

**A STUDY OF THE ACTION OF ALUMINUM CHLORIDE
ON 2,2-DIMETHYLPENTANE**

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**Thesis submitted to the Faculty of the Graduate School of
the University of Maryland in partial fulfillment of
the requirements for the degree of
Doctor of Philosophy
1943**

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ACKNOWLEDGEMENT

The author wishes to express his appreciation to Dr. Nathan L. Drake for suggesting this problem, and for his guidance throughout the course of this research. The author also wishes to thank Dr. Fred E. Kendall for his advice and assistance in the performance of the low temperature distillation and freezing point work.

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INTRODUCTION

The majority of the investigations on the isomerization of paraffin hydrocarbons has dealt with the normal or straight chain structures, and most of this work has been upon petroleum refinery products instead of pure compounds. The patent literature is rich in references in which are described the isomerization of straight chain paraffin hydrocarbons, e.g. by-products from cracking processes, to suitable blending agents for gasoline. Such isomerizations to more highly branched paraffin hydrocarbons are brought about by the use of a variety of catalysts and varied conditions of temperature, pressure, and contact time with the catalyst (1,2,3,4).

The study of the isomerization of branched chain paraffin hydrocarbons on the laboratory scale in recent years has led to some interesting results which prompted this investigation. 2-Methylpentane has been isomerized to 3-methylpentane and 2,3-dimethylbutane, by treatment with 2-3 mole percent of aluminum bromide in the liquid phase at room temperature (5). In another experiment 3-methylpentane gave some 2-methylpentane when subjected to the action of 2-3 mole percent of aluminum bromide at room temperature. 2,2-Dimethylbutane underwent a cracking instead of an isomerization when treated in the liquid phase with aluminum chloride plus hydrogen chloride at 80° (5,6). 2,3-Dimethylbutane, however, under the same conditions formed 3.8 percent of normal hexane and 64.6 percent of "methylpentanes".

2,2,4-Trimethylpentane (isooctane) was found by Ipatieff and Grosse to yield, upon treatment with aluminum chloride and dry hydrogen chloride at 50°, 23 percent of isobutane, 1 percent of pentanes, 38

percent of higher boiling paraffin hydrocarbons boiling over a fairly wide range, 12 percent of unchanged isooctane, and 23 percent of an unsaturated polymer (7).

These investigations comprise all the published work to date on the action of isomerization catalysts upon isoparaffins alone. This study of the action of aluminum chloride on 2,2-dimethylpentane was undertaken in this Laboratory because of the relatively small amount of work that is recorded in the literature upon the isomerization of branched chain paraffin hydrocarbons, especially the heptanes. It was also undertaken as a possible method of preparing the more highly branched isomer 2,2,3-trimethylbutane, an isomeric heptane of superior anti-knock value (8).

EXPERIMENTAL

I. Preparation of the Hydrocarbon:

2,2-Dimethylpentane used in the reaction was prepared by the method of Moller (9) through the use of di-n-propyl zinc and tertiary butyl chloride. The method consists of slowly adding the tertiary alkyl chloride dissolved in an equal weight of dry toluene to the alkyl zinc dissolved in an equal weight of dry toluene. The reaction was carried out in an atmosphere of carbon dioxide, and the reaction mixture was kept cooled to 25-35°. At the end of the addition of the chloride the mixture was decomposed by dilute hydrochloric acid, cooling the flask in an ice bath during cautious addition of the acid. The mixture was then washed with water, dried several hours over a suitable drying agent, and separated from the toluene by distillation through an efficient column. The yield of 2,2-dimethylpentane boiling at 79.0-79.3° was 574 grams from 2163 grams of di-n-propyl zinc (40 percent of the theoretical amount).

The di-n-propyl zinc was prepared by the method of Moller (9,10) from 8 percent copper-92 percent zinc alloy turnings, n-propyl iodide, and n-propyl bromide. A suitable reaction flask equipped with an efficient reflux condenser and a heavy stirrer was filled with 750 grams (approximately 12 moles) of clean, dry, alloy turnings, and then flamed gently while being swept with dry carbon dioxide. After cooling in a stream of dry carbon dioxide, 42.7 grams (.25 mole) of n-propyl iodide and 30.3 grams (.25 mole) of n-propyl bromide was quickly added through the top of the condenser. The mixture was heated with an oil bath with stirring, dry carbon dioxide sweeping across the top of the condenser constantly to prevent an influx of air. In about half an hour the reaction began

to fume. The fuming was allowed to continue for several minutes, after which 676.5 grams (5.5 moles) of n-propyl bromide were added through the top of the condenser at a rate which allowed the reaction to proceed smoothly. Holler's procedure calls for the use of equimolar quantities of the alkyl iodide and alkyl bromide, and adding all the halides at the start of the reaction. The reaction was found to be easily controlled if it was started with .25 mole of the iodide and .25 mole of the bromide, then completed with the more economical bromide. After adding all the propyl bromide, heating was continued until reflux stopped, after which the stirrer assembly was removed and the reflux condenser replaced with a downward condenser. The crude alkyl zinc was distilled off under reduced pressure (30 millimeters of mercury). When the vacuum was released, dry carbon dioxide was admitted to the apparatus. The average yield of crude di-n-propyl zinc from this size run was 303.7 grams (63 percent of the theoretical amount).

II. Apparatus:

Apparatus for the Reaction of the Hydrocarbon with Aluminum Chloride:

The apparatus used to carry out the reaction of aluminum chloride on 2,2-dimethylpentane is shown on Plate I. The general plan of this apparatus was obtained from the work of Ipatieff and Grosse (7) who studied the isomerization of 2,2,4-trimethylpentane by aluminum chloride, and L. Goldman (11) of this Laboratory, who carried out some investigations on the dehydrogenation of cyclic compounds.

A is a constant temperature bath controlled by a bimetallic strip thermoregulator. B is a four-necked round-bottom flask equipped with standard taper joints. The hydrogen chloride inlet, C, extends below the level of the liquid in the reaction flask, and D is the carbon dioxide inlet. A dropping funnel for introducing the hydrocarbon

is shown at E, and F is a mercury sealed Hirschberg type stirrer assembly. The stirrer blades are made of double strand No. 22 Chromel wire. G is an efficient large cold finger condenser which may be packed with alcohol and solid carbon dioxide. The gas reservoir, H, equipped with an overflow trap, I, allows continuous collection of gaseous products while transferring the gas collected in the carbon dioxide absorber, J, into the gas holder, K. The reservoir and the gas holder are filled with a saturated solution of magnesium sulfate, due to the low solubility of hydrocarbon gases in this solution, and the carbon dioxide absorber contains 50 percent potassium hydroxide solution. The volume of gases collected are measured by displaced magnesium sulfate solution collected in graduated cylinder M. The capacity of flask E is either 500 milliliters or one liter; the reservoir H is a two-liter round-bottom flask, and the gas holder K is a ten-liter bottle. The volume of the carbon dioxide absorber J is 300 milliliters. The gas reservoir, carbon dioxide absorber, and gas holder are all equipped with leveling bulbs as shown in the diagram.

The carbon dioxide used for sweeping the apparatus before and after a run was taken from a tank of the compressed gas and dried by passing it through a train of calcium chloride, calcium sulfate, and magnesium perchlorate. The hydrogen chloride used in the reaction was generated by dropping concentrated sulfuric acid onto a sodium chloride slurry, and dried by bubbling the gas through concentrated sulfuric acid. The hydrogen chloride was tested to be sure it contained no air before introducing it into the reaction mixture by passing it through 50 percent potassium hydroxide in a gas absorber like the absorber J in the diagram.

