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Division 11

NATIONAL DEFENSE RESEARCH COMMITTEE

of the

OFFICE OF SCIENTIFIC RESEARCH AND DEVELOPMENT

CHARACTERISTICS OF THE OXYGEN ABSORBENTS ETHOMINE AND FLUOMINE

to June 30, 1945

by

Robert L. von Berg
W. E. Catterall

Report OSRD No. 5407

Copy No. 63

Date: July 31, 1945

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"The data here reported on the ethoxy and fluoro derivatives of the oxygen absorbent "Salcomine" were obtained to facilitate the design of apparatus for separating atmospheric oxygen. Other engineering data on oxygen absorbents is reported by the same contractor in the following: OSRD No. 291; OSRD No. 613; OSRD No. 1539; OSRD No. 1579; OSRD No. 1620. These reports, taken together, represent a complete report of work done under Contract OEmar-4."

This is a final report under Contract 11-69, OEmar-4 with Massachusetts Institute of Technology.
CHARACTERISTICS OF THE
OXYGEN ABSORBENTS
ETHOMINE AND FLUOMINE

Final Report to Division 11
National Defense Research Committee

June 30, 1945

Robert L. Von Berg, Author
W. E. Catterall, Supervisor

Contract 11-69, OEMsr-4
Massachusetts Institute of Technology
Cambridge, Massachusetts
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I. SUMMARY

The methods of modern warfare have created an urgent demand for oxygen producing equipment which is light and portable, as well as simple and reliable in operation. This need by the armed forces led to the consideration of oxygen production by means of chemical absorbents which remove oxygen from the air. This study deals with a phase of the development of such absorbent type oxygen producing units.

The particular problem considered here is that of obtaining sufficient basic data on the behavior of the absorbent to enable preliminary design of oxygen units. Only two compounds are discussed: (1) ethomine, on which most of the experimental work was done and which compound was the basis for most of the units designed; (2) fluomine, a new compound which proves to be better than ethomine in every way. Both compounds are derivatives of the organic chelate salcomine, cobalt salicylaldehyde ethylenediamine.

Because of the very immediate need for design data, considerable engineering absorption and desorption experiments were made, i.e., determinations were made of the rate of absorption of oxygen from air passed through a bed of ethomine (an arbitrarily chosen 1/2" jacketed copper tube) and the rate of evolution of this oxygen upon heating the bed. However, to search out the mechanism of the reaction, more basic data were also obtained. This consisted of equilibrium studies and rate studies using pure oxygen rather than air.
Analysis of these basic experiments on ethomine revealed that from 0 to 90 per cent of saturation the rate of oxygen absorption was directly proportional to the fraction of deoxygenated ethomine present; that is, the reaction was first order with respect to deoxygenated ethomine. The function of pressure was best correlated as \( p^{1.5} \) although no theoretical reason for the 1.5 power could be found. The relation between the specific reaction rate constant and temperature could not be successfully determined from theoretical studies and recourse to an empirical expression was made.

The rate of reaction of ethomine and oxygen in the range -10° to 60°C and 0 to 1000 mm. Hg oxygen partial pressure can be approximated as follows:

\[
\frac{dx}{dt} = \left[ 4.9 \ (10^{-4})_e - 1.1 (10^{-5}) (t-29)^2 \right] p^{1.5} \ \frac{a-x}{a} \]

where
\( x \) = weight per cent oxygen absorbed
\( s \) = " " " at saturation
\( t \) = °C
\( p \) = oxygen partial pressure in mm. Hg
\( t \) = time in minutes

Although the ethomine-oxygen system is not a true monovariant heterogeneous system (the equilibrium vapor pressure is a function of both temperature and composition), its general properties are comparable to such a monovariant system as \( \text{CaCO}_3 - \text{CaO} - \text{CO}_2 \).

Differential equations were set up for the absorption of oxygen from air by ethomine in an isothermal bed, assuming...
the chemical rate of reaction to be controlling. These were solved by the calculation of finite increments in a stepwise procedure and the solution put into graphical form. This solution checked the experimental data very well over a wide range of conditions.

The desorption process is controlled by the heat flow to the compound rather than the chemical rate of desorption. An adaptation of the graphical Schmidt method was applied as an analytical solution of this problem of heat transfer to a bed of desorbing ethomine. Remarkably good checks with experiment were obtained.

By these methods both absorption and desorption data for a bed of ethomine can be predicted with considerable accuracy. It is possible, therefore, to make preliminary designs without constant recourse to experimental work.

Experimental work on fluomine showed it to have the same general properties as ethomine. The optimum absorption temperature and the equilibrium desorption temperature were approximately the same as those of ethomine but fluomine had a higher rate of reaction and a higher oxygen capacity (4.2 per cent as compared to 5.5 for ethomine).

A comparison was also made of the life characteristics of salcombe, ethomine, and fluomine when run under ideal cyclical conditions as predicted by the most recent theories on deterioration. Fluomine showed a life considerably better than either salcombe or ethomine on the basis of oxygen produced. Its rate of deterioration was less than half that of ethomine and at 50 per cent deterioration, it had produced 70 times its weight of oxygen.
II. INTRODUCTION

Gaseous oxygen of high purity can be obtained on a commercial scale by the rectification of liquid air, and from an economic viewpoint, this is the preferred process. However, modern warfare has placed many varied and special demands on oxygen supplies. The distributing of oxygen for general use in distant outposts, supplying oxygen for shock treatment on the battlefield, and the furnishing of a life sustaining atmosphere for high altitude flying are problems faced by our armed forces. Because the standard commercial methods are not easily adaptable to small scale light weight plants or to intermittent operation, considerable interest has been shown in other methods of producing oxygen.

Certain chelate compounds have the unique property of forming a loose combination with oxygen which will decompose on heating. Such a compound makes possible a chemical system of oxygen production, and an investigation of its potentialities was deemed quite worthwhile. Researches were carried out both from the chemical standpoint of discovering new compounds and improving methods of making those already known, and from the engineering standpoint of developing methods of utilizing the oxygen absorbent and of evaluating the compounds furnished by the chemist.

This investigation was concerned mainly with the physical-chemical properties of ethomine and fluomine, the two most promising compounds on a basis of practical
utilization. The research had a twofold purpose: (1) to obtain specific data immediately necessary for the design of large units to utilize the oxygen-producing properties of the compounds and (2) to obtain sufficient basic data to enable the prediction of the behavior of a given compound with respect to the several variables involved (temperature, pressure, composition, and time).
In 1937 Tsumake (13) reported on the oxygen-absorbing properties of a metallic organic compound, cobalt salicylaldehyde ethylenediamine. This compound, now known as salcomine, has an oxygen-absorbing capacity of 4 per cent of its own weight and a rapid rate of absorption and desorption at temperatures of 20°C and 100°C respectively.

Calvin (1), Diehl (2), Geissman (3) and their associates have investigated a large number of compounds of the same general chelate form and found only a few that would react with oxygen reversibly. For the most part, these are either derivatives of the parent compound salcomine or of cobalt salicylaldehyde propylenetriamine which was developed by Calvin. Salcomine and its derivatives differ from the cobalt salicylaldehyde propylenetriamine and its derivatives in that the former absorb a half molecule of oxygen per molecule of chelate and have reasonable absorption rates at atmospheric pressure whereas the latter absorb one molecule of oxygen per molecule of chelate but require extremely high oxygen pressures.
Listed below are the derivatives of saloomine that were investigated. A brief summary of properties is given when these are available.

From the table, it appears that the 3-position is especially important and that the rates of absorption can be controlled by substitution there. The oxy-group (with the exception of the 3-F) produces the most active compound. Also, it is at least suggested that as the chain length of the oxy-group is increased, the absorption rate will increase, the desorption temperature will rise, and the material will become more hygroscopic.

Since the compounds are chelate in nature and have some weak and easily shifted bonds, they are subject to chemical attack and do deteriorate materially with use. This will be discussed more fully in the section on deterioration. Saloomine has what is considered good life characteristics but is a comparatively slow absorber. On the other hand, the 3-ethoxy saloomine (called ethomine) has a sufficiently high absorption rate and can be used in a much more favorable temperature range but has poorer life characteristics than the parent compound.

A search for a more stable compound which would have the same general properties as ethomine yielded the 3-fluoro saloomine (called fluomine). It not only has better life characteristics than saloomine but a higher absorption rate and higher saturation value than ethomine. It is, however, exceedingly difficult to make and as yet can be produced only on laboratory scale at very high cost.
<table>
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<tr>
<th>Compound</th>
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<th>Practical Absorption Temp. °C.</th>
<th>Absorption Rate</th>
<th>Remarks</th>
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<tr>
<td>salcomine</td>
<td>60°</td>
<td>0°</td>
<td>Absorbs slowly at 1 atm.</td>
<td></td>
</tr>
<tr>
<td>3-hydroxy</td>
<td></td>
<td></td>
<td></td>
<td>Inactive</td>
</tr>
<tr>
<td>3-methoxy</td>
<td>65°</td>
<td>0°</td>
<td>Faster than salcomine</td>
<td>Extremely hygroscopic</td>
</tr>
<tr>
<td>3-ethoxy</td>
<td>93°</td>
<td>10°-40°</td>
<td>Very fast</td>
<td>Hygroscopic but water driven off at desorption temp.</td>
</tr>
<tr>
<td>3-n-propoxy</td>
<td>95°</td>
<td></td>
<td>Very fast</td>
<td>Very hygroscopic</td>
</tr>
<tr>
<td>3-n-butoxy</td>
<td>95°</td>
<td>0°</td>
<td>Very fast</td>
<td>Extremely hygroscopic</td>
</tr>
<tr>
<td>3-ethyl</td>
<td></td>
<td></td>
<td>slow</td>
<td>Poor oxygen carrier</td>
</tr>
<tr>
<td>3-nitro</td>
<td></td>
<td>25°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-fluoro</td>
<td>93°</td>
<td>10°-40°</td>
<td>Extremely fast</td>
<td>Higher total capacity than ethamine.</td>
</tr>
<tr>
<td>3-bromo</td>
<td></td>
<td></td>
<td></td>
<td>Inactive</td>
</tr>
<tr>
<td>3-ethyl-4-methoxy</td>
<td></td>
<td></td>
<td></td>
<td>Good oxygen-carrying properties</td>
</tr>
<tr>
<td>3-nitro-5-methoxy</td>
<td></td>
<td></td>
<td></td>
<td>Inactive</td>
</tr>
<tr>
<td>4-methoxy</td>
<td></td>
<td></td>
<td></td>
<td>Good oxygen-carrying properties</td>
</tr>
<tr>
<td>4-methyl-6-methyl</td>
<td></td>
<td></td>
<td></td>
<td>Inactive</td>
</tr>
<tr>
<td>5-hydroxy</td>
<td></td>
<td></td>
<td></td>
<td>Carries oxygen - no other data</td>
</tr>
<tr>
<td>5-methoxy</td>
<td></td>
<td></td>
<td></td>
<td>Inactive</td>
</tr>
<tr>
<td>5-ethoxy</td>
<td></td>
<td></td>
<td></td>
<td>Carries oxygen - no other data</td>
</tr>
<tr>
<td>5-methyl</td>
<td></td>
<td></td>
<td></td>
<td>Inactive</td>
</tr>
<tr>
<td>5-phenyl</td>
<td></td>
<td></td>
<td></td>
<td>Carries oxygen - no other data</td>
</tr>
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</table>
Mixed aldehyde compounds have been made which have properties quite different from those predicted by consideration of the separate constituents. Such mixtures, are, however, not mixed molecules but mixed crystals. Their properties are probably governed to a major extent by this crystal structure.
IV. ETHOMINE

Ethomine, in the oxygenated form, is a fine crystalline black powder while in the deoxygenated form it is a beautiful orange-brown. If proper care is exercised and a small percentage of talc added, it can be pressed into pellets. The ethomine used in this work was for the most part granulated pellets, 10-20 mesh, with a bulk density of 1.1. Such granules are rather soft and tend to powder easily, making the material difficult to handle. The heat conductivity of the granules is very low and the transfer of heat into and away from the material becomes one of the major engineering problems involved. Breathing of the vapors or dust which have an odor approaching that of vanilla causes irritation of the nasal and throat passages and results in a condition simulating a cold. For this reason, a respirator should be worn when handling the material.

The color change from orange-brown to black may be observed to take place with only several minutes exposure to air at room temperature. The commercial material will absorb about 3.6 per cent oxygen by weight and initially should be heated to over 100°C in a vacuum for a short time to drive off any water that might have been absorbed. Rapid absorption of oxygen occurs over a considerable temperature range, 0° to 50°C, while evolution of this oxygen requires a temperature of 95°C or greater at atmospheric pressure.
A. Method of Attack

In order to obtain a definite picture of the mechanism of oxygen absorption and desorption, and knowledge sufficient to predict the behavior of the absorbent, the following basic information was considered necessary:

1. The rate of oxygen absorption as a function of temperature, oxygen partial pressure, and composition (amount of oxygen in combination with absorbent).

2. The rate of oxygen desorption as a function of temperature, oxygen partial pressure, and composition.

3. The oxygen vapor pressure over the absorbent as a function of temperature and composition.

4. The heat of reaction.

5. The specific heat and density.

In addition X-ray data which would establish the molecular structure and indicate phase changes should prove to be helpful.

From an engineering design standpoint, it is necessary to know how the compound will act when under conditions of practical operation; that is, when the compound is in some type of container, equipped to remove the heat of reaction and furnish the heat of desorption, through which air is passed to furnish oxygen. The information tabulated above should be sufficient to predict the action of the compound. However, to expedite results and to check such predictions, some engineering data were also considered necessary and were obtained in a standard jacketed copper tube, selected somewhat...
arbitrarily as the container. The data collected are listed below:

(1) The overall oxygen absorption rate determined at various jacket temperatures, air pressures, and air rates.

(2) The rate of oxygen desorption determined at various jacket temperatures and oxygen pressures.
B. Apparatus and Experimental Methods

Basic Absorption Rates

The basic absorption rate data were obtained by measuring the amount of oxygen required to maintain the oxygen pressure constant over a bed of ethomine held at substantially constant temperature. From the data of each experimental run, a plot of weight per cent oxygen absorbed (composition) versus time could be made. The actual rate of absorption is the slope of this curve. Hence a series of such runs over a range of temperatures and pressures gave the rate of absorption relative to the three variables, temperature, pressure, and composition.

A diagram of the apparatus used is given in Figure 1. It is divided into two parts: (1) the reservoir section consisting of a "vacuum"* and an oxygen reservoir each with a manometer, (2) the absorption section consisting of a powder holder, Sprengel pump, and manometer. By means of valves, oxygen can be bled into the absorption section or out of the section into the "vacuum" reservoir.

The powder holder consists of a jacketed piece of 3/8" O.D. brass tubing. Glass wool plugs hold the 5 grams of powder in place. Heat transfer calculations (Appendix E) show that with reasonable absorption, the average temperature rise of the powder may be several degrees. However, the ease of packing and simplicity of construction were advantages which warranted the selection of the present holder.

