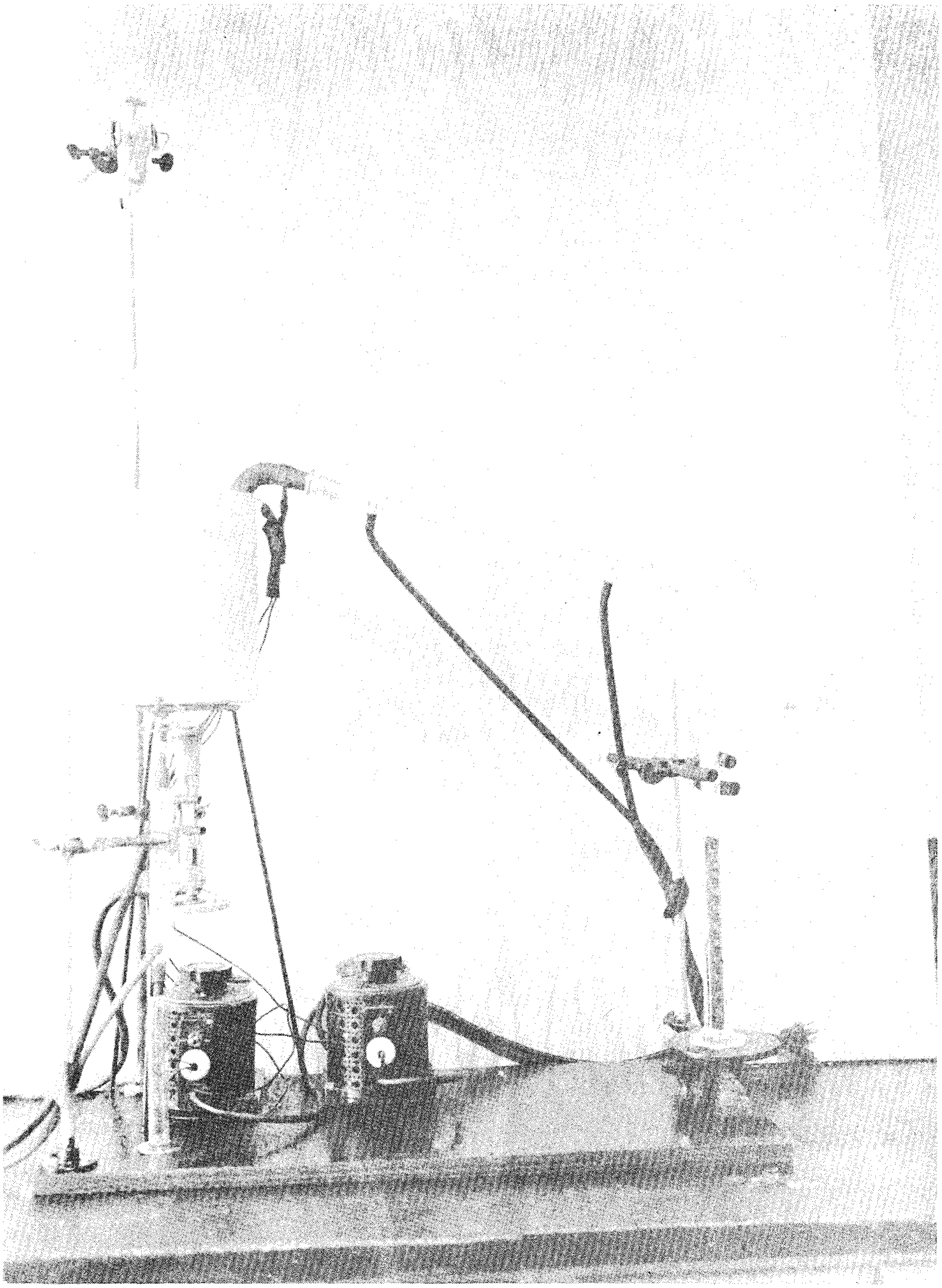

FIGURE 2

sampling of the solution, liquid could be siphoned from the flask into graduate R. The first 15 ml. of this liquid were returned to the flask by way of thistle tube C. The next 10 ml. of the solution were used as a solution sample which was analyzed for carbon dioxide concentration. The distillation was continued, samples being taken after 100, 200, 300, 500, 1000, 1500, and 2000 ml. of distillate had been collected. Whenever analyses of samples taken at any of these points showed that the carbon dioxide concentration in the solution was so small that accurate determinations were beyond the scope of the analytical method, no further samples were taken.

### C. Analytical Methods.

The analysis of the solution for carbon dioxide concentration is described in Standard Method SM-5 (see Appendix). Essentially, it consists in acidifying a given volume of the amine solution with phosphoric acid and measuring the carbon dioxide thus liberated by means of a gas burette.

### D. Experimental Data.

The data obtained in this investigation on the relative steam requirements for the reactivation of 2.5 N amine solutionsare shown in Table I. The concentrations of carbon dioxide in the solutions after various volumes of distillate had been collected are given in V/V at S.C.(volumes of carbon dioxide at 760 mm. of Hg and 0°C. per volume of solution at room temperature). The indentification number of each compound is taken from Girdler Report No. T2.20-2-2 which gives the physical properties of the amines. The pH values for the amine solutions at 90°C. and the differences between the pH values at 25°C. and 90°C. ($\Delta$ $pH25^\circ C.-pH_{90^\circ C.}$) are also given. These data are taken from Girdler Report No. T2.28-1-1.

## IV. DISCUSSION:

### A. Evaluation of the Method.

Duplicate sets of data are given in Table I on the reactivation of monoethanolamine. These data represent the results obtained for two independent determinations on the reactivation of this solution. The analytical method employed for the analysis of the solution for carbon dioxide is accurate to within 0.5 of a volume/volume. The averages of the two values obtained are, therefore, within analytical error. It may be concluded from these results that the method gives reproducible values, provided the equipment employed meets the proper specifications.

In reproducing these results the following factors should be carefully controlled:

(1) The volume of solution should be 1500 ml.

(2) The distillation flask should be of such dimensions that the maximum solution depth is exactly 4 inches. This height governs the amount of contact between the solution and steam and, therefore, is critical.

(3) The flask should be so insulated that it is heated only through a circular opening of exactly 7 cms. diameter.

(4) The free space in the distillation flask and steam carry over tube should be supplied with sufficient heat to maintain a temperature slightly above the boiling point of the solution to prevent reflux of water vapor.

## TABLE

## The Relative Steam Requirements from Amine

| Amine | Identification Number | pH at 90°C. | $\Delta$ pH ($pH_{25^\circ C.} - pH_{90^\circ C.}$) |
|---|---|---|---|
| Monoethanolamine | 111 | 10.6 | 1.5 |
| Diethanolamine | 133 | 10.2 | 1.4 |
| Triethanolamine | 143 | 10.1 | 1.1 |
| Isobutanolamine | 120 | 10.5 | 1.3 |
| 2-Amino-2-methyl-1-propanol | 124 | 10.7 | 1.5 |
| Methyl diethanolamine | 145 | 10.4 | 1.4 |
| Ethyl diethanolamine | 144 | 10.5 | 1.3 |
| 2(2-Dimethylaminoethoxy)ethanol | 148 | 10.6 | 1.3 |
| Diethylaminoethanol | 142 | 10.2 | 1.1 |
| Aminoethyl morpholine | 240 | 10.8 | 1.0 |
| Diethylaminopropylamine | 63 | 10.9 | 1.7 |
| Alkaline salt of $\alpha$-alanine | - | 13+ | nil |
| Sharples mixed ethylethanolamines #161 | 2M | 10.8 | 1.5 |
| 50% Diethanolamine<br>50% Methyldiethanolamine | 133<br>145 | 10.3 | 1.5 |
| 50% Diethyleneglycolamine*<br>50% Methyldiethanolamine | 122<br>145 | 10.6 | 1.3 |
| 75% Diethyleneglycolamine*<br>25% Methyldiethanolamine | 122<br>145 | 10.7 | 1.3 |

* Carbide and Carbon sample.

## I

## for Removal of Carbon Dioxide

## Solutions

| Concentration of Carbon Dioxide in the Solution | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 0 ml | 50 ml | 100 ml | 200 ml | 300 ml | 500 ml | 750 ml | 1000 ml | 1500 ml | 2000 ml |
| 26.0 | 16.8 | 13.5 | 9.7 | 8.6 | 6.0 | 4.9 | 2.7 | 2.1 | 1.5 |
| 24.9 | 15.7 | 12.8 | 10.6 | 9.0 | 4.9 | 3.8 | 2.9 | 1.8 | 0.9 |
| 24.6 | 11.2 | 7.0 | 3.0 | 2.1 | 1.7 | 1.1 | 0.6 | 0.3 | 0.3 |
| 3.9 | 2.3 | 1.4 | 0.9 | 0.6 | 0.3 | 0.1 | - | - | - |
| 21.6 | 14.5 | 10.6 | 7.9 | 6.4 | 4.2 | 3.1 | 1.9 | 1.0 | - |
| 30.9 | 16.9 | 8.3 | 5.4 | 2.1 | 1.4 | 0.7 | 0.3 | - | - |
| 12.4 | 3.7 | 1.3 | 0.9 | 0.5 | 0.3 | - | - | - | - |
| 12.9 | 3.9 | 1.7 | 1.2 | 0.6 | 0.3 | - | - | - | - |
| 12.6 | 5.3 | 3.4 | 1.3 | 0.4 | 0.4 | - | - | - | - |
| 26.3 | 15.6 | 9.3 | 5.2 | 3.8 | 2.5 | 1.5 | 1.1 | - | - |
| 18.4 | 10.2 | 8.1 | 5.4 | 3.9 | 2.6 | 1.9 | 1.3 | - | - |
| 24.7 | 19.3 | 15.5 | 13.7 | 11.6 | 8.9 | 6.9 | 6.3 | 3.5 | 2.0 |
| 29.0 | 21.8 | 20.1 | 15.0 | 13.0 | 10.2 | 7.9 | 6.9 | 5.4 | 4.4 |
| 21.9 | 9.8 | 6.2 | 3.1 | 2.6 | 1.4 | 0.6 | 0.5 | - | - |
| 19.0 | 7.6 | 4.6 | 2.6 | 1.9 | 1.2 | 0.5 | - | - | - |
| 19.6 | 12.1 | 8.3 | 5.5 | 3.7 | 2.6 | 1.6 | 1.2 | - | - |
| 23.0 | 16.5 | 11.8 | 8.1 | 6.4 | 3.8 | 3.1 | 2.3 | 1.4 | 1.0 |

(5) Three Hengar boiling granules should be used.

(6) The distillation rate should be controlled to yield 6 ml. of condensate per minute.

(7) The flask should be heated with the oxidizing flame from a Mekker burner.

## B. The Relative Steam Requirements for Reactivation of Amine Solutions.

The purpose of this investigation was to compare the relative steam requirements of the amine solutions tested with the relative requirements of solutions of monoethanolamine, diethanolamine, or triethanolamine, for which design data are available. The results shown in Table I are shown in graphical form in Graph I as the steam required in pounds per gallon of solution versus the concentration of carbon dioxide in the solution contacted with the quantity of steam indicated. No points taken from Table I are shown since the curves fall so close together. Not all of the data given in the table are plotted since the degree of reactivation produced was insignificant after the solution had been contacted with 3 pounds of steam per gallon of solution, a value corresponding to approximately 500 ml. of distillate.

In general the energy or steam required for reactivation can be divided into two components, (1) the sensible heat required to raise the temperature of the solution to its boiling point, and (2) the heat required to produce the steam required for stripping the carbon dioxide from the solution. The method used in this investigation for determining the relative steam required for reactivation measures only the second factor, that is, the steam required for stripping. In commercial size plants where the height of the absorber is limited, the extent to which equilibrium is realized is limited by the absorption rate of the amine. The quantity of amine solution circulated for the removal of a given quantity of carbon dioxide is influenced by the absorption rate and the net capacity of the amine, that is, the difference between the capacity of the amine solution as it leaves the absorber and that of the solution that enters the absorber. Therefore, the total steam required for reactivation is influenced by (1) the absorption rate of the amine, (2) its net capacity for the absorption of carbon dioxide, and (3) the steam required for stripping the carbon dioxide from the solution.

From the data contained in Table I and Graph I the relative steam requirements for reactivation of the solutions investigated may be compared qualitatively to that for monoethanolamine, diethanolamine, or triethanolamine in the following manner:

Amines similar to monoethanolamine are:

(1) Isobutanolamine
(2) A mixture composed of 75% (by wt.) diethyleneglycolamine and 25% (by wt.) methyldiethanolamine.

Amines similar to diethanolamine are:

(1) A mixture composed of 50% (by wt.) diethyleneglycolamine and 50% (by wt.) methyldiethanolamine.
(2) Diethylaminoethanol
(3) 2-Amino-2-methyl-1-propanol
(4) Sharples mixed ethyl ethanolamines #161.
(5) A mixture composed of 50% (by wt.) diethanolamine and 50% (by wt.) methyldiethanolamine.
(6) Aminoethyl morpholine.

Amines similar to triethanolamine are:

(1) 2-(2-Dimethylaminoethoxy)ethanol
(2) Ethyl diethanolamine
(3) Methyl diethanolamine

Solutions of the potassium salt of $\alpha$-alanine and diethylaminopropylamine required considerably more steam for reactivation than any of the ethanolamines employed as standards.

The solutions investigated originally contained concentrations of carbon dioxide approximately equivalent to their capacities. Therefore, it should be emphasized that this capacity is that concentration which may be attained only in an absorption tower designed to effect a close approach to equilibrium between the solution and the gas being purified. For some of these solutions, the tertiary amines in particular, such design would probably be impractical since their reaction rates are so slow. For example, while diethylaminoethanol which has a carbon dioxide capacity of 34 V/V at S.C. seems from the data in Table I and Graph I to have steam requirements similar to those of diethanolamine. in actual practice this probably would not be true since the relative carbon dioxide absorption rate of diethylaminoethanol is appreciably less than that for diethanolamine. (See Girdler Report No. T2.11-2-1). Therefore, a higher circulation rate would be required in the case of the tertiary amine and the energy requirements would be much greater than the data contained in this report indicate.. The same is true for all tertiary amines because of their low absorption rates. Diethanolamine required less steam per pound of carbon dioxide reactivated than monoethanolamine. Nevertheless, the absorption rate of diethanolamine is less than that for monoethanolamine and, consequently, the actual steam requirements for reactivation in plant practice may be no less for diethanolamine and could be greater than that for monoethanolamine.