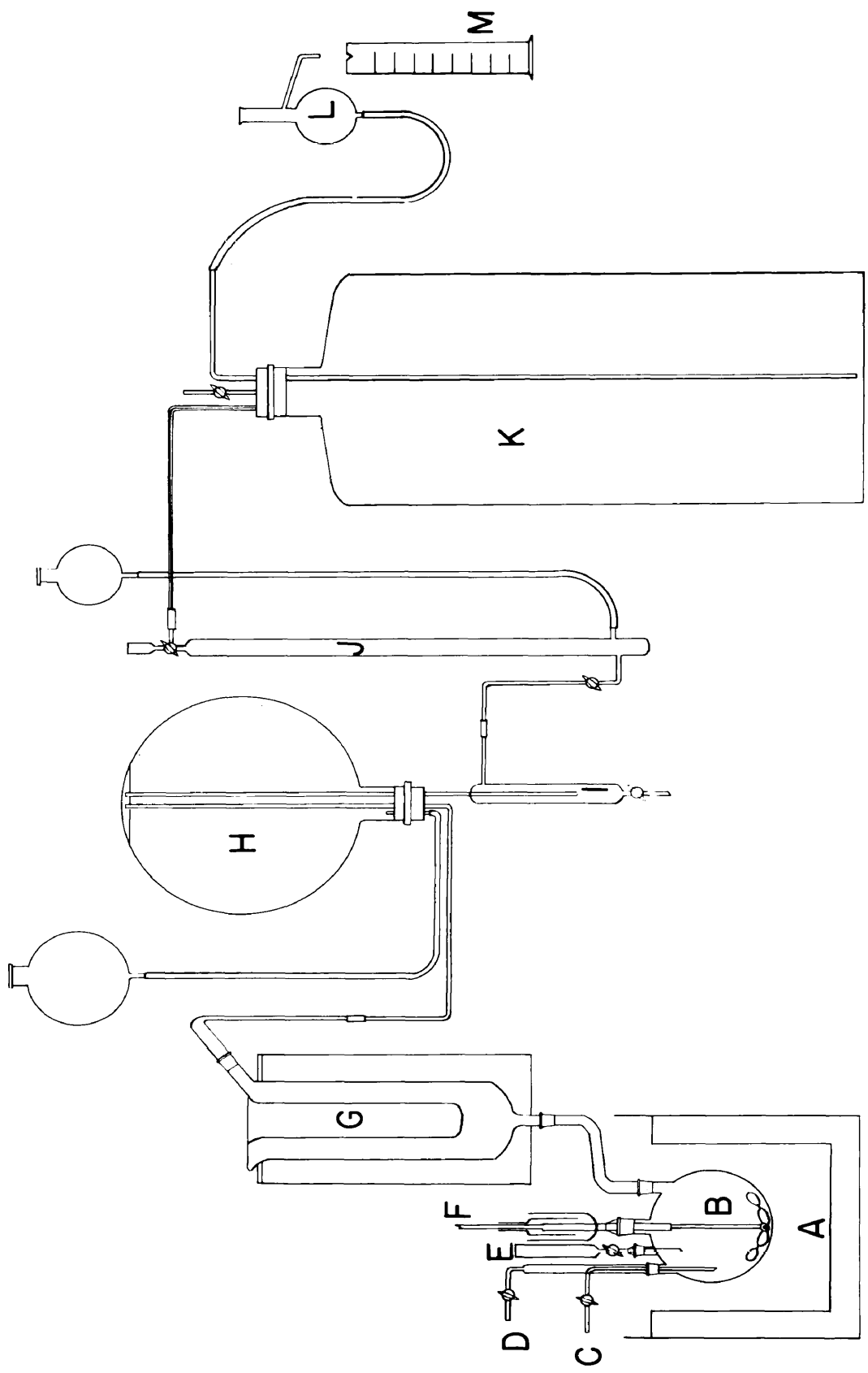


PLATE I

Low Temperature Fractionating Columns:

The apparatus used for the purification and identification of the gaseous hydrocarbons obtained in the reaction of aluminum chloride on 2,2-dimethylpentane is a simplified form of the column developed by Booth and his associates (12), which is in turn a modified form of a Podbelniak precise laboratory distillation column (13,14). A sketch of the apparatus used in this research is shown on Plate II and Plate III; photographs of the apparatus are on Plate IV and Plate V.

The apparatus is constructed principally from 7 millimeter (outside diameter) Pyrex tubing. The back line, A, constructed of 12 millimeter (outside diameter) Pyrex tubing, is connected to a HyVac pump which evacuates the entire apparatus. The ampoules, B, made of 15 centimeter lengths of 24 millimeter (outside diameter) Pyrex tubing, are for the collection and storage of samples with the aid of a refrigerant. C is a detachable ampoule, 10 centimeters in length, equipped with a stopcock and a 10/30 standard taper joint. This ampoule allows the introduction of samples into the apparatus. Gas may be transferred from any one ampoule into another, into the stillpots, Y, or into the freezing point cell, Z, by the proper manipulation of the stopcocks. The charcoal tube, D, also attached to the back line, is identical with ampoules B except it is packed with activated Columbia charcoal. This attachment is capable of producing a very high vacuum in the system by immersing it in liquid air and opening it to the system after the HyVac pump has pumped out the apparatus for one half hour.

Each section of the apparatus where gas is liquefied is connected to an open mercury safety manometer, labeled as E on the

sketch. These manometers not only serve as a safety device in case of excessive pressures, but also allow observation of the pressure in the closed portions of the apparatus. These manometers are constructed of 7 millimeter (outside diameter) Pyrex tubing, and have a trap on the bottom as shown made of a 15 centimeter length of 24 millimeter (outside diameter) Pyrex tubing.

In order to insure that the system be dry, a phosphorus pentoxide drying tube, E, 30 centimeters long and 24 millimeters in diameter, is also attached to the back line. To dry the apparatus it is filled with dry air drawn through this tube and evacuated about twelve times.

The fractionating columns, F, identical in their construction, are 110 centimeters long and are made from 11 millimeter (outside diameter) Pyrex tubing. A detailed description of the stillheads will follow later. A dripper, X, is sealed into the base of the column to allow observation of the reflux as it drops into the pot, Y. A small hole in the side of the funnel allows the ascending vapor to pass the descending liquid without interference.

The columns are packed with a Dufton wire spiral (15), made of No. 22 gauge Chromel wire which fits snugly over an 85 centimeter length of 7 millimeter (outside diameter) Pyrex tubing sealed at both ends. The spiral reaches from the dripper X to the bottom of the stillhead, and fits snugly into the column. The columns are insulated by a jacket of 64 millimeter (outside diameter) Pyrex tubing, filled with 20 mesh ground cork.

Stillpot Y is a 50 milliliter Pyrex distilling flask sealed into the bottom of the column. It is heated by a coil of four turns of

No. 20 gauge Nichrome wire shaped to fit the bottom of the stillpot. The amount of current passing through the coil, and hence the rate of boiling, is governed by a lamp bank placed in series with the heating coil.

The take-off side arm is attached to an open end manometer, N, N', before it goes into the back line. The manometer is made of 7 millimeter (outside diameter) Pyrex tubing, and each arm is 100 centimeters in length. A piece of platinum wire is fused into the bottom of the manometer and a piece of copper wire is inserted into the open arm to complete the circuit. Variation of the pressure in the head makes and breaks the circuit as the mercury level changes.

The stillheads, G and H, are shown in detail on Plate III, Figure 1 and Figure 2. The two heads are identical, but one uses liquid air (Figure 1) and the other carbon dioxide snow and alcohol (Figure 2) as refrigerant. The liquid air cooling head is made of a copper tube, I, 24 centimeters long, 3 centimeters in diameter, and is held in place over the distilling column by paraffined corks. Two small copper tubes, J and K, serve as inlet and exit tubes for the circulating liquid air. The whole head is insulated with heavy magnesia steam pipe insulation.

The liquid air is held in an unsilvered wide-mouth Dewar flask, L, equipped with a liquid air exit tube, J, an exhaust tube, F, and a large tube for adding liquid air. The Dewar is sealed with a sponge rubber gasket, M, compressed between two wooden blocks held by four end-threaded rods. When the pressure in the column rises, contact is made at point 2 in the manometer, N, which activates the relay sounder key, O, and closes the exhaust line, F, from the Dewar, L. The liquid air is then injected into the cooling head through inlet J by the pressure developed by the evaporating liquid air. The temperature drop causes a pressure

drop, which breaks the contact at point 2 and disconnects the relay sounder key, opening the exhaust line F. The liquid air then no longer injects into the head, but instead escapes through the exhaust line until sufficient pressure develops again to repeat the operation.