---

*Used to signify an evacuated vessel.
To prevent blocking of the surface of the compound by the accumulation of inertes present in small amounts in the cylinder oxygen used, a mercury circulation pump was used to sweep the oxygen through the powder. Gas flow rates of 50 to 100 cc. per minute were maintained. This flow was sufficient since runs made with cylinder oxygen and those made with pure oxygen (better than 99.98%) checked very well.

Jacket temperatures were controlled by use of steam for high temperatures, steam and water mixing for temperatures between 20° and 100°C, and normal butyl alcohol cooled by dry ice for low temperatures.

The volume of both reservoirs, the powder holder, and the remainder of the absorption section were accurately determined. Hence with a knowledge of the pressure in any section, the volume of gas in it could be calculated. These calculations were somewhat complicated by the fact that the manometer volume was an appreciable fraction of the total volume.

In operation, the procedure was as follows: the compound was desorbed, the tube evacuated and sealed off from the rest of the system. The jacket temperature was adjusted and time allowed for the powder temperature to become constant. At the same time the absorption system was filled with oxygen to a pressure such that with the opening of the valves on the powder holder, the desired pressure was obtained. The mercury pump was then started, and the valves on the powder holder were opened — absorption started immediately. The desired pressure in the system was then maintained by
continuously bleeding oxygen into the system from the reservoir, while readings on the oxygen reservoir manometer were taken at definite time intervals. From these readings the amount of oxygen absorbed was calculated.

At the end of a run the system was quickly brought to atmospheric pressure and sealed. Then steam was introduced into the jacket, and the oxygen given off was bled into the "vacuum" reservoir. The volume obtained here, after the correction for gas expansion in the powder bed due to temperature change had been applied, should check the absorption.

Basic Desorption Rates

Attempts by other investigators to obtain chemical desorption rate data have all met with failure. In all cases the controlling factor in the desorption was not the chemical rate of reaction but the ability to furnish the heat necessary for the reaction.

Since no apparatus was conceived that represented improvements over those already tried, no experimental attempt was made to determine these data directly.

Engineering Absorption Rates

In the design of a unit to produce oxygen from air, the powder holder represents one of the main problems. Its design will depend on the method of heating and cooling (air, water, steam, etc.), heat transfer to the powder necessary to limit the temperature rise during absorption and to give a reasonable desorption time, cycle length and balance, life characteristics of the compound, etc. Because
of the many considerations involved, a powder holder was rather arbitrarily selected for use in evaluating the compound from an engineering standpoint and in obtaining the initial design data.

A 1/2" jacketed copper tube was used and is shown in Figure 3. This tube was generally filled with 42.6 grams of oxygenated compound which gave a bed depth of about 50 cm. Such a tube, heated by steam and cooled with water or other liquid, had heat transfer characteristics sufficiently good to allow cycles of reasonable length and good balance of absorption and desorption times. This holder was easily constructed and incorporated into apparatus, quite strong and quite easy to load and unload.

Absorption obtained by passing air through a bed of powder differs from the absorption obtained in the basic absorption rate experiments because the oxygen partial pressure varies through the bed depth, and absorption is, therefore, a function of air flow rate and bed depth as well as temperature, total pressure, and composition.

These data were obtained by two different methods. The first consisted of passing air through the bed of compound and after a definite time interval, desorbing the compound to determine the amount of oxygen absorption. The second method utilized a Pauling oxygen meter to analyse the exit air. From this analysis the oxygen removed could be calculated. With the first method each run gave a point on the absorption versus time curve whereas the second method gave the complete curve in one run. For this
STD. 3/8" COPPER PIPE
I.D.- 0.493"
O.D.- 0.675"

COPPER JACKET

36" 33"

STEAM AND COOLING WATER JACKET

1/8" WALL

POWDER SAMPLE

COPPER SCREEN

0.162"

GLASS BEADS

COPPER SCREEN

5/16" O.D.
COPPER TUBING

FIGURE 3
STANDARD 1/2" TUBE UNIT

CONFIDENTIAL
reason the second method was preferred if it proved sufficiently accurate.

The Pauling meter does not respond immediately but has a definite lag — an accurate analysis of the characteristics of the meter are given in Appendix F. In a series of tests, it was found that assumption of a 10 second lag throughout gave very good results. The greatest difficulty was, of course, encountered at the beginning of the run where the concentration changes are large. By checking the calculations against a desorption at the end of the run, any difference was assumed to be due to inaccurate measurements at the initial part of the run. In this way the Pauling meter calculations were corrected to check the desorption. This correction was usually quite small.

For practical engineering data the advantage of the rapid and continuous Pauling meter method far outweighed the greater accuracy and reliability of the so termed point method. Checks between the two methods were usually better than 5 per cent.

It should be pointed out that in both methods the exit gas flow was held constant by bleeding through a throttling valve since this gave greater ease of control and greatly simplified the oxygen material balances. This means, however, that air flow through the bed was not constant; the greater absorption at first will cause a greater flow. Correction to constant air flow would make only slight changes in results; moreover, constant exit conditions are more likely to be met in actual units which makes the data obtained all the more appropriate.
A diagram of the apparatus used is given in Figure 4. Essentially it consisted of a tube through which air was passed. The pressure was maintained by a pressure regulator, and the air was throttled to approximately atmospheric pressure at the top of the tube. It then passed through a capillary flow meter, Pauling oxygen meter, and wet test meter. Connected to the tube was a "vacuum" reservoir used in measuring the oxygen evolved upon desorption.

The procedure of operation was simple but required rapid handling and adjustment of valves. The tube of compound, initially in the desorbed state, was evacuated with the jacket fluid at the temperature required. The pressure regulator was adjusted to the correct pressure and upon starting, the valve at the bottom of the tube was opened and the throttling valve at the top adjusted for the required flow according to the capillary flow meter. Readings on both the Pauling meter and the wet test meter were taken initially and at definite time intervals. At the end of a run, the air supply was cut off and the tube brought quickly to atmospheric pressure, the manometer and first valve to the reservoir opened, and the tube sealed off. The compound was then heated with steam in the jacket and the evolved oxygen bled into the "vacuum" reservoir through the sensitive needle valve on that system, maintaining atmospheric pressure in the tube.

It should be noted that any oxygen absorbed after the end of the run will upon desorption return the tube system exactly to atmospheric pressure and not be drawn into the
Figure 5
Absorption Rate Apparatus
Using Pauling Meter
"vacuum" reservoir. Also at the beginning of the desorption, there is air in the powder bed, and the oxygen pressure is not one atmosphere. However, with the evolution of oxygen, this air is swept out and an atmosphere of comparatively pure oxygen is maintained around the granules.

**Engineering Desorption Rates**

All observations in this laboratory indicate that the rate at which oxygen is evolved from ethylene or other like compounds is governed only by the rate with which heat may be supplied. This may or may not be true but will certainly apply to compounds in any practical powder holder. No exact method of calculating such heat transfer has been developed, and approximate methods are not very applicable. Hence actual laboratory tests were the easiest method of obtaining these most important engineering data.

The apparatus used was that described in the previous section, Figure 4. The compound was saturated with oxygen, using cylinder oxygen rather than air. It was held at jacket temperature long enough (5 to 10 minutes) to insure uniformity of powder temperature and then the jacket was quickly raised to the arbitrarily selected desorption temperature. The oxygen evolved was continually bled off into the reservoir maintaining the proper pressure in the tube system. Readings were made on the reservoir manometer at definite intervals. At low desorption pressures (below 1 atmosphere) the capacity of one reservoir was not sufficient to handle all the oxygen, hence two were used. The two had practically the same volume and could be used interchangeably.
Equilibrium Vapor Pressure

Some vapor pressure data have been reported by Calvin (1). He found that the approach to equilibrium was extremely slow, and that times of three weeks to a month were required for a single reading. With the hope of avoiding such time-consuming methods, an attempt was made to obtain some approximate equilibrium data in a much simpler manner.

The data obtained were that of the relationship of composition to temperature at constant vapor pressure. If curves were obtained for several pressures, the usual constant temperature vapor pressure curves could be approximated by interpolation. Moreover, these constant pressure curves were of considerable interest since they represent the equilibrium desorption temperature.

By raising the temperature of the compound very slowly during a constant pressure desorption and observing the oxygen evolved at each new temperature, a plot of composition versus temperature was obtained. By allowing sufficient time for complete desorption at any one temperature, equilibrium should be closely approximated. This was partially substantiated by the fact that with a shift in temperature of only one or two degrees, a change to absorption occurred.
G. Experimental Data

Basic Absorption Rate Data

Ethomine especially prepared from C.P. chemicals by Rumford Chemical Company was used for all these absorption experiments — in all other experimental work except life tests, commercial ethomine also prepared by Rumford Chemical Company was used.

A summary of the series of absorption runs made is given below. The different pressures (mm. Hg) used at any one temperature are listed in the column headed by that specific temperature.

<table>
<thead>
<tr>
<th>Basic Absorption Runs</th>
</tr>
</thead>
<tbody>
<tr>
<td>-10° 0° 10° 20° 30° 40° 50° 60° 70° T.°C</td>
</tr>
<tr>
<td>--- --- 40 40 40 40 --- --- ---</td>
</tr>
<tr>
<td>80 80 80 80 80 80 80 80 --- ---</td>
</tr>
<tr>
<td>160 160 160 160 160 160 160 160 ---</td>
</tr>
<tr>
<td>320 320 320 320 320 320 320 320 ---</td>
</tr>
<tr>
<td>640 640 640 640 640 640 640 640 640</td>
</tr>
</tbody>
</table>

The results are all of the same general character except for the appearance of an "induction" period at conditions of low pressure and high temperature. Curves of absorption versus time are given for runs at 20° and 50°C in Figures 6 and 7. The initial period of accelerating rate or "induction" period is quite noticeable in the latter.

Engineering Absorption Rate Data

Runs were made by the point method at pressures of 20 psig. and 1 atmosphere, temperatures of 20° and 40°C, and
Figure 6
Oxygen Absorption
Ethomine 20°C

Time (Minutes)
a range of air flow rates, 1 to 15 cubic feet per hour through a 1/2 " tube. Pauling meter runs were made at pressures of 20 and 75 psig., a temperature range of -10° to 80°C, and a range of air flow rates, 1/2 to 2 cubic feet per minute per pound of ethomine in a 1/2" tube.

The results of the Pauling meter runs at 1 CFM/# and 20 psig. are given in Figure 8. A comparison of results obtained by the two methods at 20 psig., 40°C, and several air flow rates is given in Figure 9.

**Engineering Desorption Data**

A table of the series of runs made is given below. The different desorption jacket temperatures used at any one pressure are listed in the column headed by that specific pressure.

**TABLE III**

<table>
<thead>
<tr>
<th>CO₂</th>
<th>1/4 atm.</th>
<th>1/2 atm.</th>
<th>1 atm.</th>
<th>1-1/2 atm.</th>
<th>2 atm. P</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.4</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>&quot;</td>
<td>110</td>
<td>110</td>
<td>110</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>130</td>
<td>130</td>
<td>130</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>2.0</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>2.0</td>
<td>115</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>2.0</td>
<td>130</td>
<td>&quot;</td>
<td>130</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

Figures 10 and 11 give typical desorption curves.

**Equilibrium Vapor Pressure Data**

Approximate equilibrium desorptions at constant pressure were made at pressures of 1/2 and 1 atmosphere oxygen pressure. These are plotted in Figure 12.
Figure 6

Oxygen Absorption
From Air

Submerging in 1/2" Tube
44.0 M.S.
Air Rate = 1 CFM/Lb.
Air Pressure = 20 psi.
(Temperature Refers
to Cooling Medium)
Figure 9

Oxygen Absorption

Air Rate  Run No.
0.5     A-3
1.0     A-4
2.0     A-6

--- Pauling Meter Runs
- - Values Interpolated from Point Runs

Oxygen Absorption from Air
Ethomine in 1/2" Tube
42.5 Gaa.
Temperature = 46°F
Air Pressure = 20 P41
(Temperature refers to cooling medium)
Figure 10

Absorption Rate
Ethylene in 1/2" Tube
Saturated to 5.4%
Desorption Temp. 130°C
Initial Temp. 40°C.
Figure 11

Desorption Rate
Exposure in 1/2" Tube
Saturated to 5.4% Desorption Pressure 1 Atm.
Initial Temp. 40°F

Time (Minutes)
Figure 12

Equilibrium Curves at Constant Pressure

Temperature °C

1 Atm.

1/2 Atm.
D. Data of Other Investigators

Vapor Pressure

The oxygen vapor pressure of ethomine has been determined by Calvin (1) using standard equilibrium methods. His results are given in the following table.

**TABLE IV**

<table>
<thead>
<tr>
<th>Temp.</th>
<th>Pressure (mm. Hg)</th>
<th>% Oxygenated</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°C</td>
<td>0.37</td>
<td>3.6</td>
</tr>
<tr>
<td>•</td>
<td>0.38-1.0</td>
<td>38.4</td>
</tr>
<tr>
<td>•</td>
<td>0.88</td>
<td>78.0</td>
</tr>
<tr>
<td>•</td>
<td>3.4</td>
<td>91.0</td>
</tr>
<tr>
<td>25°C</td>
<td>0.50</td>
<td>5.23</td>
</tr>
<tr>
<td>•</td>
<td>1.20</td>
<td>16.1</td>
</tr>
<tr>
<td>•</td>
<td>1.90</td>
<td>55.6</td>
</tr>
<tr>
<td>•</td>
<td>4.70</td>
<td>77.8</td>
</tr>
<tr>
<td>•</td>
<td>11.50</td>
<td>93.0</td>
</tr>
</tbody>
</table>

Heats of Reaction

Heats of reaction have been reported by both Calvin (1) and Hetherington (4). The values vary somewhat with composition and the specific material used but all fall between 19,000 and 20,000 calories per mol of oxygen.

Coefficient of Conductivity

McCrosky (3) obtained a value of 0.027 Btu/sq. ft. hr. °F/ft. for salomine granules, 10-20 mesh, in ambient air. Somewhat higher values for ethomine were obtained by Hetherington (4). He suggests 0.0368 Btu/sq. ft. hr. °F/ft. as an average value for ethomine, 10-20 mesh, in ambient air.
Specific Heat

Determinations by Hetherington (4) gave approximately 0.28. This value was used in the calculation of the coefficient of conductivity.

Density

The bulk density of 10-20 mesh granules will vary with the sample and packing. Generally it is between 0.6 and 0.7 g./cc.
E. Correlation of Basic Absorption Rate Data

Introduction

The analysis of a large amount of experimental data taken under various conditions with respect to the fundamental variables must, of necessity, be a stepwise procedure. If at all possible, the effect of each variable should be investigated separately. The method used here is that most commonly used in analysis; namely, the postulation of a chemical and physical picture of the mechanism of reaction built upon basic physical chemistry theories and the application of tests of such a postulation to the experimental results.

If the tests fail, the original picture is wrong. However, if the results fit the picture that is not proof that the picture is correct — others may fit just as well. Since it is impossible to establish positive proof of the mechanism, the most reasonable one is usually accepted as the most probable picture and used as an end to understanding and predicting the behavior of the chemical compound.