From the data shown in Table I it is apparent that neither the pH of these solutions at 25°C. nor the pH at 90°C. has much influence on the relative energy requirements for reactivation. This is not unexpected since as was pointed out in Girdler Report No. T2.28-1-1, the decline in pH over a temperature range of 25-90°C. is practically constant for all the amines tested and does not greatly exceed that which would be estimated as resulting from the change in pH of water over this temperature range.

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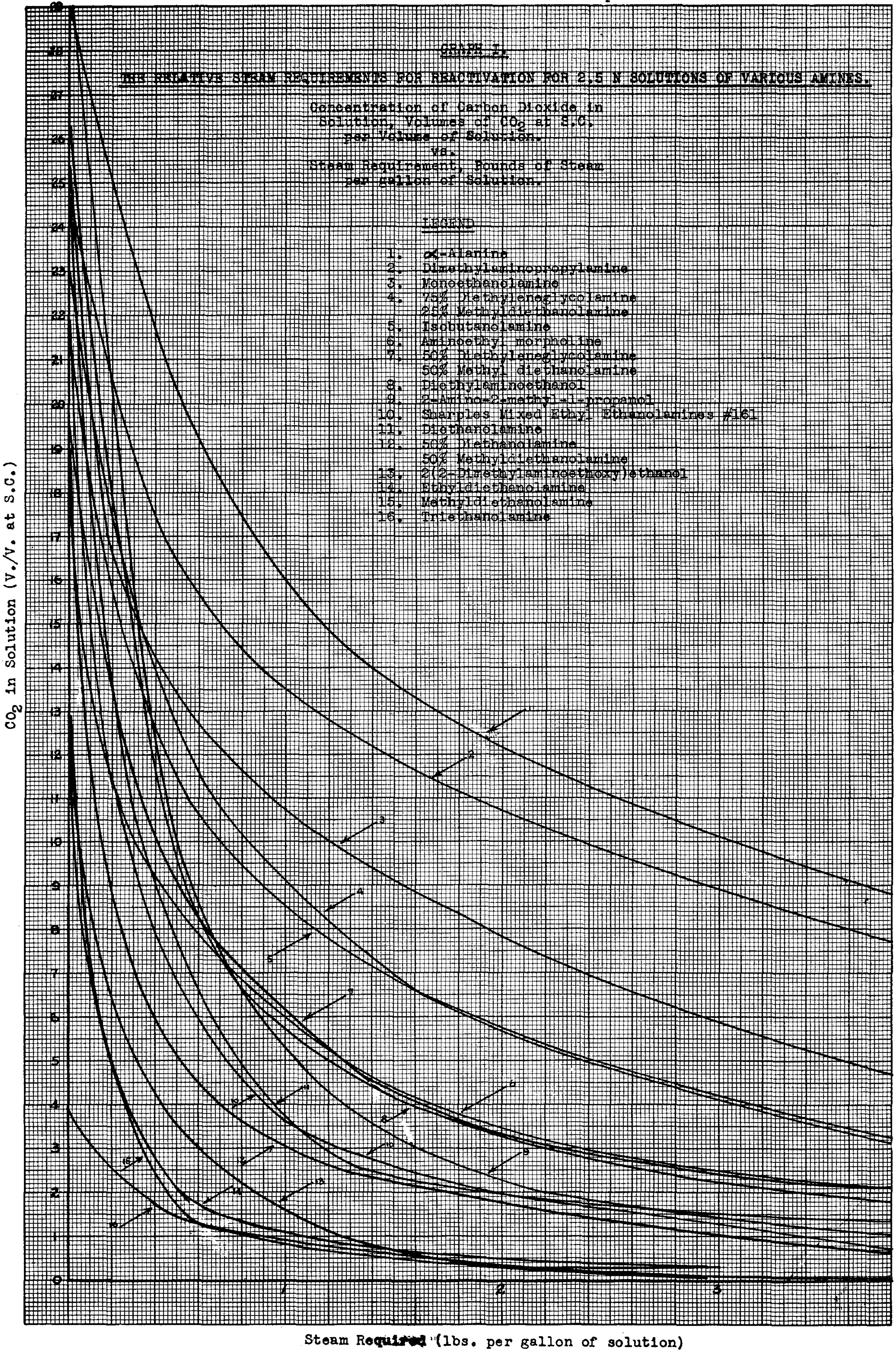

GRAPH I.

THE RELATIVE STEAM REQUIREMENTS FOR REACTIVATION FOR 2.5 N SOLUTIONS OF VARIOUS AMINES.

Concentration of Carbon Dioxide in
Solution, Volumes of $CO_2$ at S.C.
per Volume of Solution.
vs.
Steam Requirement, Pounds of Steam
per gallon of Solution.

Report No. T2.15-1-31

THE GIRDLER CORPORATION
GAS PROCESSES DIVISION
PROCESS DEVELOPMENT AND RESEARCH LABORATORIES
LOUISVILLE, KENTUCKY

# A PROLONGED OXIDATION TEST ON AMINE SOLUTIONS RESISTANT TO OXIDATION.

May 25, 1950

| Work by: | Report by: |
|---|---|
| R. C. Kindrick<br>R. E. Reitmeier<br>M. R. Arnold | R. C. Kindrick |

## Sentence Summary

Eleven 2.5 N amine solutions have been subjected to an oxidation test consisting of contacting the solutions for forty days at 85°F. with a gas mix composed of 5% carbon dioxide and 95% air.

## I. INTRODUCTION:

In the literature search (Girdler Report No. T2.20-2-2) all except approximately forty materials were eliminated from consideration as possible absorbents for carbon dioxide from submarine atmospheres. On the basis of the results of an accelerated oxidation test it was possible to eliminate all of these remaining compounds with the exception of thirteen materials and four mixtures. (Girdler Report No. T2.15-2-30). Two of these thirteen remaining compounds were eliminated on the basis of low carbon dioxide capacities (Girdler Report No. T2.11-3-2).

In the accelerated oxidation test the solutions studied were subjected to conditions especially conducive to rapid oxidation. Those compounds which showed the highest resistance to oxidation under these conditions were selected for further consideration. The purpose of the present report is to describe the results of a prolonged oxidation test on thirteen materials chosen on this basis. In the present investigation solutions of these compounds were studied under conditions similar to those where oxygen (air) contact will occur in plant operation. From the alkalinity losses of these materials over a period of forty days, their relative alkalinity loss which may be expected in plant operation may be estimated. Since the advantages of certain mixtures of amines were discovered late in this investigation, there was insufficient time to complete the prolonged oxidation tests so the results could be included in this report, therefore, the results of these tests will be presented in a later report.

## II. SUMMARY AND CONCLUSIONS:

(1) Solutions of eleven compounds have been tested for relative resistance to oxidation by means of a prolonged oxidation test under conditions similar to those to be employed in removing carbon dioxide from submarine atmospheres.

(2) There were no significant differences in the relative alkalinity losses of most of the amines investigated, the only exceptions being diethylaminopropylamine and diethylamino ethanol.

(3) Certain relative corrosive properties of the amine solutions have been tabulated.

(4) There are no significant differences in the corrosive properties of the materials investigated with the exception of the salts of the amino acids which were found to be extremely corrosive toward low carbon steel.

## III. INVESTIGATIONAL PROCEDURE AND EXPERIMENTAL DATA:

### A. Source of Reagents.

The source of the reagents employed in this investigation may be found in Girdler Report Nos. T2.20-2-2 and T1.15-3-30.

### B. Apparatus and Procedure.

The procedure employed in the prolonged oxidation test consisted in contacting a gas mixture consisting of 5% carbon dioxide and 95% air with 100 ml. of the solutions at a rate of 100 ± 10 cc. per minute at 85 ± 0.5°F. for forty days. The solutions were analyzed before and after the test.

The apparatus employed is shown in Figures 1 and 2. The tubes labeled H in Figure 1 contained exactly 100 ml. of the 2.5 N amine solutions to be investigated. A coil of type 304 stainless steel wire (39 B and S gauge), approximately 15 feet in length, was in contact with each amine solution during the test. This aided in simulating the conditions of plant operation. The weight of this wire before and after the test provided an indication of the relative corrosive properties of the solution toward this alloy. Scrubbers J contained exactly 50 ml. of N/10 sulfuric acid. The apparatus was assembled as shown in Figure 2. A gas mixture composed of 5% carbon dioxide and 95% air was prepared by passing carbon dioxide and air into mixing chamber C at appropriate rates as indicated by flow meters A and B. The resulting homogeneous gas mixture flowed into water saturator D where it was saturated with water vapor at room temperature. The gas was sampled at point E for Orsat analysis. The concentration of carbon dioxide was maintained at 5 ± 0.2% throughout the test. The gas entered tubes H by way of manifold F which was constructed of 1/4" copper tubing. The contents of these tubes were held at 85 ± 0.5°F. by means of water bath L. The gas was contacted with the solution by means of coarse fritted dispersion tubes (Harshaw catalog No. H 27020 coarse) at a rate of 100 ± 10 cc. per minute controlled by adjustment of the screw clamps at G. This rate was indicated by wet test meters K. In condensers I, water and amine vapor in the effluent gas was condensed back into tubes H. Since these condensers operated at approximately 15°C., it was necessary periodically to bypass water saturator D to prevent dilution of the amine solution. Thus, the volume of the solution was maintained at approximately 100 ml. throughout the test. Any alkaline material, such as ammonia, not removed by the condensers was absorbed by the standard acid in scrubbers J.

Samples of the original solution were analyzed for free amine concentration, primary amine concentration, total organic nitrogen concentration, iron content, and iron capacity. After forty days the solutions were removed from the tubes and were weighed together with the washings from the tubes and condensers to within 0.1 gm. From these weights and the specific gravities the final volumes of the resulting solutions were determined. These solutions were analyzed for the above components and the analytical results corrected to compare directly with the values obtained on the original solution by multiplying the results by the final volume/the original volume. The acid in scrubbers J was back-titrated with standard sodium hydroxide using methyl orange as the indicator. The results of this determination were calculated as ammonia.

### C. Analytical Methods.

The analytical methods employed in this investigation are discussed under Analytical Methods, 1, 2, 3, 5, and 6 of Girdler Report No. T2.15-2-30.

### D. Experimental Data.

The results obtained on the prolonged oxidation test on thirteen compounds are shown in Table I. The free amine concentration is expressed in equivalents per liter before and after the test. The loss in free amine incurred during the test is expressed in percent. The primary amine concentration which was determined by the Van Slyke Method whenever primary amine was present, is also expressed in the same manner. The total organic nitrogen concentration is expressed in gram atomic weights per liter before and after the test and the resulting loss is given in percent. The ammonia evolved during the test is

# LEGEND

A. Flow meter for measuring the rate of air flow.

B. Flow meter for measuring the rate of carbon dioxide flow.

C. Gas mixing chamber constructed of iron pipe having a volume of approximately 2-1/2 liters packed with Raschig rings.

D. Water saturator.

E. Glass "T" outlet for sampling gas.

F. A gas manifold constructed of 1/4" copper tubing.

G. Rubber tubing connections from manifold equipped with screw clamps for adjusting rate through each manifold outlet.

H. Pyrex test tubes of 200 ml. capacity equipped with coarse fritted gas dispersion tubes.

I. Friedricks condensers.

J. Gas scrubbers equipped with Folin bell dispersion tubes.

K. Wet test meter.

L. Water Bath.

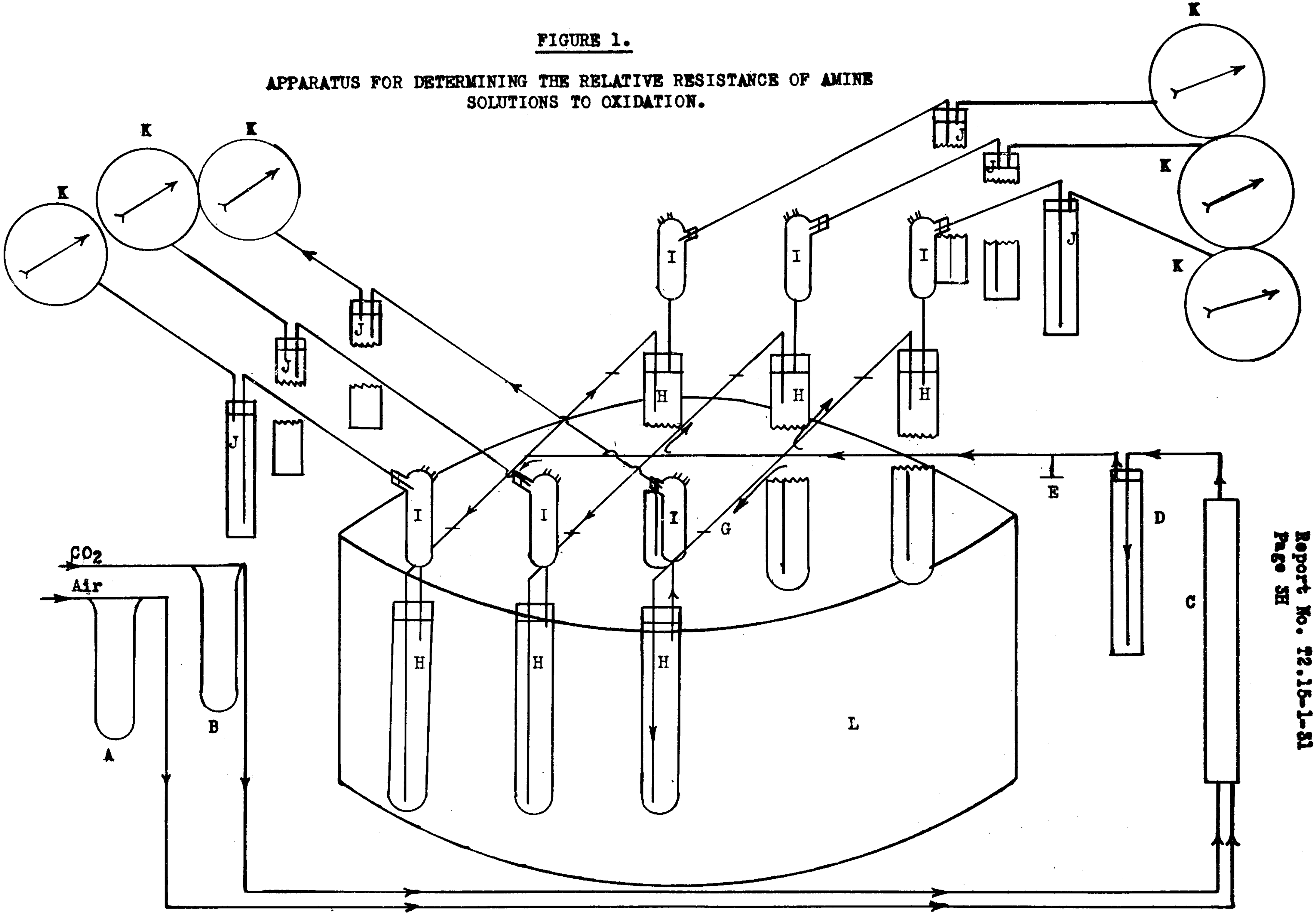

FIGURE 1.