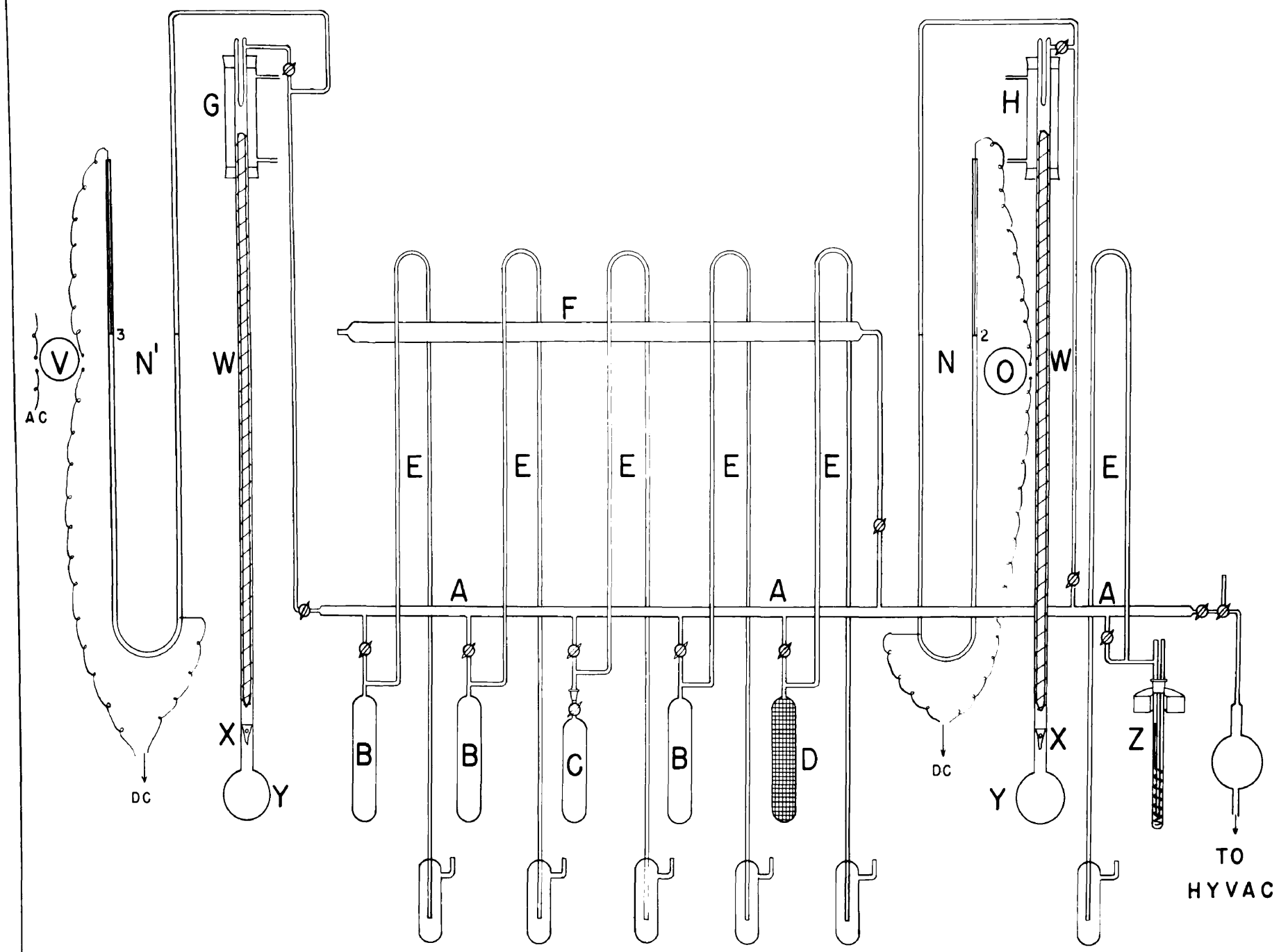
The carbon dioxide-ethyl alcohol cooling head, Q, has the same dimensions as the liquid air cooling head, and is held in place over the distilling column by rubber stoppers. It is likewise insulated with a layer of magnesia steam pipe insulation.

A small centrifugal pump, R, circulates the cold alcohol through the cooling head. The pump is below the surface of the liquid in Dewar flask S, hence no packing is required. The shaft of the pump is directly attached to a small motor, T. The circulating liquid is cooled by pumping it through the copper coil in Dewar flask, U, which is filled with a slush of alcohol and carbon dioxide snow. The motor, T, is activated by a relay, V, whenever there is sufficient pressure in the column to cause the manometer, N, to make contact at point 3. When the pressure drops the contact at point 3 is broken, and the motor stops circulating the cooling liquid until the pressure is sufficient to repeat the process.

The carbon dioxide-alcohol head is equipped with a three junction copper-constantan thermocouple, and the liquid air head with a two junction copper-constantan thermocouple. The millivoltage produced is read on a Rubicon potentiometer. The thermocouples are inserted in wells made from 10 centimeters of 4 millimeter (outside diameter) Pyrex tubing.

The freezing point cell, Z, constructed of 10 millimeter (outside diameter) Pyrex tubing, is 23 centimeters long and is divided 4 centimeters from the top by a 14/35 standard taper joint. A two junction copper-constantan thermocouple is inserted in a well made of

4 millimeter (outside diameter) Pyrex tubing which runs the entire length of the cell. The contents of the tube are stirred by a glass spiral which has attached to it a small tube containing a piece of iron. The stirrer is moved by a solenoid placed around the cell and fixed above the stirrer, made of several turns of copper wire wrapped around a soft iron pipe. A circuit breaker in series with the solenoid causes the stirring, and a lamp bank in series with the solenoid controls the strength of the magnetic field. The freezing point cell is attached directly to the back line, and is also equipped with a safety manometer. E.