In many cases the search for a probable mechanism that fits the experimental results fails. Then recourse to mathematics that will fit the data is made, and an empirical correlation is developed. Such correlations give no insight into the basic physical and chemical properties but do, nevertheless, allow predictions of the behavior of the material considered.
Composition

The overall reaction between ethomine and oxygen may be represented by the equation:

\[ 2M + O_2 \rightleftharpoons M_2O_3 \]

This may in turn be considered to go in two distinct steps:

(a) \( M + O_2 \rightleftharpoons NO_2 \)
(b) \( NO_2 + M \rightleftharpoons M_2O_3 \)

The experimental data give the total amount of oxygen going into combination with ethomine. Hence, regardless of whether the reaction proceeds in one or several steps, it gives only the difference in oxygen taken up by the forward reactions and that released by the reverse reactions. At low temperatures the vapor pressure of the oxygenated ethomine becomes very small and the back reactions releasing oxygen can be neglected. Hence, at low temperatures the data may be considered as representing the oxygen absorption reactions only.

For a first order reaction with respect to deoxygenated ethomine, we may write

\[ \frac{dx}{dc} = k' \frac{s-x}{s} \]

where
- \( x \) = per cent oxygen by weight on ethomine
- \( s \) = per cent oxygen at saturation
- \( c \) = time (minutes)
- \( k' \) = proportionality factor

For such a heterogeneous reaction (solid and gas) \( k' \) is constant for conditions of constant temperature and pressure

---

*The molecular form \( M_2O_3 \) has been proven by Calvin (1) with X-ray diagrams.
$k' = k\varnothing(p)$ (specific reaction rate constant) (function of pressure)

Integrating (1)

$$-\ln(s-x) = \frac{k'}{s} \Theta + c$$

At $\Theta = 0$, $x = 0$, $c = -\ln s$

Hence

(2) $-\log (s-x) = \frac{k'}{2.303 s} \Theta - \log s$

or

(3) $-\log (s-x) = \Theta - \log s$

A plot of $\log (s-x)$ versus $\Theta$ should give a straight line of slope $-k'$ if the reaction is first order. Such a plot for ethomine at $-10^\circ C$ is given in Figure 13. Straight lines are obtained over the range of $0$ to approximately $90$ per cent of saturation.

If the reactions were second order a plot of $\frac{1}{s-x}$ versus $\Theta$ should yield a straight line of slope $k'$. Such a plot for ethomine at $-10^\circ C$ is given in Figure 14.

The fact that the experimental data deviate from a first order reaction as saturation is approached, the rates becoming slower than that predicted was to be expected. In the first place changes of phase occur at approximately 5 and 80 per cent of saturation according to Calvin (1).

Below 5 per cent saturation, there is a single phase system of oxygen dissolved in deoxygenated ethomine. Between 5 and 80 per cent, there is a two-phase region of oxygenated and deoxygenated compound. Above 80 per cent saturation, there is a shift to a single phase of deoxygenated ethomine dissolved in the oxygenated. When this second single phase region is reached, it is not out of the question to expect
Figure 14

Second Order Test

Ethomine \(-10^\circ C\)
a different mechanism of reaction. As saturation is approached, the oxygen vapor pressure rises rapidly and in all probability the back reaction can no longer be neglected. Also, from a physical standpoint, it is not difficult to reason that with increasing oxygenation, it becomes increasingly difficult for oxygen to reach unoxidized molecules in the interior of the granules and that diffusional effects should be considered.

It is only logical to assume that the rate of the reverse reaction (releasing of oxygen) should be a function of the oxygen in combination with the ethomine. If the reverse reaction is first order, the rate equation is as follows:

\[ \frac{dx}{dt} = k_1 \frac{s-x}{s} - k_2 \frac{s}{s} \]

While \( k_1 \) is a function of both temperature and pressure, \( k_2 \) should be a function of temperature only.

Rearranging (1)

\[ (\frac{d}{dt})(\frac{s}{x}) = k_1 \frac{s-x}{s} - k_2 \]

A plot of \( (\frac{d}{dt})(\frac{s}{x}) \) versus \( \frac{s-x}{s} \) should give a straight line of slope \( k_1 \) and intercept \( -k_2 \). Such a plot for ethomine at 30°C is given in Figure 15. It is difficult to obtain an accurate intercept value since all the lines apparently pass through the origin.

However, if equation (1) were rearranged in another fashion; namely,

\[ \frac{dx}{dt} = k_1 \frac{s}{s-x} - k_2 \frac{s}{s-x} \]

a plot could be made of \( (\frac{d}{dt})(\frac{s}{x}) \) versus \( \frac{s}{s-x} \) and the

\[ ^* (\frac{dx}{dt}) \]

is the rate of oxygen absorption — the slope at any point on the per cent oxygen absorbed versus time curve.
Figure 1b
Determination of Back Reaction Constant Ethomine 30°C

\[ \frac{\text{Fe}(\text{Fe})}{\text{Fe}} \]

640 mm.

320 mm.

160 mm.

80 mm.
slope would be \(-k_a\). Figure 16 shows the 30°C data plotted that way. Although the points scatter, the slopes appear to be zero.

The same reasoning may be applied with the assumption that the reverse reaction is second order. The results obtained are substantially the same. However, if the experimental results at high temperatures are tested for the single rate of reaction constant as was done at low temperatures, all give good straight lines. A graph of log \((s-x)\) versus time is given for ethylmone at 30°C, Figure 17. It appears that if there is a substantial back reaction, its effects are contained in this one rate constant.

Langmuir's (6) theory on heterogeneous systems, particularly for the reaction

\[ \text{CaO} + \text{CO}_2 \xrightleftharpoons[k_2]{k_1} \text{CaCO}_3 \]

may give some help here.

If this reaction is considered from a kinetic point of view,

\[
\frac{d\Theta_1}{dt} = k_1 \theta_2 \theta_1 \\
\frac{d\Theta_2}{dt} = k_2 \theta_2
\]

where \(\theta_1\) and \(\theta_2\) are the fractions of reacting surface that are \(\text{CaO}\) and \(\text{CaCO}_3\) respectively.

At equilibrium

\[ k_1 \theta_2 \theta_1 = k_2 \theta_2 \]

\[ K_{eq.} = \frac{k_2}{k_1} = \frac{p_{\text{CO}_2}}{\theta_1/\theta_2} \]

Since \(K_{eq.} = p_{\text{CO}_2}\) in a monovariant system,

\[ \frac{\theta_1}{\theta_2} = 1 \text{ or } \Theta_1 = \Theta_2 \]
Figure 16

Determination of Back Reaction Constant
Ethomine: 30°C

640 mm.
320 mm.
160 mm.
80 mm.

\( \frac{d^2y}{dx^2} = \frac{8 - x}{x - 0} \)
Figure 17

First Order Test
Ethoxime 30°C.

Time (Minutes)

Wt. % Oxygen
This is explained by the assumption that reaction occurs only at the interfacial boundaries. Hence a change in one phase area results in an identical change in the other. In the case of CaCO₃ – CaO the CO₂ diffuses through the relatively porous CaO and reacts on the surface of the CaCO₃ crystals. Such a CaCO₃–CaO mass would have definite crystal boundaries as is actually the case — these facts fit the phase rule.

From the above, it appears that the rate of combination or decomposition would be a function of the phase interfacial boundaries which in turn would be some function of the extent of reaction and previous history.

If in the case of ethylene the reacting surface were proportional to the deoxygenated compound, the rate equation would have the following form:

\[
\frac{dX}{dt} = k_1 \frac{X}{s} - k_2 \frac{X}{s}
\]

\[
\frac{dX}{dt} = (k'_1 - k_2) \frac{X}{s}
\]

\[
(8) \frac{dX}{dt} = k' \frac{X}{s}
\]

Such an equation will yield only one constant when tested under conditions of constant pressure and temperature. However, \(k'_1\) and \(k_2\) should have different temperature coefficients and mention of this will be made in the discussion of temperature influence.
A table of the single first order \( k' \)'s is given below.

**TABLE V**

\[ k' = k\Phi(p) = 2.303 \text{ sK} \]

<table>
<thead>
<tr>
<th>( p(\text{mm Hg}) )</th>
<th>-10°</th>
<th>0°</th>
<th>10°</th>
<th>20°</th>
<th>30°</th>
<th>40°</th>
<th>50°</th>
<th>60°</th>
<th>70°</th>
<th>T°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>640</td>
<td>1.99</td>
<td>3.28</td>
<td>5.07</td>
<td>7.31</td>
<td>8.00</td>
<td>7.11</td>
<td>4.83</td>
<td>2.70</td>
<td>1.20</td>
<td></td>
</tr>
<tr>
<td>320</td>
<td>0.69</td>
<td>1.13</td>
<td>1.75</td>
<td>2.50</td>
<td>2.68</td>
<td>2.67</td>
<td>1.96</td>
<td>---</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>160</td>
<td>0.30</td>
<td>0.42</td>
<td>0.66</td>
<td>1.03</td>
<td>0.97</td>
<td>0.80</td>
<td>0.66</td>
<td>0.115</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>0.13</td>
<td>0.16</td>
<td>0.24</td>
<td>0.33</td>
<td>0.32</td>
<td>0.24</td>
<td>0.084</td>
<td>---</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>---</td>
<td>---</td>
<td>0.097</td>
<td>0.107</td>
<td>0.073</td>
<td>0.031</td>
<td>---</td>
<td>---</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A plot of the single order \( k' \)'s is given in Figure 18. The values taken from the smooth curve are used in all the pressure and temperature correlations.

For practical purposes knowledge that the reaction is first order with respect to deoxygenated ethomine over a range of 0 to 90 per cent saturation is sufficient. In engineering applications, the compound is seldom carried to saturation and greatest interest is in the rate of reaction within the range mentioned above. Hence for this investigation it will be assumed that the reaction of ethomine with oxygen is a first order reaction, remembering, however, that deviation from this rule occurs at high saturation values.

**Pressure**

The ideas of Langmuir (6) on heterogeneous equilibrium may be applied to this problem as follows:

\[ \frac{dX}{d\Theta} = (k_p - k_s) F \]

where \( F \) is a function of the interfacial boundaries. It is
Figure 18

Values of $k^1$

Ethomine

Temperature °C.
here assumed that the forward or absorption reaction is
proportional to the oxygen concentration and therefore
proportional to the oxygen pressure. At equilibrium

\[ K = \frac{k_2}{k_1} = p_0 \quad \text{or} \quad k_2 = k_1 p_0 \]

where \( p_0 \) is the equilibrium oxygen pressure.
Hence

\[ \frac{dX}{dP} = (k_1 p - k_1 p_0) F \]

or

\[ (10) \frac{dX}{dP} = k_1 F (p-p_0) \]

From the previous discussion it appears that

\[ F = \frac{d^2k}{d} \]

and

\[ (11) \frac{dX}{dP} = k_1 (p-p_0) \frac{d^2k}{d} \]

From equation (1)

\[ k' = \frac{dX}{dP} = 2.303 \frac{d^2k}{d} \]

Substituting in equation (11)

\[ (12) \ k' = k_1 (p-p_0) \]

To test this equation, \( k' \) was plotted versus \( p \). Such a
plot for ethomine at 30°C is shown in Figure 19. If the
equation fitted the data, the plot would be a straight
line of slope \( k_1 \) and intercept on the abscissa of \( p_0 \).
All experimental data gave curves that were concave up-
ward. The abscissa intercept could not be determined
accurately but was much higher than the equilibrium pressure.

A table of estimated oxygen vapor pressures for
ethomine at 40 per cent saturation is given below. The
pressures were calculated from the small amount of equilibrium
data available assuming the Clausius-Clapeyron to hold. Forty per cent saturation was selected because it is near the middle of the flat portion of the constant temperature vapor pressure curve, the average pressure in the single phase region.

TABLE VI

<table>
<thead>
<tr>
<th>Temp. °C.</th>
<th>Vapor Pressures (mm. Hg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.1</td>
</tr>
<tr>
<td>10</td>
<td>0.3</td>
</tr>
<tr>
<td>20</td>
<td>1.0</td>
</tr>
<tr>
<td>30</td>
<td>3.0</td>
</tr>
<tr>
<td>40</td>
<td>8.4</td>
</tr>
<tr>
<td>50</td>
<td>21.6</td>
</tr>
<tr>
<td>60</td>
<td>52.6</td>
</tr>
<tr>
<td>70</td>
<td>121.4</td>
</tr>
</tbody>
</table>

The fact that the plots of $k'$ versus $p$ curved upward suggested that $k'$ might be a power function of $p$. The relationship would be

(13) $k' = kp^n$

Taking the logs of both sides

(14) $\log k' = n \log p + \log k$

A plot of $\log k'$ against $\log p$ would give a straight line of slope $n$ if such a relationship fitted. This is shown in Figure 20. Straight lines of slope 1.5 were obtained over most of the range of data. The experimental results deviate at the low pressures in the very high and low temperature regions.
Figure 20

Correlation of \( \kappa \) with Pressure

Ethanol

\[ \kappa = k \, y^{1.5} \]
The correlations could be made slightly better by the use of \( (p-p_c) \) rather than \( p \) but the additional term gave a much more difficult expression to handle without a great increase in accuracy. At constant temperature the reaction rate equation may be expressed as follows:

\[
\frac{dx}{dt} = k p^{1.5} \frac{s-x}{s}
\]

where

- \( k \) = specific reaction rate constant
- \( x \) = wt. per cent oxygen absorbed
- \( s \) = wt. per cent oxygen/saturation
- \( t \) = time in minutes
- \( p \) = oxygen partial pressure in mm. of Hg.

A table of values of \( k \) over the temperature range investigated is given below.

**TABLE VII**

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>( k )</th>
</tr>
</thead>
<tbody>
<tr>
<td>-10</td>
<td>( 1.23 \times 10^{-4} )</td>
</tr>
<tr>
<td>0</td>
<td>2.03</td>
</tr>
<tr>
<td>10</td>
<td>3.14</td>
</tr>
<tr>
<td>20</td>
<td>4.52</td>
</tr>
<tr>
<td>30</td>
<td>4.94</td>
</tr>
<tr>
<td>40</td>
<td>4.41</td>
</tr>
<tr>
<td>50</td>
<td>2.99</td>
</tr>
<tr>
<td>60</td>
<td>1.67</td>
</tr>
<tr>
<td>70</td>
<td>0.74</td>
</tr>
</tbody>
</table>
The correlations could be made slightly better by the use of \( (p-p_0) \) rather than \( p \) but the additional term gave a much more difficult expression to handle without a great increase in accuracy. At constant temperature the reaction rate equation may be expressed as follows:

\[
(15) \frac{dx}{dt} = k p^{1.5} \frac{e^{-x}}{s}
\]

where

- \( k \) = specific reaction rate constant
- \( x \) = wt. per cent oxygen absorbed
- \( s \) = wt. per cent oxygen/saturation
- \( \Theta \) = time in minutes
- \( p \) = oxygen partial pressure in mm. of Hg.

A table of values of \( k \) over the temperature range investigated is given below.

