CATALYSIS AND EQUILIBRIA IN THE CYCLOHEXANE-

METHYLCYCLOPENTANE SYSTEM

By

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CHAPTER I

INTRODUCTION

Isomerization may be defined as the rearrangement of the molecular configuration of a compound without change in molecular weight. This thesis will not consider geometrical or optical isomerization, but only structural isomerization.

Hydrocarbon isomerization is a reversible, first-order reaction. Equilibrium favors the more branched, compact molecules, at low to moderate temperature.

Much work has been done on the catalytic conversion of cyclohexane into methylcyclopentane. Separation of products from the catalyst is accomplished by distillation at low temperature (to avoid further reaction), washing with water, or both. The reaction products have been examined by means of several instruments: (1) refractometer, (2) cryoscopic apparatus, (3) infrared spectrophotometer, (4) mass spectrometer, and (5) Raman spectrograph.

Industrially the isomerization is best done vapor-phase, at high temperatures, over nickel-silica-alumina catalyst; but the present work is concerned with use of metal halide catalysts of the Lewis-acid type in liquid phase.

It is now accepted that a pure aluminum chloride or aluminum bromide catalyst, or even one promoted with hydrogen halide, does not affect pure cyclohexane and methylcyclopentane. However, aluminum halide catalysts promoted by exposure to water, oxygen, and olefin promotes

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the rearrangement (cf. Chapter II).

A literature search shows that nothing is known of the catalytic value of any halides except aluminum chloride and aluminum bromide for this isomerization. The equilibrium constant has been measured, but for temperatures above 80° the values are few and inconsistent. The present work has aimed at extending our information in both these areas.

CHAPTER II

HISTORICAL BACKGROUND

General Methods and Results

Aschan[4] was the first to observe that cyclohexane isomerizes into methylcyclopentane when refluxed with aluminum chloride.

In 1911 Ipatieff and Dowgelewitsch[22] reported that when cyclohexane was heated with aluminum chloride at 500-510° and 110-120 atmospheres pressure for four hours, only a small amount of methylcyclopentane was recovered from the reaction product.

Later Grignard and Stratford[17] studied the action of aluminum chloride on cyclohexane and alkylcyclohexanes at 120-150° with the amount of catalyst being 20-30% of the weight of hydrocarbon. It was found that (1) cyclohexane and methylcyclohexane remained unchanged. (2) Some methyl groups shifted to the 3-position when 1,2- and 1,4-dimethylcyclohexanes were tried. (3) The products of isomerization of ethyl- and propylcyclohexanes were 1,3-dimethylcyclohexane, 1,3-diethyl-cyclohexane and tetramethylcyclohexanes. Only small amounts (1-5%) of acyclic compounds formed from the cracking of the side chains. (4) With the three butylcyclohexanes, the cracking increased to 13-15%. Butane was formed from normal and secondary butylcyclohexanes. The tertiary butyl isomer gave a mixture of n-butane and isobutane. The main product was a mixture of tetramethylcyclohexanes. (5) With pentyl and isoamylcyclohexanes, 70 and 42% cracking occurred respectively.

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Both yielded butane, methylcyclohexanes, and polymethylcyclohexanes.

Skraup and Beifuss[57] found that when cyclohexane was heated three days at 420° in an alkali-glass tube, only 5 per cent of it was converted to methylcyclopentane.

Zelinskii[61] in 1929 treated cyclohexane with aluminum bromide for twelve hours at 180°. Only a slight change in the cyclohexane resulted. Later work of Zelinskii with Turova-Pollak[63,64] showed that a rearrangement of cyclohexane into methylcyclopentane and a dimethylcyclobutane occurred when cyclohexane was heated for 24 hours with aluminum bromide on a steam bath. These authors claimed that the action of aluminum bromide and aluminum chloride does not stop with the formation of methylcyclopentane, the end product apparently being a dimethylcyclobutane.

Nenitzescu and Contuniari,[34] on the contrary, observed that isomerization proceeded only to the formation of methylcyclopentane when cyclohexane was heated for three hours with aluminum chloride. No evidence of the formation of a dimethylcyclobutane was obtained. This isomerization was markedly aided by the presence of a small amount of water. In fact, when the aluminum chloride used was as nearly anhydrous as possible, the cyclohexane was practically unchanged. The reported equilibrium mixture for the reflux temperature consisted of 22 per cent methylcyclopentane and 78 per cent cyclohexane.

In 1939 Ipatieff and Komarewski[23] investigated the effect of aluminum chloride-hydrogen chloride on cyclohexane. The treatment was carried on for 24 hours at 150° in closed autoclaves. The reaction mixture contained, besides methylcyclopentane, some hydrogen, isobutane, 1,3-dimethylcyclopentane (6.5%), dimethylbicyclopentyl (9%), bicyclohexyl (3%), and unaltered cyclohexane.

Glasebrook and Lovell[13] confirmed the inertness of anhydrous

aluminum chloride toward the hydrocarbons under discussion. In treatment of boiling cyclohexane with aluminum chloride activated with water, a 16 per cent yield of methylcyclopentane was obtained; only 5 per cent of the cyclohexane entered into side reactions.

In 1938 and 1939 a number of investigators demonstrated that the yield of methylcyclopentane can be increased by using other catalysts under severe conditions. Puchkov and Nikolaeva[48] reported a 62 per cent yield of methylcyclopentane when 102.2 grams of cyclohexane at 400° under 140-365 atmospheres of hydrogen pressure was stirred for 26 hours in the presence of 10.1 grams molybdenum sulfide catalyst. Serious side reactions led to the formation of 19 per cent hexane and 15 per cent isohexane; only 4 per cent of the cyclohexane was unchanged. Gases, unsaturated hydrocarbons (50%), and aromatic hydrocarbons (9%) developed as additional products at 500° during one hour reaction time. Prokopets and Filaretov[47] reported practically complete isomerization when cyclo- hexane was treated with molybdenum sulfide-cobalt sulfide catalyst for one hour at 500° under 100 atmospheres initial pressure of hydrogen. The molybdenum sulfide-cobalt catalyst was more active as a hydrogenation and isomerization catalyst than the molybdenum sulfide.

Ando,[1] a Japanese chemist, observed that 67.7 per cent of methyl- cyclopentane was formed along with 0.4 per cent of unsaturated hydro- carbons and 0.6 per cent of aromatic hydrocarbons when cyclohexane was passed over molybdenum sulfide supported on granular Japanese acid clay in a vertical reaction chamber at 379° to 411° and under 200 atmospheres hydrogen pressure. Under milder conditions, molybdenum sulfide, supported on a Japanese acid clay which had been activated previously with mineral acids, was effective in forming 17.2 per cent of methyl- cyclopentane.[2] A few years later the catalytic isomerization of

cyclohexane over molybdenum sulfide was restudied by Maslyanskii.[28] His findings indicated that the rate of the reaction is dependent only upon the partial pressure of cyclohexane and is independent of hydrogen partial pressure. However, an increase of hydrogen pressure helps to preserve the catalyst activity.

The composition of the equilibrium mixture is highly dependent upon temperature. Increase in temperature increases the equilibrium amount of methylcyclopentane until at 140°, it reaches that of the cyclohexane.[55] The experiments were carried out with aluminum chloride-hydrogen chloride over the temperature range 20 to 110° and aluminum chloride alone at 140°. The reaction time was 10 hours for each run. At lower temperatures (20° to 80° C) the isomerization is only slightly impeded by side reactions (0.6-1.0%). The side reactions become highly pronounced if the temperature is raised above 80°. At temperatures higher than 140° the disproportionation increased rapidly, and it was impossible to obtain reliable results for the equilibrium constant at these temperatures.

The effect of the temperature is shown[13] by a curve representing the experimental composition of the equilibrium mixture of cyclohexane and methylcyclopentane (aluminum chloride catalyst) at 10° intervals over the range of 25° to 77.4°. The methylcyclopentane contents of the mixture (average mole per cent) were 12.5 per cent at 25° and 25.6 per cent at 77.4°. From these equilibrium mixture values the thermodynamic constants for the isomerization were calculated. These values, with the exception of the ones[36] based on early and somewhat uncertain combustion data (see line II of Table I), agree closely with the values recorded in later literature by several other investigators.[32,33,55,59]

Moore and Parks[33] made an extensive and very precise investigation of the heats of combustion of cyclohexane [11126.7 (± 2.1) cal./gram]

TABLE I

THERMODYNAMIC DATA FOR THE REACTION

CYCLOHEXANE (LIQUID, 25°) $\rightleftarrows$ METHYLCYCLOPENTANE (LIQUID, 25°)

Basis of Calculation	ΔH, cal./mole	$\Delta F°$, cal./mole	ΔS, e.u.
Equilibrium measurements[13]	3510	1150	7.9
Thermochemical data of Parks and Huffman[36]	-1100	-4100	10.0
Thermochemical data of Moore and Parks[33]	3930	950	10.0
Equilibrium measurements of Mizusima and Morino[32]			9.2 ± 1.2
Equilibrium measurements of Stevenson and Morgan[59]	4015 ± 550	1183 ± 272.9	9.50 ± 1.1
Equilibrium measurements of Schuit, Hoog and Verheus[55]		-1201.9*	

*(ΔF = -3930 + 9.15T)

and methylcyclopentane [11173.4 ($\pm$ 3.6) cal./gram]; from these values Δ H, ΔS, and ΔF were calculated. These thermodynamic values are listed in Table I for comparison with the ones derived by Glasebrook and Lovell.[13]

In 1941 Mizusima, Morino and Huzisiro[32] proved by the use of Raman spectra that in the presence of moist aluminum chloride, cyclohexane is isomerized to give 12.6% methylcyclopentane at 30° and 26.5% at 78.5°.

A few years later Stevenson and Morgan[59] investigated the equilibrium mixtures at 27°, 59° and 100° with the aid of infrared and mass spectrometers. The infrared analysis showed that aluminum bromide isomerized 11.5% of the cyclohexane to methylcyclopentane at 27°, and 19.3% at 59°. In the same way aluminum chloride caused isomerization of 33.5% ($\pm$ 0.6) of the cyclohexane at 100°.

Recent workers have found good agreement between composition of the equilibrium mixture obtained at atmospheric pressure and that obtained in the presence of a substantial hydrogen pressure.[27] This shows its independence of pressure. The methylcyclopentane contents of the equilibrium mixtures of cyclohexane and methylcyclopentane at 100°, 160°, and 167° were reported to be 33.8, 50.8, and 52.6 per cent respectively.

The rate of isomerization of alkanes and cycloalkanes with even the most active catalysts known is so low at room temperature that commercial processes have always been operated at or above 80°.

The rate of isomerization is dependent on the pressure; increased pressure tends to inhibit the reaction. Gronikberg, Plate, and Gavrilova[14] observed this inhibition under high pressure of hydrogen at 80°. Thus, at 25, 130 and 615 atmospheres of hydrogen, the yields of cyclohexane within three hours were 61, 48.5 and 17.8 per cent

respectively; on the other hand, under 1, 140, 460, and 660 atmospheres

of nitrogen, the corresponding yields of cyclohexane were 60.5, 60, 48.5

and 38.5 per cent respectively. This is in accord with the work by

Lien and D'Ouville,[27] who studied the specific reaction rate for the

isomerization of cyclohexane at 100°. The yield decreased within ten

minutes from 27.6 per cent to 21.6 per cent methylcyclopentane as the

hydrogen pressure was raised from zero to 1000 pounds per square inch.

<div align="center">Mechanism</div>

In order to present a more complete picture of the subject, this

review of mechanism will not be limited strictly to the isomerization of

cyclohexane and methcyclopentane, but will include some work on alkanes

and cycloalkanes, since they behave fundamentally alike.

Although Gunness[20] could say as recently as 1951 that the mechanism

of isomerization remains uncertain, it appears now that the carbonium-ion

theory is highly favored. The facts that the reaction requires acid

catalysis and that the action of activators, regulators, and inhibitors

can all be explained in terms of their action on carbonium ions, point

to this theory. In accordance with this idea, the steps in isomerization

are as follows.

(a) The formation of a carbonium ion, not directly from the

paraffins but from impurities or preliminary substitution

products.

(b) Attack of this carbonium ion on the alkane or cycloalkane.

$$C\text{-}C\text{-}C\text{-}C + R^{\oplus} \longrightarrow RH + \underset{\oplus}{C\text{-}C\text{-}C\text{-}C} \rightleftharpoons \underset{\oplus}{C\text{-}C\text{-}C\text{-}C}$$
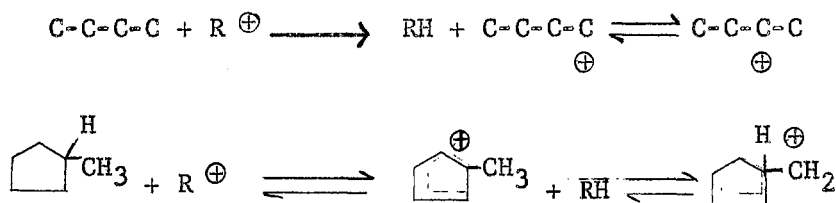
(c) Rearrangement (isomerization) of the carbonium ion by internal

shifts.

$$C\text{-}C\text{-}\overset{\oplus}{\underset{}{C}}\text{-}C \rightleftharpoons C\text{-}\overset{}{\underset{C}{C}}\text{-}C \oplus \rightleftharpoons C\text{-}\overset{\oplus}{\underset{C}{C}}\text{-}C$$
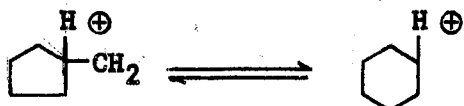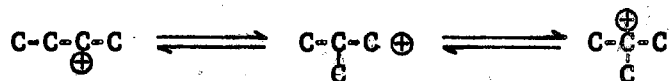
(d) Continuation of these steps.

$$C\text{-}\overset{\oplus}{\underset{C}{C}}\text{-}C \;+\; C\text{-}C\text{-}C\text{-}C \longrightarrow C\text{-}\overset{H}{\underset{C}{C}}\text{-}C \;+\; C\text{-}C\text{-}\underset{\oplus}{C}\text{-}C$$
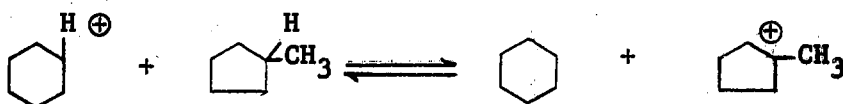
In 1946 Pines and Wackher[43] formulated the mechanism of paraffin

isomerizations which were promoted with a small amount of oxygen in the

presence of aluminum chloride or aluminum bromide catalysts. This

mechanism was discussed in two series of hypothetical equations.