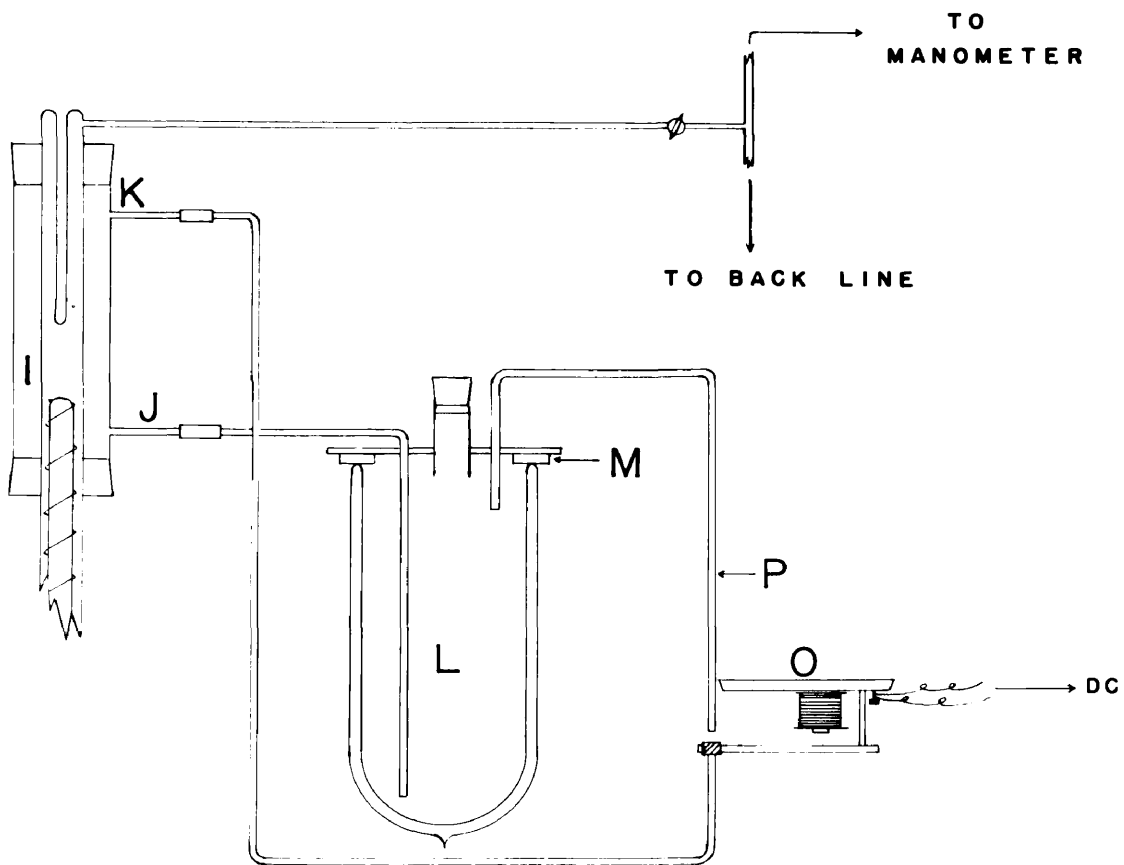


FIGURE 1

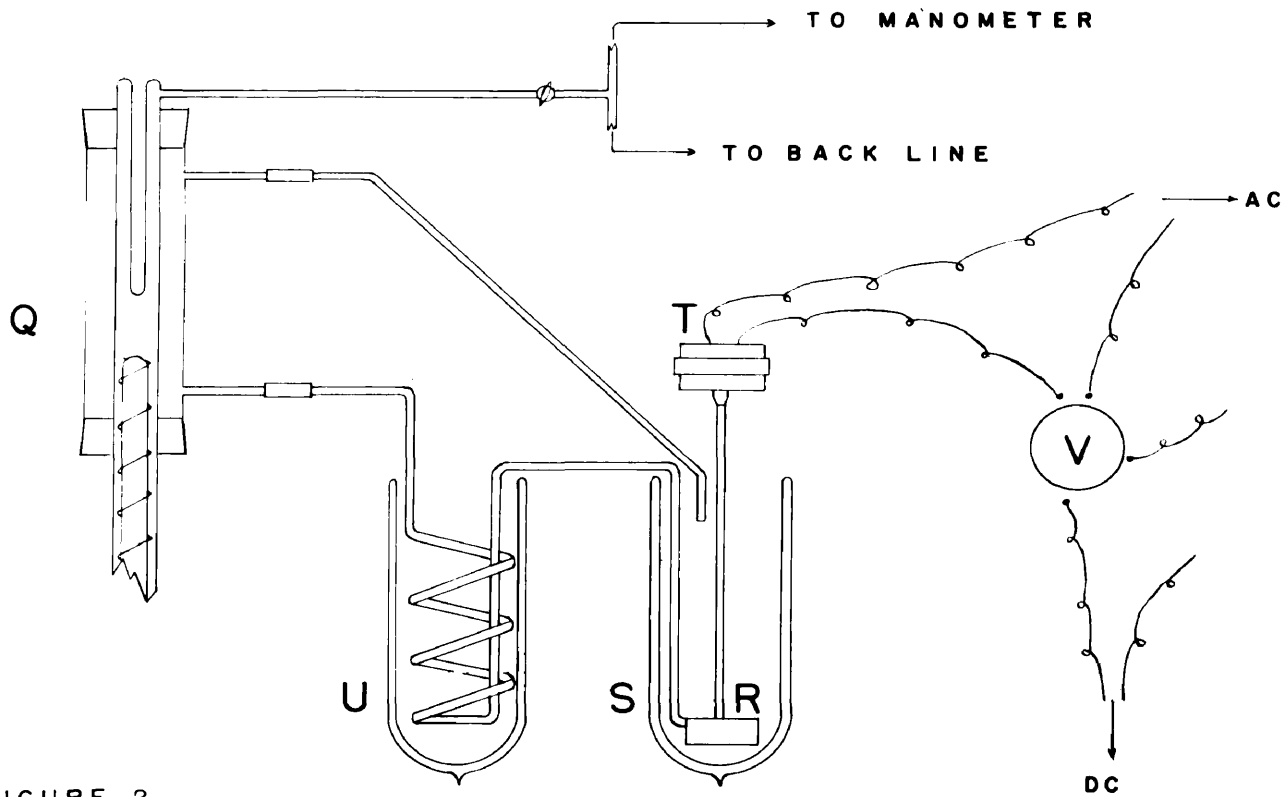


FIGURE 2

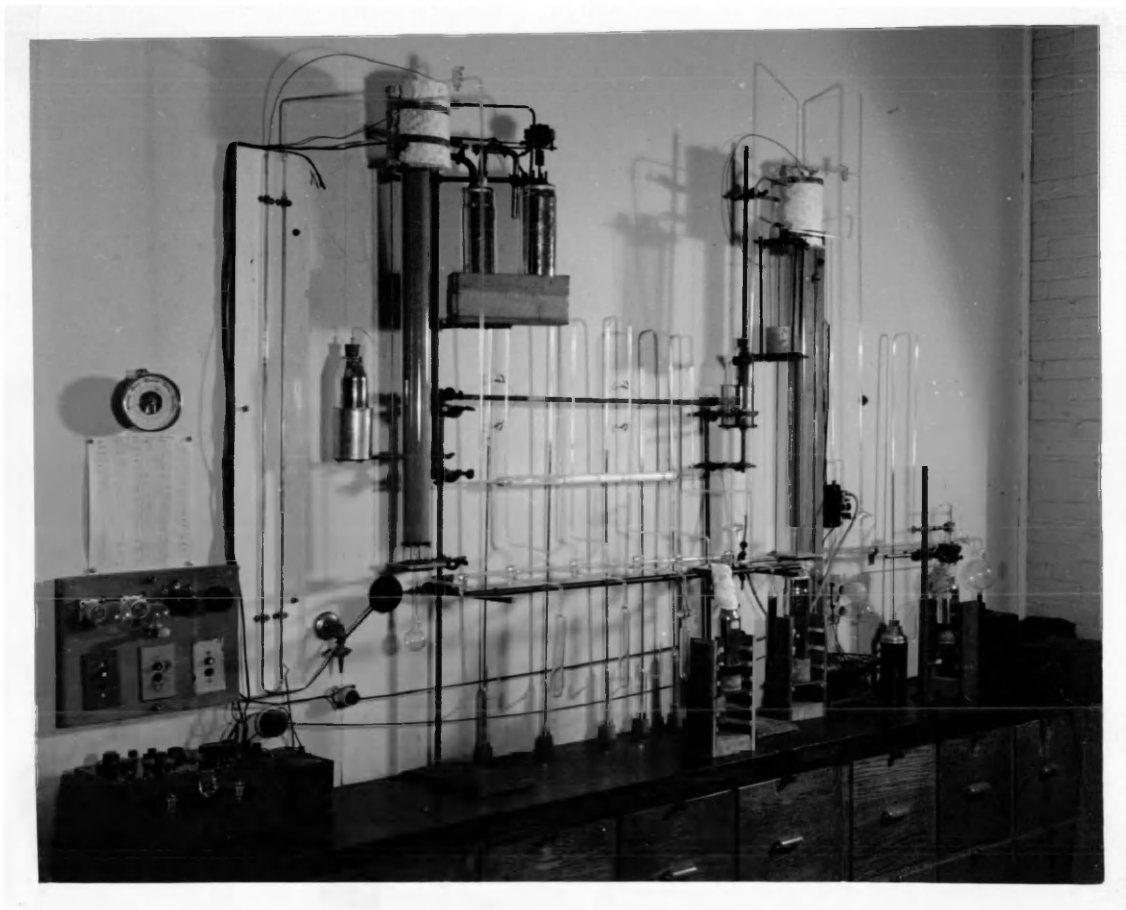


PLATE IV

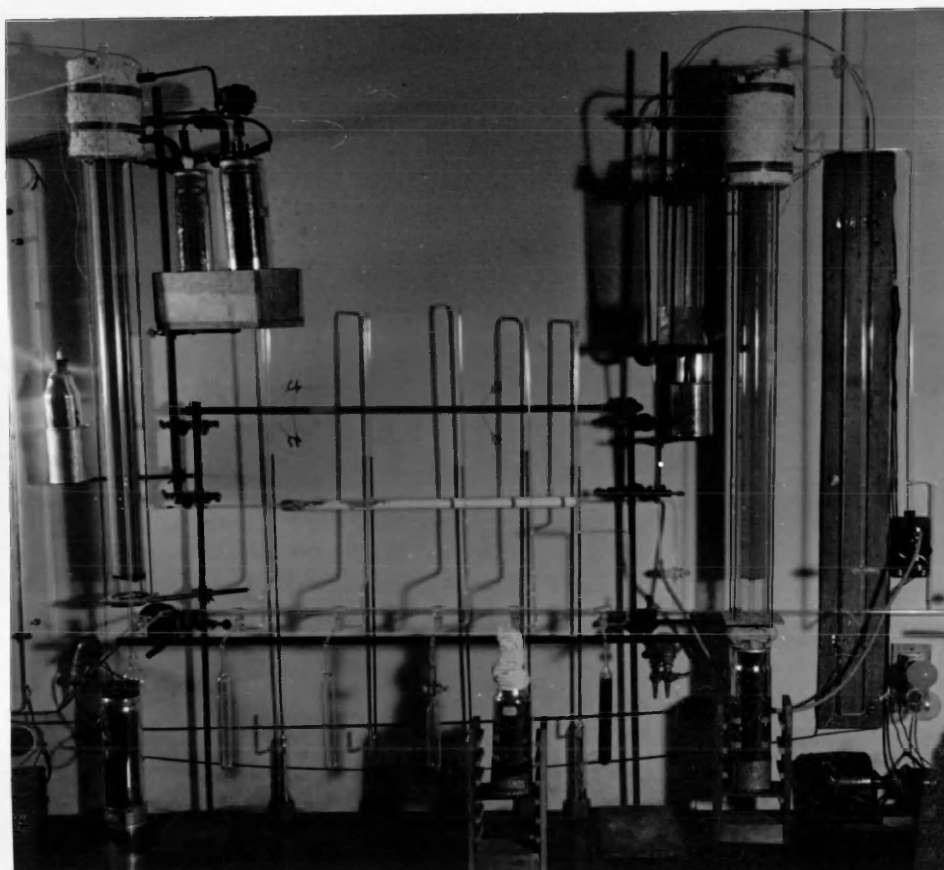


PLATE V

Fractionating Column for Liquid Products:

The liquid residues from the reaction of aluminum chloride on 2,2-dimethylpentane were distilled through a liquid column equipped with a stillhead with an automatic adjustment of the reflux ratio. The column is made from a four foot length of 13 millimeter (outside diameter) Pyrex tubing, and has 24/40 standard taper joints on each end. The packing for the column is single turn soft glass helices, 4 millimeters in diameter, which are held in place by a glass cross sealed into the bottom of the column. The column contains four feet of packed space, which is insulated by a jacket of 54 millimeter (outside diameter) Pyrex glass tubing filled with 20 mesh ground cork. The column is not heated.

The distilling head is one made by the Ace Glass Company, Vineland, New Jersey (Ace Glass Company, Catalog "40", item No. 6530). It holds a pivoted funnel below the condenser, which has sealed into its side a piece of iron. This funnel is operated by a magnetic coil, strapped to the side of the stillhead adjacent to the funnel, which has in series with it an adjustable circuit breaker. By adjusting the time interval on the circuit breaker the rate of take off can be adjusted. When the circuit is closed, the magnet pulls the pivoted funnel over the receiver, and when the circuit is broken, the funnel falls back to its vertical position and returns the reflux to the column. The entire head is wrapped with a layer of glass wool for insulation during a distillation. The stillhead is equipped with a 24/40 standard taper joint and fits directly on the column. Temperatures are taken by a thermometer with an enclosed scale, equipped with a 10/30 standard taper joint which fits into the standard taper thermometer well on the stillhead.

Burrell Gas Analyzer

The gas analyses of the gaseous products of the reaction of aluminum chloride on 2,2-dimethylpentane were carried out with a Burrell Universal Gas Analyzer, Build-Up Model.[†] The apparatus used was equipped with a carbon dioxide absorption pipette with a helical coil, two absorption pipettes of the Francis Auto Bubbler type for oxygen absorption and absorption of unsaturated hydrocarbons, a heated copper oxide tube for the removal of hydrogen, and a slow combustion pipette for the determination of saturated hydrocarbons. The carbon dioxide absorber contained 30 percent potassium hydroxide. The pipette for the absorption of unsaturated hydrocarbons contained a mixture developed by Tropch and Dittrich (16, 17). The reagent is prepared from 15 volumes of 0.6 percent silver sulfate in concentrated sulfuric acid and one volume of a saturated solution of nickel sulfate in sulfuric acid. Tropch and Dittrich claim this absorbent is superior to fuming sulfuric acid for the removal of unsaturated hydrocarbons in that it does not dissolve saturated hydrocarbons, and it eliminates the necessity of the passage of the gas after bubbling through the absorbent through potassium hydroxide to remove sulfur trioxide. The oxygen is removed in the other Francis Auto Bubbler pipette by use of a solution developed by Fieser (18). This reagent is prepared by dissolving 16 grams of 36.7 percent sodium hydrosulfite, 13.3 grams of sodium hydroxide, and 4 grams of 95 percent sodium anthraquinone- β -sulfonate in 100 milliliters of water.

[†]The author is grateful to Dr. D. T. Bonney of the Chemical Engineering Department, University of Maryland, for the use of this apparatus.

III. Experiments:

Experiment No. 1

After generously sealing all joints with triethylene citrate-tetraethylene citrate cement, seven grams of anhydrous aluminum chloride (Mallinckrodt technical grade) were placed in the reaction flask and sweeping with carbon dioxide was begun. After sweeping the apparatus overnight, micro bubbles were obtained in the carbon dioxide absorber. While continuing the sweeping, the large condenser was filled with solid carbon dioxide and alcohol and the reaction flask was surrounded by an ice bath. Then the flow of carbon dioxide was stopped and after the carbon dioxide stopped bubbling out of the absorber, 100 milliliters of pure 2,2-dimethylpentane was added to the flask through the dropping funnel. Stirring was then commenced, and air-free hydrogen chloride was bubbled into the reaction mixture. The mixture in the flask was stirred continuously for three hours at 0°, with hydrogen chloride constantly being run into the flask. Throughout this time a small amount of a gas collected in the carbon dioxide absorber and was transferred into the gas holder by closing the stopcock at the base of the absorber, opening the three way stopcock at the top of the absorber to the gas holder, and pushing the gas into the gas holder by raising the bulb on the absorber. After three hours reaction time it was evident little or no reaction was taking place, so the flow of hydrogen chloride was shut off, the stirring was stopped, and sweeping with carbon dioxide was begun. After sweeping the apparatus three quarters of an hour with carbon dioxide, bubbles of very nearly micro size were obtained in the carbon dioxide absorber. The gas obtained by sweeping was also transferred to the gas holder, giving

a total volume of gases of 90 milliliters. The gas from this run was discarded, as there was an insufficient quantity for duplicate analyses. The substance remaining in the reaction flask was water-white, and only in one layer. The aluminum chloride was bright yellow, and apparently unreacted. The contents of the flask were poured into a large separatory funnel containing crushed ice, shaken, and then allowed to separate. The upper layer was washed twice with five percent sodium bicarbonate solution and twice with water, dried several hours over calcium chloride in the icebox. The results of the liquid distillation are shown in Table I.

Table I

Liquid Distillation, Experiment No. 1

Charge = 90 ml.

<u>Fraction No.</u>	<u>Vol. Distilled</u>	<u>B. P. (corr.)</u>	<u>Reflux ratio</u>
1	26 ml. ⁺	76.0° - 79.0°	50:1
2	39 ml.	79.0°	10:1
3 (holdup)	23 ml.		

Experiment No. 2

The second experiment differed from the first in the temperature, time of reaction, and the grade of catalyst. Twenty grams of anhydrous aluminum chloride (Mallinckrodt Analytical Reagent Grade) were placed in the reaction flask and the apparatus was swept with carbon dioxide overnight after sealing all joints with triethylene citrate-tetraethylene citrate lubricant; micro bubbles were obtained in the absorber after sweeping for this length of time. In this experiment crushed ice

⁺This relatively large amount of forerun in comparison to the volume of recovered hydrocarbon is due to the fact that the 90 ml. charge was insufficient for the size column used to fractionate efficiently. In subsequent experiments larger volumes of hydrocarbon were used to give larger charges for liquid distillations.

was placed in the large condenser instead of solid carbon dioxide and alcohol, and the reaction flask was surrounded by a water bath at room temperature, 23° . The temperature of the reaction was maintained at $23 \pm 1^{\circ}$ throughout the course of the reaction. After stopping the sweeping with carbon dioxide and when bubbling ceased in the absorber, 250 milliliters of pure 2,2-dimethylpentane was added to the flask through the dropping funnel. The stirrer was started, and hydrogen chloride was passed into the reaction mixture as before. The reaction mixture was stirred continuously for ten hours, hydrogen chloride being bubbled into the reaction mixture constantly. Throughout the course of the experiment gases were collected in the absorber, in larger quantities than in Experiment 1, and were transferred at intervals into the gas holder. After ten hours time, the hydrogen chloride flow was shut off, stirring was stopped, and sweeping with carbon dioxide was begun. After ten hours sweeping, micro bubbles had not been obtained in the absorber, but a gas was collecting at a constant rate. Apparently something was being swept over from the reaction flask, so sweeping was stopped, and all gases transferred to the gas holder. The volume of gas collected at standard temperature and pressure was 2902 milliliters. The mixture in the reaction flask was slightly pink in color, but as in the first experiment there was only one layer, the aluminum chloride was bright yellow and apparently unreacted. The mixture was hydrolyzed and washed as in the first experiment, and dried several hours over calcium chloride in the icebox. The results of the liquid distillation are given in Table II.

Table II

Liquid Distillation, Experiment No. 2

Charge = 170 ml.