<table>
<thead>
<tr>
<th>Temp. °C</th>
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<tbody>
<tr>
<td>-10</td>
<td>( 1.23 \times 10^{-4} )</td>
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<td>60</td>
<td>1.67</td>
</tr>
<tr>
<td>70</td>
<td>0.74</td>
</tr>
</tbody>
</table>
It is difficult to offer an explanation for the function of pressure being the 1.5 power. Surface adsorption might be considered the governing factor rather than pressure. However, all such theories lead to powers of less than 1.0 on the pressure. Since the actual meaning of the reaction rate constant $k$ is in considerable doubt, the use of $p^{1.5}$ should be considered an empirical correlation without a theoretical basis.

**Temperature**

Application of the theory of Langmuir on heterogeneous systems led to the following rate equation at constant temperature and pressure:

$$\frac{dx}{dt} = (k_1' - k_s) \frac{S - x}{s}$$

This can be extended to include the influence of temperature and pressure by assuming both $k_1'$ and $k_s$ have temperature coefficients according to the Arrhenius equation and that $k_1'$ alone is a function of pressure.

$$(16) \frac{dx}{dt} = \left[ k_1' e^{-\frac{E_1}{RT}} - k_s e^{-\frac{E_s}{RT}} \right] \frac{s-x}{s}$$

At low temperatures where the back reaction can be neglected $E_1$ can be calculated. For ethomine

$$E_1 = 7000 \text{ cal./g. mol } O_2$$

$$E_2 = \Delta H + E_1 = 19,500 + 7000 = 26,500 \text{ cal./g. mol } O_2$$

At constant pressure, the two rate constants are the only unknowns if the solution for $E_1$ and $E_2$ is correct. These may be determined by trial. However, values could not be found that would fit the data well. By varying $E_1$ and $E_2$ the fit could be improved but in all cases the
The experimental data gave a curve much like the normal probability curve, and an equation of that type was used. The general form is as follows:

\[ y = Ae^{-K(x-x_0)^2} \]

or in this case

\[ k = ae^{-b(t-t_0)^2} \]

By trial the axis was found to be 29°C. The best average fit gave the following equation:

\[ (17) \quad k = 4.9 \times 10^{-4} - 1.1 \times 10^{-3}(t-29)^2 \]

Figure 21 shows a graph of the k values obtained from the pressure correlation compared to the ones predicted by the above equation.

It must be remembered that equation (17) does not obey the necessary boundary condition of desorption at high temperature (negative k). Desorption does occur at 93°C and 1 atmosphere and at a lower temperature corresponding to a lower pressure which value can be approximated by use of the Clausius-Clapeyron equation.

General Correlation

The rate of reaction of ethamine and oxygen in the range -10°C to 60°C and 0 to 1000 mm. oxygen partial pressure
Figure 21

$4.9 \times 10^{-4} - 1.1 \times 10^{-3} (t-29)^2$

Specific Reaction Rate Constant for Ethylamine

o - k from Exp. Data

Temperature °C
can be approximated as follows:
\[
\frac{dx}{dt} = \left[4.9 \times 10^{-4} e^{-1.1(10^{-3})(t-29)^2}\right]^{1.5} \frac{s-x}{s}
\]

where
- \(x = \) wt. per cent oxygen absorbed
- \(s = \) wt. per cent oxygen at saturation
- \(t = {^\circ}C.\)
- \(p = \) oxygen partial pressure in mm. of Hg
- \(\phi = \) time in minutes.

The integration of equation (18) will yield
\[
(19) \ln \frac{s-x}{s} = A s e^{-b(t-29)^2} p^{1.5} \phi
\]

where
- \(A = 4.9 \times 10^{-4}\)
- \(b = 1.1 \times 10^{-3}\)

If \(\ln \frac{s-x}{s}\) is plotted versus \(\frac{1}{s} e^{-b(t-29)^2} p^{1.5} \phi\), a straight line is obtained and experimental points may be placed on the same plot to check the correlation. Such a plot is shown in Figure 22. The points were taken from data covering the complete temperature and pressure range and absorption times up to 5 minutes.

Above a value of \(\frac{s-x}{s}\) of 10 (90 per cent oxygenated), the experimental points deviate greatly from the equation but do fall rather well on a common curve. Since the first order reaction does not hold at such \(\frac{s-x}{s}\) values, this deviation was expected.

On the plot shown practically all the experimental points are within 10 per cent of the calculated value with a maximum deviation of about 35 per cent. From an engineering standpoint this is an excellent check.
FIGURE 22
GENERAL CORRELATION ETHOMINE

\[ \frac{S}{S-X} = e^{-b(1-29)^2} \]

\[ A = 4.9 \times 10^{-4} \]

\[ b = 1.1 \times 10^{-3} \]
Comparison to Other Monovariant Systems (CaCO₃ and CdCO₃)

Zawadzki and Bretsznajder (14) have reviewed considerable work on monovariant heterogeneous systems. Most experimental work was done on the association and dissociation of CaCO₃ and CdCO₃. Experiments on decomposition of CaCO₃ have also been reported by Maskill and Turner (7) and Huttig and Kappel (5). Certain general properties of such systems deviating from the classic theories of chemical kinetics are indicated, and these will be outlined briefly.

Experiments showing the effect of composition on association and dissociation rates gave considerable difficulty and the results are poor. Indications are that decomposition is first order with respect to the carbonate. Association is probably the same type of function with respect to the oxide.

The general properties of the systems are shown by the graphs in Figure 23. The overall rate of reaction, \( v \), is the initial rate and therefore independent of the function of composition. It is a function of pressure and temperature, equivalent to \( k' \) used in the correlation of ethylene data.

A study of the graphs in Figure 23 will reveal the following fundamental properties:

1. At low pressures, \( p/p_0 < 2 \), the overall rate of reaction is proportional to \( p - p_0 \). Association or dissociation occurs depending on the sign of \( p - p_0 \). (Graph 1)

2. At high pressures, \( p/p_0 > 4 \), the rate increases out of proportion to \( p - p_0 \). (Graph 2)
FIGURE 23
PROPERTIES OF MONOVARIENT
HETEROGENEOUS SYSTEMS
3. Over considerable range the rate is proportional to \( p - p'_0 \), where \( p'_0 \) is a pseudo equilibrium pressure. (Graph 2)

4. Rates are identical for association and dissociation for equal values of \( p-p'_0 \) and \( p'_0-p \). (Graph 3)

5. The equilibrium pressure follows the Clausius-Clapeyron relationship. (Graph 4)

6. The variation of rate with temperature goes through a maximum falling off rapidly on each side. (Graphs 5 and 6)

7. At certain temperatures and low pressures a definite "induction" period is observed. (Graph 7)

Ethomine checks the above properties exceptionally well, with absolutely no basic refutations. Calvin has reported the proportionality of pressure and rate at low pressures and his equilibrium data as well as the author's appear to follow the Clausius-Clapeyron equation. The relationship of rate to temperature fits the type of curve given for \( \text{CdCO}_3 \) very closely. However, no measurements of dissociation rates were made, nor were sufficient low pressure data taken to check the pseudo equilibrium.
F. Method of Predicting Engineering Absorption Data

Basic Equations

The determination of absorption when air is passed through a bed of ethomine requires a knowledge of rate relations, material balance, and temperature conditions of the bed as governed by heat transfer. The partial differential equations for a rigorous solution of the problem can be set up. However, the solution of such a set of equations mathematically is entirely too difficult to be considered here.

The assumption that the bed is isothermal throughout the absorption time greatly simplifies the problem. Consider a section of such a bed of ethomine of unit cross sectional area.

At any time Q

\[ N = \text{mols of } N_2/(\text{minute})(\text{unit cross section}) \]
\[ R = \text{mols of } O_3/\text{mol of } N_2 \]

Mols \( O_2 \) entering/min. = \( NR \)
Mols \( O_2 \) leaving/min. = \( N \left[R + \frac{2R}{2L} dL\right] \)
Accumulation = \( -\frac{2R}{2L} dL \)

\( O_2 \) absorbed by the section = \( \rho \beta \frac{2x}{20} \) dL

where \( x = \) weight per cent \( O_2 \) in combination
\( \rho = \) bulk density of ethomine
\( \beta = \) conversion factor to mols
Hence
\[ \rho \beta \frac{2x}{s} \frac{dL}{d\theta} = -N \frac{\beta P}{sL} \frac{dL}{d\theta} \]
The rate equation at constant temperature is
\[ \frac{4x}{s} = k \rho_0 \frac{1.5}{s-X} \]
But
\[ P_0 \left[ \frac{R}{R+1} \right]^P \]
where \( P = \) total air pressure
Substituting for \( P_0 \)
\[ (2) \frac{4x}{s} = k \rho \frac{1.5}{s-X} \left[ \frac{R}{R+1} \right]^1.5 \]
The solution of equations (1) and (2) must satisfy the boundary conditions of (1) entering gas being air, (2) initial bed condition of \( x_0 = 0 \), (3) \( L_0 = 0 \), and (4) \( \phi_0 = 0 \). Constant gas flow at the entrance rather than the exit (as was used experimentally) was assumed because the assumption of constant exit flow would have only complicated an already formidable problem.

No mathematical solution to the partial differential equations was found. Graphical or stepwise methods of finite increments were therefore investigated.

The equations were first examined to see if a general solution was possible. Equations (1) and (2) can be rearranged and put into the following form:
\[ (1a) \frac{\partial (x)}{\partial [\rho \frac{kpl.5}{s} \phi]} = \frac{\partial R}{\partial \left[ \frac{\rho \beta kpl.5}{N} L \right]} \]

*General in the sense that it would hold for all values of the constants (\( \rho, \beta, s, k, N, \) and \( P \)) with fixed boundary conditions.
The variables involved are now four dimensionless groups, namely, \((x/s), R, \frac{K P^{1.5}}{S}, G = Q', \) and \(\frac{K P^{1.5}}{N} L = L'.\) However \((x/s)\) and \(R\) are directly related and the solution may be given in terms of the two independent variables \(Q'\) and \(L',\) and either \((x/s)\) or \(R.\) Any particular solution, no matter how obtained, which gives the value of \((x/s)\) and \(R\) for any \(Q\) and \(L\) can be transformed to the more general solution by putting it into terms of the dimensionless groups.

The rate-pressure relationship of \(PQ^{2}\) causes the term \(\frac{R}{N+1}\) in equation (2a) to carry a power factor of 1.5. This factor restricts the general solution to ethomine or compounds of the same rate-pressure relationship since the particular rate characteristic of ethomine is not removed by the rearrangement of terms.

**Stepwise Solution**

As an approximation, the continuous passage of gas up through a bed of powder, may be considered a series of finite batch processes. A slug of air equivalent to that which would pass through the bed in a small increment of time is allowed to remain in a small section of the bed for that increment of time. The slug of gas remaining is then moved to the section of bed above and allowed the same time of contact, etc. After this slug has been carried the entire

\begin{equation}
\frac{d}{d\left[\frac{K P^{1.5}}{S} Q\right]} = \left[\frac{R}{N+1}\right]^{1.5} \left[1 - \left(\frac{Q}{Q'}\right)\right]
\end{equation}

*Solution with particular values for the constants.*
height of bed, a second slug of air, representing the second increment of time is carried through the bed in the same fashion. Such a procedure will approximate the calculus of integrating with respect to L and G. The accuracy of such a method will depend on the size of the increments of time and bed height used.

In such a series of calculations the rate equation (2) is used to determine the absorption in a section and the oxygen composition of the gas figured by material balance (1).

\[
\frac{dx}{dt} = k \left( \frac{R}{1+R} \right)^{1.5} \frac{G}{s-x}
\]

\[(4) \, \Delta \Theta (R_0 - R) = \beta \delta L (x-x_0)\]

Elimination of R between (3) and (4) gives an equation of the form:

\[
\frac{dx}{dt} = \frac{a(b-x)^{1.5} (s-x)}{(c-x)^{1.5}}
\]

This is an extremely complicated form and was not integrated.

To obtain an expression for the absorption during the time \( \Theta \) equation (1) was integrated assuming the pressure driving force \( p^{1.5} \left( \frac{R}{R+1} \right)^{1.5} \) to be constant. The value of driving force used could possibly be some average of the initial and final conditions. By integration

\[
(5) \, x = s - s - x_0 \frac{\frac{k}{6} \Delta \Theta \left( \frac{R}{R+1} \right)^{1.5}}{e^{An}}
\]

or

\[
(6) \, x = s - s - x_0 \frac{\frac{k}{6} \Delta \Theta \left( \frac{R}{R+1} \right)^{1.5}}{e^{An}}
\]

where

\[
A = \frac{k}{6} \Delta \Theta \left( \frac{R}{R+1} \right)^{1.5}
\]

\[
n = \left[ \frac{R}{R+1} \right]^{1.5}
\]
n was arbitrarily taken as
\[ \left[ \frac{R_0}{R_0 + 1} \right]^{1.5} + \left[ \frac{R_F}{R_F + 1} \right]^{1.5} \]
\[ \frac{2}{2} \]

This average driving force resulted in numerical values which were substantially correct since the final value of x was independent of the magnitude of the \( \Delta \Theta \) employed. The final value of R corresponding to x could be obtained from equation (4). The actual numerical calculation required a knowledge of \( R_F \) to calculate x and hence was a trial and error solution between equations (4) and (5).

This stepwise integration was carried out for a tube of ethylene. The conditions assumed were temperature 40°C, air rate 1 CFM/# in 1/2" tube, pressure 20 psig. The increment of bed height \( \Delta L \) used was such that the values obtained were within 1 per cent of those obtained with an increment one half as large. Since the calculation was numerically exact for the integration with respect to \( \Theta \), the solution should be quite accurate.

The results were converted to values of \( (x/s)_{ave} \), \( L' \), and \( \Theta' \). \( (x/s)_{ave} \) is the average value of \( (x/s) \) over the range of \( \Theta \) to \( L \). A plot was then made of \( (x/s)_{ave} \) versus \( L' \) at constant \( \Theta' \) values. A cross-plot was used to obtain \( \Theta' \) values as integers. Calculations and tables of values are included in Appendix C. The final plot is given in Figure 24.

In using the plot N, P, \( \rho \), \( \beta \), k, s, and L may be in any consistent system of units. L' is calculated and corresponding
FIGURE 24
OXYGEN ABSORPTION BY
ETHOMINE IN AN
IsoTHERMAL BED

\[
\frac{k \cdot \rho_{\text{i}}}{S} \theta = L' = \frac{k \cdot \rho_{\text{i}}}{N} \theta L
\]
values of \((x/x)_{ave}\) and \(\Theta'\) are read from the chart. These values are then converted to \(x\) and \(\Theta\).

In applying the chart to design work the restrictions resulting from basic assumptions must be kept in mind. These assumptions are:

1. Isothermal bed.
2. Absorption is controlled by chemical rate and not by diffusion.
3. Chemical rate equation holds over entire range of composition.
4. Constant entrance conditions.

Figures (25, 26, 27) show the calculated absorption as compared to actual experimental data in a 1/2" tube. The experimental results are reported on the basis of jacket temperature. The average bed temperature may rise as much as 10 to 15°C above the jacket at some time during the run. Hence the experimental results should be shifted to a higher average bed temperature. In general this is the case. The variation between calculated and experimental data is of the same order of magnitude as variations between individual experimental runs.
Figure 25

Engineering Absorption Correlation

Exp. Data

$O_2$%  

$0-40^\circ C$ Jacket Temp.