APPARATUS FOR DETERMINING THE RELATIVE RESISTANCE OF AMINE SOLUTIONS TO OXIDATION.

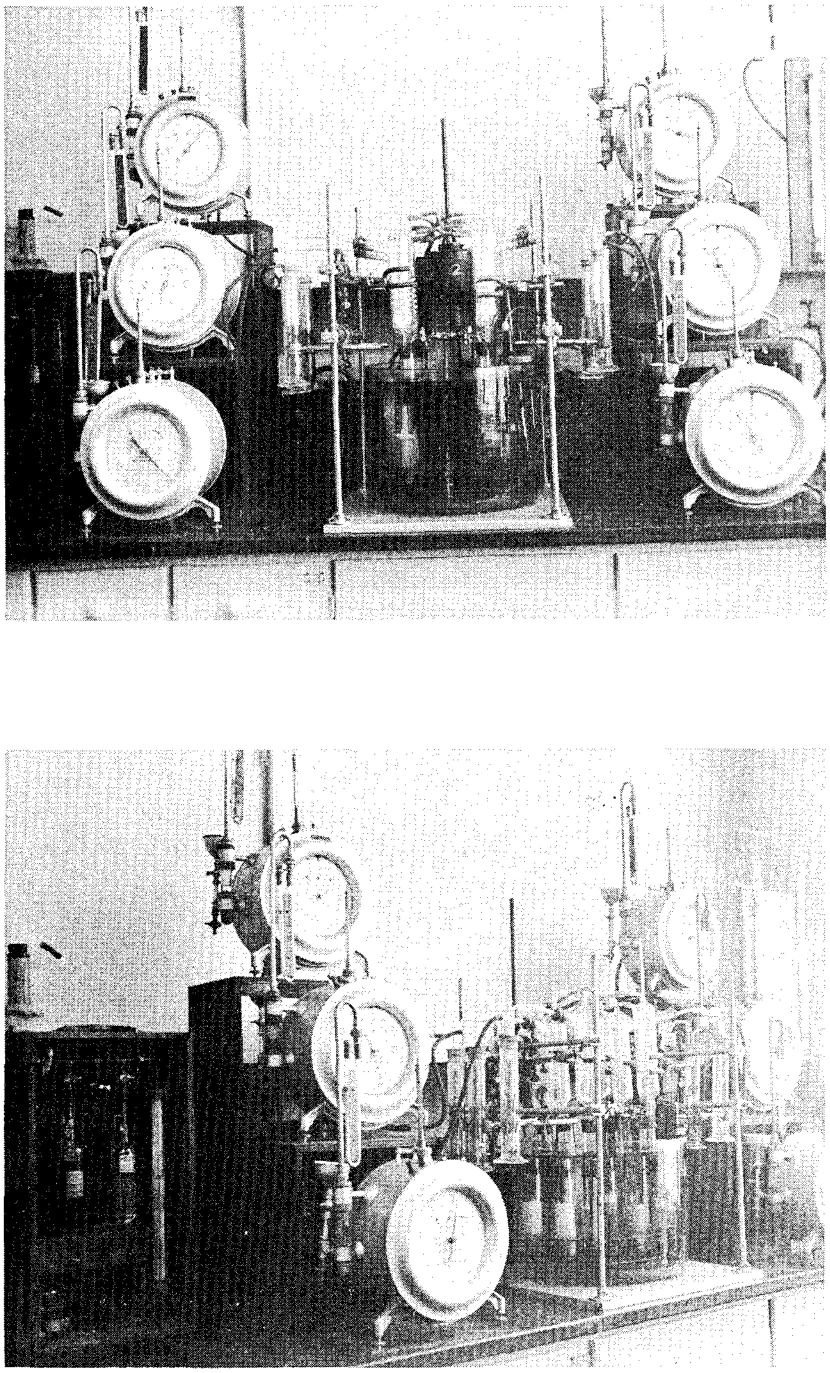

FIGURE 2

presented in equivalents per liter of amine solution. The nitrogen material balance is expressed as percent of the organic nitrogen concentration accounted for as final organic nitrogen content and as ammonia evolved.

Data obtained on the relative corrosive properties of the solutions are presented in Table II. The iron contents of the solutions are given in parts per million before and after the test. These values show the concentrations of iron dissolved in the solutions. The iron capacities are also expressed in parts per million. These data show the relative corrosive properties of the solutions toward low carbon steel. The loss in weight of the stainless steel wire is expressed in inches of penetration per year. This value was calculated from the following formula which is valid since the weight loss of specimen was negligible in all cases:

$$IPY = \frac{Q \times 365}{D \times A}$$

Q = milligrams lost per day
A = area of 1 gram of wire in square inches
D = density of wire in milligrams per cubic inch

## IV. DISCUSSION:

### A. Evaluation of the Method.

The data presented in Tables I and II of this report are subject to the same errors inherent in the accelerated oxidation test. For a complete discussion of these errors Girdler Report No. T2.15-1-30 should be consulted. Briefly these errors consist in:

(1) The control of the conditions of the oxidation test.

Losses in alkalinity occurring in amine solutions subjected to this test are probably reproducible to within only 1-2 percent of the total alkalinity present.

(2) Certain analytical errors.

These include inaccuracies in the Van Slyke Method for determining primary amine concentration where steric hindrance interferes, inaccuracies in the Kjeldahl method for total organic nitrogen concentration when compounds difficult to reduce to ammonia are present, difficulties in control of the iron capacity test which determines the relative corrosive properties of the solutions to low carbon steel and inaccuracies in the determination of the concentration of iron dissolved in the solution.

### B. Relative Resistance of the Amines Tested to Prolonged Oxidation.

The primary purpose of this investigation was to determine the relative resistance of the amines tested to alkalinity loss over an extended length of time when subjected to conditions similar to those employed in plant operation. Therefore, the values for "percent free amine loss" are the most significant data presented in Table I.

## TABLE

## The Relative Resistance
## to the Prolonged

| Amine | Formula | No. |
|---|---|---|
| Isobutanolamine | $(CH_3)_2C(OH)CH_2NH_2$ | 120 |
| 2-Amino-2-methyl-1-propanol | $(CH_3)_2C(NH_2)CH_2OH$ | 124 |
| Methyl diethanolamine | $CH_3N(C_2H_4OH)_2$ | 145 |
| Ethyl diethanolamine | $C_2H_5N(C_2H_4OH)_2$ | 144 |
| 2(2-Dimethylaminoethoxy)ethanol | $(CH_3)_2NC_2H_4OC_2H_4OH$ | 148 |
| Triethanolamine | $(HOC_2H_4)_3N$ | 143 |
| Diethylaminoethanol | $(C_2H_5)_2N(C_2H_4OH)$ | 142 |
| Aminoethyl morpholine | $OC_2H_4N(C_2H_4NH_2)CH_2CH_2$ | 240 |
| Diethylaminopropylamine | $(C_2H_5)_2NC_3H_6NH_2$ | 63 |
| Alkaline salt of α-alanine | $H_2NCH(CH_3)COOK$ | |
| Alkaline salt of NN'-dimethyl glycine | $(CH_3)_2NCH_2COOK$ | |

* Equivalents per liter
** Percent loss of amine, by wt.
*** Gram atomic weights per liter

I

of Amine Solutions

Oxidation Test

| Free Amine | | | Primary Amine | | | Total Organic Nitrogen | | | | N2 |
|---|---|---|---|---|---|---|---|---|---|---|
| Before, E/L* | After, E/L* | Loss, %** | Before, E/L* | After, E/L* | Loss, %** | Before, GA/L*** | After, GA/L*** | Loss, %** | NH3 Lost | Mat'l. Bal. |
| 2.51 | 2.48 | 1.20 | 2.56 | 2.52 | 1.56 | 2.61 | 2.57 | 1.53 | .01 | 99. |
| 2.51 | 2.46 | 2.0 | 2.61 | 2.61 | 0.00 | 2.64 | 2.57 | 2.60 | .02 | 98. |
| 2.50 | 2.50 | 0.00 | nil | nil | - | 2.61 | 2.61 | 0.00 | .004 | 100. |
| 2.56 | 2.54 | 0.8 | nil | nil | - | 2.68 | 2.66 | 0.7 | .004 | 99. |
| 2.46 | 2.49 | -1.21 | nil | nil | - | 2.53 | 2.51 | 0.7 | .02 | 100. |
| 2.54 | 2.47 | 2.75 | nil | nil | - | 2.61 | 2.54 | 2.68 | .003 | 97. |
| 2.51 | 2.38 | 5.17 | nil | nil | - | 2.56 | 2.66 | -3.91 | .03 | 105. |
| 2.60 | 2.58 | 0.8 | 2.30 | 2.34 | 0.4 | 4.58 | 4.68 | -1.7 | .03 | 104. |
| 2.60 | 2.50 | 3.84 | 1.23 | 1.23 | 0.00 | 2.54 | 2.54 | 0.00 | .02 | 102. |
| 2.04 | 2.02 | 1.0 | 2.12 | 2.21 | -4.24 | 2.08 | 2.21 | -6.3 | .04 | 107. |
| 2.00 | 2.04 | -2.0 | nil | nil | - | 2.03 | 2.02 | 0.5 | .01 | 100. |

## TABLE II.

## CORROSIVE PROPERTIES OF SOLUTIONS

| | Iron Capacity | | Iron Content | | Corrosion of |
|---|---|---|---|---|---|
| **Amine** | Before Test (p.p.m.) | After Test (p.p.m.) | Before Test (p.p.m.) | After Test (p.p.m.) | Stainless Steel (IPY) |
| Isobutanolamine | 30 | 30 | 30 | 30 | $4.5 \times 10^{-5}$ |
| 2-Amino-2-methyl-1-propanol | 40 | 80 | 40 | 60 | NL |
| Methyl diethanolamine | 50 | 30 | 50 | 30 | NL |
| Ethyl diethanolamine | 80 | 30 | 50 | 30 | $2.2 \times 10^{-5}$ |
| 2(2-Dimethylamino ethoxy)ethanol | 30 | 30 | 30 | 40 | NL |
| Triethanolamine | 30 | 30 | 30 | 30 | NL |
| Diethylaminoethanol | 40 | 40 | 40 | 40 | $7.6 \times 10^{-6}$ |
| Aminoethyl morpholine | 30 | 60 | 30 | 80 | NL |
| Diethylaminopropylamine | 40 | 30 | 40 | 30 | NL |
| Alkaline salt of α-alanine | 2500 | 3000 | 30 | 60 | $2.2 \times 10^{-5}$ |
| Alkaline salt of NN' dimethyl glycine | 4550 | 4500 | 30 | 90 | NL |

NL = No Loss

Most of the amines investigated lost 3% or less in alkalinity. As previously stated these losses are probably reproducible only to within 1-2% of the total alkalinity present. Therefore, it is probable that there are no significant differences in the relative resistance of these amines to alkalinity loss. The only exceptions are diethylaminopropylamine, which lost 3.84% of its original amine concentration and diethylaminoethanol which lost 5.17% in total alkalinity. These two amines, therefore, may be considered to be the least desirable of the amines tested on the basis of resistance to prolonged oxidation.

C. Relative Corrosive Properties of the Solutions.

In general the data presented in Table II confirm the results obtained in the accelerated oxidation test (Girdler Report No. T2.15-1-30.) The solutions tested showed very slight tendencies toward corrosion of the stainless steel employed. The weight loss of the metal itself was so low as to be almost insignificant. This is seen from the data presented for the corrosion rate of the stainless steel wire.

The iron contents of the solutions remained virtually unchanged throughout the test. These values show the concentration of dissolved iron in the solutions.

The iron capacities, which indicate the relative corrosive properties of the solutions toward low carbon steel, remained approximately unchanged throughout the test. It should be noted that the salts of the amino acids exhibited high iron capacities before and after the test.

It must be emphasized that the corrosion results given in this report are very limited in scope. Before an amine solution may be definitely stated to be non-corrosive toward any material prolonged corrosion tests on a pilot plant scale are required.

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Report No. T2.20-2-4

THE GIRDLER CORPORATION
GAS PROCESSES DIVISION
PROCESS DEVELOPMENT AND RESEARCH LABORATORIES
LOUISVILLE, KENTUCKY

# SUMMARY OF A STUDY OF AMINES RESISTANT TO OXIDATION AS ABSORBENTS FOR CARBON DIOXIDE.

May 29, 1950

| Work by: | Report by: |
|---|---|
| R. C. Kindrick | R. C. Kindrick |
| Kenton Atwood | R. E. Reitmeier |
| M. R. Arnold | |
| R. E. Reitmeier | |

## Sentence Summary

Ten materials are evaluated as absorbents for the removal of carbon dioxide from submarine atmospheres.

The purpose of the present investigation was to evaluate certain materials as absorbents for the removal of carbon dioxide from submarine atmospheres. The scope of the investigation was limited to the study of those materials which show the greatest immediate promise for the solution of this problem, namely the water soluble amines and alkaline salts of amino acids. The investigation was further limited to those materials available commercially or those that will be available within the next two years. The use of such a material for carbon dioxide removal would involve the circulation of an aqueous solution of the amine or amino acid, with the carbon dioxide being absorbed from the air in one part of the cycle and being desorbed from the solution at an elevated temperature in another part of the cycle. The solution, essentially free of carbon dioxide, would then be cooled and returned to the first part of the cycle for absorption of more carbon dioxide.

The use for which this process is intended demands that in addition to giving reasonably complete removal of carbon dioxide from the atmosphere the process should exhibit the following characteristics.

(1) There should be a minimum of atmospheric contamination with materials not normally present in air.

(2) The amine or amino acid employed should have sufficient stability toward oxygen that the degradation over a period of sixty days would not influence the operation of the process within the limits of plant design.