I. $AlX_3 + 1/2\ O_2 \rightleftharpoons AlOX + X_2$

$C_4H_{10} + X_2 \rightleftharpoons C_4H_9X + HX$

$C_4H_9X \rightleftharpoons CH_3\text{-}CH_2\text{-}\overset{\oplus}{C}H\text{-}CH_3 + HX$

$CH_3\text{-}CH_2\text{-}\overset{\oplus}{C}H\text{-}CH_3 \rightleftharpoons CH_3\text{-}\underset{CH_3}{\overset{\oplus}{C}H}\text{-}CH_2$

$CH_3\text{-}\underset{CH_3}{\overset{\oplus}{C}H}\text{-}CH_2 \rightleftharpoons CH_3\text{-}\underset{CH_3}{\overset{\oplus}{C}}\text{-}CH_3$

$CH_3\text{-}\underset{CH_3}{\overset{\oplus}{C}}\text{-}CH_3 + C_4H_{10} \rightleftharpoons CH_3\text{-}\underset{CH_3}{\overset{H}{C}}\text{-}CH_3 + CH_3\text{-}CH_2\text{-}\overset{\oplus}{C}H\text{-}CH_3$

II. $C_4H_{10} + 1/2\ O_2 \xrightarrow{AlX_3} C_4H_9\ OH$

$C_4H_9\ OH + AlX_3 \longrightarrow C_4\ H_9\ OAlX_2 + HX$

$C_4\ H_9\ OH + HX \longrightarrow C_4\ H_9\ X + H_2O$

$C_4\ H_9\ X \rightleftharpoons CH_3-CH_2-\overset{\oplus}{C}H-CH_3 + HX$

$CH_3-CH_2-\overset{\oplus}{C}H-CH_3 \rightleftharpoons CH_3-\underset{\underset{CH_3}{|}}{C}H-\overset{\oplus}{C}H_2$

$CH_3-\underset{\underset{CH_3}{|}}{C}H-\overset{\oplus}{C}H_2 \rightleftharpoons CH_3-\underset{\underset{CH_3}{|}}{\overset{\oplus}{C}}-CH_3$

$CH_3-\underset{\underset{CH_3}{|}}{\overset{\oplus}{C}}-CH_3 + C_4H_{10} \rightleftharpoons CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-CH_3 + CH_3-CH_2-\overset{\oplus}{C}H-CH_3$
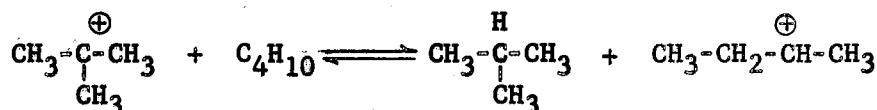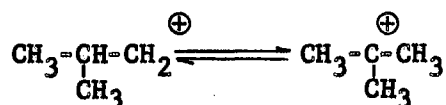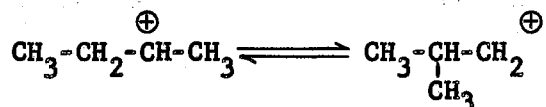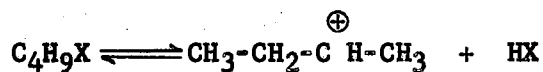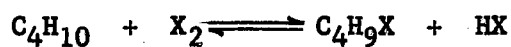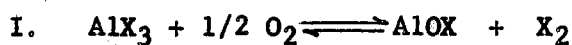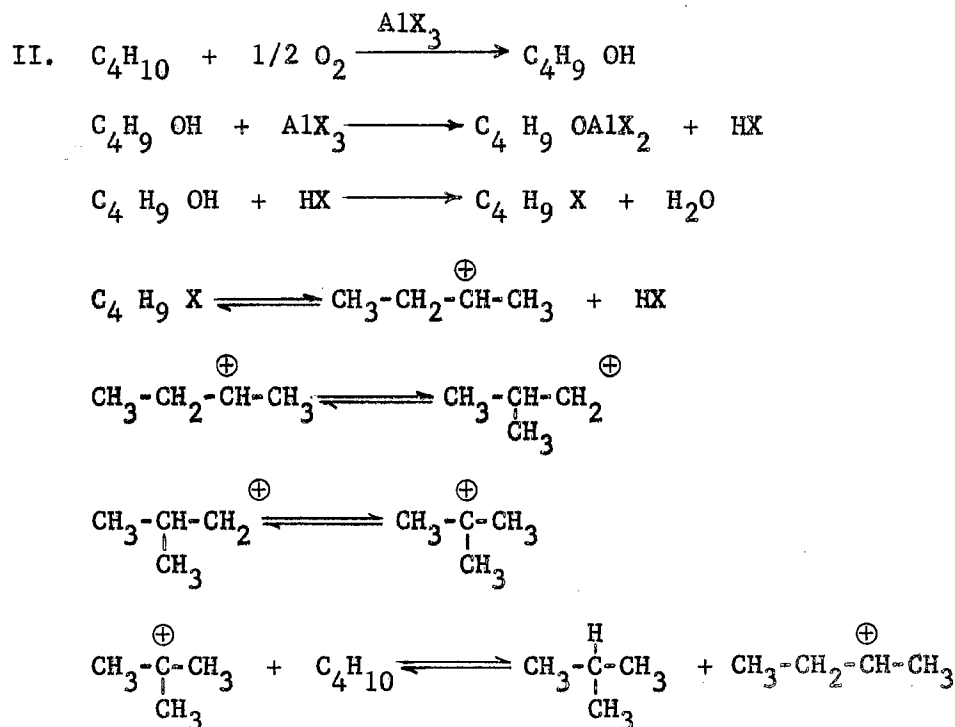
A more specific mechanism is the one suggested recently by Pines, Abraham and Ipatieff,[38] who concluded from their work that olefins are necessary as promoters for the initiation of the reaction. This mechanism which is similar to that of Block, Pines, and Schmerling[5] for n-butane, is given stepwise below:

R° (olefins) $+ HBr \rightleftharpoons RBr$

$RBr + AlBr_3 \rightleftharpoons \left[R\overset{\oplus}{} \quad Al\ \overset{\ominus}{Br_4} \right]$
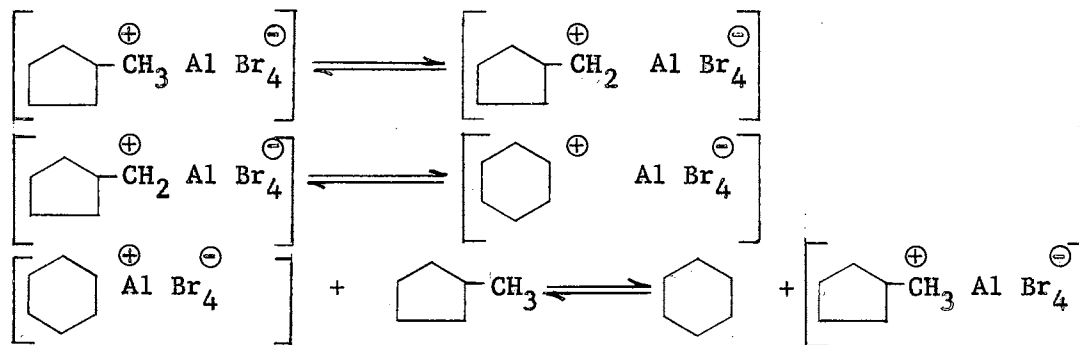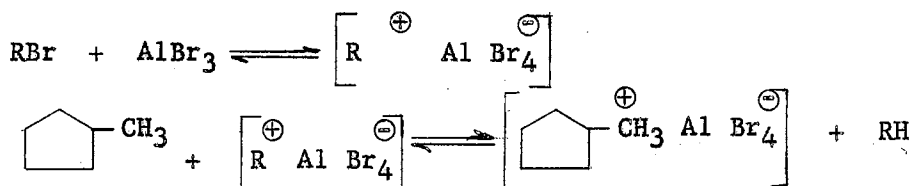
These are in accord with mechanism studies utilizing $CH_3-CH_2-C^{13}H_3$, which was found to isomerize to $CH_3-C^{13}H_2-CH_3$ over aluminum bromide at a normal rate but never to yield any $CH_3-C^{13}H_2-C^{13}H_3$. In other words, the isomerization is intramolecular, and does not involve cleavage and recombination of fragments as believed earlier.[10] Some similar work has been done on isomerization of $C^{14}H_3-CH(CH_3)-CH_2-CH_3$.[49]

Side Reactions

Side reactions in isomerization of alkanes become more serious as the molecular weight of the hydrocarbons increases. Whereas the butane-isobutane transformation is clean, n-pentane gives some trouble, n-hexane more, and n-heptane has not been successfully isomerized, commercially at least. Among cycloalkanes the cyclohexane-methylcyclopentane conversion is fairly smooth, but isomerization of larger ones becomes more complicated. Side reactions make analysis of the product difficult, give unwanted products, and often combine with the catalyst to cut its useful life. The reactions themselves are very complex, involving disproportionation, cracking, self-alkylation, and so on. They are manifested in products boiling lower and higher than the desired isomers,[3,27,63,64] and in a catalyst inactivated by a sludge, this apparently being unsaturated.

The reported side reactions for the interconversion of cyclohexane and methylcyclopentane involve from 5 to 38 mole per cent of the hydrocarbons, depending upon the nature of catalyst, temperature, pressure, and promoters. For example, under mild conditions (one atmosphere pressure and reflux temperature) hydrated aluminum chloride catalyst converted only 5 per cent of cyclohexane into undesired products,[13,55] these being a mixture of branched-chain hexanes, methylcyclohexane, 1,3-dimethylcyclohexane, bicyclohexyl, and dimethylbicyclopentyl.

Aluminum bromide substituted for aluminum chloride increased the extent of side reactions, isobutane, isopentane, isomeric hexanes and some gases being among the reaction products. Cyclohexane exposed to MoS_2 under severe conditions (500° and 140-365 atmospheres) completely cracked and dehydrogenated into gaseous and liquid products, including unsaturated and aromatic hydrocarbons.[48]

An improvement was made by Ciapetta[6] for repressing the side reactions of cyclohexane at temperatures ranging as high as 280 to 300°, by employing standard nickel-silica-alumina catalyst. In this way only 2.4 mole per cent of the cyclohexane is converted to hexanes and lower molecular weight alkanes, and 1.9 mole per cent is dehydrogenated to benzene.

Argument formerly existed among investigators over the alleged formation of cyclobutane and dimethylcyclobutanes as a result of the action of moist aluminum bromide on cyclohexane.[63,64] It has now been determined by mass-spectrometric analysis that C_3H_8, C_4H_{10}, C_5H_{12}, C_6H_{14}, C_7, C_8, and C_9 napthenes and C_{17} binaphthanes are among the products of side reactions, but no evidence could be found for the formation of cyclobutane, cyclopropane and dimethylcyclobutane.[34,59,62]

Various regulators have been tested and recommended to minimize these side reactions. It appears likely that the regulators function by destroying most of the isoparaffin carbonium ions by reacting with them before these ions can either lose a proton and irreversibly foul the catalyst, or disproportionate, or alkylate another molecule.[51] Using aluminum along with aluminum chloride reduces catalyst consumption.[18] A much more common practice is to effect isomerization at 500-1000 pounds/square inch pressure of hydrogen, even though some hydrogenolysis[24] occurs and the hydrogen hinders the catalytic reaction.[14] Naphthenes at

5-10 volume per cent or benzene at 0.25-0.5 per cent represses side reactions in the isomerization of n-pentane by aluminum chloride-hydrogen chloride at 75°; however, too much benzene stops the reaction by trapping all the alkylcarbonium ions.[9,30] The most recent suggestion is that excess isobutane, which is known to take part in the catalytic dispro-portionation of isoalkanes,[52] can suppress side reactions and catalyst loss in isomerization of n-pentane (or of n-hexane, but less effectively).[56]

Factors Affecting Isomerization

The factors affecting isomerization are worth individual discussion.

1. Physical state of the hydrocarbon, i.e., vapor phase or liquid phase. Some isomerizations are called "vapor-phase" and some "liquid-phase,"[37] but actually the carbonium ion intermediate cannot exist in the vapor or even the nonpolar liquid environment, and available evidence indicates the reaction occurs at solid surfaces, ordinarily the catalyst surface.[7,27,35,58]

2. Concentration of the hydrocarbon.

3. Solvent, if any. It is obviously difficult to find an inert, cheap solvent in which to carry out the catalytic isomerization.