<u>Fraction No.</u>	<u>Vol. Distilled</u>	<u>B. P. (corr.)</u>	<u>Reflux Ratio</u>
1	21 ml.	78.2° - 79.0°	50:1
2	132 ml.	79.0°	10:1
3 (holdup)	25 ml.		

us Product, Experim
Low Temperature Distillation of Gaseous Product, Experiment No. 2:

The gas collected in the gas holder was drawn into the detachable ampoule of the low temperature distillation apparatus. In the process of pulling over the gas an air block formed; some of the gas could not be condensed in the ampoule surrounded by liquid air, and hence detained the condensation of the condensable gases into the ampoule. For this reason it was necessary to pull this air into the charcoal tube. Some small amount of a liquid gas was condensed in the ampoule, and a fractionation was attempted in the solid carbon dioxide-alcohol distilling column on this substance. The attempted fractionation was unsuccessful because the substance boiled too high for the refrigerant, and the column continually flooded. Evidently the use of crushed ice instead of solid carbon dioxide and alcohol in the large reflux condenser during the reaction allowed some of the starting material to be swept over into the gas holder.

Experiment No. 3:

This experiment was carried out at the same temperature as the preceding one, but solid carbon dioxide and alcohol was used in the reflux condenser as in the first experiment instead of crushed ice. The object of the experiment was to verify that the large volume of gas obtained in the gas holder during the second run was entrained starting material, and not a reaction product.

As before, the joints were sealed with triethylene citrate-tetraethylene citrate lubricant after placing 30 grams of anhydrous aluminum chloride (Mallinckrodt, Analytical Reagent Grade) in the reaction flask. After sweeping with carbon dioxide overnight, micro bubbles were obtained in the absorber. The large reflux condenser was packed with solid carbon dioxide and ethyl alcohol, and the reaction flask was surrounded by a water bath at room temperature, 24°. The temperature of the bath was maintained within $\pm 1^\circ$ of this temperature throughout the reaction. After stopping the sweeping as before, 375 milliliters of pure 2,2-dimethylpentane was introduced into the flask through the dropping funnel. Stirring was started, and hydrogen chloride was bubbled into the flask and continued throughout the reaction as in the previous experiments. The reaction mixture was stirred for ten hours, but in this case only a small amount of gas passed through the absorber and into the gas holder as in the first experiment. After ten hours time, sweeping with carbon dioxide was begun after stopping the flow of hydrogen chloride. Inside of one hour of sweeping micro bubbles were observed in the absorber. One hundred eighty-three and four-tenths milliliters of gas at standard temperature and pressure was the volume of gas obtained in this experiment. The mixture in the reaction flask was the same in appearance as in the previous two runs; the liquid was in only one layer, and the aluminum chloride was bright yellow and apparently unreacted. The mixture was hydrolyzed, washed, and dried as before; the result of the liquid distillation are given in Table III.

Table III

Liquid Distillation, Experiment No. 3

Charge = 355 ml.

<u>Fraction No.</u>	<u>Vol. Distilled</u>	<u>B. P. (corr.)</u>	<u>Reflux Ratio</u>
1	20 ml.	78.0° - 79.0°	50:1
2	306 ml.	79.0°	10:1
3 (holdup)	26 ml.		

Gas Analysis of Gaseous Product, Experiment No. 3:

The gas collected in the gas holder was analyzed in the Burrell Universal Gas Analyzer. The results of the analysis are tabulated in Table IV.

Table IV

Gas Analysis, Experiment No. 3

	<u>Percent</u>
Carbon dioxide	5.2
Unsaturates	0.0
Oxygen	23.0

The analysis indicates clearly that the gas obtained in the gas holder during this experiment was carbon dioxide, which escaped absorption in the absorber, and air, which leaked into the system sometime during the reaction.

Experiment No. 4:

In the fourth experiment the only condition that was varied from the third experiment was the temperature.

As in the preceding experiment, 21 grams of anhydrous aluminum chloride (Mallinckrodt, Analytical Reagent Grade) was put into the flask, the joints were sealed, and the apparatus was swept until micro bubbles

appeared in the carbon dioxide absorber. Solid carbon dioxide and alcohol were placed in the reflux condenser, the flask was placed in the constant temperature bath shown in Plate III, and the temperature was maintained at $50 \pm 0.5^\circ$ throughout the course of the reaction. Sweeping was stopped, 250 milliliters of pure 2,2-dimethylpentane were added to the flask, stirring was begun, and hydrogen chloride was bubbled into the reaction mixture and continued throughout the reaction. After one and one half hours, a constant rapid reflux was noted in the large reflux condenser, and a thick frost appeared on the adapter connecting the condenser to the flask. It was also noted that soon after this reflux began, the aluminum chloride attained a dirty brown color. The reaction was allowed to proceed for ten hours, during which time a relatively large amount of gases collected in the absorber, which were transferred at intervals to the gas holder. At the end of ten hours, the heater was turned off, the flow of hydrogen chloride was stopped, and stirring was stopped. The solid carbon dioxide and alcohol was removed from the reflux condenser and crushed ice placed therein; the warm water was removed from the constant temperature bath and crushed ice substituted. The object of this procedure was to try and hold back any original heptane or isomerization product, but sweep over any low boiling reaction product into the gas holder. However, after three and one half hours of sweeping with carbon dioxide, micro bubbles did not appear in the absorber, yet the gas was collecting at a constant rate, so sweeping was discontinued at this point. There was present in the gas holder at the end of the reaction 4218 milliliters of gas at standard temperature and pressure. The substance remaining in the reaction flask was quite different in appearance than

in previous experiments. It was in two layers, a lower layer of dark brown viscous liquid, and a slightly yellow upper layer. The aluminum chloride that remained was dirty brown in appearance, apparently coated with some of the substance in the lower layer. The upper layer was separated as well as possible from the brown viscous material, washed and dried as in previous experiments. The results of the distillation of this liquid are tabulated in Table V.

Table V

Liquid Distillation, Experiment No. 4

Charge = 200 ml.

<u>Fraction No.</u>	<u>Vol. Distilled</u>	<u>B. P. (corr.)</u>	<u>Reflux Ratio</u>
1	15 ml.	up to 64.5°	total reflux
2	51 ml.	64.5° - 79.0°	50:1
3	90 ml.	79.0°	10:1
4 (holdup and residue)	30 ml.		

Fraction No. 1 was obtained by attaching a solid carbon dioxide-alcohol trap to the vent of the liquid fractionating column; it is apparently some isobutane that was dissolved in the higher boiling liquid. Fraction No. 4 includes the 25 milliliters holdup of the column, plus a small volume of residue which remained in the distilling flask when all the volatile substance had been distilled off.

Vacuum Distillation of Residue from Liquid Distillation.Experiment No. 4:

The thirty milliliters of residue plus column holdup (Fraction No. 4) were separated further by a vacuum distillation. It was necessary to take off the volatile holdup by distillation in a Claisen flask at 760 millimeters, then to apply a vacuum to separate the high boiling

substance. Under 10 millimeters pressure, a forerun came off at 35-66°, and a few drops of a brown viscous liquid boiling at 65-67° at 10 millimeters pressure came over after changing the receiver. This fraction proved to be some of the dark brown lower layer observed in the reaction flask at the end of experiment four which became dissolved in the upper layer. Both this fraction obtained in the vacuum distillation and the lower layer from the reaction flask had a kerosene-like odor, and when tested for unsaturation were found to take up bromine in carbon tetrachloride and to decolorize alkaline potassium permanganate solution.

Gas Analysis of Gaseous Product, Experiment No. 4:

A gas analysis with the Burrell Universal Gas Analyzer on a portion of the gas collected during the reaction showed the results which are in Table VI.

Table VI

Gas Analysis, Experiment No. 4	
	Percent
Carbon dioxide	1.4
Unsaturation	2.8
Oxygen	2.0
Hydrogen	1.2
C_4H_{10}	89.7

The analysis of the gas indicates it was principally one of the butanes; it was shown by fractionation and freezing point to be isobutane, described in the next section. The small percentages of carbon dioxide, unsaturation, oxygen and hydrogen tabulated above may be explained by the slight solubility of isobutane in the reagents

used. The results of the analysis are within the limit of experimental error.

Low Temperature Distillation of Gaseous Product.