(3) The physical size and weight of the equipment should be as small as possible.

(4) The power requirements for the operation of the process should be at a minimum.

(5) The amine or amino acid employed should not be corrosive toward the materials of fabrication.

It is necessary that any evaluation of materials to be used in such a process should be based on these five requirements. Therefore, from an investigation of certain properties of the aqueous solutions of these materials the relative extent to which the solutions might be expected to fulfill these process requirements in plant operation was indicated. The properties investigated included:

1. Resistance to oxidation.
2. Vapor pressure.
3. Capacity for the absorption of carbon dioxide.
4. Reaction rate with carbon dioxide.
5. Energy requirements for reactivation.
6. Cost per equivalent unit of active absorbent.
7. Degree of "fogging".
8. Solubility of amine and its corresponding carbonate in water.
9. Thermostability.
10. Corrosiveness toward materials of fabrication.

From several of these studies (See Girdler Report Nos. T2.20-2-2, T2.15-1-30, T2.11-3-2, and T2.11-3-1) it was possible to eliminate from consideration all but 10 compounds. The elimination was made on the basis that the compound failed completely to meet one or more of the five process requirements.

The ten remaining compounds are:

(1) Primary Amines

Isobutanolamine
2-Amino-2-methyl-1-propanol

(2) Tertiary Amines

Triethanolamine
Diethylaminoethanol
Methyldiethanolamine
Ethyldiethanolamine
2(2-Dimethylaminoethoxy)ethanol

(3) Diamines

Diethylaminopropylamine
Aminoethyl morpholine

(4) Alkaline salts of Amino acids.

$\alpha$-Alanine

Not all of these materials if employed in a cyclic process for the removal of carbon dioxide from submarine atmospheres would fulfill equally well all of the requirements previously stated as desirable. The relative suitability of these compounds depends to a great extent upon which of the specifications is considered to be most important. The purpose of this report, therefore, is to indicate which of these materials are best qualified to fulfill each of these individual requirements and to discuss briefly the relative merits of each compound.

## Atmospheric Contamination.

If maintaining the atmosphere free of contaminants is considered to be the most important of the five process requirements previously mentioned, it would be necessary to select an amine with a very low vapor pressure. For example, if an amine such as monoethanolamine having a relatively high vapor pressure in comparison with those amines having appreciably higher boiling points, were at equilibrium with the gas phase, approximately 0.5 pounds of amine would be introduced into each 1,000,000 S.C.F. of gas as a result of the amine vapor pressure. This quantity of amine might not only affect the personnel but might also cause serious corrosion of the equipment in the area involved. On the other hand, the vapor pressure of those materials having considerably higher boiling points is so low that the quantity of amine introduced into the atmosphere as a result of their vapor pressure would be negligible. Of the 10 materials to be evaluated the following compounds have the lowest vapor pressures and would, therefore, be the most desirable from this standpoint: the alkaline salt of $\alpha$-Alanine, Triethanolamine, 2(2-Dimethylaminoethoxy)ethanol, Ethyldiethanolamine and Methyldiethanolamine.

## Alkalinity Loss.

If the resistance of the material to alkalinity loss through oxidation is the most important factor to be considered, the following compounds would be the best qualified for the intended use since they showed very low oxidation rates in both an accelerated oxidation test (Girdler Report No. T2.15-1-30) and a prolonged oxidation test (Girdler Report No. T2.15-1-31): α-Alanine, Isobutanolamine, Ethyldiethanolamine, Methyldiethanolamine, 2(2-Dimethylamino-ethoxy)ethanol, and Triethanolamine.

## Equipment Size.

If limitation of the equipment size is the most critical factor to be considered, it is necessary to select a material which will maintain the carbon dioxide concentration in the atmosphere at the desired level by contacting a given volume of air with the least volume of solution. Such being the case, the relative rates at which these materials react with carbon dioxide (Girdler Report No. T2.11-3-1) and the capacities of their solutions under the conditions of operation as well as the ease of reactivation become the most important properties to be considered. Such a material would have to possess a high solution capacity for carbon dioxide as well as low steam requirements for reactivation since these determine the amount of carbon dioxide which may be absorbed by a given volume of the solution under specific operating conditions. In addition the compound would have to react with carbon dioxide at such a rate that its capacity might be approached rapidly, otherwise the benefit of a high capacity would be negligible when small-scale equipment was used. Of the 10 compounds to be considered the following showed high capacities and relatively low steam requirements together with the highest relative absorption rates: Isobutanolamine, Aminoethyl morpholine, and 2-Methyl-2-amino-1-propanol. If contamination of the atmosphere and relative resistance to oxidation are considered relatively unimportant in comparison to compactness of the plant, monoethanolamine or similar amines might be used, although they are not included in the group of the 10 best qualified materials because of their low resistance to oxidation.

## Energy Requirements.

Most of the necessary power requirements for such a process would be involved in the removing of carbon dioxide from the solution. The amount of heat necessary to remove a given volume of carbon dioxide from a given volume of solution, and the rate at which this solution must be circulated are both important factors in determining the total energy requirements. The solution circulation rate is determined by the volume of solution necessary to effect the desired level of gas purification. As previously stated this factor is determined by the carbon dioxide capacity, the ease of reactivation and the absorption rate of the solution. Therefore, if the power requirement is the most critical factor involved, an amine should be selected which has a relatively high carbon dioxide absorption rate, high capacity and a relatively low energy requirement for reactivation. Of the 10 materials under consideration those which are best qualified to fulfill these requirements are: 2-Amino-2-methyl-1-propanol, Aminoethyl morpholine, and Isobutanolamine.

## Corrosion.

The corrosiveness of the materials investigated was not considered as a primary criterion for evaluating these compounds for the intended use, since the materials of fabrication will be alloys highly resistant to corrosion. However, it may be stated that the tertiary amines showed lower corrosive tendencies than the other materials investigated.

In the foregoing discussion those compounds among the 10 materials to be considered which are best qualified to meet each of the 5 basic requirements for plant design have been indicated. In the following discussion the relative merits of each of these ten compounds will be summarized.

### Isobutanolamine.

This amine is characterized by a high resistance to oxidation, a relatively high carbon dioxide capacity and absorption rate, and an energy requirement for reactivation comparable to that for monoethanolamine. However, it is relatively volatile and in addition to this it possesses a strong disagreeable odor which may render it undesirable for the intended use.

### 2-Amino-2-methyl-1-propanol.

Solutions of this compound showed a relatively high resistance to oxidation. They were found to have a very high capacity for carbon dioxide and a fairly high reaction rate. However, this compound is comparatively volatile and from the standpoint of atmospheric contamination it would probably be undesirable for the intended use.

### Triethanolamine.

This amine has the desirable properties of high resistance to oxidation and a low vapor pressure. However, it has a low capacity for carbon dioxide as well as a low absorption rate. These two factors along with the relatively high steam requirements for stripping make the energy requirement for reactivation appreciably greater than that for monoethanolamine.

### Methyldiethanolamine.

This material also has a low vapor pressure and exhibits a high degree of resistance to oxidation. It has a relatively low capacity for carbon dioxide and although it shows the highest carbon dioxide absorption rate of the tertiary amines under consideration, it compares unfavorably with primary amines in this respect. Again this factor has an undesirable effect on the energy requirements for regeneration of the solution although its relatively low steam requirements for stripping tends to offset this.

### Ethyldiethanolamine.

This amine, in general, exhibits the same properties as methyldiethanolamine except for a slightly lower carbon dioxide absorption rate.

### Diethylaminoethanol.

Although this amine has a very high capacity for carbon dioxide, it has a low absorption rate which tends to offset the advantages of its high capacity. Another undesirable characteristic of diethylaminoethanol is its high volatility. This compound also demonstrated lower resistance to oxidation in a prolonged oxidation test than the other amines. These factors probably render this amine the least desirable of the compounds under consideration.

## 2(2-Dimethylaminoethoxy)ethanol.

This compound shows the characteristics of a typical tertiary amine namely, a low vapor pressure, a high resistance to oxidation, a relatively poor carbon dioxide capacity and absorption rate. In addition to these properties however, it posseses a strong highly disagreeable fish-like odor which may render it less desirable than some of the other tertiary amines.

## Diethylaminopropylamine.

This material is characterized by a high carbon dioxide capacity and absorption rate. However, the energy required to remove carbon dioxide from the solution is greater than that required for solutions of monoethanolamine. This compound showed relatively poorer resistance to oxidation in the prolonged oxidation test than some of the other materials. The most serious objection to the use of this amine is that a high degree of atmospheric contamination would undoubtedly result since diethylaminopropylamine not only has a relatively high vapor pressure but also exhibits the phenomonen of "fogging".

## Aminoethyl morpholine.

This compound has a relatively low vapor pressure, a fair resistance to oxidation, and a fairly high carbon dioxide capacity and absorption rate. It required slightly more energy for reactivation than diethanolamine. The only objectionable characteristic manifested by this amine is its strong disagreeable odor.

## The alkaline salt of $\alpha$-Alanine.

This amino acid was found to have a high capacity and absorption rate for carbon dioxide. Since it is a solid material in the pure form at atmospheric temperature the vapor pressure should be extremely low. However, the relative energy requirement for the stripping of carbon dioxide from this solution was found to be appreciably greater than that for monoethanolamine. A possible objectionable property of this material is the low degree of solubility of the carbonate when the concentration of carbon dioxide in the solution becomes high. This does not occur, however, until this concentration exceeds the capacity of the solution under the normal conditions of plant operation. Although it is extremely corrosive toward carbon steel, alloy steel may offer considerably more resistance.

Relatively late in this investigation it was discovered that when certain types of tertiary amines such as methyldiethanolamine are combined in solution with certain primary or secondary amines such as diethyleneglycolamine or diethanolamine, the desirable properties of both components of the mixture are retained. The aqueous solutions of the resulting mixtures showed high resistance to oxidation typical of tertiary amines and high capacities and absorption rates for carbon dioxide which characterize the primary and secondary amines. These mixtures also have low vapor pressures since they are composed of materials having high boiling points. Although data pertaining to these are included in the present series of reports, no attempt will be made to evaluate these materials at this time, since information is incomplete and work is now in progress to complete and verify these data. The evaluation of these amine mixtures will be covered in a later report. Also to be included in this later report will be information pertaining to the dipiperidyls. Samples of these materials were received too late to be included in the present series of investigations.

It was impossible to obtain any samples of methyl alanine or its alkaline salt, "Alkazid M". Since the salt of this amino acid is known to be a rapid absorbent for carbon dioxide, this compound might be particularly adaptable to the problem at hand.

REPORT BY: ______________________________ DATE: ______________

READ AND UNDERSTOOD BY: ____________________ DATE: ______________

Distribution:

T.F., P.D.F., P.F., U.O.F., R.E.R., M.R.A., K.A., R.C.K.

jc

# APPENDIX

## SM5 DETERMINATION OF $CO_2$ IN AMINE SOLUTIONS

**Method:** A one ml. sample of the amine solution being tested is acidified with 2 mls. of 50% phosphoric acid, which liberates the $CO_2$ from the amine solution. The evolved $CO_2$ is measured in a gas measuring burette and the volume of $CO_2$ obtained corrected to standard conditions and reported as volumes of $CO_2$ (S.C.) per volume of amine solution, or converted to SCF (standard cubic feet) of $CO_2$ per gallon of amine solution.

**Reagents:** 50% phosphoric acid (Note 5)
Confining solution prepared by dissolving 200 grams $Na_2SO_4$ in a solution composed of 800 mls. of water and 40 mls. of conc. $H_2SO_4$. (Note 3)
Mercury

**Apparatus:** See sketch No. S117 (Note 8). The apparatus consists of two gas burettes. The reaction burette contains mercury and the measuring burette contains a gas confining solution. The reaction burette is fitted with three two-way stopcocks, "C", "E", and "G" (Note 1) and two small tubes, "A" and "B"; "B" is graduated in ml. Between stopcocks "E" and "G" is a calibrated tube (Note 7) with a mark at 1 ml. at "F". This volume is measured down to the top of the mercury meniscus from "E", when the latter is closed. Stopcock "C" has a discharge tube "D" used for cleaning the reaction burette. The measuring burette is calibrated in 0.5 ml. divisions and is equipped with one two-way stopcock "H".

**Procedure:** Tube "A" is filled with the sample to be examined. "B" is filled with 50% phosphoric acid (Note 5). The mercury leveling bulb is raised and any air or water present is run out of the reaction burette thru "D". Stopcock "C" is then opened to "A" and a small amount of mercury is forced up into "A" in order to insure the absence of air in the system. The mercury leveling bulb is then carefully lowered until the level of the mercury is at "F", when stopcocks "E" and "G" are closed (Note 2). There is now one ml. of the liquid in the calibrated portion of the reaction burette. Stopcock "G" is opened and the mercury is lowered until all this liquid is below stopcock "G". Stopcock "E" is then opened slowly to "B" and 2 or 3 ml. of 50% phosphoric acid allowed to run in from "B". "E" is then closed (Note 10).

The mercury is raised and lowered several times in order to mix the acid and the solution thoroughly. The measuring burette which is full of gas confining solution is then opened thru "H" to "G". "G" is opened to "H" and the gas in the reaction burette is pumped thru "G" and "H" into the measuring burette. "H" is then closed and "G" is turned thru 180 deg. and the reaction burette from "E" down is evacuated by lowering the mercury. "G" is again opened to "H" and the gas is pumped into the measuring burette. This process is repeated until no further gas is obtained on evacuating the reaction burette. This drives out all the $CO_2$ dissolved in the acidified solution.

With stopcock "H" closed the gas confining solution leveling bulb is raised or lowered until its level is the same as the level inside the burette (Note 4). The volume of gas is then read to the nearest 0.25 ml.

Record the room temperature and barometric pressure.

Run determinations in duplicate and report the average. Duplicate determinations should check within 0.50 ml. in gas volume.

**Calculation:** For routine testing, the volume of $CO_2$ obtained may be reported directly as volumes of $CO_2$ per volume of solution at ____ deg. F (or deg. C) and ____ mm. pressure.

It is preferable to correct the $CO_2$ volumes obtained to dry $CO_2$ at 0 deg. C. and 760 mm. absolute pressure, correcting for room temperature. This can be done by referring to charts 5 and 6 which include the corrections. (Note 9). They will then be reported as volumes of $CO_2$ per volume of solution (V/V) corrected to 0 deg. C and 760 mm. or V/V S.C

Volumes of $CO_2$ per volume of solution, corrected to 0 deg. C and 760 mm., multiplied by 0.141 gives standard cubic feet (SCF) of $CO_2$ per gallon of solution.