$40^\circ C$ and $20^\circ C$

$50^\circ C$

Wt. % Oxygen Absorbed

<table>
<thead>
<tr>
<th>Time (Minutes)</th>
<th>0.0</th>
<th>1.0</th>
<th>2.0</th>
<th>3.0</th>
<th>4.0</th>
<th>5.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethamol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50 cm. Tube</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air Rate 1 GPM/ft</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>in 1/2&quot; Tube</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temp. + Compound Temp.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Saturation 5.5%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 24

2 GPM/\#  1 GPM/\#  0.5 GPM/\#

Exp. Data

Jacket Temp. 40°C
Air Rate

O 0.5 GPM/\#
O 1.0 \#
A 2.0 #

Engineer Absorption Correlation

Cyanine

50 ft. Tube
20 psig. Air
Air Rate GPM/\#
in 1/2" Tube
Temp. = Compound Temp.
Figure 27. Engineering Absorption Correlation

Ethomine

- 50 cm. Tube
- 20 Psig. Air
- Air Rate 1 CFM/#
- 1/21 Tube

Exp. Data
Temp. °C
- 50°
- 60°
- 70°
- 80°
- 90°
- 100°
Method of Predicting Desorption Data

Ethomine in the desorption temperature range takes up considerable heat in evolving oxygen. Considered purely from the standpoint of heat input, this heat added could be imagined due to heat capacity since the temperature is not strictly constant but does slowly rise. According to this viewpoint ethomine in the desorption range has an exceedingly large, variable heat capacity which is a definite function of temperature. The problem of heat transmission through such a material has been treated mathematically by Nessi and Nissile (9) and Sawada (10). Such treatment is out of the scope of this paper. The approximate Schmidt (11) method may be used by applying the correction of varying slab width with temperature. The complexity of such a construction is hardly justified by the accuracy obtained.

The mechanism of desorption may be simplified by the following assumptions:

1. Desorption takes place at constant temperature (actually better than 50 per cent of the oxygen is driven off within a range of 5°C at constant pressure).

2. The rate of desorption is dependent only upon the rate of heat conduction to the compound.

Calculation of heat transfer to a bed of ethomine assuming the above simple mechanism is still beyond the scope of simple mathematics. However, such heat transfer calculations may be approximated by applying the graphical Schmidt method.
In using the graphical Schmidt method for a cylinder, equally distant concentric layers are plotted on a logarithmic scale. Otherwise the treatment is exactly the same as that used for a slab. A derivation of the above is given in Appendix D. The following assumptions were made in carrying out the construction:

(1) The center line temperature represents the uniform temperature of the layer.

(2) When the average desorption temperature is reached at the center line of the layer, the point is fixed until desorption is complete.

(3) The temperature gradients at the center line represent the driving force for heat transfer into and out of the layer.

(4) Heat transfer follows the simple relationship

\[ q = k A (A_{\text{in}} - A_{\text{out}}) \]

where \( A \) is the area of the center of the layer.

The exact method of construction and calculation is described in Appendix D. The result as compared to experiment for desorption of ethylene in a 1/2" tube at one atmosphere and 130°C from an initial bed temperature of 40°C is shown in Figure 28. An equilibrium desorption temperature of 93°C, \( k \) of 0.027 Btu/hr. sq. ft. °F/ft., and \( C_p \) of 0.25 Btu/°F lb. were assumed. The value of \( k \) is in doubt and should probably be higher. No determinations of \( k \) have been made under conditions of gas flow through the bed.

The check of calculated and experimental results is
Figure 28
Desorption Calculated by Schmidt Method

Ethanene 1/2" Tube
Initial Temp. 40°C
Desorption Temp. 150°C in Jacket
o - Exp. Data

$S_{Desorbed}$

Time (Minutes)
only fair but is sufficiently good to predict desorption times for preliminary design work. For other reactors it may be necessary to modify the graphical method somewhat but the basic principles will remain unchanged.
V. FLUOMINE

A. Method of Attack

Introduction

In general, the same apparatus and procedures were used as with ethomine. The same fundamental types of data were obtained, namely:

(1) Basic absorption rate data using pure oxygen.
(2) Engineering absorption rate data using air with the compound in a standard tube.
(3) Desorption rate data with the compound in a standard tube.
(4) Equilibrium vapor pressure data at constant pressure. Samples of fluomine used in this work were furnished by Calvin and were made in his laboratory.

Experimental Results

A. Basic absorption rate data were taken over a range of temperatures of \(-10^\circ\) to \(50^\circ C\) and pressures of 20 to 320 mm. of Hg. Results at \(20^\circ\) and \(50^\circ C\) are shown in Figures 29 and 30. These curves are typical of all the data. A marked induction period appeared in runs at high temperatures and low pressures.

B. All engineering absorption data were obtained by use of the Pauling meter apparatus exclusively. Pressures of 1 atmosphere, 20, and 75 psig. were used. Typical absorption curves are given in Figures 31 and 32.

C. Only a few desorption runs were made since it became apparent that the results were quite comparable to
Figure 29

Oxygen Absorption
Fluorine 20°C

320 mm.
160 mm.
80 mm.
40 mm.
20 mm.

Mg. % Oxygen Absorbed

Time (Minutes)

P  Run No.
320 mm.  8
160 mm.  9
80 mm.   2
40 mm.   3
20 mm.   10

1.0
1.5
2.0
2.5
3.0
3.5
4.0
Figure 30

Oxygen Absorption
Fluorine 50°C

320 mm.  
160 mm.  

(80 mm. - No Absorption in 2 Minutes)

Time (Minutes)
**Figure 31**

Oxygen Absorption from Air

- Fluorine in 1/2" Tube
- 42.5 Gms.
- Air Rate = 1 CFM/
- Air Pressure = 1 Atm.
- (Temperature refers to Cooling Medium)

<table>
<thead>
<tr>
<th>Temp.</th>
<th>Run No.</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>20°</td>
<td>A-123</td>
<td>2 CFM #</td>
</tr>
<tr>
<td>25°</td>
<td>A-126</td>
<td>25°C</td>
</tr>
<tr>
<td>30°</td>
<td>A-125</td>
<td></td>
</tr>
<tr>
<td>40°</td>
<td>A-126</td>
<td></td>
</tr>
<tr>
<td>50°</td>
<td>A-127</td>
<td></td>
</tr>
</tbody>
</table>
Oxygen Absorption From Air
Fluorine in 1/8" Tube
42.5 Gms.
Air Rate = 1 CFM/
Air Pressure = 20 Psig
(Temperature Refers to Cooling Medium)
these obtained for ethomine. Such a desorption curve is given in Figure 53.

D. Equilibrium data giving the relationship of composition and temperature at constant pressure were obtained at 1/2 and 1 atmosphere oxygen pressure, Figure 54. The oxygen absorption rate apparatus was used for this work.
B. Correlation of Basic Rate Data

Introduction

The experimental data obtained for fluomline show it to be very similar to ethomline in its properties. Desorption temperature and vapor pressure relations are almost identical with ethomline. However, fluomline has a higher saturation value and its rate of absorption is higher with the optimum at a somewhat lower temperature. Because of the general similarity, analysis of the experimental data was carried out in much the same manner as with ethomline.

Composition

The data were first tested to determine the order of reaction with respect to deoxygenated fluomline. Plots of \((s-x)\) versus \(\theta\) at -10° and 30°C are given in Figures 35 and 36. A straight line on such a plot indicates a first order reaction. As with ethomline, straight lines were obtained over the range of \(\theta\) to approximately 90 per cent of saturation at all temperatures. The induction effect which is more pronounced for fluomline than ethomline causes deviation from a straight line during the first part of the oxygen absorption. A similar test for second order reaction was made. This failed.

The equation for the first order reaction at constant pressure and temperature is

\[
\frac{dx}{dt} = k' \frac{s-x}{s}
\]
where \( k' = k \phi (p) \)

A table of values of \( k' \) is given below.

**TABLE VIII**

\[ k' = k \phi (p) \text{ (Experimental)} \]

<table>
<thead>
<tr>
<th>( p \text{ (mm Hg)} )</th>
<th>-10°</th>
<th>0°</th>
<th>10°</th>
<th>20°</th>
<th>30°</th>
<th>40°</th>
<th>50°</th>
<th>T°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>320</td>
<td>11.12</td>
<td>13.17</td>
<td>12.76</td>
<td>9.55</td>
<td>7.50</td>
<td>4.90</td>
<td>2.66</td>
<td></td>
</tr>
<tr>
<td>160</td>
<td>4.35</td>
<td>5.73</td>
<td>5.80</td>
<td>4.73</td>
<td>5.70</td>
<td>2.16</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>1.60</td>
<td>2.34</td>
<td>2.60</td>
<td>2.24</td>
<td>1.97</td>
<td>0.80</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>0.65</td>
<td>0.89</td>
<td>1.34</td>
<td>0.85</td>
<td>1.21</td>
<td>---</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>---</td>
<td>0.32</td>
<td>0.58</td>
<td>0.18</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td></td>
</tr>
</tbody>
</table>

A plot of \( k' \) versus temperature is shown in Figure 37.

Values of \( k' \) read from the smooth curves of this cross plot are given below.

**TABLE IX**

\[ k' = k \phi (p) \text{ (smooth cross-plot)} \]

<table>
<thead>
<tr>
<th>( p \text{ (mm Hg)} )</th>
<th>-10°</th>
<th>0°</th>
<th>10°</th>
<th>20°</th>
<th>30°</th>
<th>40°</th>
<th>50°</th>
<th>T°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>320</td>
<td>11.1</td>
<td>13.0</td>
<td>12.6</td>
<td>10.5</td>
<td>7.6</td>
<td>4.8</td>
<td>2.65</td>
<td></td>
</tr>
<tr>
<td>160</td>
<td>4.3</td>
<td>5.7</td>
<td>5.8</td>
<td>5.0</td>
<td>3.6</td>
<td>2.12</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>1.60</td>
<td>2.35</td>
<td>2.60</td>
<td>2.26</td>
<td>1.64</td>
<td>0.97</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>0.67</td>
<td>1.04</td>
<td>1.22</td>
<td>1.03</td>
<td>0.67</td>
<td>---</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.21</td>
<td>0.41</td>
<td>0.51</td>
<td>0.44</td>
<td>0.28</td>
<td>---</td>
<td>---</td>
<td></td>
</tr>
</tbody>
</table>

**Pressure**

Values of \( k' \) at constant temperature were plotted against pressure, Figure 38. Comparatively good straight lines were obtained which, however, did not pass through the origin but cut the x-axis at positive values of pressure. This means that
\[ k' = \kappa \varphi(p) = k(p - p'_0) \]

where \( p'_0 \) = pseudo equilibrium pressure. This is the type of relationship obtained for the CaO - CaCO\(_3\) system over an intermediate range of pressures.

Within the range of pressure investigated, the above relation holds but, as with CaO - CaCO\(_3\), it probably fails at both higher and lower pressures. Approximate values of \( k \) and \( p'_0 \) are given below.

**TABLE X**

\[
\frac{dx}{dp} = k(p-p'_0)^{\frac{\varphi-x}{x}}
\]

<table>
<thead>
<tr>
<th>Temperature</th>
<th>( k )</th>
<th>( p'_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>-10°C</td>
<td>2.94 x 10(^{-2})</td>
<td>15 mm</td>
</tr>
<tr>
<td>0°C</td>
<td>3.63</td>
<td>15 mm</td>
</tr>
<tr>
<td>10°C</td>
<td>4.01</td>
<td>11 mm</td>
</tr>
<tr>
<td>20°C</td>
<td>3.40</td>
<td>9 mm</td>
</tr>
<tr>
<td>30°C</td>
<td>2.47</td>
<td>6 mm</td>
</tr>
<tr>
<td>40°C</td>
<td>1.80</td>
<td>21 mm</td>
</tr>
<tr>
<td>50°C</td>
<td>0.90</td>
<td>36 mm</td>
</tr>
</tbody>
</table>

In order to check the possibility of correlating the data on the basis of \( \varphi(p) = p^n \), a plot of log \( k' \) versus log \( p \) was made, Figure 39. At constant temperature, straight lines of slope 1.15 were obtained. This is quite reasonable since a slope slightly greater than 1.0 was expected on the basis of the previous correlation. The values of \( k \) for different temperatures are given as follows:
Figure 89

Correlation of $k'$ with Pressure

Fluorine

$k' = k p^{0.15}$

Pressure (mm Hg)
This second pressure correlation is the better if the equation is to be used over a considerable range of pressure. It represents the experimental data reasonably well at low pressure where the relationship \( \phi (p) = (p-p_0) \) fails completely. Judging from the results obtained with ethomine, it can be expected to give a much better prediction of absorption rates above the range of pressure covered by experiment also. Hence, this correlation is recommended as the more accurate. It is, however, the more complex from a mathematical point of view.

**Temperature**

The relationship of \( k \) to temperature for both pressure correlations is given graphically in Figure 40. No attempt was made to obtain either theoretical or empirical equations for these curves.

**TABLE XI**

\[
\frac{dx}{dt} = k \frac{p^{1.15}}{s-x}
\]

<table>
<thead>
<tr>
<th>Temperature</th>
<th>( k )</th>
</tr>
</thead>
<tbody>
<tr>
<td>-10°C</td>
<td>( 1.20 \times 10^{-2} )</td>
</tr>
<tr>
<td>0°C</td>
<td>1.55</td>
</tr>
<tr>
<td>10°C</td>
<td>1.68</td>
</tr>
<tr>
<td>20°C</td>
<td>1.41</td>
</tr>
<tr>
<td>30°C</td>
<td>1.02</td>
</tr>
<tr>
<td>40°C</td>
<td>0.62</td>
</tr>
<tr>
<td>50°C</td>
<td>0.31</td>
</tr>
</tbody>
</table>

\[ \text{This second pressure correlation is the better if the equation is to be used over a considerable range of pressure. It represents the experimental data reasonably well at low pressure where the relationship } \phi (p) = (p-p_0) \text{ fails completely. Judging from the results obtained with ethomine, it can be expected to give a much better prediction of absorption rates above the range of pressure covered by experiment also. Hence, this correlation is recommended as the more accurate. It is, however, the more complex from a mathematical point of view.} \]

\[ \text{**Temperature**} \]

\[ \text{The relationship of } k \text{ to temperature for both pressure correlations is given graphically in Figure 40. No attempt was made to obtain either theoretical or empirical equations for these curves.} \]
Specific Reaction Rate Constant for Fluorescein

\[ \phi' = \frac{df}{dp} = k \left( \frac{P - P_c}{P_c} \right)^{1.5} \left( \frac{A}{A_c} \right) \]

\[ \Delta = \frac{df}{dp} = k \left( \frac{P - P_c}{P_c} \right)^{1.5} \left( \frac{A}{A_c} \right) \]

Temperature °C

No. 3421-1005 Diestatic Graph Paper
2 Cycles x 10 Inches Per Inch
General Correlation

Two equations were found which fit the data equally well.