Experiment No. 4

The 4218 milliliters of gas collected in the fourth experiment was drawn into the detachable ampoule of the low temperature distillation column, and then transferred to the stillpot of the liquid air column. It had a volume of twelve to fifteen milliliters when liquefied. The cooling system was manipulated manually for twenty minutes until the temperature of the head was below that of the anticipated boiling point, after which the spiral became wet with the descending liquid. The heating coil was then strapped to the stillpot and a current of 1.12 amperes was run through the heater. It was not necessary to surround the heater and stillpot with a Dewar flask, which is the customary practice. After allowing the column to operate automatically on total reflux until the temperature became constant at -14.5° , and there was a minimum of fluctuation in the manometer, the column was in equilibrium. The rate of dropping at the base of the column was 75 drops a minute at this time. The slightly lower temperature than anticipated was attributed to an air block; when this was bled off into the charcoal tube for a period of twenty minutes the temperature attained constancy at -10.5° . The distillate was then collected in one of the ampoules for one hour and twenty five minutes, during which time the boiling point remained constant at the above value of -10.5° . The manometer was adjusted at the start so the pressure throughout the distillation was atmospheric pressure, 756.1 millimeters of mercury. After the period of one hour and twenty five minutes when the boiling point began to rise slightly showing a change in composition, the ampoule containing the pure

fraction boiling at -10.5° at 756.1 millimeters was closed, and the second ampoule was opened to the back line. After one half hour, during which time the stillhead temperature rose to approximately -1° , nothing had collected in the second ampoule, the stillpot was dry, the distillation was assumed to be complete, and the column was shut down. The volume of liquid collected in the first ampoule was approximately eight milliliters.

During the course of the distillation the rate of take off was checked by closing the take off stopcock for ten minutes and watching the temperature in the stillhead closely. Such a procedure is valuable when fractionating a mixture of gases, where it is possible to obtain a constant temperature in the stillhead from a mixture of components due to an inadequate reflux ratio. It is important in separating a mixture of gases by fractional distillation to insure the ratio of reflux to take off is greater than the minimum required to effect the separation. The procedure used to check the reflux ratio is as described above; the take off stopcock is closed several minutes and the temperature in the head is observed. If the reflux ratio is too small, the temperature of the head will fall, since the column delivers a fraction richer in the lower boiling component to the head due to the increased reflux ratio when on total reflux. However, if the rate of take off is above the minimum, the temperature will not change when the column is thrown onto total reflux in this manner. When this procedure was followed in this distillation, no change in the boiling point was observed, so the reflux ratio was satisfactory.

Freezing Point Determination of Gaseous Product, Experiment No. 4:

The pure fraction which boiled at -10.5 degrees Centigrade in

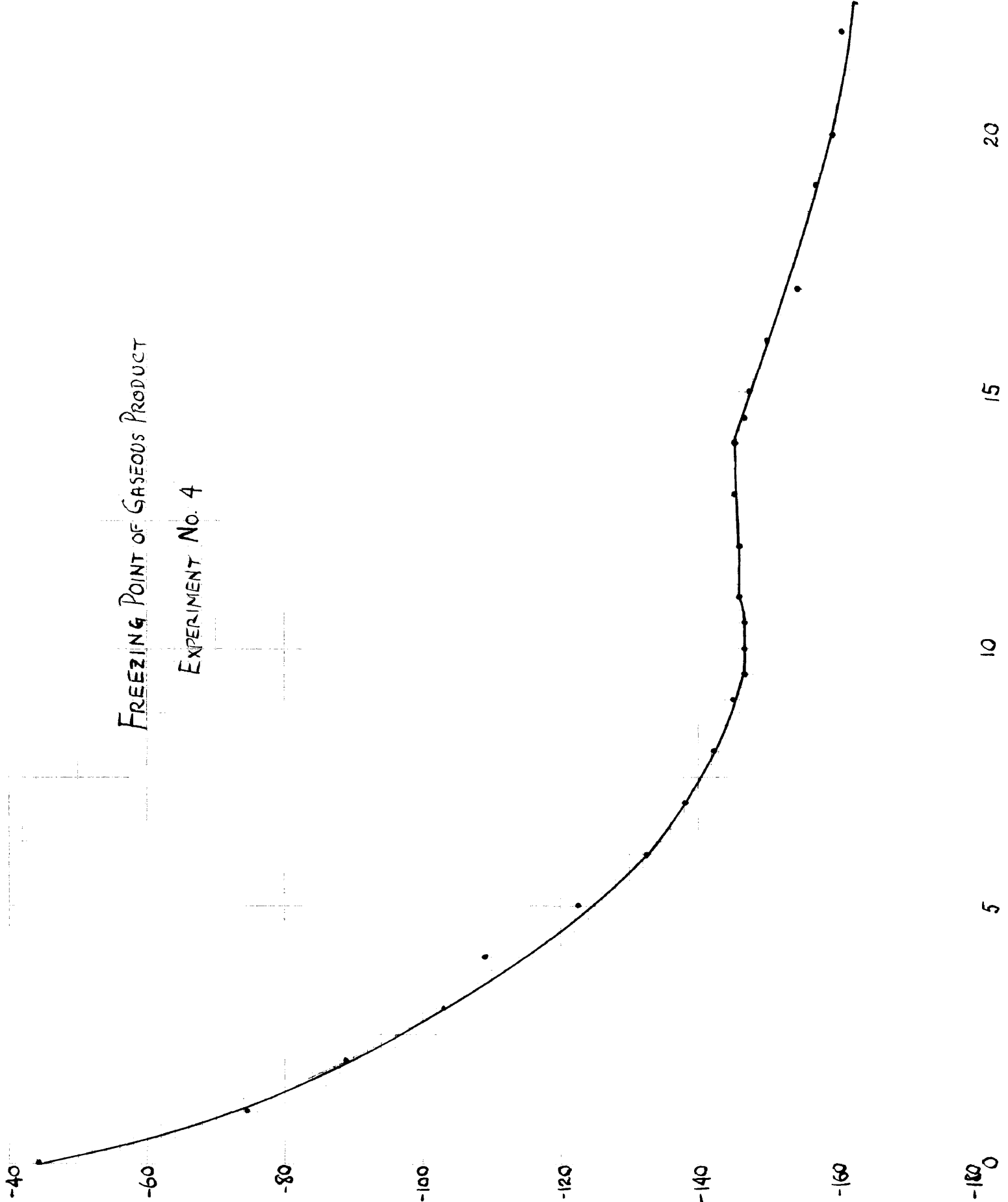
the low temperature distillation described in the previous section was drawn into the freezing point cell of the apparatus. The stirrer was started, and the cell surrounded by an empty small crude Dewar flask constructed of a 17 millimeter by 150 millimeter Pyrex test tube and a 22 millimeter by 200 millimeter test tube held together at the lips by a bored cork. This tube was then surrounded by a Dewar of liquid air, and the millivoltage read from the potentiometer. The freezing point of the purified sample was found to be -145.4° ; this value was checked by repeating the operation two more times. The freezing point data are given in Table VII and on the curve shown on Page 30.

Table VII

Freezing Point of Gaseous Product, Experiment No. 4

<u>Millivoltage</u>	<u>Temperature</u>	<u>Time</u>
3.22	-44.2	0
5.20	-74.6	1
6.05	-88.9	2
6.85	-102.9	3
7.20	-109.1	4
7.90	-122.5	5
8.40	-132.6	6
8.65	-138.0	7
8.85	-142.3	8
8.98	-145.0	9
9.05	-146.8	9 1/2
9.05	-146.8	10
9.05	-146.8	10 1/2
9.02	-145.9	11
9.02	-145.9	12
9.00	-145.4	13
9.00	-145.4	14
9.05	-146.8	14 1/2
9.10	-147.7	15
9.20	-149.9	16
9.40	-154.5	17
9.50	-156.9	19
9.60	-159.3	20
9.65	-160.7	22

FREEZING POINT OF GASEOUS PRODUCT
EXPERIMENT NO. 4



DISCUSSION OF RESULTSExperiment No. 1

The results of this experiment, conducted at 0°, indicate that the heptene was not affected by aluminum chloride at this temperature. The small volume of gas which was collected in the gas holder can be attributed to an air leak in the apparatus, or to a dead space in the apparatus not reached by sweeping with carbon dioxide; air was noted in the gas analyses of subsequent experiments. The appearance of the reaction mixture after the experiment was completed also substantiates the fact that no reaction occurred at this temperature. Always when aluminum chloride is placed in contact with a paraffin hydrocarbon there is observed, when a reaction does take place, an "upper layer" of saturated hydrocarbons and a "lower layer" of an unsaturated polymer (7). The catalyst in such cases is also reported to be coated with the same viscous polymer, which reduces the activity of the catalyst. In this experiment it will be noted that the mixture in the flask was in one layer, and the aluminum chloride was clean and apparently unreacted. Likewise the recovery of the starting hydrocarbon in the liquid distillation verifies the conclusion that there was no reaction of 2,2-dimethylpentane with aluminum chloride at 0°.