When determinations are made on both rich and lean amine solutions the difference between the two values obtained will be the net $CO_2$ removal or recovery effected by the solution.

The net recovery of $CO_2$ in V/V S.C. multiplied by the circulation rate in gallons per minute and then multiplied by 0.99 gives the $CO_2$ recovery in pounds per hour.

Cleaning the Apparatus: Stopcock "H" is opened to "I" and the confining liquid is raised to drive the gas out thru "I". (Note 4).

Stopcocks "C" are opened to "A" and the liquid remaining in "A" allowed to drain into the reaction burette. Stopcock "C" is then opened to "D" and the contents of the reaction burette are discharged thru "D". "A" is then filled with water and drained into the reaction burette and then pumped out thru "D". Two water washes are sufficient. It is not necessary to disturb the acid in "B" during the washing.

Note 1: The stopcocks must be well ground and greased to prevent leaks.

Note 2: Discharge the first sample of liquid through "D" and measure out a second before proceeding with the determination, as the walls of the reaction burette are usually wet and result in a slight dilution of the sample.

Note 3: This is a confining solution proposed by Kobe and Kenton (Ind. Eng. Chem., An. Ed. 10, 76 (1938).

$CO_2$ is much less soluble in this solution than in water.

For rough determinations, water is a suitable confining liquid provided the gas volumes are measured quickly.

Note 4: It is preferable to run the tube between "G" and "H" full of confining solution before beginning the determination. After all the gas has been run from the reaction burette into the measuring burette during the determination, run enough of the acidified sample over to fill the tube from "G" to "H" with liquid. After the gas volume has been read, run the liquid back into the reaction burette, run the gas out at "I", and refill the tube from "G" to "H" with confining solution. The slight mixing of the acidified sample with the confining solution does no harm.

Note 5: Fifty per cent phosphoric acid may be purchased from most suppliers of laboratory chemicals. Technical or USP grades are both suitable for this determination. Seventy or 85% syrupy phosphoric acids are both suitable for use in this determination, either full strength, or diluted to 50%. Sulphuric acid (1-1) prepared by adding one volume of concentrated sulphuric acid to one volume of water (Caution!) may also be used, but phosphoric acid is preferred because it is less dangerous to handle.

Note 6: If the amine solution contains other substances which become gases when the sample is acidified, these will be measured with the $CO_2$. Such interfering substances are $H_2S$, $SO_2$, and $N_2O_3$.

When $H_2S$ is present in the amine solution along with $CO_2$, it is necessary to add 3 ml. of 10% sodium or potassium bichromate to the amine solution sample in the reaction burette to oxidize the $H_2S$ to sulphur before the sample is acidified. This procedure is given in detail in SM7.

$SO_2$ is not normally present in amine solutions containing $CO_2$. It can also be removed by the treatment given in SM7.

$N_2O_3$ ($NO_2$ + NO) is present in amine solutions in some cases where the gases being scrubbed contain nitrogen oxides in addition to $CO_2$. In such cases, the apparent $CO_2$ contents obtained by SM5 will be in error.

Note 7: Before a new reaction burette is used, the volume of the measuring tube should be calibrated accurately by determining the weight of mercury it contains. This may be done by inverting the reaction burette and drawing mercury by suction up to the mark in the measuring tube thru tube "G". This mercury is then run into a weighed flask thru tube "H", taking care that no drops adhere to the glass, and its weight determined, and from that the volume of the measuring tube. If this varies appreciably from 1 ml., a volume correction factor should be applied to the results obtained.

Note 8: This equipment may be obtained from the following suppliers by referring to Girdler drawing CS-28, entitled Carbonimeter and Van Slyke Testing Apparatus.

Corning Glass Works
Corning, New York

Yonkers Supply Company
515 West 132nd Street
New York, New York

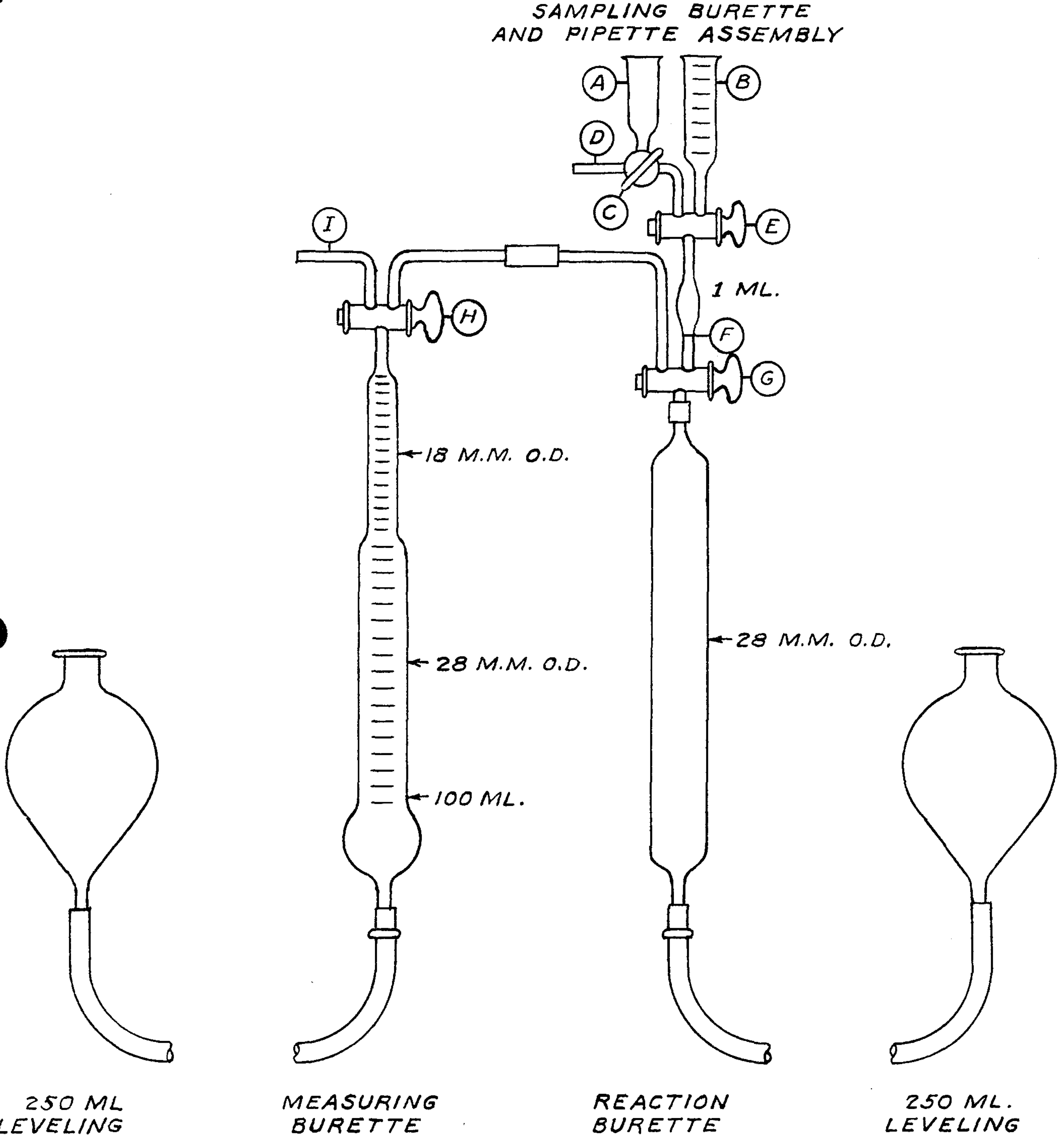
Scientific Glass Apparatus Co.
Bloomfield, New Jersey

Note 9: If temperatures below 14 deg. C are encountered during the determination, special charts similar to No. 5 and 6 may be obtained from the Process Development and Research Laboratories of the Gas Processes Division for this lower temperature range.

Note 10: It is also permissible to pipette the sample directly into funnel "B". It is then washed into the reaction burette with a little water. This method is especially useful when the amount of $CO_2$ is small and larger samples are necessary.

SM-5

SM-7



| | | | | |
|---|---|---|---|---|
| 1 | 3-1-48 | NOTE AND RUBBER CONNECTING SLEEVE ADDED | VKH | RYB |
| NO. | DATE | REVISION | BY | CKD. |

**THE GIRDLER CORPORATION**

**GAS PROCESSES DIVISION**

**LOUISVILLE, KENTUCKY**

| | | | | |
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| SCALE | | | PROJ. DR. | |
| DRAWN | HODGES | 10-13-48 | CHIEF DR. | |
| CHECKED | | | ENGINEER | |

FOR:

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CARBONIMETER

S-117

SM-5
SM-7

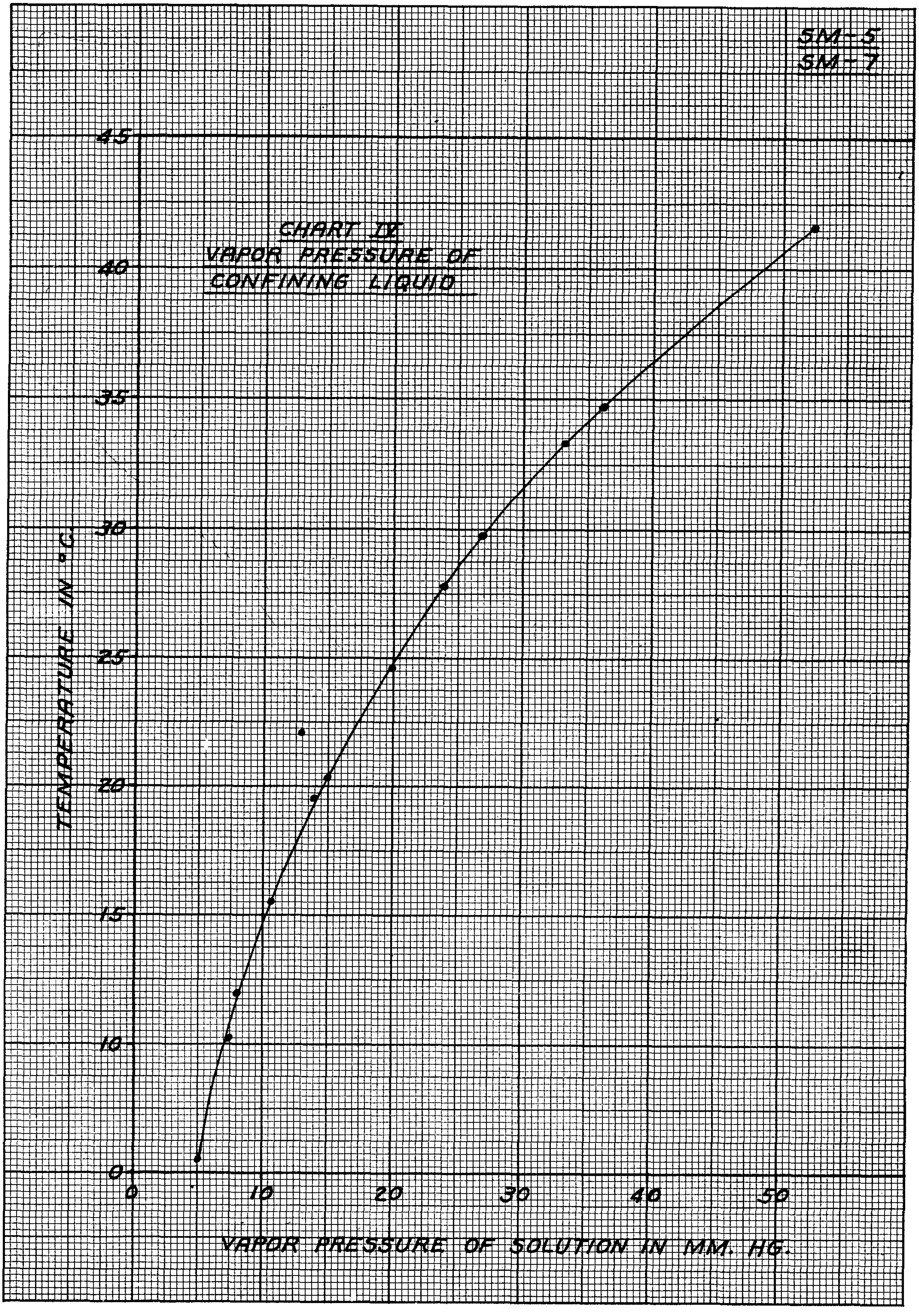
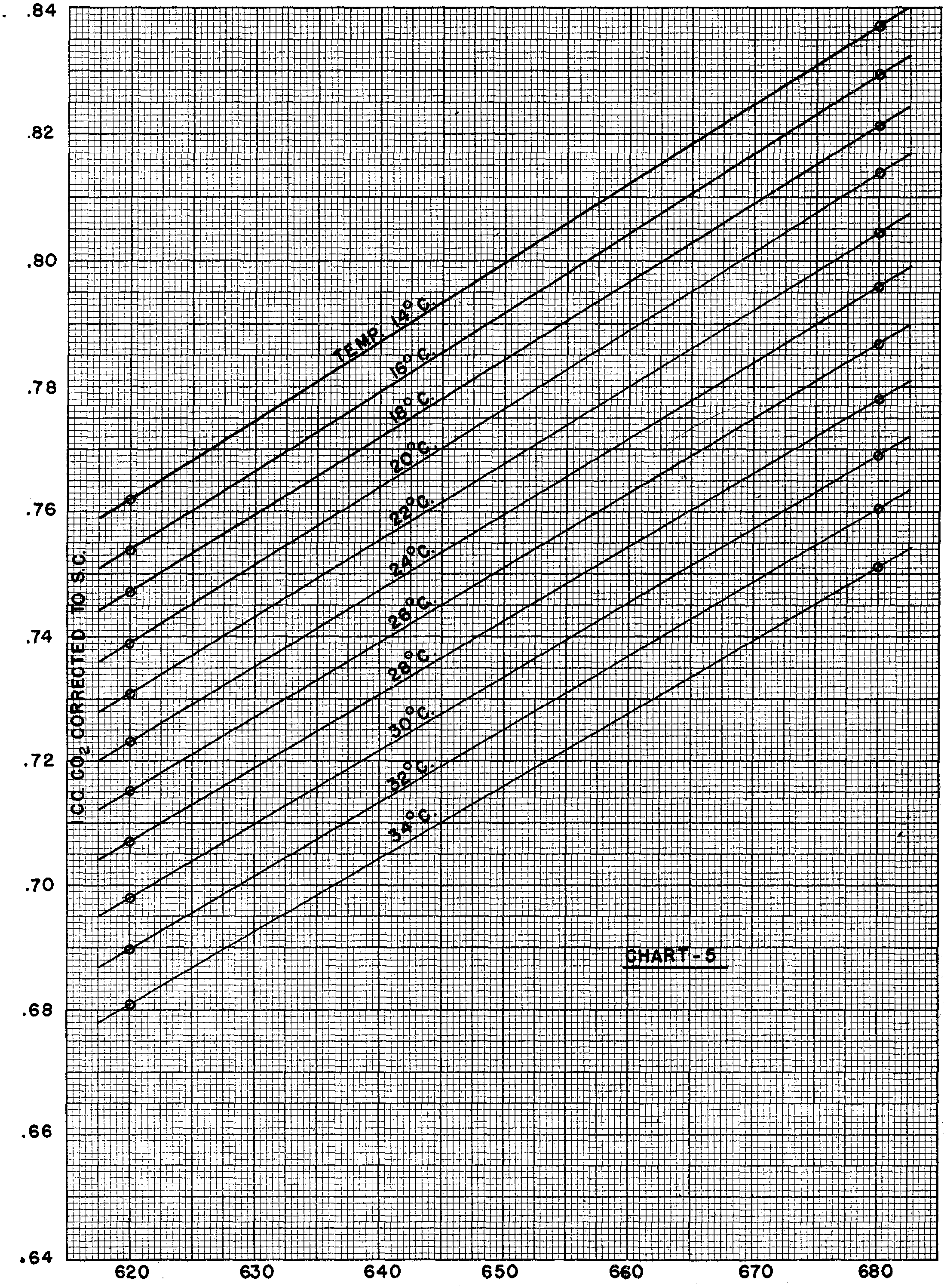