4. Catalyst.

    a. Nature. Both pure compounds and the variety of promoted ones need to be discussed here. Careful work has made it clear that pure anhydrous aluminum halide will not affect pure n-alkanes[41] and/or cycloalkanes,[13,31,34,38,58] although $AlBr_3$-HBr is claimed to attack n-hexane or n-heptane even at 0°C.[31]

In 1943 and 1945 Leighton and Heldman[26] and Powell and Reid[46] advanced a theory of isomerization involving the presence of hypothetical strong complex acids, $HAlX_4$.[11] They believed that the presence of these acids was responsible for the catalytic activity of the aluminum halide.

The more recent work of Pines and Wackher[42,43b] and Abraham and Ipatieff[38] substantiates this theory but shows that substances other than a hydrogen halide must be present along with an aluminum halide in order to convert the AlX_3 or AlX_3-HX mixture into an active catalyst for isomerization of paraffins and cycloparaffins. These promoters are now identified as olefins,[38,41,42,43b,58,43a] water, oxygen, cyclohexyl bromide,[38] etc. It is suggested[58,43b] that water converts aluminum chloride (or rather Al_2X_6) into intermediate compounds of the form $Al_2X_{6-n}(OH)_n$ (where $1 \leqslant n \leqslant 5$), any of which may have catalytic activity. The use of radioactive hydrogen (tritium)[46] or heavy hydrogen (deuterium) as tracers in butane undergoing isomerization with AlX_3-HX has shown rapid exchange of hydrogen between the HX and the hydrocarbon. This indicates that hydrogen chloride or hydrogen bromide is involved directly in the reaction mechanism; however, $HAlX_4$ has been proved incapable of independent existence, so that it can be postulated to form only in the presence of an acceptor for the proton, such as an olefin.[37]

A less well-known catalyst for isomerization of alkanes is boron trifluoride activated with an alkyl fluoride.[52,53,54] Little information on its relative efficiency is available. Concentrated sulfuric acid is clearly a much weaker catalyst, which can shift methyl groups along a chain or around a ring but not produce any net gain in branching.[15,25,50,60] The only isomerization that has been observed to be caused by concentrated H_2SO_4 (99.8 per cent) is that of these alkanes and cycloalkanes having tertiary carbon atoms. No evidence of a ring

enlargement was observed for methylcyclopentane. An elaborate study of isoalkane-sulfuric acid hydrogen exchange and isomerization showed that the two are not necessarily connected; one can occur without the other.[60]

Another class of catalysts, as already noted, is that which has been developed for isomerization from general hydroforming catalysts. These are combination cracking (silica-alumina)-hydrogenation (nickel, platinum, cobalt, or molybdenum)[1,10,28,47,48] catalysts used at 450-500° and 500-1000 pounds H_2/square inch pressure, and are of recent appearance. The Platforming catalyst is not very specific, yielding only 52 per cent n-heptane isomerized, and 14 per cent recovered per pass;[21] in contrast, molybdenum sulfide catalyst isomerized 79.4 per cent of cyclohexane. Tungsten sulfide showed quite extensive hydrogenolysis and is a poor catalyst for selective isomerization. Close regulation of the H_2/n-pentane ratio between 0.3 and 0.8 permits molybdena-alumina to give 40-55 per cent isomerization per pass and up to 95 per cent ultimately, apparently by a balance between carbon deposition on the catalyst (if too little hydrogen) and hydrocracking to lower alkanes (if too much).[8,16] The broadest claims are made for nickel-silica-alumina, which is said to be far superior to the aluminum chloride type of catalyst.[6,7,12] Excessive cracking activity is avoided by high-temperature steaming to reduce surface area.

    b. Surface characteristics. This has been little studied except for the cracking-hydrogenation high-temperature catalysts.

5. Reaction time (contact time). Long reaction time (sometimes weeks) is required for the reactions at lower temperatures, but as the reaction temperature increases, the contact time decreases.

6. Temperature. A proper choice of temperature may result in the formation of a desired isomer. Increasing the reaction temperature increases the rate of reaction, but shifts equilibrium toward the normal paraffin and increases the proportion of side reaction.[39]

7. Pressure. Other things being equal, increased pressure should favor isomerization over disproportionation, since the latter involves an increase in volume. Pressure increase should also favor the formation of the isomer of greatest density.

Measuring The Yield Of Isomers and Byproducts

Separation of products from catalyst is done either by distillation at low temperature (to avoid further reaction), or washing with water, or both.

Thereafter, the most common procedure is fractional distillation. In the exceptionally favorable case of cyclohexane⇌methylcyclopentane, fractional distillation must be very carefully done, with a 60-100 plate column and high reflux ratio, to get maximum separation of what is usually a complex mixture.

The separate cuts are then often examined further to characterize them. Densities, refractive indices, and melting points are easy to measure. The parachor is capable of distinguishing isomers differing in the number of methyl side chains.[10] Much more elaborate and powerful tools are the infrared spectrophotometer and the mass spectrometer, both of which have frequently been applied. The Raman spectrograph has been used very little, and of course instruments for the ultraviolet, while excellent for aromatics, are useless for alkanes and cycloalkanes. It has repeatedly been shown that refractive index alone is a good index of composition, but this simple method is safe only for an essentially

binary system.

The Schaarschmidt method of selective chlorination with antimony pentachloride, described by Egloff et al.,[10] has some value for determining isomers containing tertiary carbon atoms; but it is slow, it measures points of chain branching rather than isomers, and it is not at all clear-cut. The segregation of straight-chain alkanes by urea complexing may serve the purpose, but unfortunately the complexes do not form with chains as short as six carbon atoms.

In a few instances the degree of chain branching or even the identity of isomers has been derived from motor-method octane number determination.

CHAPTER III

SOURCES OF CHEMICALS

The cyclohexane used in the experiments for the identification of
reaction products was of a technical grade from Eastman Organic Chemicals
Department. The refractive index of this cyclohexane was 1.4247 at
20°C. Distillation of this material revealed the presence of some higher
and lower boiling impurities such as benzene and water.

The methylcyclopentane, with a refractive index of 1.4091, was
supplied by Phillips Petroleum Company.

A chemically pure grade of anhydrous aluminum bromide requiring no
further purification was used. This came from City Chemical Corporation.

Anhydrous aluminum chloride from Matheson, Coleman and Bell
Incorporated was used throughout. This had become partially hydrated
and further purification was necessary, except for the study of
equilibrium constants, where impurities should have no noticeable effect
on the values obtained.

Several other chemicals (C. P. grade) were used and are listed
below, along with the company that supplied them:

    Activated alumina....................Baker Chemical Company

    Ferric chloride anhydrous...........Matheson, Coleman, and Bell Inc.

    Antimony pentachloride..............Baker Chemical Company

    Titanium tetrachloride..............Fisher Scientific Company

    Stannic chloride....................Baker Chemical Company

    Concentrated sulfuric acid..........Baker Chemical Company

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Purification Of Chemicals

The fractionating column used for distillation was a vacuum-jacketed Oldershaw bubble-plate having 30 plates, a high hold-up (45 cc), and a timer set at 10 per cent takeoff. Cyclohexane and methylcyclopentane were purified by the use of this column and the constant-boiling fractions were used.

Various methods and types of apparatus were used in an effort to obtain pure catalysts, which were placed in sealed, breakable capsules, and to cut down on the time required for each run. Each method tried had its own advantages and disadvantages that will not be explained further.

A. Sublimation

The simple apparatus shown schematically in Figure 1 is used in a very quick and crude method of subliming the catalysts. A bulb (a,b) of 10 to 12 mm in diameter is blown in a short piece of 5-mm Pyrex tubing. After introduction of the catalyst in one end of the tube, a tight-fitting glass rod K is inserted behind it to prevent catalyst vapors from escaping during the sublimation of the catalyst into the bulb. When sufficient catalyst has been sublimed into the bulb, the latter is sealed off. The catalysts produced by this method were not of sufficient purity for the purpose of this work.

Another method for purification of solid catalysts is shown in Figure 2. Catalyst is placed in the bulb K, which is then attached to the bulb containing the hand-blown thin-walled capsules ab and cd. Nitrogen gas is passed through the system; and, when heat is applied, the purified catalyst is collected in the capsules, which are sealed off at the points a,b,c and d. Further modification of this apparatus is
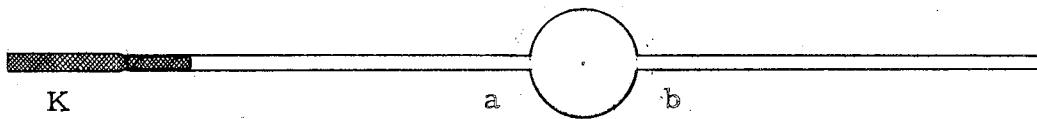
Sublimation Apparatus I

Figure 1
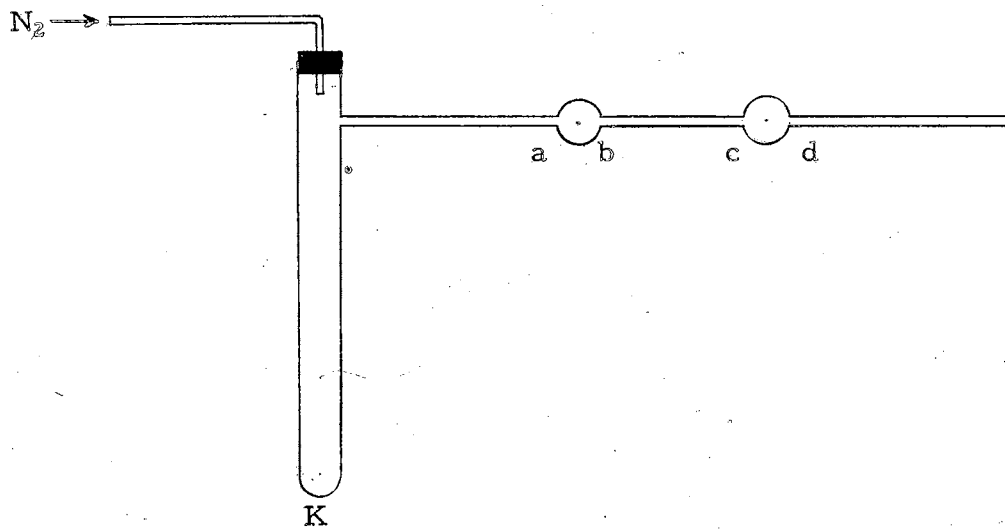
Sublimation Apparatus II

Figure 2

depicted schematically in Figure 3, the difference in use being that sublimation is done under vacuum. Several other difficulties were then encountered--the undue length of time spent to prepare the capsules, and trouble in sealing off the tube containing the catalyst. Glass surfaces covered with the catalysts (aluminum chloride or ferric chloride) or their residues do not flow properly when the glass is melted, and would not give seals.

Figure 4 shows the apparatus used in the quickest and most effective method of all. Catalyst is placed in K through opening M and then nitrogen gas is flushed through the system. Tube AB is heated up to about 200° by means of an electric current through the nichrome wire wrapped around the tube. When heat is applied at K, the catalyst sublimes and condenses on the side walls of the glass tubing above the capsules. Then, with the help of a Bunsen burner, it is transferred into the capsules. The excess sublimed catalyst is collected in tube L. In this method the capsules are blown in the end of 3-mm Pyrex tubing which is joined to the rest of the apparatus by the use of ball-joints E and F. In this way several capsules containing catalyst can be made in each run.