Experiment No. 2:

When 2,2-dimethylpentane was treated with anhydrous aluminum chloride at room temperature, 24-25°, no reaction occurred. This conclusion is evident from the attempted low temperature distillation of the substance collected in the gas holder during this experiment. The original hydrocarbon has an exceptionally high vapor pressure, and it is quite understandable that during ten hours reaction time a relatively

large volume of vaporized 2,2-dimethylpentane collected in the gas holder. It will be remembered that ice was used in the reflux condenser instead of solid carbon dioxide and alcohol in experiment two, and evidently was not capable of holding back the heptane in the flask. In all subsequent runs this error was eliminated by using exclusively a better refrigerant in the reflux condenser.

The data on the distillation of the liquid residue in the reaction flask verifies the conclusion that the hydrocarbon is unreactive at room temperature. Recovery of the starting material was the result, with a relatively small fraction of forerun. As in the first experiment, the clean appearance of the catalyst after ten hours, and the absence of a layer of polymerized unsaturation hydrocarbons in the reaction flask is good evidence that no reaction had taken place between the hydrocarbon and the aluminum chloride.

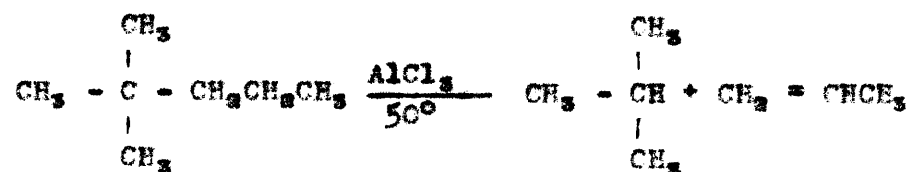
Experiment No. 3

This experiment, also conducted at room temperature, was carried out as a check on the previous one. It verified further that 2,2-dimethylpentane gave no reaction with aluminum chloride at 24°C. The use of solid carbon dioxide and alcohol instead of crushed ice as refrigerant in the reflux condenser held back the volatile heptane, preventing the collection of a large volume of gas in the gas holder. The small volume of gas which did collect in this experiment eliminated the possibility of a low temperature distillation, but the gas analyses of this substance showed that the sample was only a small amount of carbon dioxide which escaped absorption in the potassium hydroxide absorber, and air which could have either leaked into the apparatus or have been present in a dead space in the apparatus.

As in the previous experiments the liquid distillation shows a good recovery of the starting material. Again the reaction mixture after ten hours appeared unchanged, and the catalyst was still in very good condition. Hence it may be stated conclusively from the results of this experiment and the preceding one that at 24° aluminum chloride has no effect on 2,2-dimethylpentane.

Experiment No. 4

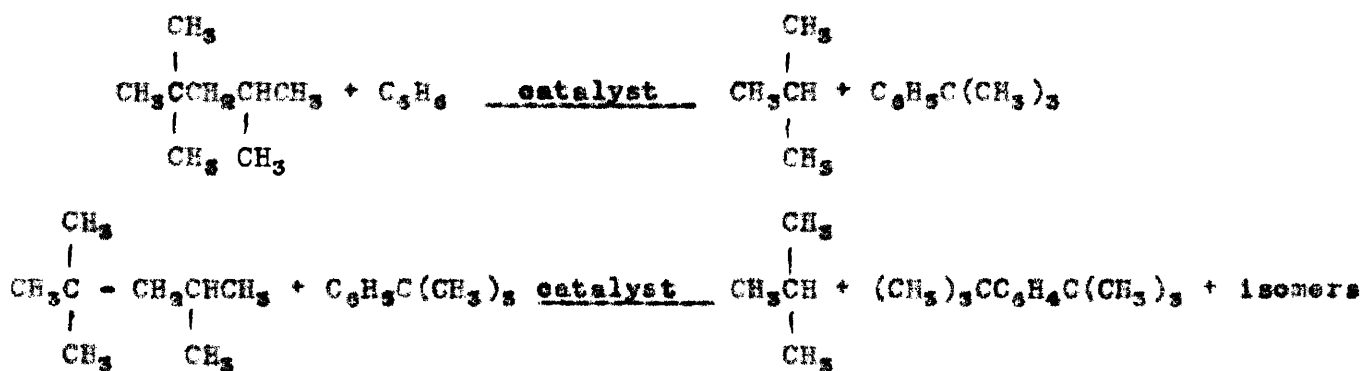
When the temperature of the reaction is raised to 50°, the results show considerable evidence that 2,2-dimethylpentane is cracked by anhydrous aluminum chloride. It will be noted that in this experiment the reaction mixture after ten hours appeared quite different than when the reaction was attempted at lower temperatures. The lower layer, which gave positive tests for unsaturation with bromine in carbon tetrachloride and alkaline potassium permanganate solution, was undoubtedly composed of polymerized olefin. In the case of 2,2-dimethylpentane, the olefin that arises from cracking would be propylene, given by the reaction:



The isobutane produced in the above equation was positively identified by the gas analysis of a portion of the gaseous product collected during the reaction, in conjunction with the low temperature distillation and freezing point determination of the same gaseous product. The boiling point obtained, -10.5° at 756.1 millimeters (-10.3° at 760 millimeters), and the freezing point obtained, -145.4°, correspond very closely to the literature values for isobutane (boiling point, -10.2°; freezing point, -145.0° (19)). It will be noted from the data on the low

temperature distillation that -10.5° at 756.1 millimeters was the constant temperature at which almost all the substance distilled; the freezing point data and the corresponding curve show that -145.4° was the point at which the temperature remained constant on cooling. Hence it can be said with certainty that isobutane was the only gaseous product of the reaction of aluminum chloride on 2,2-dimethylpentane.

An interesting parallel to the reaction studied is an investigation by Grosse and Ipatieff on the reaction of paraffins with aromatic hydrocarbons (20). It has been found by these investigators that paraffins will react with aromatic hydrocarbons in the presence of catalysts under mild conditions. The mechanism proposed is the splitting of the paraffin into a lower molecular weight paraffin and an olefin, which alkylates the aromatic hydrocarbon immediately. An example of such a reaction is that of benzene with 2,2,4-trimethylpentane in the presence of aluminum chloride to yield isobutane and t-butylbenzenes. With aluminum chloride the reaction takes place at $25-50^{\circ}$ and ordinary pressure in about four hours. Hydrogen chloride is added to promote the action of the catalyst. The reaction may be formulated as:



The octane can be practically completely converted into isobutane and the t-butylbenzenes.

The investigations of Schuit, Hoeg, and Verheus on the action of aluminum chloride on 2,2-dimethylbutane agrees with the results of

this research (6). It was found by these investigators that 2,2-dimethylbutane instead of isomerizing underwent a cracking when treated with anhydrous aluminum chloride and hydrogen chloride.

It seems from the above evidence and from the results obtained in this research that any paraffin hydrocarbon containing a tertiary alkyl group is liable to undergo cracking instead of isomerization when treated with anhydrous aluminum chloride and hydrogen chloride, or any other isomerization catalyst. This is a logical postulation, since the weaker tertiary carbon-carbon bond would be expected to be broken before a primary carbon-carbon bond scission would occur.

It has been shown that olefins will alkylate paraffins forming higher paraffins (21). It would be interesting therefore to investigate further the lower layer of the reaction mixture, or perhaps even better carry out a more precise distillation of the upper layer of the reaction mixture of 2,2-dimethylpentane and aluminum chloride. The olefin produced by the cracking reaction may combine with the original heptane by an alkylation reaction to give small amounts of higher paraffins.

SUMMARY

1. 2,2-Dimethylpentane has been treated with anhydrous aluminum chloride and hydrogen chloride at 0° and 24° and found not to react.

2. When the reaction was heated to 50°, the hydrocarbon was found to crack in the presence of anhydrous aluminum chloride and hydrogen chloride to give isobutane and propylene. The isobutane was identified by its boiling point and freezing point, and the propylene appeared in the reaction mixture as an unsaturated polymer, which was not investigated further.

3. The construction and operation of a simplified low temperature distilling column suitable for laboratory purification and identification of gases have been described.

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