CHART IV
VAPOR PRESSURE OF
CONFINING LIQUID



.84
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.80
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1 CC. CO₂ CORRECTED TO S.C.
TEMP. 14° C.
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18° C.
20° C.
22° C.
24° C.
26° C.
28° C.
30° C.
32° C.
34° C.
620
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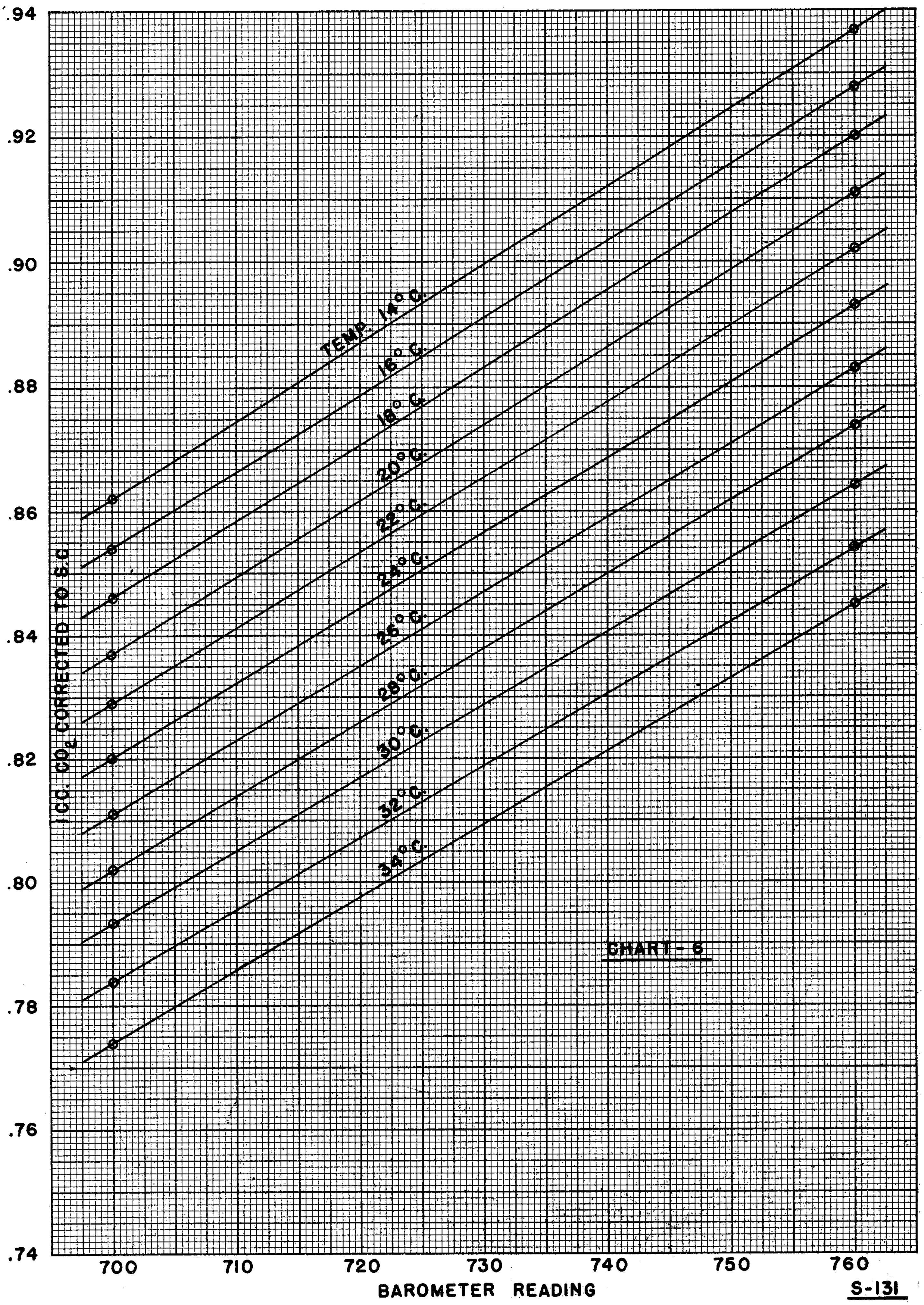
660
670
680
BAROMETER READING

CHART - 5


.94
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.86
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.78
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.74
1 CC. $CO_2$ CORRECTED TO S.C.
TEMP. 14° C.
16° C.
18° C.
20° C.
22° C.
24° C.
26° C.
28° C.
30° C.
32° C.
34° C.
700
710
720
730
740
750
760
BAROMETER READING

CHART - 6

## SM-17 - DETERMINATION OF TOTAL MEA IN PLANT SOLUTIONS

Method: The method, a modification of that proposed by D. D. Van Slyke (Ber. 43 3170-81,1910), is based on the reaction between nitrous acid and a primary aliphatic amine.

$$RNH_2 + NaNO_2 + Acid \longrightarrow ROH + NaSalt + H_2O + N_2$$

The nitrogen evolved is exactly twice that present in the primary amine. Due to partial decomposition of the nitrous acid formed in the reaction, considerable nitric oxide is also liberated and must be removed before the volume of nitrogen is read. Any hydrogen sulphide or carbon dioxide present in the amine solution is also liberated by the reaction and must be removed from the nitrogen.

Reagents: 17% by wgt. phosphoric acid (Note 10)
Saturated water solution of Sodium Nitrite
2% solution of Oxalic Acid
225 mls. solution containing 13.5 g. Potassium Permanganate and 5.6 g. Sodium Hydroxide.

Apparatus: The apparatus required for the determination is illustrated in Blue Print #S110, attached (Note 9). The Reaction Burette is filled with Mercury and the 100 ml. Burette with a 2% water solution of Oxalic Acid. The Permanganate Scrubber is filled to the graduation E with 225 ml. of a solution containing 5.6 g. Sodium Hydroxide, and 13.5 g. Potassium Permanganate.

Procedure: Before making a determination (Note 11) the Scrubber should be completely filled as described. Fill the 100 ml. Burette completely, closing Stopcock C. Set Stopcock D open thru the Manifold between Stopcocks C and F with the passageway to graduation E closed off. Fill the Reaction Burette with Mercury up thru the tube between Stopcocks A and F, filling the capillaries in Sample Tubes G and H so that no air will be trapped when the solutions are poured into the Sample Tubes. In filling the Reaction Burette, force any water floating on the Mercury out into the discharge line thru Stopcock A before passing Mercury into the Sample Tubes. Close Stopcock F. Set Stopcock A for passage from Sample Tube G into the Reaction Burette and Stopcock B for passage from Sample Tube G into the Reaction Burette.

Pour at least 5 ml. of the Solution to be tested into Sample Tube G. (Note 12). By manipulating the Leveling Bulb and opening Stopcock F draw the Solution down into the measuring tube (Note 5) to the 1 ml. mark. Open Stopcock A to the discharge line, and force the solution out the discharge line. This will rinse any water out of the measuring tube. Then open Stopcock A to the reaction burette and draw exactly 1 ml. of the solution into the measuring tube and close Stopcock F. Close Stopcock B and open Stopcock F. Pour approximately 5 ml. of the Sodium Nitrite Solution into Sample Tube H and draw the greater part of it into the Reaction Burette by opening Stopcock B. Close Stopcock B while there is still a small quantity of Sodium Nitrite in the capillary of the Sample Tube so that no air enters the apparatus.

Pour approximately 5 ml. of 17% Phosphoric Acid into Sample Tube H. Lower the Leveling Bulb so as to pull a partial vacuum on the Reaction Burette and allow the greater part of the Phosphoric Acid to flow into the Reaction Burette by opening Stopcock B. Considerable gas will be evolved in the Reaction Burette and the Leveling Bulb must be held low enough that no gas escapes up thru Stopcock B. Close Stopcock B before all of the Phosphoric Acid has run out of the capillary of the Sample Tube to prevent air entering the apparatus. Close Stopcock F, open Stopcocks A and B to the drain line and open Stopcocks C and D to the 100 ml. Burette.

Raise and lower the Mercury Leveling Bulb several times to mix the liquids in the Reaction Burette and pump the evolved gas into the 100 ml. Burette, by opening and closing Stopcock F, until approximately 100 ml. have been collected. Do not permit any liquid to pass thru Stopcock F. Close Stopcock F and allow the liquid in the Reaction Burette to stand under a slight vacuum. Set Stopcocks C and D for flow from the 100 ml. Burette into the Permanganate Scrubber and pump the gas into and out of the Scrubber until the Nitric Oxide and Hydrogen Sulphide or Carbon Dioxide are removed and the gas volume becomes constant by manipulating the Leveling Bulb and Stopcock C. When all of the impurities have been removed draw the gas back into the 100 ml. Burette and bring the Permanganate Solution up to graduation E. Close Stopcock C and read and record the volume of Nitrogen gas.

In the meantime more gas has collected in the Reaction Burette. Open Stopcocks C and D and pump this gas into the 100 ml. Burette by opening Stopcock F. Close Stopcock F and allow the mixture to stand in the Reaction Burette as before. Set Stopcock D as before and pump the gas in and out of the Permanganate Scrubber until all of the Nitric Oxide has been removed and record the volume of Nitrogen as before. Continue the process of taking gas from the Reaction Burette, removing the Nitric Oxide and recording the volume until the volume of Nitrogen is constant. Record the final volume (V) of Nitrogen. Record the atmospheric temperature and the barometric pressure at the time the final volume of Nitrogen is read.

Calculations: The data from the analysis are V, the volume of nitrogen obtained, and the atmospheric temperature and the barometric pressure read at the time of the determination. From Charts I or II, attached, the weight (W) of nitrogen in one c.c. of moist gas under the conditions of the determination may be found.

The total MEA in the plant solution, in per cent by weight may then be calculated from the following formula:

$$\% \text{ MEA} = \frac{0.218 \times V \times W}{\text{SpG of Sample} \times \text{Vol. of Sample}} \quad \text{(Note 8)}$$

Note 1: The Reaction Burette should be washed immediately after the determination because Nitric oxide continues to be evolved and may force the Mercury out of the Reaction Burette. Water should be added first thru Sample Tube H, then thru Sample Tube G, and discharged to the drain line thru Stopcock A. If a check determination is to be made on the same Solution, the Reaction Burette may be washed thru Sample Tube H without disturbing the contents of Sample Tube G.

Note 2: If Permanganate is drawn up into the Manifold during a determination, a small volume of water from the 100 ml. Burette may be pumped thru the manifold as a wash. A small quantity of Oxalic Acid is carried in this water to decolorize any Permanganate which contaminates it.

Note 3: When the solution in the Permanganate Scrubber is "spent", a heavy deposit of Manganese Dioxide will be found on the walls of the Scrubber. This may easily be removed by washing the Scrubber with a water solution of Oxalic Acid acidified with Sulphuric Acid. The Scrubber should then be washed thoroughly with water before it is charged with fresh solution.

Note 4: When the apparatus is not in use, all the Stopcocks should be rotated periodically to prevent their freezing.

Note 5: Before a new reaction burette is used, the volume of the measuring tube should be calibrated accurately by determining the weight of Mercury it contains. This may be done by inverting the reaction burette and drawing Mercury by suction up to the mark in the measuring tube thru Tube G. This Mercury is then run into a weighed flask thru Tube H, taking care that no drops adhere to the glass, and its weight determined, and from that the volume of the measuring tube. If this varies appreciably from 1 ml., a volume correction factor should be applied to the results obtained.

Note 6: With MEA solutions stronger than 20% the volume of Nitrogen evolved may be more than 100 ml. In these cases, about half of the Nitrogen may be left in the Reaction Burette, and the balance scrubbed to constant volume, and its volume recorded. It is discharged out of the 100 ml. Burette to the air, and the balance of the Nitrogen then scrubbed and measured. The total volume of Nitrogen will be the sum of the two volumes obtained.

An alternate procedure for concentrated MEA solutions is to dilute them accurately to below 20%, and carry out the determination on the diluted solution, converting the results back to the basis of the original solution.

Note 7: The determination should always be made on lean (regenerated) MEA solution to minimize the amount of Hydrogen Sulphide or Carbon Dioxide present.

Note 8: If a comparison is to be made between the MEA content of plant solution as determined by Van Slyke analysis with the MEA as determined by titration (SM1M) the specific gravity of the sample should be taken as 1.0 unless the actual specific gravity is applied as a correction factor to the result obtained by SM1M.

Note 9: This equipment may be obtained from the following suppliers by referring to Girdler drawing CS-28, entitled Carbonimeter and Van Slyke Testing Apparatus.

Corning Glass Works,
Corning, New York.