1. \( \frac{dx}{dt} = k(p-p_0) \frac{s-x}{s} \)

   Good between -10° and 50°C and 40 and 320 mm. Hg.
   This equation is not recommended over a greater pressure range.

2. \( \frac{dx}{dt} = k \frac{p^{1.15}}{s} \frac{s-x}{s} \)

   Good between -10° and 50°C and 0 and 320 mm. Hg.
   This equation will probably give good results over pressures much above 320 mm. Hg.

For values of \( k \) given in Tables X and XI

\( x \) = wt. per cent oxygen absorbed
\( s \) = wt. per cent oxygen at saturation
\( p \) = oxygen partial pressure in mm. of Hg
\( t \) = time in minutes
VI. DETERIORATION

A. Cycling Life

Optimum Cycle

The cycling life of these compounds is not a main consideration of this paper. This phase of the problem has been investigated in considerable detail by A. M. Smith (12). His experiments indicated that deterioration was a function of the oxygen produced and the number of cycles. His work also showed that most of the deterioration occurred during the desorption period. Lowering of the desorption temperature and pressure reduced the rate of deterioration.

On this basis a very general picture of the deterioration mechanism may be postulated.

(1) Chemical deterioration occurs when the compound is brought into contact with oxygen. This may be considered a chemical reaction and is a function of the oxygen pressure and temperature at the point of reaction.

(2) Chemical deterioration is also a result of the absorption and desorption process, due mainly to the straining and shifting of molecular structure.

(3) Physically, the structure is reduced by each heating and cooling cycle.

This picture suggests the following necessary conditions for maximum oxygen production with respect to the compound life:

(1) A minimum number of cycles.
(2) As low an average compound temperature as possible throughout the cycle.

(3) Low oxygen pressure when compound is at high temperature.

Such an optimum cycle would be one in which:

(1) Compound is carried practically to saturation each cycle.

(2) Desorption is not complete (80 to 90 per cent desorbed) and a moderate jacket temperature, 30 to 40°C above equilibrium desorption temperature, is used.

(3) Desorption pressure maintained low (0.1 to 0.2 atmospheres).

(4) Absorption preceded by a cooling period.

The reasoning involved in such a choice is quite simple. Absorption is carried to saturation to obtain as much oxygen as possible per cycle, hence minimizing the number of cycles. Desorption is not complete which means that for the most part the compound never rises above the equilibrium desorption temperature. A low oxygen pressure at this point reduces the chemical deterioration which is a function of this pressure and also lowers the equilibrium desorption temperature and consequently the compound temperature. Such a reduced pressure also reduces the time of desorption at a given jacket temperature. A cooling period prevents high pressure air from contacting hot compound.
Experimental Procedure and Results

Tests were carried out to determine approximate optimum cycles for ethomine and fluomine. The deterioration under these conditions was then determined experimentally. The apparatus used was essentially the same as the automatic equipment used by Smith. (12). Only minor changes and adaptations were made. The results obtained are shown in Figure 42. Included is the best cycle for salcomine according to Smith.

All tests were carried out in standard 1/2" tubes. Silica gel dried air was used throughout. The dew point was maintained below -30°C at 1 atmosphere. The general characteristics of the cycles are given in the table below.

<table>
<thead>
<tr>
<th>TABLE XII</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fluomine</strong></td>
</tr>
<tr>
<td>Total cycle length</td>
</tr>
<tr>
<td>Absorption time</td>
</tr>
<tr>
<td>Blowdown time</td>
</tr>
<tr>
<td>Desorption time</td>
</tr>
<tr>
<td>Cooling time</td>
</tr>
<tr>
<td>Cooling water temperature</td>
</tr>
<tr>
<td>Steam temperature</td>
</tr>
<tr>
<td>Air pressure (psig.)</td>
</tr>
<tr>
<td>Air rate (CFM/#)</td>
</tr>
<tr>
<td>Desorption pressure (atm.)</td>
</tr>
</tbody>
</table>
Figure 41
Cycling Apparatus
for Fluomine
The plot of ethomine life represents the average of 7 samples run for different lengths of time. The fluomine test was carried out on a single sample with considerably more care and with more refined apparatus. Oxygen production was determined at 0.1 atmosphere for fluomine while production for ethomine and salcomine was taken at 1.0 atmosphere.

Figure 42 shows clearly the very decided advantage of fluomine over both salcomine and ethomine from a cycling life standpoint.
B. Effect of Deterioration on Reaction Rate

Procedure

A sample of ethomine was packed in a standard 1/2" tube and subjected to a jacket temperature of 130°C and an air pressure of 80 psig. with slight flow for approximately 40 hours. The saturation value of the ethomine was determined at intervals.

The ethomine was then removed and mixed well. A 5 gram sample was then placed in the oxygen absorption rate apparatus and the absorption rate determined at several pressures. Several checks on the saturation value were also made.

Results

Figure 43 gives a plot of the per cent approach to saturation with time for the deteriorated sample as compared to a good sample of ethomine. These results are for tests under identical conditions of jacket temperature and oxygen pressure. The deteriorated sample had a saturation value of 1.5 per cent, the good sample 3.5 per cent.

Discussion

From the curve of the results, it can be seen that not only is the absorption rate of the deteriorated sample greater on a percentage basis but for a considerable time period the actual volumetric uptake of oxygen is also greater. Such results were not anticipated and are certainly not obvious in explanation.

The results obtained can be vaguely explained in several
Figure 43
Rate of Absorption of Deteriorated Ethylene
different ways but all such explanations involve rather unreasonable premises. For example, the following general picture will suffice as an explanation:

(1) Good (unused) compound is made up of molecules of varying absorption rates.

(2) The deterioration process used selectively killed the molecules of low reaction rate.

(3) The deterioration process also activated the good molecules left.

It is not known whether cycling deterioration will produce the same effect on the rate of absorption. Such experiments would be of great interest. Certainly in the future, study of deterioration should concern itself with the rate of absorption as well as activity (saturation value). Such study would no doubt lead to new insight into the mechanism of compound degradation.
APPENDIX A

Oxygen Absorption Apparatus

Volume of Components of System

The volume of various parts of the apparatus was determined experimentally by allowing air to flow from a vessel of known volume into the part and noting the changes in pressure. The volume was then calculated with the aid of the gas laws. All values are calculated only to the 100 cm. reading of the manometric leg connected to the apparatus.

Volumes

*Oxygen reservoir (reservoir and tubing to controlling needle valve)* - 290 cc.

"Vacuum" reservoir (reservoir and tubing to controlling needle valve) - 231 cc.

Absorption system (with 70 cc. mercury in pump but excluding powder tube and connections) - 181 cc.

*Powder tube with 5 grams of powder (including connections to valves)* - 18 cc.

Oxygen and system reservoir manometer tube - 0.285 cc./cm.

"Vacuum" reservoir manometer tube - 0.196 cc./cm.

Reservoir Volume Plots and Factors

The manometers were calibrated so that the pressure difference could be determined from a single leg reading. This was done to make reading easier and also so that the position of the mercury columns would be known for any pressure difference since the gas in the manometer leg was an appreciable amount of the reservoir volume.

From the above knowledge, a plot of the volume of gas in the reservoir against the single leg manometer reading was made. A standard barometer was assumed, and the gas was
measured at 760 mm. and reservoir temperature. Calculations were made according to the following formula:

\[ \text{vol} = \left[ \text{Res. vol.} + \text{mano. tube vol.} \right] \left[ \frac{\text{Ap of manometer}}{76} + 1 \right] \]

For example: Oxygen reservoir at Ap = 50 cm.

Left leg reading = 75.7; right leg (app. side) reading = 25.7

\[ \text{vol.} = \left[ 290 + 0.283 \times (100-25.7) \right] \left[ \frac{50}{76} + 1 \right] = 516.5 \text{ cc.} \]

Graphs for both the oxygen and "vacuum" reservoirs are given in Figures 44 and 45.

If the barometer is not standard 760 mm. the plots are not exact. However, the error is negligible as will be shown. Let \( V_1 \) be the original and \( V_2 \) the final volume of the reservoir.

Then

\[ V_1 \left[ \frac{\Delta \text{P} + \text{Bar.}}{760} \right] - V_2 \left[ \frac{\Delta \text{P} + \text{Bar.}}{760} \right] = \Delta \text{vol. at 760 mm.} \]

The barometer is usually 760 ± 10 mm., hence

\[ V_1 \left[ \frac{\Delta \text{P} + 760}{760} \right] - V_2 \left[ \frac{\Delta \text{P} + 760}{760} \right] + \left[ V_1 - V_2 \right] \frac{10}{760} = \Delta \text{vol.} \]

Maximum \((V_1 - V_2)\) is about 6 cc.

Maximum error = \( \pm 6 \times \frac{10}{760} = 0.1 \text{ cc.} \) and the maximum percent error is less than 0.1.

The volume plots gave straight lines, hence the slopes were used in all calculations rather than readings from the graphs.

Oxygen reservoir slope = 8.50 cc./cm.

"Vacuum" reservoir slope = 7.25 cc./cm.

**Expansion Volume Correction**

On desorption, heating the tube of compound not only drove off the oxygen combined but also pushed out some of the gas in the tube originally due to the expansion of this
Figure 44

Oxygen Reservoir Calibration

Volume is Total Gas in Reservoir Measured at 760 mm. and Reservoir Temperature.

Left Leg of Manometer (cm.Hg.)
Figure 46

"Vacuum" Reservoir
Calibration

Volume is Total Gas
in Reservoir Measured
at 760 mm. and Reservoir
Temperature.

Right Leg of Manometer (Gm. Hg)
gas. Hence the gas volume obtained on desorption must be corrected by this amount.

This expansion volume for the tube with 5 grams of compound was determined experimentally and found to be on the average 0.027 cc./°C at reservoir temperature. Δ°C represents the difference between absorption and desorption temperatures.

Starting Corrections

When making a run the tube was maintained evacuated until the starting time and the remainder of the absorption system was adjusted to a pressure such that upon opening the tube valves, the complete system was at the desired pressure. An example of the calculation of this additional pressure is given below.

Desired pressure = 80 mm.
Left leg reading = 160 cm.; right leg reading = 84.0 cm.

\[
\frac{80}{760} \left[ \frac{(181 + 18) + (100-84)(0.283)}{(100-83.6)(0.283)} \right] = \frac{97.6}{80} \left[ 181 + (100-83.6)(0.283) \right]
\]

\[ p = 87.6 \]

difference 87.6 - 80 = 7.6 mm.
or \[ \frac{7.6}{2} = 3.8 \] mm. on each leg of manometer.

<table>
<thead>
<tr>
<th>P (mm.)</th>
<th>Correction (mm.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>2.0</td>
</tr>
<tr>
<td>80</td>
<td>3.8</td>
</tr>
<tr>
<td>160</td>
<td>7.5</td>
</tr>
<tr>
<td>320</td>
<td>15.0</td>
</tr>
<tr>
<td>640</td>
<td>28.0</td>
</tr>
</tbody>
</table>
Factors for Converting to Wt. % Absorption

For ethylene:

5 grams of compound, saturation 3.5%, in tube.

\[ 5 \times \frac{100}{103.8} = 4.83 \text{ g. deoxygenated ethylene} \]

Wt. % absorbed = \( \text{factor} \times \frac{273}{T_{\text{res.}}} \times [\Delta(\text{mano. leg reading of 0\textsubscript{a} res.})] \)

\[ \text{factor} = 8.50 \times \frac{32 \times 100}{22,400 \times 4.83} = 0.252 \]

Wt. % desorbed = \( \text{factor} \times \frac{273}{T_{\text{res.}}} \times [\Delta(\text{mano. leg reading of "vacuum" reservoir}) - (0.027 \times \frac{A^\circ C}{7.26})] \)

\[ \text{factor} = 7.26 \times 0.0296 = 0.215 \]

For fluomine, similarly:

Absorption factor = 8.50 x 0.0298 = 0.253

Desorption factor = 7.26 x 0.0298 = 0.216
APPENDIX B

Pauling Meter Apparatus

Oxygen Material Balance

For every unit volume of gas passing through the Pauling oxygen meter at standard barometer.

\[
\frac{P}{760} = \text{oxygen in the gas}
\]

\[
[1 - \frac{P}{760}] \approx 0.265 = \text{oxygen in the original air}
\]

where \( p = \text{oxygen partial pressure} \)

(1) Oxygen absorbed = \((1 - \frac{P}{760}) \times 0.2645 \times \frac{P}{760}\)

Putting into differential form

(2) \[\frac{d[O_2 \text{ absorbed}]}{d\Theta} = V \left[(1 - \frac{P}{760}) \times 0.2645 \times \frac{P}{760}\right]\]

where \( V = \text{constant exit gas flow rate} \)

Integrating (2)

(3) Oxygen absorbed = \(0.2645 V \Theta - \int \frac{1.2645 V \Theta}{760} p d \Theta\)

For \( \Theta = 1 \int p d \Theta = \text{average value of } p \text{ over the time increment} \)

Hence the equation may be written:

(4) (Oxygen absorbed in unit time) = \(V \left[0.2645 - \frac{1.2645}{760} P_{ave.}\right]\)

A plot of equation (1) for barometric pressures of 750, 760, and 770 mm. is shown in Figure 46. Interpolation for other pressures is necessary.

Reservoir Volumes

Experiment gave a value of 26.7 cc./Ap (cm.) for both reservoirs.
Expansion Volume Correction

The average expansion volume correction for the 1/2" tube filled with 42.5 grams of compound was 0.01 Ap (cm.)/Δ°C. The correction was expressed in units of reservoir manometer pressure and could be subtracted directly.

For the tube of fluomine (26.1 g.) the expansion correction was 0.007 Ap (cm.)/Δ°C.

Capillary Flow Meter

A calibration curve of the capillary flow meter is given in Figure 47. It is based on 42.5 grams of compound in a 1/2" tube.

Factors for Converting to Wt. % Absorption

For ethomine:

42.5 grams of compound, saturation 3.5%, in tube

\[
\text{wt. % absorbed} = \text{factor} \times \left( \frac{p}{p_{\text{res.}}} \right) \left( \frac{273}{T_{\text{res.}}} \right) (\text{vol. of O}_2)
\]

\[
\text{factor} = \frac{32 \times 100}{22,400 \times 41.1} = 0.003476
\]

\[
\text{wt. % desorbed} = \text{factor} \times \left( \frac{273}{41.1} \right) \left[ \Delta (p \text{ of res. mano. in cm.}) - (0.01 \times \Delta°C) \right]
\]

\[
\text{factor} = \frac{26.7 \times 32 \times 100}{22,400 \times 41.1} = 0.0927
\]

For fluomine:

26.1 grams of compound, saturation 4.2%, in a 1/2" tube

\[
\text{absorption factor} = 0.00571
\]

\[
\text{desorption factor} = 0.1525 \text{ (expansion correction 0.007 Ap (cm.)/Δ°C)}
\]

Calculations

The average value of p was figured for each minute,
Figure 47

Calibration of Capillary No. 15
at Atmospheric Pressure

Air Rate Based Upon:
42.5 g. in 1/24 tube

Pressure Drop (Cms. of Water)
however, because of the meter lag values were taken which
run from 10 sec. after the minute to 10 sec. after the next
minute. The average was taken in the usual manner except
only half weight was given the end points.