B. Distillation

A liquid catalyst is placed in a round-bottomed distilling flask A (see Figure 5), which joins the condenser H connecting it to the rest of the apparatus. Nitrogen gas is flushed along the system through opening C and out through drying tube E. The part of the system T through G is evacuated prior to the distillation by using the rubber bulb with valve K. After heat is applied at A and the catalyst condenses at H, the distillate trickles down until stopped by the Teflon-plug stopcock T. Excess distillate runs into the reservoir B. When sufficient distillate has formed at T, the stopcock is opened and the pure catalyst is forced
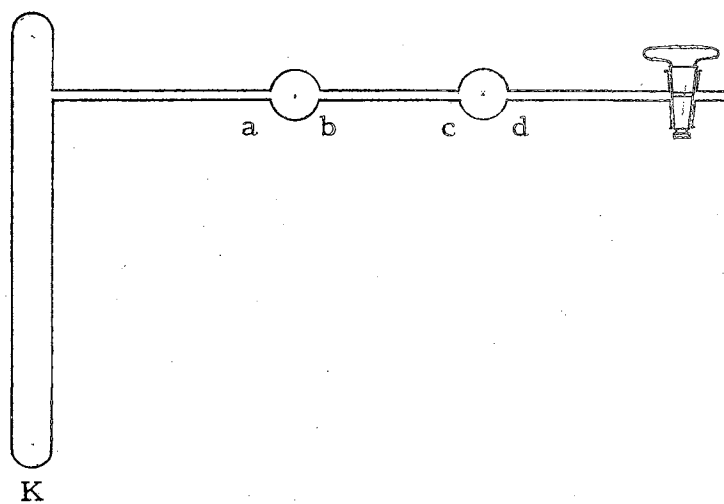
Vacuum Sublimation Apparatus

Figure 3
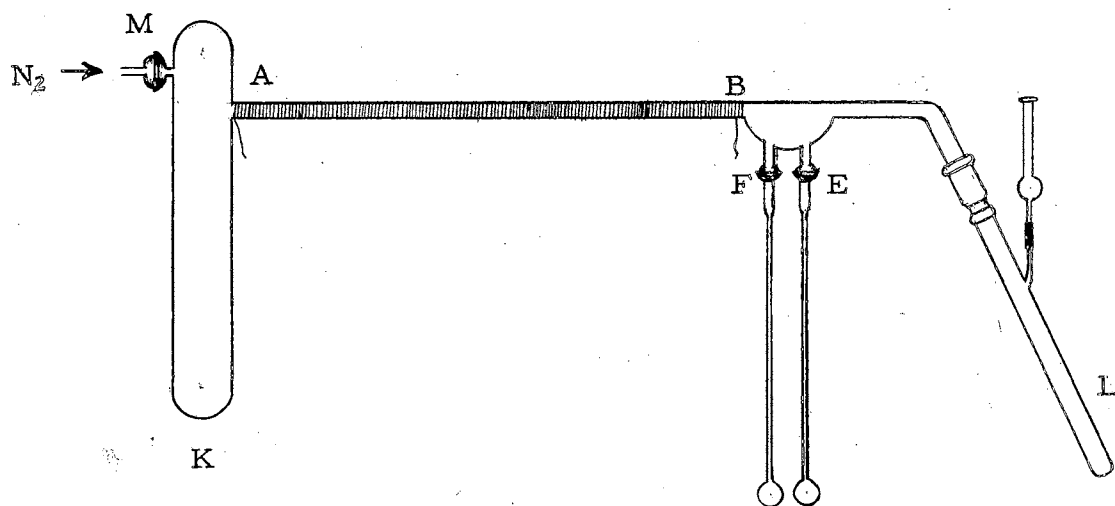
Sublimation Apparatus, Best Form

Figure 4
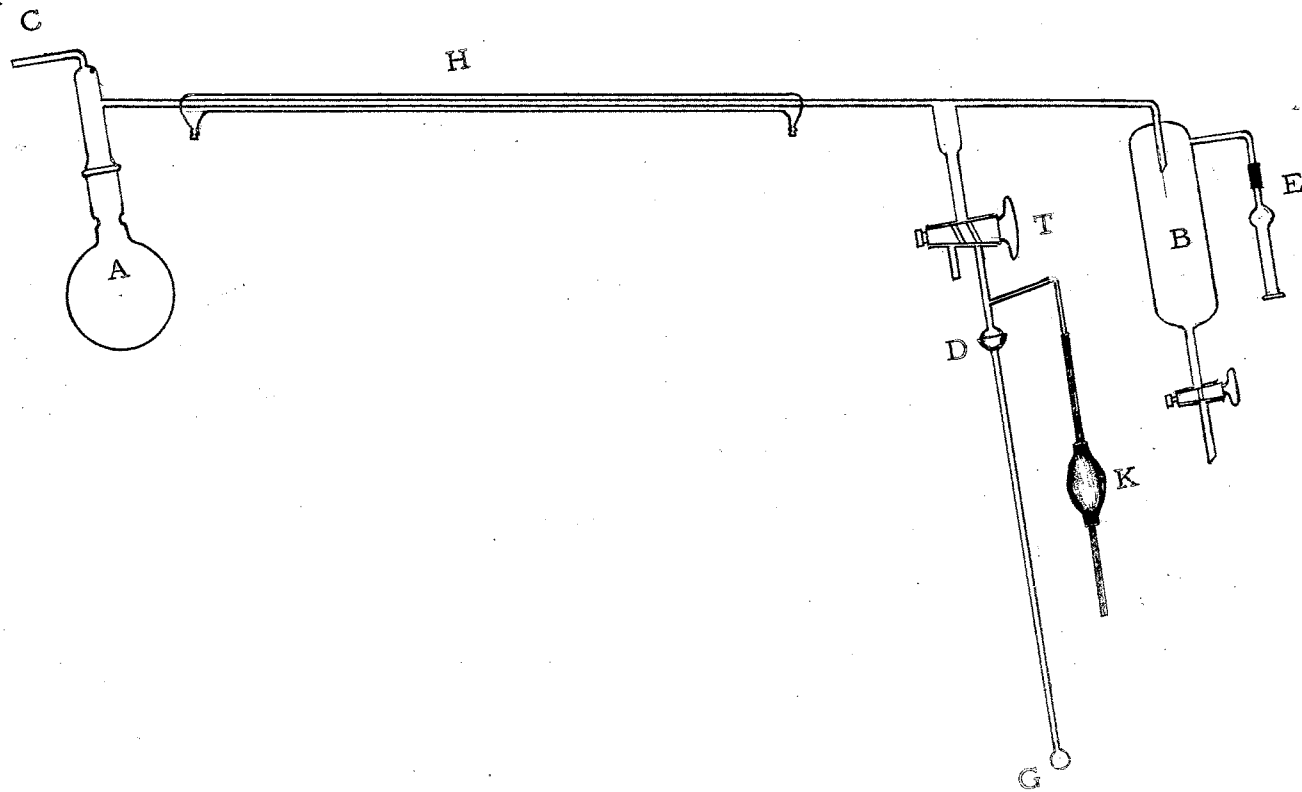
Apparatus for Distilling Catalysts

Figure 5

through the 3-mm tube into the bulb G, after which the stopcock is closed and another evacuation made to prevent a pressure build-up during the sealing off of the bulb G. The bulb-tube is removed at the ball-joint clamp D and another is clamped in place for the next run.

Stannic chloride was purified by this procedure.

Apparatus For The Reaction

Two general types of apparatus were used in this work to gain qualitative and quantitative results. One was designed to give an idea as to the ability of a catalyst to isomerize cyclohexane under partially controlled conditions. The limits of this control are illustrated by the general arrangement of the apparatus as shown in Figure 6. A 100-ml round-bottomed flask A was fitted with a long reflux condenser, the top of which was connected to containers B and C of dehydrating reagents such as activated aluminum oxide and/or phosphorus pentoxide.

For the more precise work other types of apparatus were constructed. Schematic drawings of these appear in Figures 7 and 8. The conditions under which the runs were made were carefully controlled. The apparatus shown in Figure 7 was composed of a 200-ml round-bottomed flask A, condenser L, automatic pipette E, and two manometers X and Y. It was constructed entirely of glass, with only one three-way stopcock with Teflon plug where it would come in contact with liquid cyclohexane, F. Flask A and reaction tube S could be removed from the apparatus; but the rest of the joints were fused together.

By the use of this equipment, eight hours on an average were required to produce one sample for isomerization. It was a difficult and time-consuming task. What was needed was a simplification of techniques so that more runs could be made with more frequent analysis
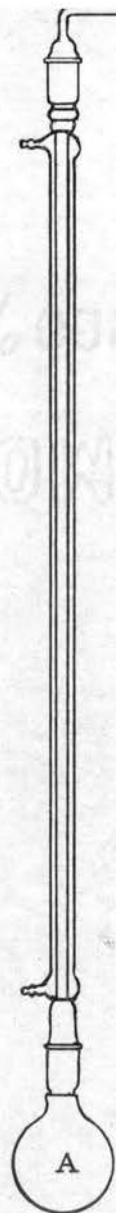
Reflux Apparatus for
Testing Catalysts

Figure 6

A

B   C
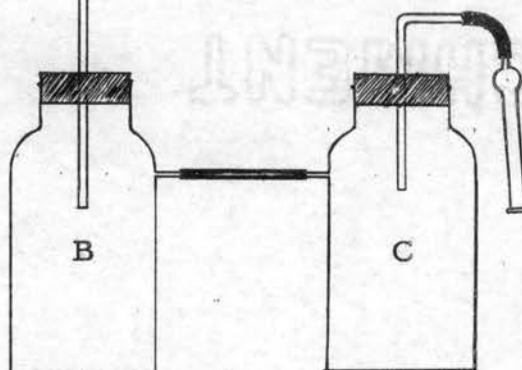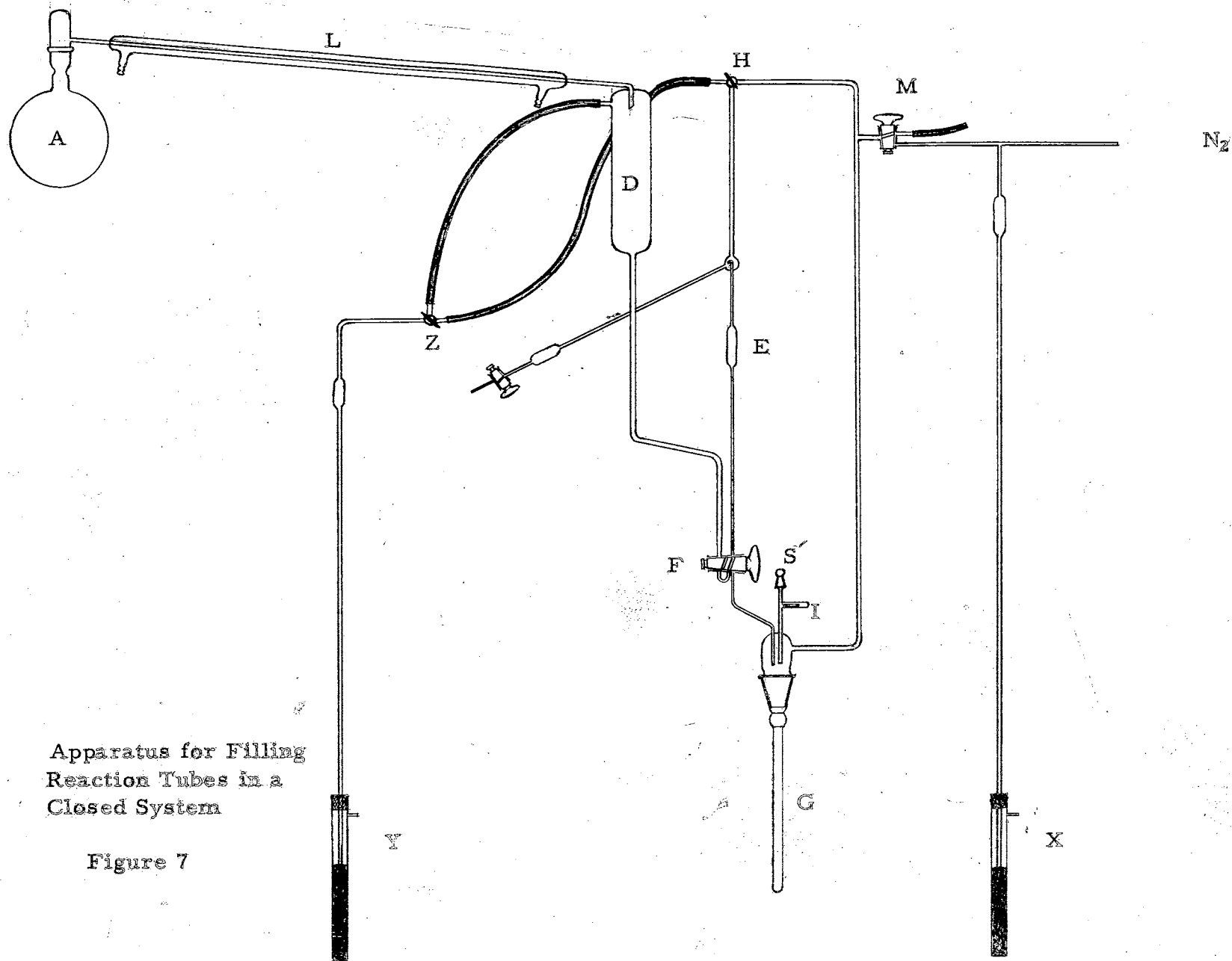
Apparatus for Filling
Reaction Tubes in a
Closed System