Yonkers Supply Company,
515 West 132nd Street,
New York, New York.

Scientific Glass Apparatus Company,
Bloomfield, New Jersey.

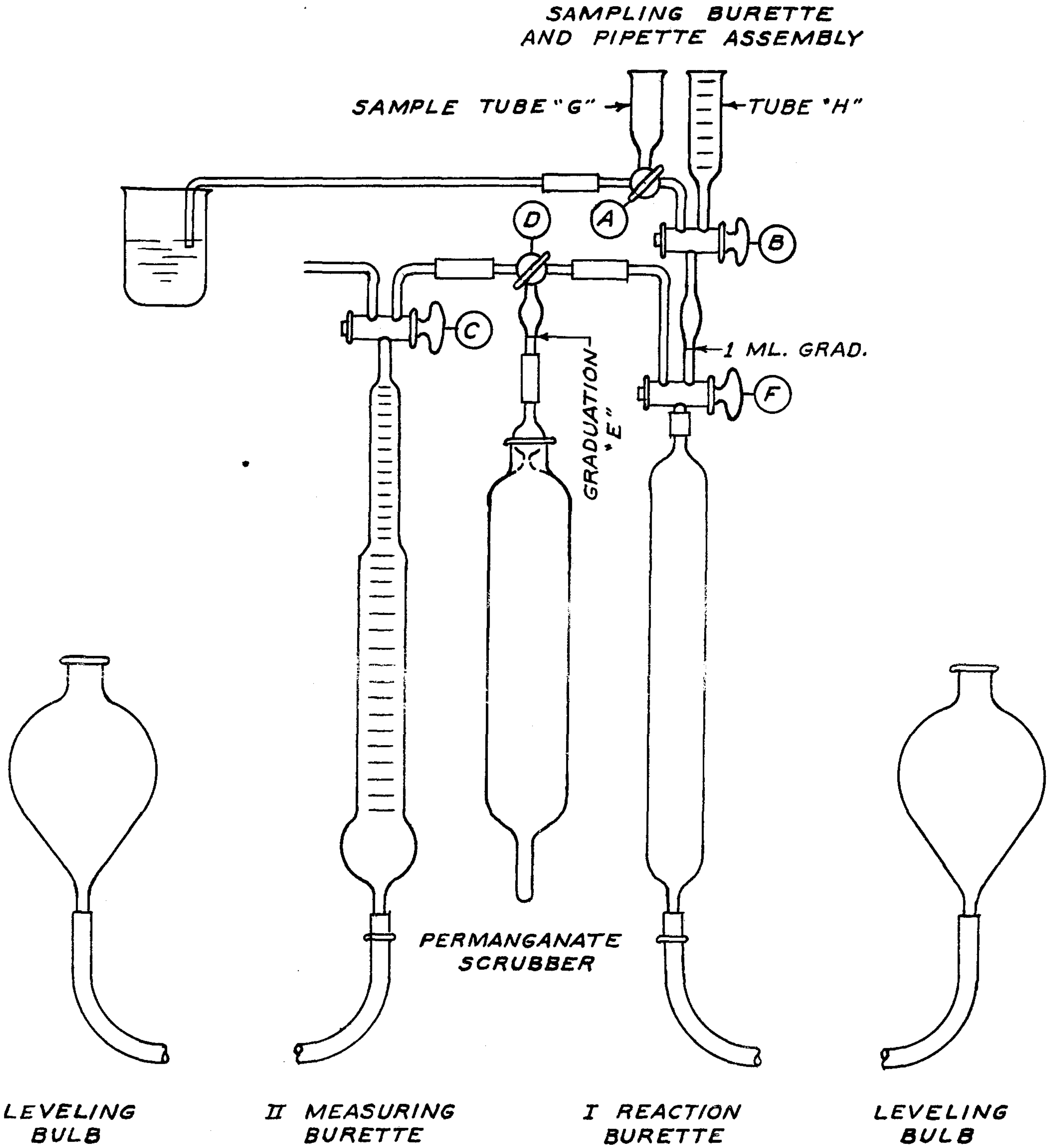
Note 10: Glacial Acetic Acid, although less desirable, may be used in place of 17% by wgt. Phosphoric Acid.

Note 11: Care must be taken to wash the manifold and reaction burette thoroughly with water before using the equipment as a Van Slyke testing apparatus after it has previously been used as a carbonimeter, otherwise, the results will be high. This is due to the tendency of MEA and MEA Phosphate to adhere to the walls of the manifold when the apparatus is used as a carbonimeter, which later liberate nitrogen when the apparatus is used in the determination of primary amine.

Note 12: It is permissible to pipette the sample directly into funnel "B". It is then washed into the reaction burette with a little water. The method is especially useful when the amount of primary amine is small and larger samples are necessary.

1-22-46

SM-17



| NO. | DATE | REVISION | BY | CKD. |
|---|---|---|---|---|
| 1 | 3-1-48 | NOTE AND RUBBER CONNECTING SLEEVE ADDED | VKH | RYB |

**THE GIRDLER CORPORATION**
**GAS PROCESSES DIVISION**
**LOUISVILLE, KENTUCKY**

| | | | |
|---|---|---|---|
| SCALE | | PROJ. DR. | |
| DRAWN HODGES | 10-13-48 | CHIEF DR. | |
| CHECKED | | ENGINEER | |

FOR:

CARBONIMETER
AND VAN SLYKE
TESTING APPARATUS

S-110

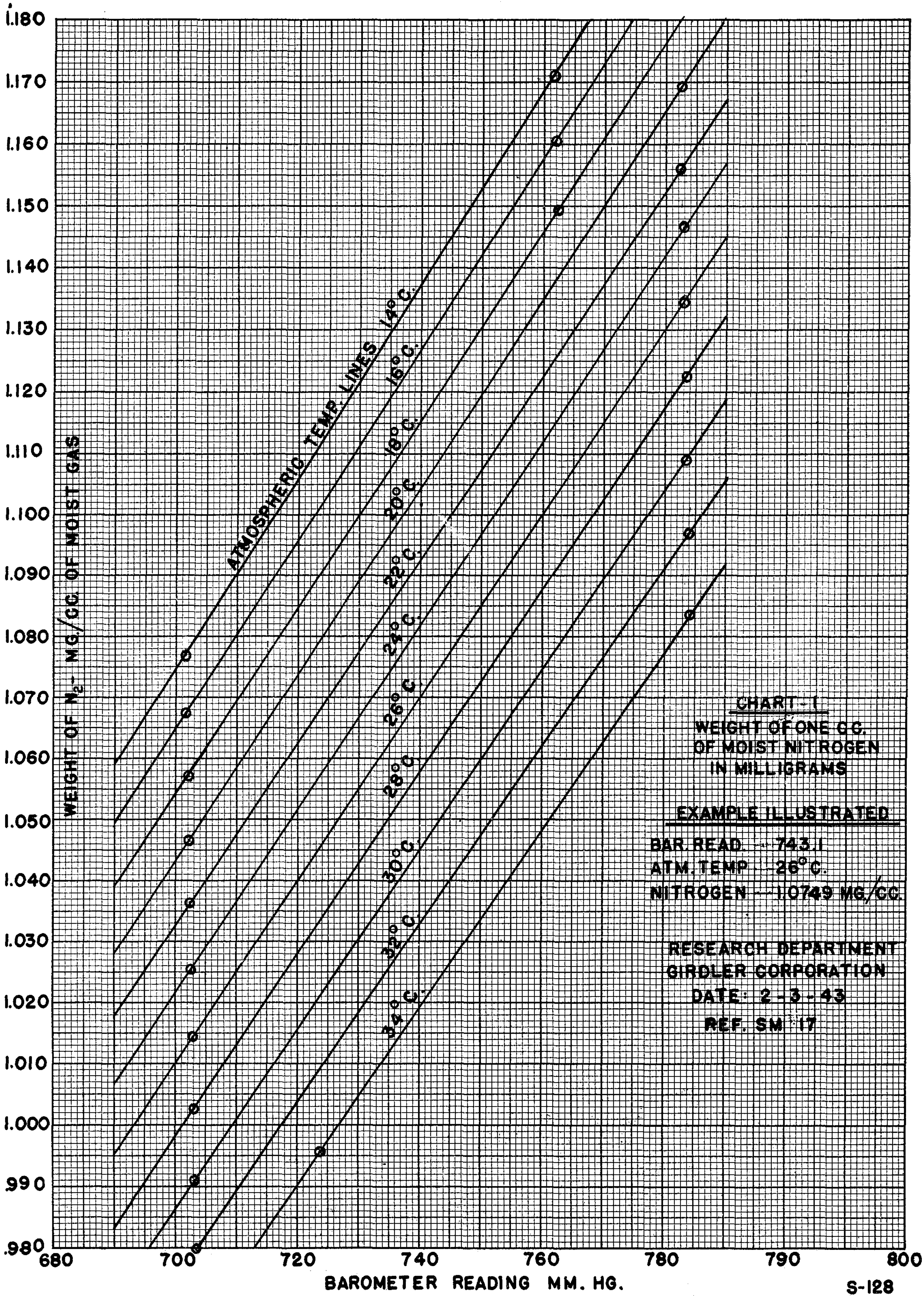


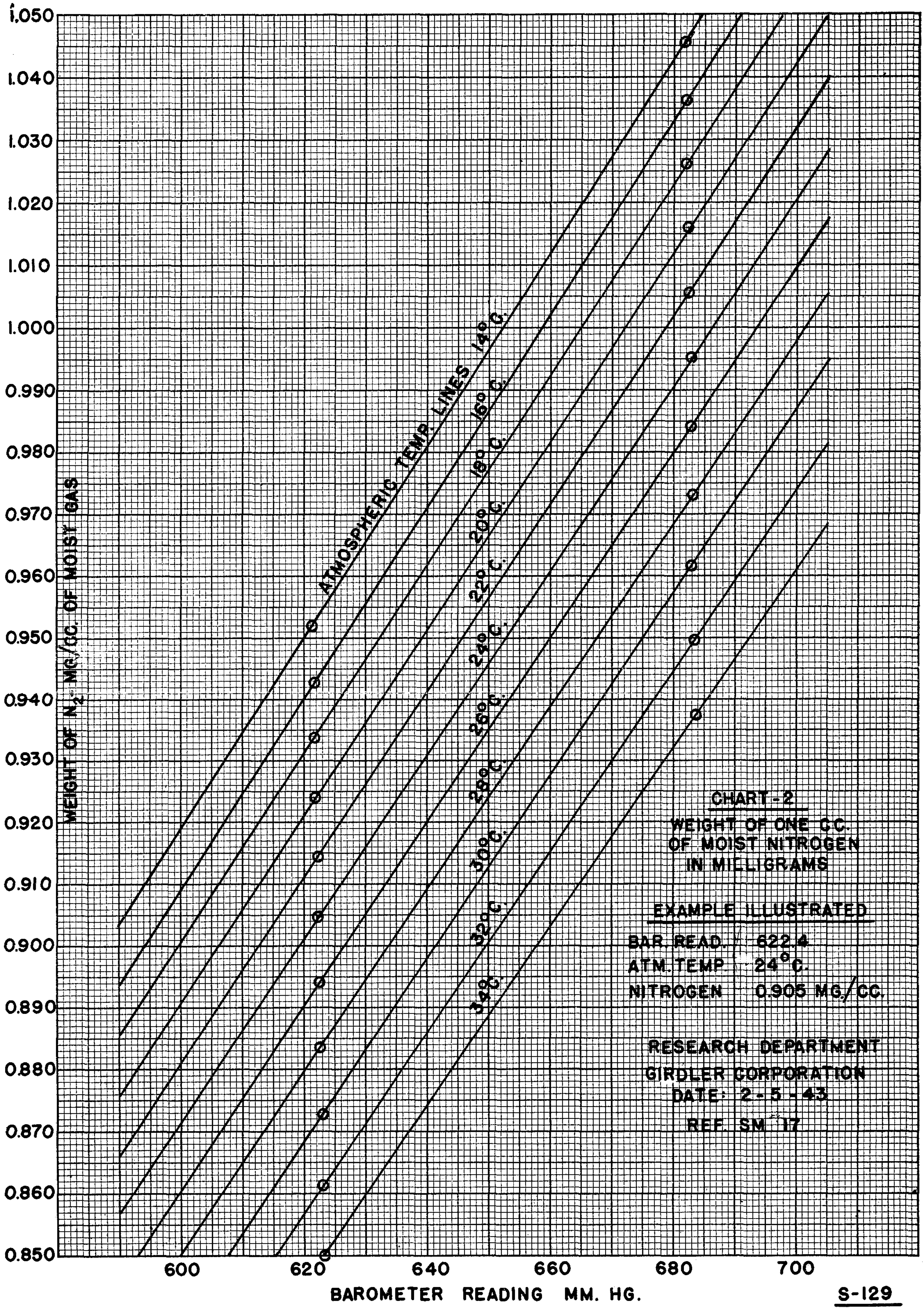
CHART - 1

WEIGHT OF ONE C.C.
OF MOIST NITROGEN
IN MILLIGRAMS

EXAMPLE ILLUSTRATED

BAR. READ. — 743.1
ATM. TEMP. — 26° C.
NITROGEN — 1.0749 MG./CC.

RESEARCH DEPARTMENT
GIRDLER CORPORATION
DATE: 2 - 3 - 43
REF. SM 17



## CHART - 2

WEIGHT OF ONE C.C.
OF MOIST NITROGEN
IN MILLIGRAMS

EXAMPLE ILLUSTRATED

BAR. READ. 622.4
ATM. TEMP. 24° C.
NITROGEN 0.905 MG./CC.

RESEARCH DEPARTMENT
GIRDLER CORPORATION
DATE: 2 - 5 - 43
REF. SM 17

## SM-25 COLORIMETRIC DETERMINATION OF IRON IN GIRBOTOL PLANT SOLUTIONS

Method: The organic matter in the solution is completely destroyed by oxidation. Iron is then determined colorimetrically with potassium thiocyanate by comparison with standard solutions in Nessler tubes.

Reference: Kolthoff and Sandell, "Quantitative Inorganic Analysis", the Macmillan Co., New York, 1937, page 635.

Reagents: Standard iron solution prepared as follows. Dissolve 0.7022 gms. $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ in one liter of 0.5N $HNO_3$ to which several drops of bromine water have been added. One ml. of this solution contains 0.1 mg. of iron.