The fraction of volume absorbed was read from the chart
and multiplied by the volume of exit gas as measured over
the minute. There was no 10 sec. lag in the volume readings.

Sample Calculations

Run #114 fluomine (See data)

Average \( P_0 \)

1st. min. = \frac{70+65+42+41.5+43+46+24}{6} = 55.3

2nd min. = \frac{24+53+59+66+72+50+48}{6} = 66.2

Corrected factors absorption

\[
\frac{764}{760} \times \frac{273}{298} \times 0.00571 = 0.00526
\]

desorption

\[
\frac{273}{298} \times 0.1525 = 0.1397
\]

Min. co. abs./cc. Vol. co. abs. Sum Wt.% \( P_0 \)

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<td>0.0225</td>
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<td>1480</td>
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Desorption 29.2 - .007 (120-30) = 28.6 \( \Delta p \)

28.6 x 0.1397 = 4.00 % \( P_0 \)

Air rate

Total air in 1st 2 min. = 1.53 + 1.51 + 0.5 = 3.54 liters

\[
\frac{3.54}{2} \times \frac{454}{28.3 \times 25} = 1.13 \text{ cu.ft./min.} \text{ (average over the 1st 2 min.)}
\]
APPENDIX C

Tube Correlation

Methods of Stepwise Solution

The equations used in the stepwise solution are taken from the section entitled "Method of Predicting Engineering Absorption Data," part IV, Section F.

(1) \[ x = s - \frac{s - x_0}{An} \]

where \( A = \frac{k}{s} \)

\[ n = \left[ \frac{R}{(R+1)^{1.5}} \right] \text{ ave.} \]

(2) \[ R = R_0 - \frac{8 \rho \Delta L}{N A \Delta} (x - x_0) \]

Arbitrary conditions were assumed - 20 p.s.i. gage,

40°C, 1 CFM/#, ethomine in 1/2" tube (50 cm. long)

The values of the several constants in metric units are as follows:

\( x_{01} = 0\% \)

\( R_{01} = 0.264 \)

\( N = 0.0655 \text{ g. mols/sq. cm.} \)

\( k = 4.41 \times 10^{-4} \)

\( s = 3.3\% \)

\( \rho = 0.65 \text{ g./cc.} \)

\( \beta = 3.12 \times 10^{-4} \)

\( P = 1800 \text{ mm. Hg.} \)

In most of the numerical calculations \( \Delta \varphi = 0.5 \) and \( \Delta l = 12.65 \) were used. On this basis the formulae were simplified.

(1a) \[ x = 3.3 - \frac{3.3 - x_0}{e^{5.1n}} \]
(2a) \( R = R_0 - 0.0782 \, (x - x_0) \)

A series of calculations for the first increment of time, moving lengthwise of the tube are given below.

\( Q = 0.5, \Delta \theta = 0.5 \text{ min.}, L = 12.65, \Delta L = 12.65 \text{ cm.} \)

Assume \( n_{\text{ave.}} = 0.077 \)

\[
\begin{align*}
n_0 &= \left( \frac{0.264}{1.264} \right)^{1.5} = 0.095 \\
x &= 3.3 - \frac{3.3}{1.489} = 1.08 \\
R &= 0.2640 - (0.0782) \, (1.08) = 0.1795
\end{align*}
\]

\[
\frac{R}{R+1} = \frac{0.095}{0.095 + 0.059} = 0.77\text{ checks assumption}
\]

\( Q = 0.5, \Delta \theta = 0.5, L = 25.3, \Delta L = 12.65 \)

\( (R_0 \text{ is now } R \text{ from last calculation}) \)

Assume \( n_{\text{ave.}} = 0.048 \)

\[
\begin{align*}
x &= 3.3 - \frac{3.3}{1.278} = 0.72 \\
R &= 0.1795 - (0.0782) \, (0.72) = 0.1232
\end{align*}
\]

\[
\frac{R}{R+1} = \frac{0.059}{0.059 + 0.036} = 0.48\text{ checks assumption}
\]

This may be carried on for any number of \( \Delta L \)'s.

Now with the second \( \Delta \theta \) the values of \( x_0 \) used are those of the \( x \) found in the previous \( \Delta \theta \) for that section.

\( Q = 1.0, \Delta \theta = 0.5, L = 12.65, \Delta L = 12.65 \)

Assume \( n_{\text{ave.}} = 0.081 \)

\[
\begin{align*}
x &= 3.3 - \frac{3.3 - 1.08}{1.527} = 1.85 \\
R &= 0.264 - 0.0782 \, (1.85 - 1.08) = 0.204
\end{align*}
\]

\[
\frac{R}{R+1} = \frac{0.169}{0.169 + 0.069} = 0.72\text{ checks assumption}
\]
\( Q = 1.0, \Delta \theta = 0.5, L = 25.3, \Delta L = 12.63 \)

Assume \( n_{\text{ave}} = 0.059 \)

\[
x = 3.3 - \frac{3.3 - 0.72}{1.350} = 1.39
\]

\[
R = 0.204 - 0.0782 (1.39 - 0.72) = 0.152
\]

\[
\frac{n}{N+1} = 0.1316 \quad n_f = 0.048
\]

\[
n_{\text{ave}} = \frac{0.069 + 0.048}{2} = 0.059 \text{ checks assumption}
\]

This series of calculations may be carried as far as those of the first \( \Delta \theta \).

Table XIII gives the values of \( x \) and \( R \) obtained by the above method of calculation. The value of \( x \) is an average value in the section \( \Delta L \) at the end of the time \( \theta \) considered. The value of \( R \) is the average value over the increment of time \( \Delta \theta \) at the end of the length \( L \) considered. Some calculations were carried out using larger \( \Delta \theta \)'s. In every case the value of \( R \) is the average value over that \( \Delta \theta \).

The values of \( x \) first obtained were converted to \( (x)_{\text{ave}} \).

These average values are the average over the range of \( L = 0 \) to \( L = 1 \) and represented the same \( x \) as obtained in the experimental work. Table XIV gives these values.

\( Q \) and \( L \) were converted to \( Q' \) and \( L' \) and a plot made of \( (x)_{\text{ave}} \) vs. \( L' \) with lines of constant \( Q' \). This was then cross-plotted to obtain integer values of \( Q' \). Values obtained from this cross-plot for the final graph, Figure 24, are given in Table XV.

The dimensionless groups were evaluated as follows:

\[
Q' = \frac{k p^{1.5} \bar{Q}}{s} = \frac{4.41 \times 10^{-4} \times 1800^{1.5}}{3.3} = 10.21 \bar{Q}
\]

\[
L' = \frac{k p^{1.5} \rho g L}{\bar{N}} = \frac{4.41 \times 10^{-4} \times 1800^{1.5} \times 0.65 \times 3.12 \times 10^{-4} \times L}{0.0665} = 0.1042L
\]
## Table XIII

Calculated Values of $x$ and $R$

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### Table XV

**Average Values of \( z \) from Cross Plot**

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<td>.135</td>
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<td>.956</td>
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<td>.134</td>
<td>.177</td>
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<td>.262</td>
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<td>.944</td>
<td>.978</td>
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<td>.079</td>
<td>.118</td>
<td>.157</td>
<td>.194</td>
<td>.232</td>
<td>.303</td>
<td>.371</td>
<td>.530</td>
<td>.656</td>
<td>.762</td>
<td>.839</td>
<td>.931</td>
<td>.972</td>
<td>.989</td>
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<tr>
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<td>.093</td>
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<td>.304</td>
<td>.441</td>
<td>.567</td>
<td>.676</td>
<td>.767</td>
<td>.869</td>
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<tr>
<td>9</td>
<td>.026</td>
<td>.052</td>
<td>.078</td>
<td>.104</td>
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<td>.154</td>
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<td>.255</td>
<td>.375</td>
<td>.488</td>
<td>.594</td>
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<tr>
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<td>.047</td>
<td>.071</td>
<td>.094</td>
<td>.118</td>
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<td>.188</td>
<td>.233</td>
<td>.347</td>
<td>.455</td>
<td>.555</td>
<td>.648</td>
<td>.797</td>
<td>.899</td>
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<tr>
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<td>.087</td>
<td>.109</td>
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<td>.173</td>
<td>.216</td>
<td>.319</td>
<td>.421</td>
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<td>.611</td>
<td>.766</td>
<td>.876</td>
<td>.954</td>
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<td>.039</td>
<td>.060</td>
<td>.080</td>
<td>.100</td>
<td>.120</td>
<td>.169</td>
<td>.199</td>
<td>.295</td>
<td>.390</td>
<td>.484</td>
<td>.576</td>
<td>.736</td>
<td>.851</td>
<td>.947</td>
</tr>
</tbody>
</table>
Sample Calculations

Problem: to calculate the rate of absorption of 42.5g. of ethomine in a 1/2" tube, 20 psi gage air, 2 CFM/#, at 40°C, sat. 3.3%.

\[
L' = \frac{4.41 \times 10^{-4} \times 1800^{1.5} \times 0.65 \times 3.12 \times 10^{-4} \times 50}{3.3} = 2.60
\]

\[
Q' = \frac{4.41 \times 10^{-4} \times 1800^{1.5} \times 0.0655 \times 2}{3.3} = 10.21 Q
\]

From Figure 2.4 corresponding values of \(Q'\) and \((\bar{x})_\text{ave.}\) are read at \(L' = 2.60\). \(Q'\) and \((\bar{x})_\text{ave.}\) are then converted to \(Q\) and \(x_\text{ave.}\), and a smooth graph drawn through these points.

<table>
<thead>
<tr>
<th>(x_\text{ave.})</th>
<th>((\bar{x})_\text{ave.})</th>
<th>(Q)</th>
<th>((x)_\text{ave.})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.113</td>
<td>0.20</td>
<td>0.37</td>
</tr>
<tr>
<td>4</td>
<td>0.219</td>
<td>0.39</td>
<td>0.72</td>
</tr>
<tr>
<td>6</td>
<td>0.314</td>
<td>0.59</td>
<td>1.04</td>
</tr>
<tr>
<td>8</td>
<td>0.401</td>
<td>0.78</td>
<td>1.32</td>
</tr>
<tr>
<td>10</td>
<td>0.481</td>
<td>0.98</td>
<td>1.59</td>
</tr>
<tr>
<td>15</td>
<td>0.649</td>
<td>1.47</td>
<td>2.14</td>
</tr>
<tr>
<td>20</td>
<td>0.766</td>
<td>1.96</td>
<td>2.53</td>
</tr>
<tr>
<td>30</td>
<td>0.902</td>
<td>2.94</td>
<td>2.98</td>
</tr>
<tr>
<td>40</td>
<td>0.960</td>
<td>3.92</td>
<td>3.17</td>
</tr>
<tr>
<td>50</td>
<td>0.984</td>
<td>4.90</td>
<td>3.24</td>
</tr>
<tr>
<td>60</td>
<td>0.995</td>
<td>5.88</td>
<td>3.28</td>
</tr>
</tbody>
</table>
Schmidt Method

Proof of Method for a Cylinder

The conduction equation for an infinite cylinder is

$$\frac{1}{\alpha} = \alpha \left( \frac{2 \pi k}{2r} \right) + \frac{1}{r^2} \frac{\partial^2}{\partial r^2}$$

where \( \alpha = \frac{k}{\rho} \)

Consider the equation from a standpoint of finite increments.

A graph of temperature in the cylinder is given below:

![Graph of temperature in the cylinder]

The subscripts indicate the position in the cylinder and

\( t_{n+1} = t_{n} + \Delta \theta \) or the next increment of time. On this basis

of finite increments the differential equation may be written

as follows:

$$\frac{1}{\alpha} \frac{\Delta \theta_n}{\Delta \theta} = \frac{(t_{n+1} - t_{n}) - (t_{n} - t_{n-1})}{(\Delta r)^2} + \frac{1}{r} \frac{t_{n+1} - t_{n-1}}{2 \Delta r}$$

or

$$\frac{(\Delta r)^2}{2 \alpha} \frac{\Delta \theta_n}{\Delta \theta} + \frac{t_{n+1} - t_{n-1}}{2} + \frac{t_{n+1} + t_{n-1}}{2} + \frac{\Delta r}{r} \frac{t_{n+1} - t_{n-1}}{2}$$

If \( \frac{(\Delta r)^2}{2 \alpha} \frac{\Delta \theta_n}{\Delta \theta} = 1 \)
Consider the actual graphical interpretation of this equation.

\[ t(o + 1) = t_0 + t_{o-1} = \frac{t_{o-1} + t_{o+1}}{2} + \frac{1}{2} \Delta r \frac{t_{o+1} - t_{o-1}}{2} \]

Solving for \( x \):

\[ x = \frac{1}{2} \frac{\Delta r^2}{r} \]

then

\[ \frac{\Delta r + x}{2\Delta r} = \frac{\Delta r + \frac{1}{2} \frac{\Delta r^2}{r}}{2\Delta r} = \frac{1}{2} + \frac{1}{4} \left( \frac{\Delta r}{r} \right) \]

Let us assume \( r \) is plotted on a log scale, then

\[ \frac{\Delta r + x}{2\Delta r} = \log \left( \frac{r}{r + \Delta r} \right) + \log \left( \frac{r - \Delta r}{r} \right) = \]

\[ \log \frac{1}{1 - \frac{\Delta r}{r}} = \frac{(\Delta r)^2}{2r} + \frac{1}{2} \left( \frac{\Delta r}{r} \right)^2 + \frac{1}{3} \left( \frac{\Delta r}{r} \right)^3 + \ldots \]

\[ \log \frac{1 + \frac{\Delta r}{r}}{1 - \frac{\Delta r}{r}} = \]

\[ \frac{1}{2} + \frac{1}{4} \left( \frac{\Delta r}{r} \right) \text{ if all differentials about 2nd order are dropped.} \]

This gives the correct ratio hence the assumption of a log
The Schmidt method is applied to a cylinder in the same manner as to a slab except that equally distant concentric layers plotted in a logarithmic scale are employed.

**Desorption Calculation Methods**

The Schmidt method was applied to the specific problem of desorbing ethylene in a 1/2" tube originally at a temperature of 40°C with steam at 130°C in the jacket. The desorption pressure was assumed 1 atmosphere which gave an average desorption temperature of 93°C.

The constants used are given below. All values are in metric units.