Figure 7

C

N₂

A   B

D

G

K
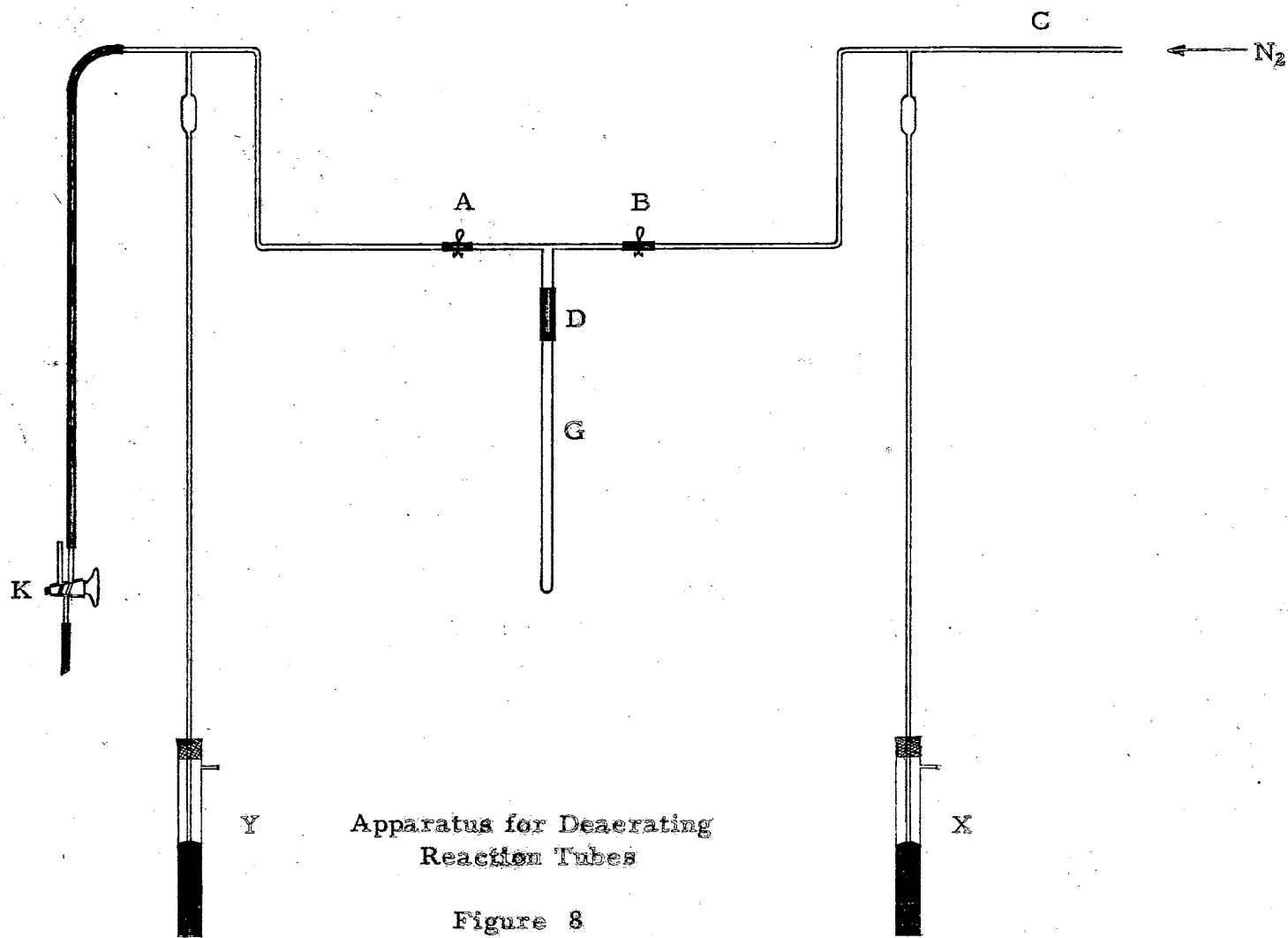
Y   Apparatus for Deaerating   X
              Reaction Tubes

Figure 8

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of products, to provide a better basis for making comparisons.

In an effort to achieve this simplification, the apparatus shown in Figure 8 was constructed. It consisted of a T-tube connected to the reaction tube on one side and to the two manometers at the other opening; the connections were made with Tygon tubing. Stopcock K served to open and close the vacuum line to the system; and nitrogen was flushed into the system from point C.

The details of each apparatus will be discussed later.

In order to keep the reactor tubes at a constant temperature, it was necessary to construct a thermostat with a thermoregulator ($\pm 0.1°$) to operate at temperatures as high as 80°C. The thermostat was filled with ethylene glycol instead of water to reduce evaporation of liquid.

Figure 9 illustrates an agitator for the sealed-reactor tubes. This rocked the fluid from one end of the tube to the other. The reactor tubes were clamped at points a-b, c-d, etc. The oscillating motion was generated by an electric automobile windshield wiper using direct current which was provided by a rectifier. The reactions at 80-160°C were carried out in a Carius-tube furnace.
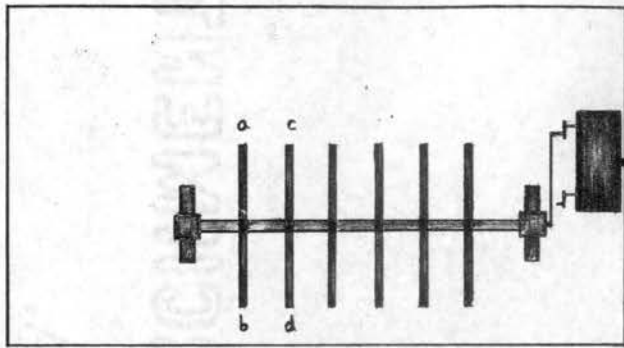
Top View
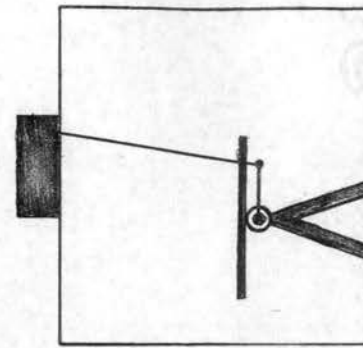
Side View
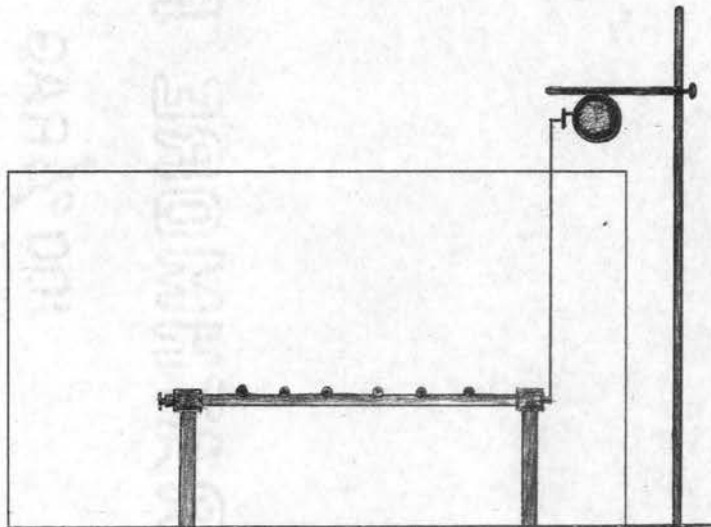
Front View

Constant Temperature Bath and Agitator

Figure 9

CHAPTER IV

EXPERIMENTAL PROCEDURES AND RESULTS

The Action of Aluminum Chloride on Cyclohexane

and Methylcyclopentane

Procedure I.

Cyclohexane (50 ml.) and 10 grams of anhydrous aluminum chloride,
activated with a small amount of water, were placed in a 100-ml. flask
equipped with a reflux condenser and connected to dehydrating-reagent
containers (see Figure 6).

The reaction mixture was boiled for 45 hours, after which the
reaction flask was cooled with a mixture of ice and salt, and the liquid
decanted and washed with ice water. After drying over activated aluminum
oxide, the product had a refractive index of 1.42173 at 20.0°, which
corresponds to 27.3 mole per cent methylcyclopentane.

The same procedure was used for the isomerization of methylcyclo-
pentane and the dried product had a refractive index of 1.42167 at 20.0°.
This refractive index corresponds to 27.4 mole per cent methylcyclopentane
and 72.6 mole per cent cyclohexane.

Procedure II.

Cyclohexane and a piece of metallic sodium were introduced into
distilling flask A (see Figure 7), and a weighed amount of catalyst con-
tained in a sealed glass capsule in reactor tube S. The system was
evacuated by opening the stopcocks at M and H. The safety column Y also

served as a manometer. Nitrogen was then introduced into the system through stopcock M. This was repeated several times to remove the air and replace it with nitrogen. When the pressure build-up from the nitrogen occurred, the excess nitrogen was run out through the mercury in the safety column X.

The cyclohexane was distilled and collected in the container D. During distillation all the stopcocks were closed except stopcock Z which served to make connection with Y acting as a safety column in case of pressure build-up from the cyclohexane vapors and/or nitrogen. Eleven ml. of cyclohexane from D were placed in the automatic pipette E through the Teflon-plug stopcock at F and let down into the reactor tube. The Teflon plug did not hold a vacuum well, and stopcock grease could not be used since it contaminated the cyclohexane. Therefore, the whole stopcock was incased in thin rubber tubing which effectively sealed it off. The cyclohexane was frozen in reactor tube S to decrease vaporizing during evacuation. The activator (if any) was placed in the reactor tube through opening S, in an open capsule. A glass-covered iron rod served to prevent the activator capsule from dropping. When the iron rod was pulled back into I by a magnet, the activator capsule was allowed to fall into the reactor tube.

The next step was the sealing off of the reaction tube. In order to facilitate this operation, the reaction tube was placed under slight vacuum as shown by a small rise in the mercury column Y. The vacuum prevented a pressure build-up and also caused the walls of the reactor to collapse during the heating.

The thin-walled catalyst capsule was then broken by striking the reaction tube sharply against a rolled magazine. Although this method may seem crude, very little difficulty from tube breakage was encountered.

The reaction tube was placed in the agitator in a constant-temperature

bath (see Figure 9). After agitation for a known time, the reactor tube

was opened, the liquid decanted and washed several times with ice water

in a separatory funnel, and the hydrocarbon layer separated from the

water and dried over activated aluminum oxide.

The weight of aluminum chloride was determined by weighing the

glass capsule before and after the experiment.

From the refractive index of the hydrocarbon mixture, the per-

centage of isomerization was determined from the binary diagram shown

in Figure II. The results of applying this method are summarized in

Table II.

Procedure III.

Fifteen ml. of hydrocarbon, measured with a pipette, was introduced

into the reaction tube G (see Figure 8) together with a weighed amount

of catalyst contained in a sealed glass capsule. The reaction tube was

connected at point D to the rest of the apparatus, the pinch clamps at

points A and B being closed. The stopcock K was opened and the system

to the left of clamp A evacuated until the mercury in the manometer Y

had risen to a maximum. The stopcock K was then closed. The reaction

tube was cooled in a mixture of ice and salt, and then clamp A was

opened, so that the tube was partially evacuated. The mercury in the

manometer fell to approximately three-fourths the original height.

Clamp A was then closed, and B was opened, admitting nitrogen to the

reaction tube. This process of evacuating and admitting nitrogen was

repeated until the mercury had fallen to the level of that in the

reservoir. With all the clamps closed, the stopcock K was again

opened and the system evacuated until the mercury had risen to a

maximum. The process of evacuating the tube and then filling with

TABLE II

RESULTS OF ISOMERIZATIONS BY PROCEDURE II

Run No.	1	2	3	4	5	6
Aluminum chloride, grams	0.8545	0.2295	0.4692	0.0917	0.2515	0.2010
Activator (H_2O), grams	--	--	0.0481	--	--	--
Temperature, °C	25	25	25	60	60	60
Reaction time, hrs.	24	24	24	1/2	1	1/2
*Refractive index of product, n_D^{20}	1.4243	1.4241	1.4241	1.4247	1.4240	1.4247
Methylcyclopentane indicated by n_D^{20}, mole %	11.7	12.8	12.8	9.3	13.4	9.3

* Determined with a Bausch and Lomb Abbe-type refractometer.

nitrogen was repeated in exactly the same manner as described above. It was believed that three to four complete evacuations were necessary to remove all air from the reaction tube.

Then the reactor tube was sealed off at G under slight vacuum and treated as described in the previous procedure.

The results of applying this method are shown in Table III. As noted later, they were quite unsatisfactory.

<div align="center">Comparison of Other Catalysts

With Aluminum Chloride</div>

Ferric chloride proved to be inactive as a catalyst for the isomerization of cyclohexane and methylcyclopentane. Runs were made using all three procedures that have been described. The products obtained from these runs remained light yellow in color after washing several times with water.

Analysis of these yellow products with the dipping refractometer gave "impossible" values; the refractive indexes were often higher than for pure cyclohexane or else for pure methylcylopentane. Consequently the reaction products were distilled. The refractive index of the colorless distillates showed them to be samples of pure cyclohexane or methylcyclopentane; no isomerization had occurred.

It was believed from the discoloration of the hydrocarbons that the ferric chloride might have been hydrated by the dissolved water in cyclohexane and the moisture of its surrounding containers. A run was made using 25 grams of anhydrous ferric chloride (from a previously unopened bottle) and placing it immediately in 50 ml. of purified cyclohexane. The reaction flask was joined to the condenser and then anhydrous hydrogen chloride was bubbled in through glass tubing inserted

TABLE III

RESULTS OF ISOMERIZATIONS BY PROCEDURE III

Run No.	1	2	3	4	5*	6*	7*	8*
Hydrocarbon used*	$CH_3C_5H_9$	$CH_3C_5H_9$	$CH_3C_5H_9$	C_6H_{12}	$CH_3C_5H_9$	$CH_3C_5H_9$	C_6H_{12}	C_6H_{12}
Aluminum chloride, g	0.0809	0.0894	0.0494	0.0376	0.3170	0.3112	0.3567	0.3737
Temperature, °C	40	40	40	40	60	60	60	60
Reaction time, hrs.	0.25	0.5	1.0	0.5	4	10	4	10
Refractive index of product, n_D^{25}	1.4058	1.4059	1.4060	1.4218	1.4066	1.4061	1.4220	1.4220
Methylcyclopentane indicated by n_D^{25}, mole %	99	98.5	97.7	1.2	94.2	97.3	0	0

* Catalyst purified in apparatus shown in Figure 4.

through the condenser. After the gas had been added for 30 minutes, the cyclohexane was refluxed for 39 hours. At the end of this period the catalyst was destroyed by the usual method and the reaction product was distilled. The distillate had a refractive index of 1.42623, which corresponds to zero isomerization.

Several other members of the Lewis-acid family were refluxed with cyclohexane, the apparatus illustrated in Figure 6 being used. The results, all negative, are summarized in Table IV. In working with these catalysts the destruction of the catalyst with water became a major problem. Since some of them, such as titanium tetrachloride and antimony pentachloride, hydrolyze violently, the heat resulting from the reaction with water caused evaporation of the hydrocarbons before the complete destruction of the catalyst occurred. To overcome this undesired feature of the reaction between catalyst and water, the hydrocarbon layer was poured in small portions into a large flask of ice water.