Concentrated $HNO_3$
3N $HNO_3$
30% $H_2O_2$
0.2N $KMnO_4$
2% KCNS

Apparatus: 0.1ml. "to contain" pipette
1 ml. pipette graduated in 0.01 ml.
1 ml. "to deliver" pipette
30 ml. micro Kjeldahl flasks
Flask tongs
Micro Kjeldahl digestion rack (may be purchased from Harshaw Scientific Co., Cincinnati, Ohio, Cat. No. A64-200)
100 ml. Nessler color comparison tubes
Nessler color comparison tube support
25 ml. graduate cylinder

Procedure: To a 0.2 ml. filtered sample (a 0.1 ml. sample should be used if the plant solution contains more than 1000 mg. of iron per liter) of the plant solution in a 30 ml. micro Kjeldahl flask is added 1 ml. of concentrated $HNO_3$ and the mixture digested to a volume of approximately 1 ml. A few drops of 30% $H_2O_2$ are added, the solution warmed, and the reaction permitted to take place without further heating. After standing for five minutes to allow the organic matter to oxidize, the solution is evaporated almost to dryness, 2-3 ml. distilled water added, and the evaporation repeated. A second 2-3 ml. portion of distilled water is added and the solution again evaporated almost to dryness. 25 ml. of distilled water, 1 ml. of 3N $HNO_3$ and 10 drops of 0.2N $KMnO_4$ are then added and the solution allowed to stand five minutes. If the purple permanganate color is not permanent, more $KMnO_4$ must be added.

The solution is transferred quantitatively to a 100 ml. Nessler tube, 10 ml. of 2% KCNS added, made up to 100 ml. and after mixing, the color (Note 1) is immediately compared with a standard prepared as follows: To a 100 ml. Nessler tube is added 10 ml. of 2% KCNS, 2 ml. of 3N $HNO_3$ and distilled water to make it up to the 100 ml. mark. This solution is then titrated with the standard iron solution until its color corresponds with that of the unknown. Report the iron content of the solution as parts per million of dissolved iron. The titration can be conveniently carried out with a 1 ml. pipette graduated in 0.01 ml.

Calculation: $\frac{\text{ml. standard iron solution x 100}}{\text{ml. of sample}}$ = parts per million of dissolved iron.

Note 1: The color which develops when the thiocyanate is added to the solution of iron tends to fade rather rapidly, and 2 ml. of 0.25% $H_2O_2$ can be added to restore the original color if necessary.

Revised 1-21-46

## SM-27 DETERMINATION OF IRON CAPACITY OF AMINE SOLUTIONS

**Method:** The amine solution after the removal of any copper present, is saturated with $CO_2$ at room temperature and contacted with iron filings at 50 deg. C after which it is filtered and the iron content of the solution determined by SM25.

**Reagents:** Hydrogen sulfide
Carbon dioxide
Iron filings, 40 mesh, degreased

**Apparatus:** Gas dispersion tube with fritted disc
Filter paper, Whatman No. 2
Test tubes, Corning No. 9820, 25 x 150 mm.
Pipe nipples, 1" x 6"
Pipe caps, 1"
Rubber stoppers, No. 5
Constant temperature bath

**Procedure:** 35 ml. of the sample after any copper present has been removed (Note 1) is saturated with $CO_2$ at room temperature by contacting it with $CO_2$ by means of a gas dispersion tube having a fritted disc. The $CO_2$ is passed thru the solution until it reaches room temperature. This may require from 10 to 20 minutes. The solution is then placed along with 20 grams of 40 mesh degreased iron filings in a Corning No. 9820, 25 x 150 mm. test tube and the latter closed with a rubber stopper. This is placed in a 1" x 6" pipe nipple which is then closed at both ends by 1" pipe caps. A small piece of rubber is placed in the cap on which the bottom of the test tube is to rest to prevent breakage. The pipe nipple and contents are placed in a suitable revolving mechanism located in a constant temperature bath held at 50 deg. C which rotates the nipple approximately 40 RPM for 20 minutes (Note 2).

The pipe nipple and its contents are then removed, cooled under tap water and opened carefully. After the solution has been filtered to remove any suspended iron, its iron content is determined by SM-25 (Note 3).

**Calculation:**

$$\frac{\text{ml. standard iron solution} \times 100}{\text{ml. of sample}} = \text{parts per million of dissolved iron}$$

**Note 1:** The copper is best removed by passing $H_2S$ into the solution to precipitate it as CuS. The solution is filtered, 20 ml. of water added and boiled to approximately the original volume before dilution. This is repeated until titration of a sample of the solution by SM6 shows no $H_2S$. If there is no copper present in the sample, it should be filtered before being saturated with $CO_2$.

**Note 2:** This mechanism rotates the tube containing the sample and iron filings so that they are maintained in constant agitation while at 50 deg. C.

**Note 3:** The iron content of the solution obtained after the above treatment is considered a measure of the corrosiveness of the solution. Only results from tests carried out in precisely the same manner are significant for comparison purposes.

2-20-46

## SM-33 THE DETERMINATION OF TOTAL AMINE BY THE MICRO KJELDAHL METHOD.

Method: The amino nitrogen in the sample is converted to ammonium sulfate by digestion with sulfuric acid. The ammonia is liberated by strong caustic and distilled into 2% boric acid. The ammonia is then titrated in the boric acid solution with 0.01 N sulfuric acid using bromo cresol green indicator.

Reference: Niederl and Niederl, Organic Quantitative Microanalysis, p. 51-58 John Wiley and Sons, 1938.
Ma and Zuazaga, Ind. Eng. Chem. Anal. Ed., 14, p. 280.

Reagents:
Sulfuric acid, 0.01 N standard solution.
Sodium hydroxide solution, 50% by wt.
Sulfuric acid, concentrated.
Potassium sulfate and copper sulfate, a 1-1 mixture.
Ammonia free water (Note 4).
Bromo cresol green indicator.

Apparatus:
50 ml. burette.
0.1 ml. pipette, calibrated to contain.
1 ml. pipettes.
5 ml. pipettes.
250 ml. Erlenmeyer flasks.
30 ml. micro Kjeldahl flasks.
Micro Kjeldahl digestion rack. Can be purchased from Harshaw Scientific Co., Cincinnati, Ohio. Cat. No. H52320.
Micro Kjeldahl distilling apparatus. Can be purchased from Scientific Glass Apparatus Co., Bloomfield, N. J., Cat. No. M-3074.

Procedure: A 0.1 ml. sample of the amine is used for the analysis. It is measured in a clean, dry 0.1 ml. "to contain" pipette and transferred to a 30 ml. micro Kjeldahl flask. The pipette must be rinsed with small portions of ammonia free water (Note 4) so that the whole sample can be transferred. 1 ml. of concentrated $H_2SO_4$ and a small amount (approximately 0.03 gm.) of $CuSO_4$-$K_2SO_4$ catalyst are added (Note 1). The flask is then placed in the Kjeldahl digestion rack and heated over a moderately low flame until the solution is a pale blue (Note 2). During the digestion it may be necessary to rotate the flask so that the acid may contact the particles of black material on the walls of the flask (Note 3). When the digestion is complete the flask is stoppered and cooled.

The distillation apparatus (see attached drawing) is prepared for use by steaming out three times with about 30 ml. of ammonia free water (Note 4) and with no water going through the condenser, H. Ammonia free water is always used in the flask, F, and is kept gently boiling during the washing operation. Water is added through funnel, A, and after it has agitated for a few minutes it is drained through D after opening E. After the third washing, the water in the flask, F, is heated until it is boiling vigorously. In the meantime, 5 ml. of 2% boric acid is added to a 250 ml. Erlenmeyer flask containing about 75 ml. of ammonia free water to which 3 drops of bromo cresol green indicator has been added (Note 5). Stop cock, D, is closed and pinch clamp E is opened. Stop cock, B, is opened and the sample added through funnel, A. The sample must be thoroughly washed out of the Kjeldahl flask with ammonia free water and at the same time the volume of the wash water must be kept at a minimum. Litmus paper is used to determine when all the acid is washed out of the Kjeldahl flask. Stop cock B is then closed and the flask, G, containing the 2% boric acid as previously prepared is placed under the condenser H, making certain that the tip of the condenser is submerged in the acid. The funnel, A, is nearly filled with 50% NaOH (about 10 ml.) and stop cock, B, is barely opened allowing the NaOH to run slowly into the bottom of the reaction tube, C, forming a layer under the sample. The stopcock, B, is again closed and the water turned on through the condenser, H. Then the pinch clamp, E, is slowly closed allowing the steam generated from the flask, F, to pass through the reaction tube, C, and to mix the sample with the NaOH. The distillation is thus carried on for 12 minutes while being closely watched to be sure that the proper conditions are maintained. Irregularities in the flame will sometimes cause too vigorous agitation in the reaction chamber and the caustic to foam into the spray trap. Sudden cooling due to air currents or to less vigorous boiling in the flask, F, will cause the acid in the flask, G, to back up into the condenser. At the end of 12 minutes the flame is turned up slightly and the flask, G, is lowered and the tip of the condenser washed off with ammonia free water. The ammonia absorbed in flask, G, is then titrated to a colorless or light pink end point using 0.01 N sulfuric acid.

In the meantime the distilling apparatus is cleaned as previously described before distilling the next sample.

Calculation:

$$\text{Wt. \% amine} = \frac{\text{ml. }_{H_2SO_4} \times N_{H_2SO_4} \times \text{mol. wt. amine}}{\text{specific gravity of sample}}$$

Note 1: Some samples are more difficult to decompose than others, especially those containing large percentages of organic matter. A little selenium catalyst or a few drops of 30% $H_2O_2$ will usually speed up the digestion.

Note 2: If the solution is brownish or yellowish green there is still a trace of organic matter and the digestion must be continued until the solution is pale blue.

Note 3: Sometimes black material will splash into the neck of the flask. These can usually be washed down with a little water. If they cannot be washed down the sample must be discarded.

Note 4: Ammonia free water is used to rinse out all apparatus and whenever wash water is needed during the determination. It is prepared by redistilling distilled water from a flask containing about 50 ml. of 85% phosphoric acid. The water thus prepared is stored in a 5 pint bottle.

Note 5: The boric acid solution should be colorless or slightly pink in the presence of bromo cresol green. If the solution is intensely red or blue it means that the mixture is contaminated with acid or base respectively, and should not be used.

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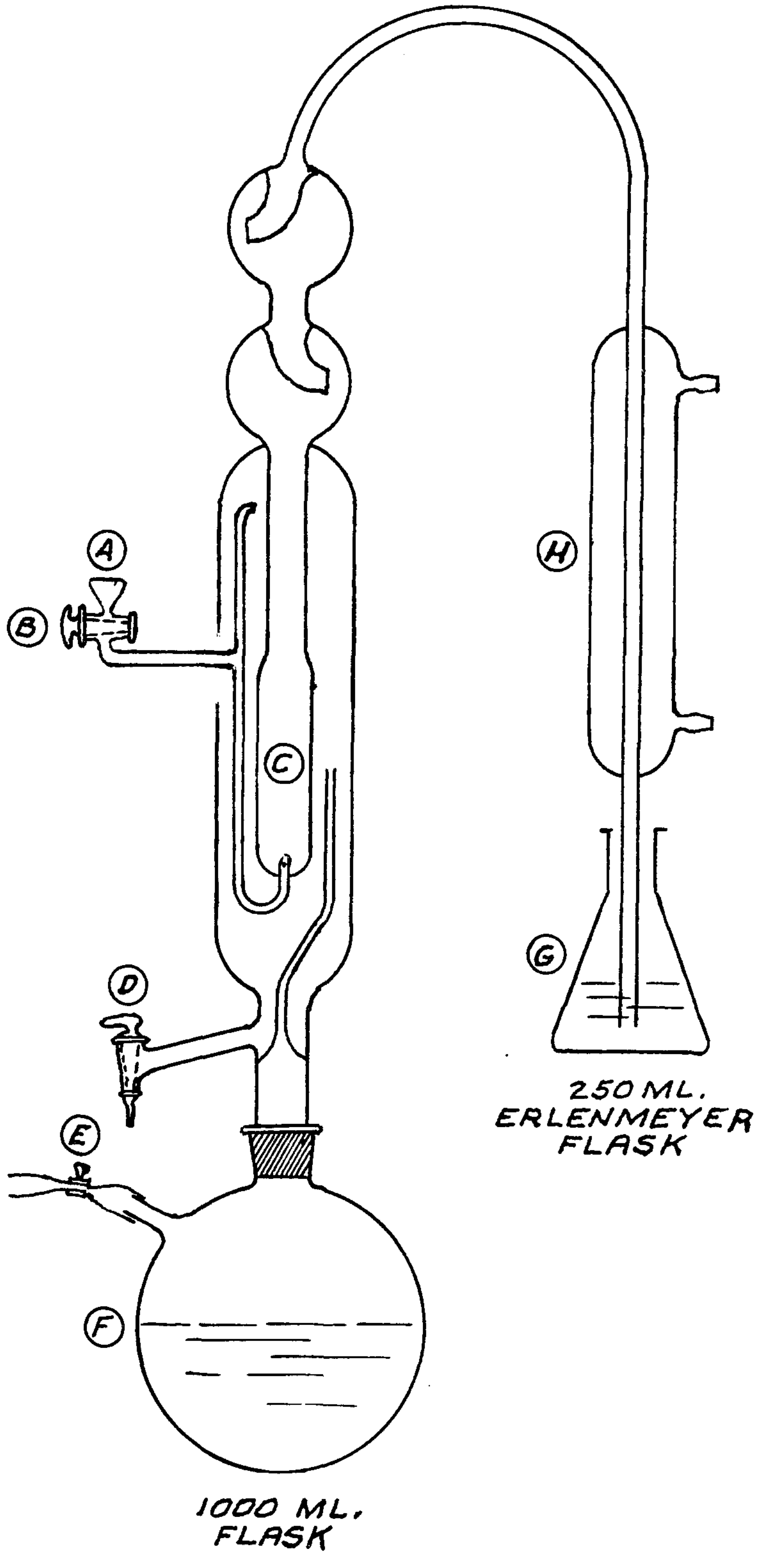
The Girdler Corporation
Louisville, Kentucky

SM-33



# THE GIRDLER CORPORATION

GAS PROCESSES DIVISION
LOUISVILLE, KENTUCKY

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| SCALE | | PROJ. DR. | |
| DRAWN HODGES | 10-13-48 | CHIEF DR. | |
| CHECKED | | ENGINEER | |

FOR:

MICRO-KJELDAHL
DISTILLING APPARATUS

SM-33