- \( k = 1.12 \times 10^{-4} \text{ cal./sec. x cm.}^2 \times ^\circ\text{C/cm.} \)
- \( e = 0.25 \text{ cal./gm. x } ^\circ\text{C} \)
- \( \rho = 0.65 \text{ gm./cc.} \)
- \( \Delta H = 19,800 \text{ cal.}/\text{g.mol. } O_2 \)
- \( r = 0.625 \text{ cm.} \)
- \( \alpha = \frac{k}{\rho e} = 6.9 \times 10^{-4} \)

The construction was made with \( \Delta r = 0.125 \text{ cm.} \); that is, 5 layers in the cylinder.

\[ \Delta t = \frac{\Delta r^2}{2 \alpha} = \frac{(0.125)^2}{2 \times 6.9 \times 10^{-4}} = 11.3 \text{ sec.} \]

The actual graphical layout is shown in Figure 48. Only the initial steps are shown so as to not complicate the diagram. The layers were drawn so that a 1/2 \( \Delta r \) occurs at the surface and the center. This was done so that the layer boundaries were at the middle of the imaginary desorption layers. Conditions at these lines were considered average.
FIGURE 48
SCHMIDT METHOD FOR CYLINDER OF ETHOMINE
for the half layer to either side. Also, since on this construction the centers of the cylinder occurred at - approved, a layer boundary could not fall at the center. At the surface a fictitious layer 1/2 ΔT thick was added to complete the half layer already there. Fictitious temperatures at this boundary were used in the construction.

Because of the extremely low heat conductivity of the compound, all resistance was assumed in the compound itself.

To obtain a better initial gradient, points were estimated for the first ΔΘ from the Gurney Lurie Charts for an infinite slab.

<table>
<thead>
<tr>
<th>Slab</th>
<th>Accomplish Temp. Ratio</th>
<th>ΔT rise</th>
</tr>
</thead>
<tbody>
<tr>
<td>Δx/2</td>
<td>0.62</td>
<td>56°C</td>
</tr>
<tr>
<td>5Δx/2</td>
<td>0.14</td>
<td>13°</td>
</tr>
<tr>
<td>5Δx/2</td>
<td>0.01</td>
<td>1°</td>
</tr>
</tbody>
</table>

After the first ΔΘ the temperature of layer 5 was very close to the desorption temperature and desorption was assumed to start at the beginning of the second ΔΘ. Had the temperature fallen higher, it would have been placed at 93°C regardless and the excess heat considered as heat of desorption (Q = swΔt).

The heat into and out of the section was considered to be governed by the temperature gradients in the two adjacent layers as given by the construction lines.
Heat of desorption/°C. = \(\frac{1 \times 0.65 \times 0.035}{32.0} \times 19,500 = 13.86 \text{ cal./cc.}\)

\[
q = \text{cal./sec.} = \frac{k A \Delta t_{\text{in}}}{1} + \frac{k A \Delta t_{\text{out}}}{1} = \frac{k A(\Delta t_{\text{in}} - \Delta t_{\text{out}})}{1}
\]

\[
q = \frac{1.12 \times 10^{-4}}{0.126} A(\Delta t_{\text{in}} - \Delta t_{\text{out}}) = 8.96 \times 10^{-4} A(\Delta t_{\text{in}} - \Delta t_{\text{out}})
\]

For 1 cm. length of tube:

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.0625</td>
<td>0.393</td>
<td>.0491</td>
<td>0.68</td>
<td>.032</td>
</tr>
<tr>
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<td>.1875</td>
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<td>.1472</td>
<td>2.04</td>
<td>.096</td>
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<td>.3125</td>
<td>1.965</td>
<td>.3457</td>
<td>3.41</td>
<td>.160</td>
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<tr>
<td>4</td>
<td>.4375</td>
<td>2.760</td>
<td>.544</td>
<td>4.76</td>
<td>.224</td>
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<tr>
<td>5</td>
<td>.5625</td>
<td>3.535</td>
<td>.442</td>
<td>6.13</td>
<td>.288</td>
</tr>
</tbody>
</table>

The construction was continued exactly as any other Schmidt method except that the desorption point \(t_s\) at first was held constant until layer 5 was desorbed. The fictitious temperature on the external half layer was found by drawing a line from the point on layer 5 through the 130° surface point to the external layer. For each new point on 5 there was a corresponding one on 6. Lines from layer 2 should have been drawn to layer 1 of the mirror image which, however, lay to the other side of \(-\infty\). Because of this difficulty, such lines were approximated by making them horizontal.

Calculations of heat transfer at the desorption layer are given below.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Q_{A\Theta} = 8.96 \times 10^{-4} \times 3.525 \times 11.3 \times \Delta = 3.58 \times 10^{-2} \Delta</th>
</tr>
</thead>
<tbody>
<tr>
<td>time</td>
<td>\Delta t_{\text{in}}</td>
</tr>
<tr>
<td>2nd (\Delta)</td>
<td>74</td>
</tr>
<tr>
<td>3rd (\Delta)</td>
<td>74</td>
</tr>
<tr>
<td>4th (\Delta)</td>
<td>74</td>
</tr>
<tr>
<td>5th (\Delta)</td>
<td>74</td>
</tr>
</tbody>
</table>

\[
\Delta \text{cal./sec.} = \frac{0.752}{0.553} = 1.352
\]

\[
\text{cal./sec.} = \frac{1.851}{0.553} = 3.343
\]

\[
\text{cal./sec.} = \frac{1.955}{0.553} = 3.546
\]

\[
\text{cal./sec.} = \frac{2.125}{0.553} = 3.852
\]
At the end of the 5th AO more than the heat of desorption had been put into the layer. This excess was assumed to raise the temperature of the layer.

$$\Delta T_{\text{rise}} = \frac{553}{228} = 1.92^\circ$$

Hence the temperature on 5 was $93 + 2 = 95^\circ C$. The ordinary Schmidt method was then carried out until Layer 4 reached a temperature of $93^\circ$ or over. On the 7th AO this temperature of $93^\circ$ was overshot by $9.3^\circ$, and this excess was calculated as heat of desorption, the point being held at $93^\circ C$.

<table>
<thead>
<tr>
<th>Layer #4</th>
<th>$Q_{\Delta \theta} = 8.96 \times 10^{-4} \times 2.750 \times 11.3 \times \Delta = 2.785 \times 10^{-2} \Delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7th AO</td>
<td>$9.3 \times .224$</td>
</tr>
<tr>
<td>8th AO</td>
<td>$18.5$ 17.6 0.9 0.025</td>
</tr>
<tr>
<td>9th AO</td>
<td>$30.2$ 10.4 19.8 0.551</td>
</tr>
<tr>
<td>10th AO</td>
<td>$24.3$ 8.6 15.7 0.437</td>
</tr>
</tbody>
</table>

This general procedure was continued until all layers were desorbed in turn. In calculating the percentage desorption vs. time, only the heat flow into the layer at the desorption temperature was considered.
APPENDIX E

Heat Transfer Calculations

Steady State Cooling of a Cylinder with Constant Heat Evolution

Consider a section of a cylinder of unit length, radius $r = r_0$, thermal conductivity $k$, heat evolution $H$ per unit volume.

Then
\[ q = - kA \frac{dT}{dr} = - 2\pi r k \frac{dT}{dr} \]

Also
\[ q = \rho \pi r^2 H = - 2\pi r k \frac{dT}{dr} \]

Integrating
\[ \int r^0 \frac{\rho H}{r} \ dr = \int_0^t 2k \ dt \]

\[ \frac{1}{4} \frac{\rho H}{k} (r_0^2 - r^2) = (t - t_0) \]

$t$ is the temperature at any radius $r$ in the cylinder.

For the average temperature difference between compound and wall we have the following:

\[ \Delta t_{ave} = \frac{\text{Volume} \times \Delta t}{\text{volume}} \]

\[ \Delta t_r = \frac{1}{4} \frac{\rho H}{k} (r_0^2 - r^2) \]

\[ \Delta t_{ave} = \frac{\int_0^r \frac{\rho H}{k} (r_0^2 - r^2) (2\pi r \ dr)}{\pi r_0^2} \]
\[ \Delta t_{\text{ave.}} = \frac{\rho H r^2}{8k} \]

Hence the average temperature difference is half the difference between the center line and wall temperatures.

**Half-Inch Tube**

Consider cooling of ethylene in a \( \frac{1}{2} \) in. tube assuming uniform absorption at the rate of 1% per minute.

\[ H = 6.1 \text{ cal./gm. min.} \]
\[ k = 1.52 \times 10^{-4} \text{ cal./sec. x cm.}^2 \text{ x } ^\circ\text{C/cm.} \]

\[ \Delta t_{\text{center}} = \frac{0.65 \times 6.1 \times 1/60}{4 \times 1.52 \times 10^{-4} (0.635)^2} = 40^\circ\text{C}. \]
\[ \Delta t_{\text{ave.}} = 20^\circ\text{C}. \]

Actually the geometrical center temperature as determined by thermocouple measurements was observed to rise approximately 12-15°C in the first several minutes at this absorption rate.

**Special Oxygen Absorption Tube**

\( 3/8 \) in. hard brass tube

- O.D. 0.375 in.
- I.D. 0.291 in.
- Wall 0.042 in.

Length filled 8" approx.

\[ \Delta t_{\text{ave.}} = \frac{0.65 \times 6.1 \times 1/60}{8 \times 1.52 \times 10^{-4}} (.389)^2 \]

\[ = 7.4^\circ\text{C} \text{ based on absorption rate of 1%/min.} \]

No thermocouple tests were made with this tube to determine actual temperature rise.
APPENDIX F

Pauling Meter Characteristics

Theory

A material which has magnetic susceptibility has an unbalanced force exerted on it when in a non-uniform magnetic field. If such a material is suspended in a non-uniform field and surrounded by gas, force is exerted on the test body according to the equation:

\[ F = V (X_V - X_G) \frac{\Delta H}{2X} \]

where

- \( F \) = force on test body
- \( V \) = volume of test body
- \( X_V \) = volume magnetic susceptibility of test body
- \( X_G \) = volume magnetic susceptibility of surrounding gas
- \( H \) = field strength
- \( \frac{\Delta H}{2X} \) = inhomogeneity of the field.

This principle can be employed to analyse gases for oxygen because oxygen has a magnetic susceptibility 300 or 400 times that of most other common gases. Hence, the concentration of other gases has little or no effect.

The Pauling oxygen meter employs a capsule of gas suspended on a quartz fiber suspended in a magnetic field produced by a permanent magnet. This is all contained in a cell through which the gas to be analysed is passed. Movement of the quartz fiber is indicated by a reflected light beam.
The Bureau of Standards reports the following characteristics:

1. 30 sec. time lag.
2. 0.1 liter/min. flow rate.
3. 1 to 2 inches of water pressure drop.

Calibration

In all the work described in this paper Pauling oxygen meter Model P, Serial No. 49 was used. It is temperature compensated between 50° and 100°F and need not be leveled exactly. This instrument was checked with oxygen-nitrogen mixtures which were analysed with an Orsat apparatus using alkaline pyrogallol. The results were as follows:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Orsat</th>
<th>Meter #49</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>160</td>
<td>159</td>
</tr>
<tr>
<td>I</td>
<td>117.3</td>
<td>116.5</td>
</tr>
<tr>
<td>II</td>
<td>90.0</td>
<td>91</td>
</tr>
<tr>
<td>III</td>
<td>62.6</td>
<td>52</td>
</tr>
<tr>
<td>N₂</td>
<td>0</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Time lag (analysis)

When gas composition is changed at the instrument, some time is required for this gas to reach the gas cell and to completely sweep out the old gas from the cell. During this time, the meter will give readings somewhere in between the values for the old and new compositions.

To check this lag, a change from air to N₂ was made at the meter and the change in reading observed. The gas flow used was 81 cc./min., which is slightly low according to the rotometer in the meter. The results are shown in Fig. 49.
Figure 49

Pauling Meter Readings
Entering Gas Changed
From Air to Nitrogen

○ Exp. Data
△ Calculated
If it is assumed that perfect mixing occurs in the cell, an expression for the rate of change of reading may be set up.

Let \( V \) = fictitious volume of cell (cc.)
\( v \) = rate of gas flow (cc./min.)
\( c \) = concentration of \( N_2 \) (cc./cc.)

then \( \frac{dc}{dt} = \frac{v - v_0}{V} \) since the flow in and out of the cell is equal.

Integrating

\[
\int \frac{dc}{1-c} = \int \frac{81}{V} \, dc = \ln(1-c) = \frac{81}{V} \, c
\]

From Figure 49 it can be seen that it took about 7 seconds for gas to reach the cell. The zero time will therefore be taken at this 7 second point.

\( G = 4.5 \) po \( = 81 \) mm.
\( c = \frac{157-81}{157} = 0.5 \) since meter apparently read
5 mm. at pure \( N_2 \)

\[ -\ln (1-0.5) = \frac{81}{5} \frac{4.5}{60} \]

\( V = 8.8 \) cc. volume of cell.

Using this value of \( V \), the meter readings may be predicted. Calculated values are shown in Figure 48 also. They check very well.

Regardless of whether the volume of the cell obtained is a true or fictitious volume, this method will predict the behavior of the meter with changing concentrations in the gas stream. The complete equation is given as follows:
\[
\log (1-c) = \frac{-2.303}{(60)(8.8)} \cdot v \cdot t
\]

where \( c \) = concentration of \( N_2 \) (cc./cc.)

\( v \) = rate of gas flow (cc./min.)

\( t \) = time (seconds)

Figure 50 gives the percentage approach to the correct reading with time. This curve is based on a gas flow rate of 94 cc./min., which is standard for instrument #49. To clarify, this curve gives the time required for the indicator to move a given percentage of the total movement finally made, with any change in gas composition. A shift of 90% requires about 13 seconds.

**Effect of Lag in a Cyclical Process**

Consider again the cell with perfect mixing of the entering gas.

Let \( c \) = entering composition

\( c' \) = cell and leaving composition (as indicated by the meter)

then \( v \cdot c \cdot d\theta - v \cdot c' \cdot d\theta = V \cdot dc' \)

Integrating \( \int v \cdot c \cdot d\theta - \int v \cdot c' \cdot d\theta = \int v \cdot dc' \)

If the process is cyclical, that is, \( \int v \cdot dc' = 0 \)

\( \int v \cdot c \cdot d\theta = \int v \cdot c' \cdot d\theta \)

This means that if the meter is used to obtain an integration of composition over a period of time, this integration is correct if the meter returns to the initial reading at the end of the time period.
Appendix G

Literature Cited

1. Calvin, Melvin, Reports to N.D.R.C., University of California, 1942-43.
2. Diehl, Harvey, Reports to N.D.R.C., Iowa State College, 1942-43.
3. Geissman, T. A., Reports to N.D.R.C., University of California at Los Angeles, 1942-43.
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ABSTRACT:

Investigation was made of oxygen production by means of chemical absorbents which remove oxygen from the air. The particular problem considered is that of obtaining sufficient basic data on the behavior of the absorbent to enable preliminary design of oxygen producing units. Two compounds are discussed; ethomine and fluomine. Both compounds are derivatives of the organic chelate saicomine, cobalt salicylaldehyde ethylenediamine. Experimental work on fluomine showed it to have the same general properties as ethomine. The optimum absorption temperature and the equilibrium desorption temperature were approximately the same as those of ethomine, but fluomine had a higher rate of reaction and a higher oxygen capacity. Fluomine showed a life considerably better than either saicomine or ethomine on the basis of oxygen produced. Its rate of deterioration was less than half that of ethomine, and at 50% deterioration, it had produced 70 times its weight of oxygen.
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