<p style="text-align:center">Analytical Procedure</p>

An Abbe-type and a Zeiss dipping refractometer were used in this work.

In the preliminary experiments the lack of an independent cooling and circulating system made it impossible to keep the thermostatic temperature at exactly 20°, the only temperature for which a literature calibration curve for cyclohexane-methylcyclopentane is available.[13] It was then decided to make up a binary diagram of composition vs. refractive index at 25°.

A series of methylcyclopentane-cyclohexane mixtures (by weight) was prepared and the refractive indices determined with a Bausch and Lomb Abbe-type refractometer with the temperature controlled at ±2°.

TABLE IV

ATTEMPTED ISOMERIZATION OF BOILING CYCLOHEXANE WITH VARIOUS CATALYSTS [a]

Reaction time, hrs.	65	35	49	48	48	48
Catalyst	$SnCl_4$ [b]	$SnCl_4$ + $FeCl_3$	Con. H_2SO_4	$TiCl_4$	$ClHSO_3$	$SbCl_5$
Volume or weight of catalyst	25 ml.	25 ml. + 9 g	50 ml.	15 ml.	15 ml.	25 ml.
Refractive index of product, n_D^{20}	1.42623	1.42618	1.42614	1.42603	1.42623	1.42679
Methylcyclopentane, mole %	0.00	0.40	0.80	1.30	0.00	c

a. 50 ml. cyclohexane used throughout these tests.

b. After purification, also tested as catalyst by Procedure III; it proved inactive here also.

c. Chlorination had evidently occurred.

A plot of the data (see Table V) is shown in Figure 10; this was used for the analysis of the products of isomerization. The resulting curve is so nearly linear with composition that it is probably just as accurate to assume it is a straight line between the values for the pure hydrocarbons. It is parallel to the ideal curve (straight line drawn between the values for the pure cycloalkanes); its failure to coincide with it is attributed to inaccuracy of refractometry and the impurities in the cyclohexane and methylcyclopentane.

After a new bath with a cooling and circulating system had been constructed, the refractive indexes were obtained at 20°C with additional accuracy by the use of the dipping refractometer.

The diagram of refractive index vs. composition for the binary system at 20°C was made after the experience with the data at 25°, by drawing a straight line between the values for the pure cyclohexane and the methylcyclopentane. This curve, which is shown in Figure 11, very nearly coincides with the experimental findings of Glasebrook and Lovell.[13]

The Effect of Temperature and Catalyst on the
Cyclohexane-Methylcyclopentane Equilibrium

Both aluminum chloride and aluminum bromide were used as catalytic agents. The runs were made by a greatly simplified procedure. Cyclohexane (25 ml.) was introduced into a combustion tube along with 10-12 grams of catalyst, and immediately frozen in a dry ice bath. The tube was then sealed off.

The reaction tubes were placed in a constant-temperature bath for the temperature range 25° to 60°. The destruction of the catalyst and drying of the hydrocarbon was done by the usual procedure.

TABLE V

REFRACTIVE INDICES $n_D{}^{25}$ FOR METHYLCYCLOPENTANE-CYCLOHEXANE MIXTURES

$n_D{}^{25}$	Methylcyclopentane, mole %	Cyclohexane, mole %
1.4220	0.00	100.00*
1.42015	10.00	90.00
1.4184	20.00	80.00
1.4167	30.00	70.00
1.4134	50.00	50.00
1.4119	60.00	40.00
1.4089	80.00	20.00
1.4056	100.00*	0.00

* Assuming the cyclohexane and methylcyclopentane to be 100% pure
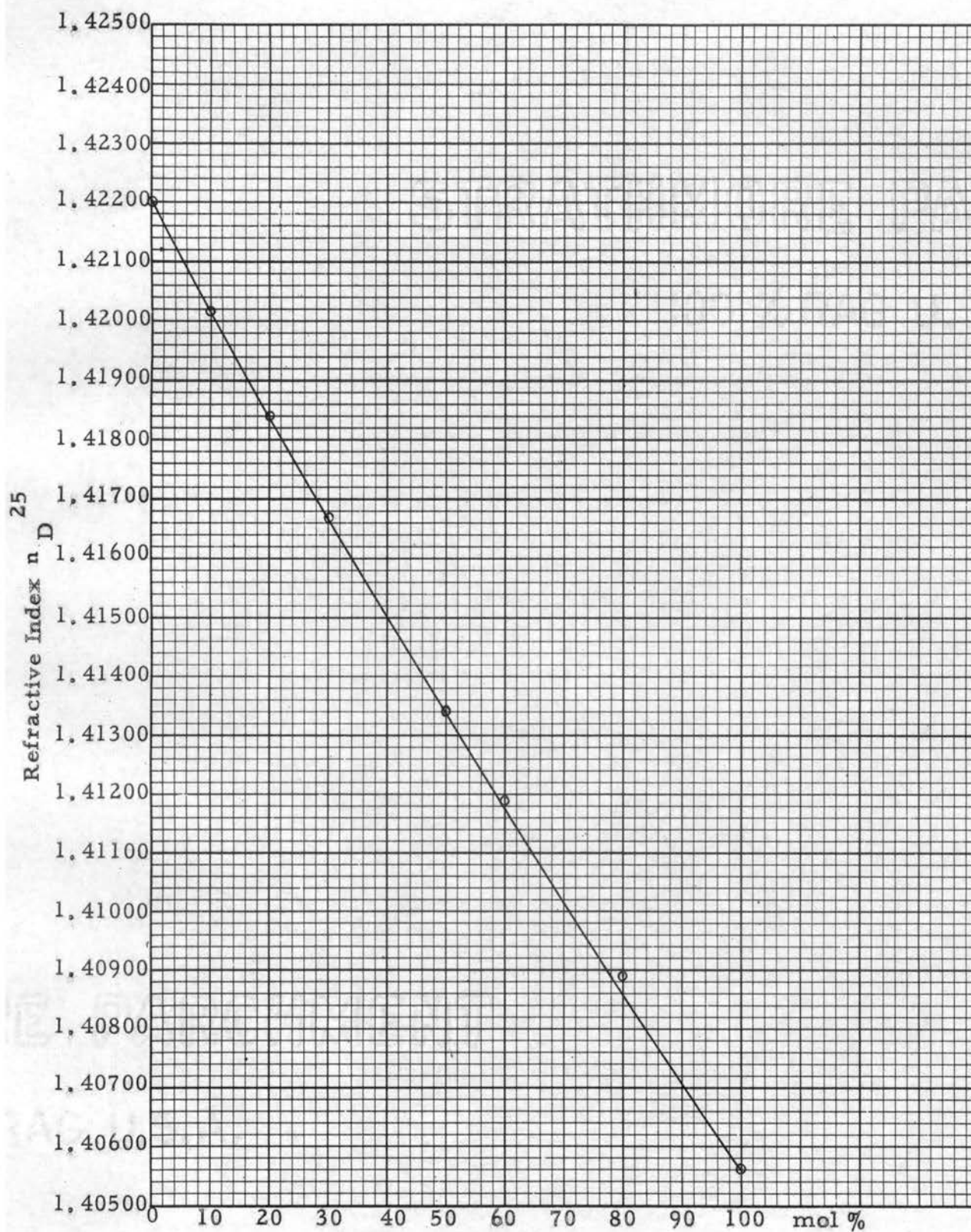
Refractive Index - Composition Diagram for the Cyclohexane -
Methylcyclopentane at 25°

Figure 10
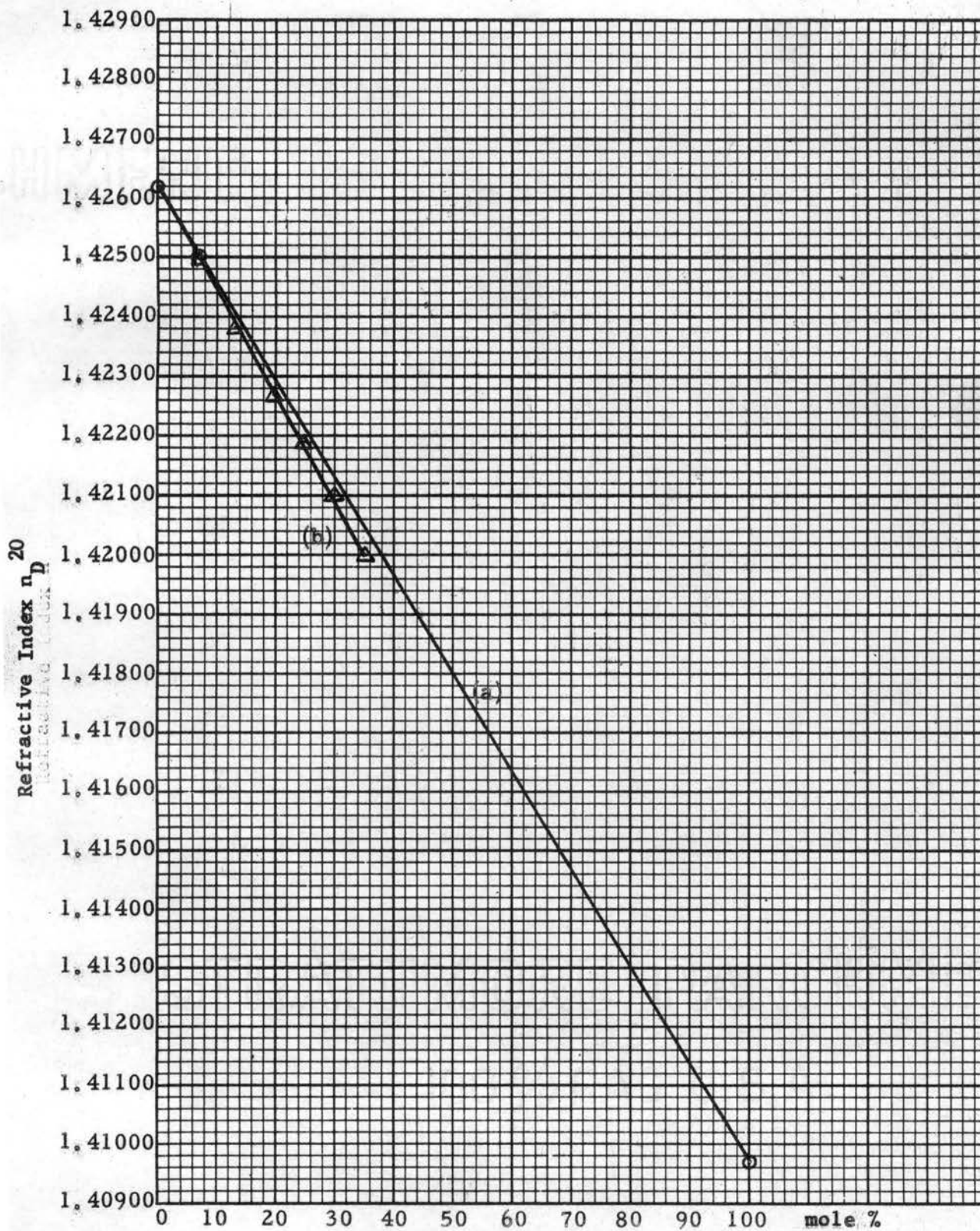
Refractive Index – Composition Diagram for the Cyclohexane – Methylcyclopentane at 20°, Various Methods (a) assumes linearity (b) Glasebrook and Lovell Values.

Figure 11

For each temperature several runs were made. The resultant values are shown in Tables VI and VII. A plot of these values as a function of temperature is shown in Figure 12 for aluminum bromide, and in Figure 13 for aluminum chloride. Figure 13 also gives published values for aluminum chloride.[13,27]

TABLE VI

EQUILIBRIUM CONCENTRATIONS OF METHYLCYCLOPENTANE IN THE
PRESENCE OF ALUMINUM BROMIDE

Run No.	Reaction time, hrs.	Reaction temp., °C	n_D^{20}	Mole % $C_5H_9CH_3$
1	23	80	1.42251	22.4*
2	14	95	1.42154	28.4
3	10	105	1.42093	32.2
4	6	120	1.41975	39.2*
5	6.75	130	1.41914	42.8
6	3.5	145	1.41849	46.8
7	3	150	1.41786	50.6
8	2	160	1.41719	54.7

* Average mole per cent of methylcyclopentane

TABLE VII

EQUILIBRIUM CONCENTRATIONS OF METHYLCYCLOPENTANE IN THE PRESENCE OF ALUMINUM CHLORIDE

Run No.	Reaction time, hrs.	Reaction temp., °C	n_D^{20}	Mole % $C_5H_9CH_3$
1	600	25	1.42593	2.0
2	624	35	1.42494	8.0
3	192	45	1.42443	10.8
4	90	55	1.42338	17.2
5	47	65	1.42275	21.2
6	24	80	1.42190	26.3*
7	12	92	1.42083	32.7
8	8.75	100	1.42002	37.7
9	6	110	1.41979	38.9
10	3	130	1.41823	48.4
11	2.5	145	1.41720	54.5
12	2	160	1.41627	60.2*

* Average mole per cent of methylcyclopentane
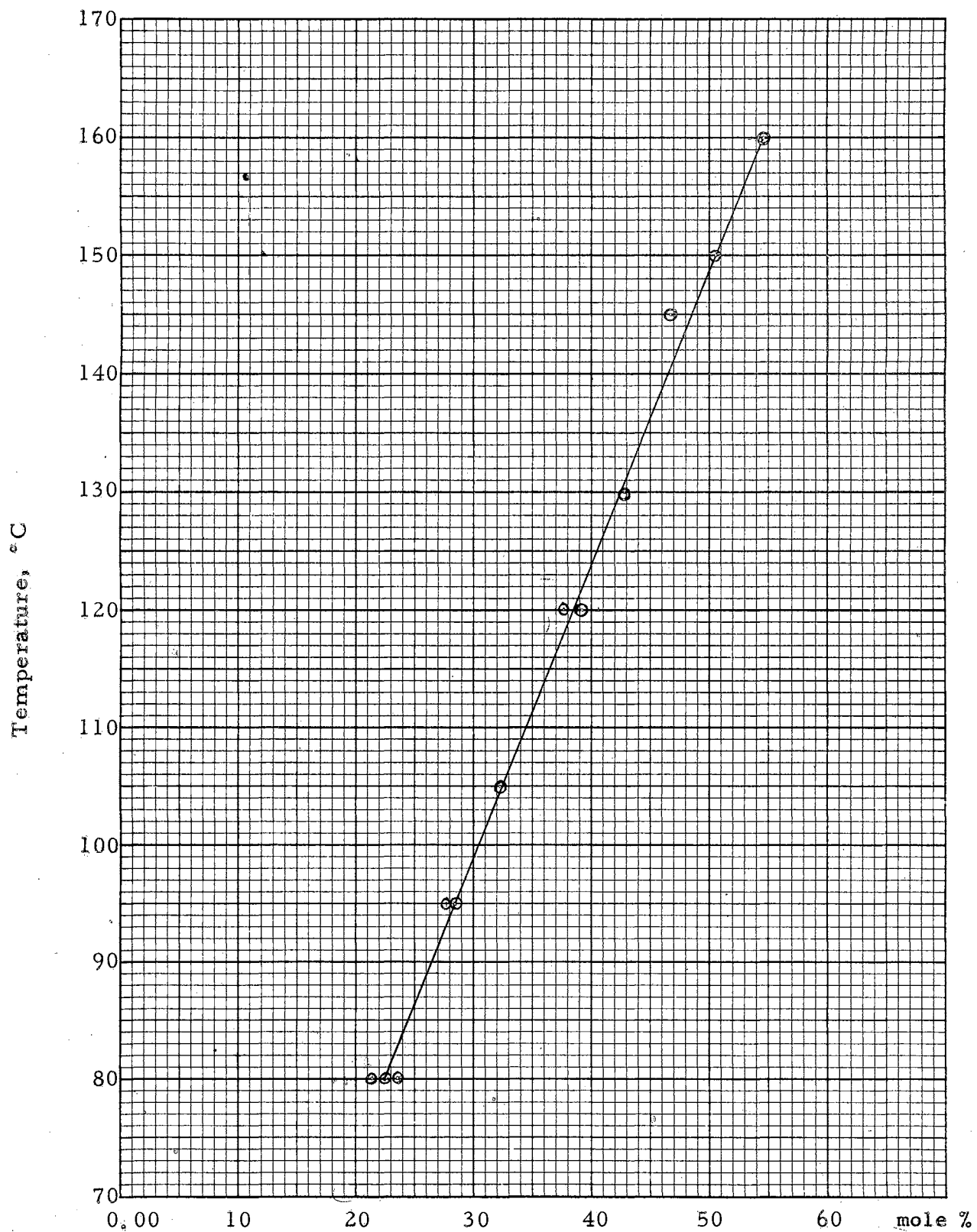
Plot of Equilibrium Composition vs Temperature for the System
Cyclohexane - Methylcyclopentane, $AlBr_3$ Catalyst

Figure 12
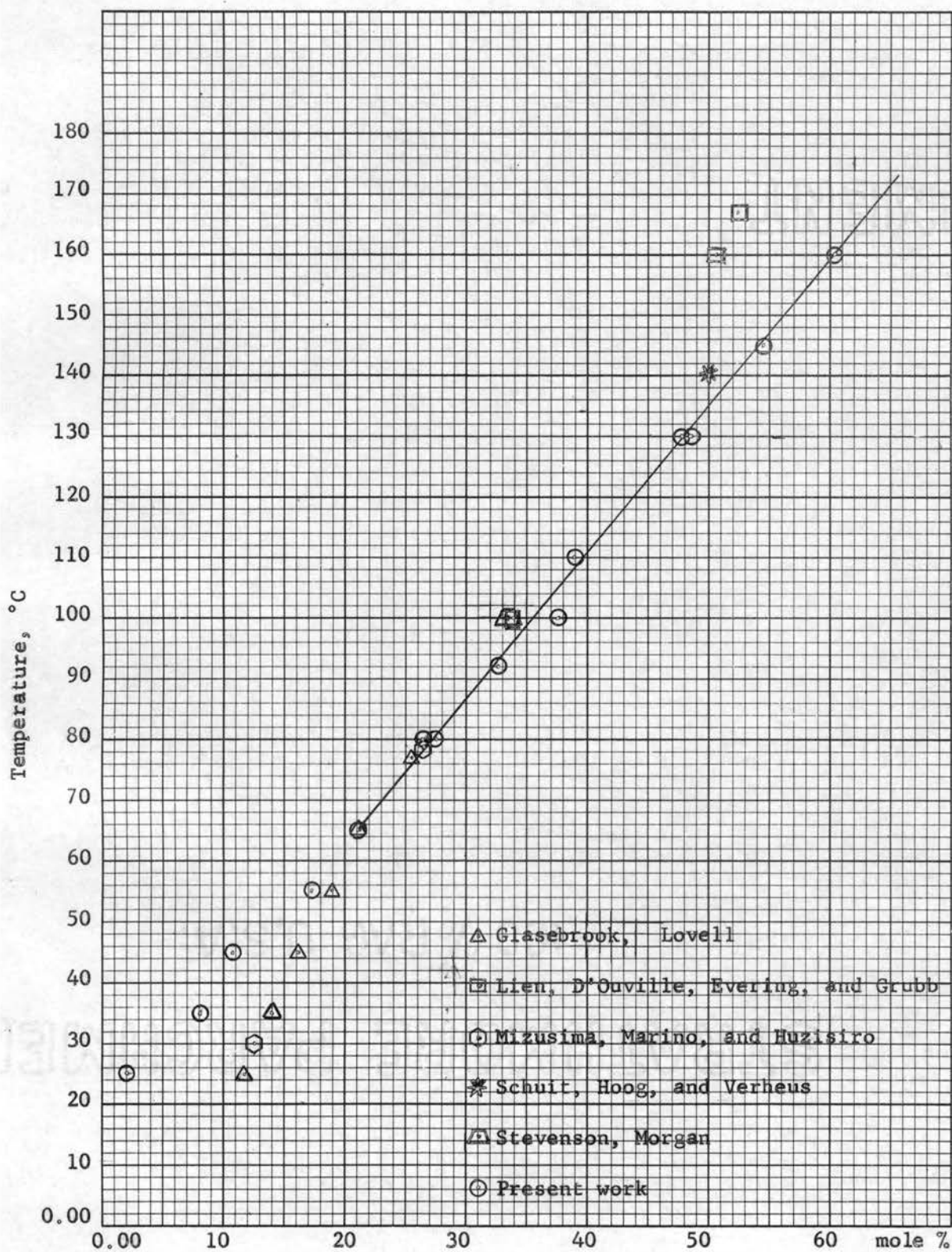
Plot of Equilibrium Composition vs Temperature for the System
Cyclohexane - Methylcyclopentane, AlCl$_3$ Catalyst

Figure 13

CHAPTER V

DISCUSSION OF THE RESULTS

In order to compare the effectiveness of various catalysts and
conditions for the isomerization of cyclohexane, a "standard" catalyst
was needed. Aluminum chloride was chosen because of the amount of
published data available.

Preliminary trials of aluminum chloride by Procedure II at room
temperature for 24 hours (Table II, runs 1, 2, and 3) show that an
equilibrium conversion of cyclohexane to methylcyclopentane was thus
attained. (According to Glasebrook and Lovell, at 25°, 12.50 mole per
cent of cyclohexane is converted into methylcyclopentane.)[13] However,
the _equilibrium_ conversion of cyclohexane to methylcyclopentane is
obviously undesirable since it permits no valid comparison of the _rate_
of reaction---i.e., catalyst effectiveness. Evidently some impurities
in the catalyst or in the cyclohexane may have acted as an activator even
when none was added.

The small differences between equilibrium values (runs 2 and 3)
obtained by this method and the one by Glasebrook and Lovell are probably
due to the lack of a bath for maintaining the temperature of the
refractometer at 20°. An Abbe refractometer was used for the analysis of
the product and was not calibrated at the time.

As noted, it was necessary to arrest the isomerization before
equilibrium was obtained. For this purpose time and temperature had to

be carefully regulated. Runs 4, 5 and 6 in Table II were made with a resublimed catalyst in a thermostat at 60°. Although none of these nearly approached giving the literature value for equilibrium conversion at 60°, which is 19.5 per cent, no isomerization at all should have occurred if activators were not present.

Many runs were tried with this procedure, but none gave the desired zero isomerization. Another disadvantage of this technique, as already remarked, was the time required for each run.

The advantages of the revised apparatus shown in Figure 8 are: (1) runs could be made in a much shorter time, and (2) there was less chance of contamination of reagents by stopcock grease, etc.

Isomerization by Procedure III was conducted using both cyclohexane and methylcyclopentane. Since the amount of conversion from the methyl-cyclopentane side is much greater than from the cyclohexane, (the concentration of cyclohexane in the equilibrium mixtures is much greater than that of methylcyclopentane), the refractometric analysis is more reliable for the methylcyclopentane runs. The low results that were obtained (Table III, runs 1 to 4) with aluminum chloride purified in the simple apparatus shown in Figure 1 indicate that not enough activators were present to promote the reaction appreciably. Nevertheless, again not one run showed zero isomerization; this seems to indicate that traces of activators were present. It seems quite likely that purifying the aluminum chloride and subliming it into capsules by the above method did not give a pure catalyst.

The need for a new apparatus for the purification of catalyst thus became apparent. The best results were obtained by using the new apparatus shown in Figure 4. Runs were made at 60° with reaction times 4 and 10 hours, using both cyclohexane and methylcyclopentane, and gave

either small degrees of isomerization (runs 5 and 6 of Table III) or none
at all (runs 7 and 8 of Table III). Therefore, it was concluded that
promoters were essentially absent and that this procedure should be used
for the comparison of other catalysts with aluminum chloride.

Aluminum bromide isomerized cyclohexane in the combustion tube
giving 22.4 mole per cent methylcyclopentane after 23 hours at 80° C. At
reflux temperature (see Figure 6) aluminum chloride produced 27.3 mole per
cent of methylcyclopentane from cyclohexane during 44 hours and left
27.4 mole per cent starting with methylcyclopentane; thus equilibrium
between cyclohexane and methylcyclopentane had been attained. On the
other hand, 78.7% of methylcyclopentane remained unisomerized when
refluxed with aluminum bromide for 44 hours. This value is obviously
far from the one obtained from the cyclohexane side. Since no other
experiments were made with methylcyclopentane plus aluminum bromide
catalyst and there is much evidence that the equilibrium composition is
about 25% methylcyclopentane, 75% cyclohexane at 80°, it must be concluded
that the isomerization of methylcyclopentane by aluminum bromide is
abnormally slow and that this one value obtained thence is untrustworthy
for equilibrium studies.

As a matter of fact, other observations also indicated that aluminum
chloride produces a higher reaction rate than aluminum bromide. The
possible reasons for this are:

a. An aluminum halide cannot initiate the isomerization reaction
unless some small quantity of promoters (H_2O, O_2, etc.) is present. The
combination of catalyst with promoters will produce an intermediate
active compound in the form of a complex.

$$AlX_3 + H_2O \rightleftharpoons HOAlX_2 + HX$$
$$HOAlX_2 + RH \rightleftharpoons Complex$$
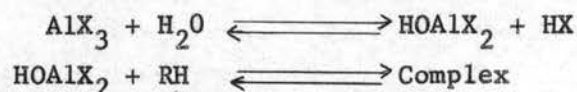
If one step of the isomerization involves separation of some of the halogen from the hydroxyaluminum dihalide as halide ion, as seems probable, then aluminum chloride should be a better catalyst than aluminum bromide. This is because the greater electronegativity of chlorine will favor its becoming chloride ion in any such competition with bromide.

b. The aluminum chloride is essentially insoluble in cyclohexane and methylcyclopentane whereas the solubility of aluminum bromide is high. It may be that aluminum bromide gives a lower rate of isomerization because it complexes more strongly with cyclohexane and methylcyclopentane than aluminum chloride does, and the stability of these complexes actually impedes the reaction.

Other acid catalysts were tried; some had very little effect and some had none. The difference between aluminum halides and other halides as catalysts is evidently much greater for this isomerization than for the Friedel-Crafts ketone synthesis.

As is shown in Figure 13, the equilibrium conversion of cyclohexane to methylcyclopentane was not attained for the temperature range of 25° to 55°. This has also been noted by other investigators. If the aluminum chloride, water and hydrocarbon are mixed and allowed to stand at room temperature for several days, very little reaction occurs. According to Glasebrook and Lovell,[13] the induction period can be over-come if the reaction mixture is heated to boiling before it is placed in the constant-temperature bath. Since the major part of this work is concerned with values gained over the temperature range of 80° to 160°, adoption of the procedure of Glasebrook and Lovell was not considered necessary.

A series of calculations were made from the thermodynamic data of A.P.I. project 44 (see Appendices A and B) to plot the theoretical

equilibrium curve. The method of calculation for log K and its values are shown in Table VIII. A plot of these values as a function of the inverse of the absolute temperature is shown in Figure 14, from which the value of log K can be read at any temperature within the range. Equilibrium concentrations of cyclohexane and methylcyclopentane at specified temperature can then be calculated.

The data from Tables VI and VII were used to calculate the equilibrium constants and ΔF values by means of the equation $\Delta F = -RT \ln K$. Other thermodynamic constants were obtained by the use of Van't Hoff's equation, $\dfrac{d(-R \ln K)}{d(1/T)} = \Delta H$, and the free energy equation $\Delta F = \Delta H - T\Delta S$. The results are summarized in Tables IX and X.

It is apparent that the experimental equilibrium constant values do not agree well with the theoretical values. This observation confirms the discrepancies of about the same order of magnitude observed by previous investigators. The extent of the side reactions, some of them irreversible, accompanying the isomerization must have had some effect on the apparent ratio of methylcyclopentane to cyclohexane. However, this is not believed to be the case for experiments conducted below 60° where the side reactions would have a negligible effect. At elevated temperatures a minimum reaction time consistent with attainment of equilibrium is very desirable to minimize these side reactions. The selection of the proper reaction time, however, was always a difficult task.

During runs at 110-160°, the aluminum chloride-hydrocarbon system changed from solid + liquid to liquid + liquid. The color of this two-liquid system changed from faint yellow to darker yellow as the reaction time increased. During longer heating a small portion of the liquid mixture formed a third phase (Tarry), which upon opening the cooled reaction tube turned to red and then slowly to black. These color

TABLE VIII

CALCULATED EQUILIBRIUM CONSTANTS FOR THE REACTION

CYCLOHEXANE $\rightleftharpoons$ METHYLCYCLOPENTANE

(Based on the relationships $\Delta F_{25}^{\circ} = \Delta F_f^{\circ}$(methylcyclopentane) - ΔF_f°(cyclohexane), and log $K = -\Delta F^{\circ}/2.303$ RT)

Temperature, °C	1/T°	log K
25	0.00335	-0.70361
126.84	0.0025	0.03824
226.84	0.0020	0.46765
326.84	0.00166	0.75757
426.84	0.00143	0.95528
526.84	0.00125	1.10084

TABLE IX

EQUILIBRIUM BETWEEN CYCLOHEXANE AND METHYLCYCLOPENTANE

CATALYZED BY $AlBr_3$

$$*\Delta F = 4722 - (11.1 \pm 0.2) T$$

Temperature, °C	K observed value	K** calculated value	ΔF, cal. observed value
80	0.289	0.549	871
95	0.397	0.699	676
105	0.475	0.794	559
120	0.645	1.048	343
130	0.748	1.096	233
145	0.880	1.314	106
150	1.024	1.397	-20
160	1.208	1.544	-163

* ΔH is assumed constant over the temperature range.

** Read from Figure 14.

TABLE X

EQUILIBRIUM BETWEEN CYCLOHEXANE AND METHYLCYCLOPENTANE

CATALYZED BY $AlCl_3$

$$*\Delta F = 4429 - (10.7 \pm 0.25) T$$

Temperature, °C	K observed value	K** calculated value	ΔF, cal. observed value
65	0.269	0.421	882
80	0.356	0.549	765
92	0.486	0.666	524
100	0.603	0.739	375
110	0.637	0.861	343
130	0.938	1.096	51
145	1.198	1.314	-150
160	1.513	1.544	-356

* ΔH is assumed constant over the temperature range.

** Read from Figure 14.

Plot of log K (values calculated from thermochem.data) vs 1/T

Figure 14
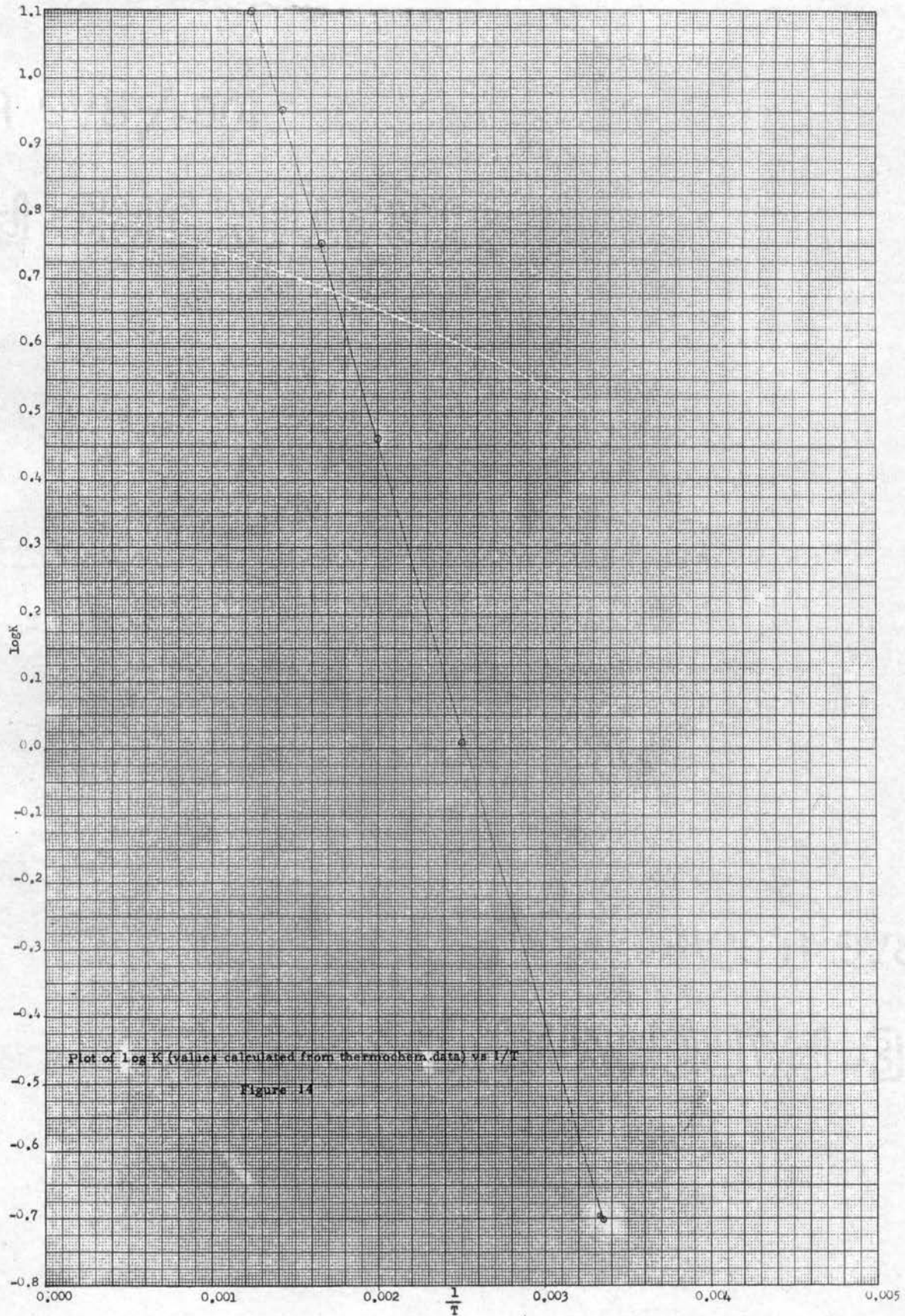
changes are thought to be due to the formation of unsaturated hydro-
carbons. The dark yellow hydrocarbon mixtures from such runs when
analyzed refractometrically gave results that could not be interpreted.

The results which are listed in Tables VI and VII were obtained
reproducibly from samples which did not show any of the physical
changes described above except development of the faint yellow color.

SUMMARY

1. The equilibrium of cyclohexane or methylcyclopentane in the presence of anhydrous aluminum chloride has been studied. The experiments confirm the lack of catalytic activity of aluminum chloride in the absence of a promoter. At 60° impurities such as water act as promoters of isomerization by aluminum halides.

2. A series of other Lewis acid-type catalysts showed no ability to catalyze the isomerization of cyclohexane refluxing under 1 atmospheric pressure.

3. Equilibrium concentrations of cyclohexane and methylcyclopentane were produced by use of both aluminum chloride and aluminum bromide catalysts, and were determined refractometrically. The experiments were carried out over the temperature range 25° to 160° with $AlCl_3$ and 80° to 160° with AlBr . Equilibrium values were then plotted as a function of temperature along with the values obtained from other investigatiors.

4. From these data, values of the equilibrium constants, free energy change, heat of reaction, and entropy change for the isomerization reaction have been computed.

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Selected Values of Physical and Thermodynamic Properties
of Cyclohexane (A.P.I. Thermodynamic data, Project 44)

Free energy function $(F°-H°)/T$ for the ideal gas state

0	298.16	300	400	500	600	700	800	900	1000	Temp., °K
0	-57.07	-57.16	-61.8	-66.39	-70.96	-75.5	-79.97	-84.4	-88.74	$(F°-H°)/T$

Entropy, $S°$, for the ideal gas state

0	298.16	300	400	500	600	700	800	900	1000	Temp., °K
0	71.28	71.44	80.18	89.24	98.30	107.14	115.65	123.8	131.59	$S°$ in cal./deg.-mole

Heat Content (Enthalpy), $(H°-H_0^°)$, for the ideal gas state

0	298.16	300	400	500	600	700	800	900	1000	Temp., °K
0	4237	4284	7352	11425	16404	22148	28536	35460	42850	$(H°-H_0^°)$ in cal./mole

Heat Capacity, C_p° for the ideal gas

0	298.16	300	400	500	600	700	800	900	1000	Temp., °K
0	25.4	25.58	35.82	45.47	53.83	60.87	66.76	71.68	75.8	C_0° in cal./deg.-mole

Heat of Formation, ΔH_f°

0	298.16	300	400	500	600	700	800	900	1000	Temp., °K
-22.01	-29.43	-29.48	-31.7	-34.08	-35.57	-36.59	-37.19	-37.46	-37.41	ΔH_f° in Kcal./mole

Free Energy of Formation, ΔF_f°

0	298.16	300	400	500	600	700	800	900	1000	Temp., °K
-20.01	7.59	7.81	20.66	34.07	47.86	61.85	75.96	90.13	104.3	ΔF_f° in Kcal./mole

Heat of formation, H_f°, at 25° (liquid phase) = -37.34 Kcal./mole
Entropy, S°, at 25° (liquid phase) = 48.85 cal./deg.-mole
Free energy of formation, ΔF_f°, at 25° (liquid phase) = 6.37 Kcal./mole
Boiling point = 80.738°C at 760 mm

n_D^{20} = 1.42623
n_D^{25} = 1.42354

Density at 20° = 0.77855 g/cc
Density at 25° = 0.77389 g/cc
Freezing point = 6.554°C in air at 1 atmosphere

Selected Values of Physical and Thermodynamic Properties
of Methylcyclopentane (A.P.I. Thermodynamic data, Project 44)

Free energy function $(F°-H°)/T$ for the ideal gas state

0	298.16	300	400	500	600	700	800	900	1000	Temp., °K
0	-65.23	-65.33	-70.45	-75.33	-80.07	-84.72	-89.26	-93.68	-97.97	$(F°-H_0°)/T$

Entropy, $S°$, for the ideal gas state

0	298.16	300	400	500	600	700	800	900	1000	Temp., °K
0	81.24	81.42	90.33	99.36	108.24	116.81	125.01	132.83	140.25	$S°$, cal./deg.-mole

Heat Content (Enthalpy), $(H°-H_0°)$, for the ideal gas state

0	298.16	300	400	500	600	700	800	900	1000	Temp., °K
0	4774	4827	7952	12015	16902	22463	28600	35235	42280	$(H°-H_0°)$, cal./mole

Heat Capacity, C_p°, for the ideal gas state

0	298.16	300	400	500	600	700	800	900	1000	Temp., °K
0	26.24	26.46	36.11	44.94	52.43	58.68	64.00	68.53	72.44	C_p° in cal./deg.-mole

Heat of Formation, ΔH_f°

0	298.16	300	400	500	600	700	800	900	1000	Temp., °K
-16.62	-25.5	-25.54	-28.07	230.11	-31.68	-32.88	-33.74	-34.29	-34.58	H_f° in Kcal./mole

Free Energy of Formation, ΔF_f°

0	298.16	300	400	500	600	700	800	900	1000	Temp., °K
-16.62	8.55	8.76	20.59	33.00	45.78	58.79	71.93	85.17	98.46	F° in Kcal./mole

Heat of formation, ΔH_f°, at 25°C (liquid phase) = -33.07 Kcal./mole
Entropy, S°, at 25° (liquid phase) = 59.26 cal./deg.-mole
Free energy of formation, ΔF_f°, at 25° (liquid phase) = 7.53 Kcal./mole
Boiling point = 71.812°C at 760 mm

dt/dp = .04274°C at 760 mm
n_D^{20} = 1.40970
n_D^{25} = 1.40700

Density = 0.74864 g/cc at 20°
Density = 0.74394 g/cc at 25°
Freezing point = -142.455°C in air at 1 atmosphere

VITA

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