

phase at 40-60°C. In order to be certain that the chlorine enters in the vapor phase, the supply line is steam jacketed. The liquid is circulated through a cooler and product corresponding to the feed is removed continuously. Distillation yields the dichlorobutane, the unreacted butylene being returned to the system.

The production of butadiene by splitting off of hydrogen chloride is carried out in empty tubes heated to 600-610°C. The best results are obtained with a 1:1 mixture of dichlorobutane to monochlorobutane, the monochlorobutane being obtained by splitting hydrogen chloride from dichlorobutane. The mixture is vaporized and passes into the reaction tubes; almost quantitative yields of butadiene are obtained.

The monochlorobutene and unreacted dichlorobutane are recycled to the decomposer.

In principle, the chlorination of propylene can be carried out in the same manner, but due to the higher boiling point, lower temperatures and higher pressures are required to maintain the liquid state.

C. Preparation of Butadiene from Butane.

The following information on the vapor-phase chlorination of butane was obtained from Dr. Waldmann.

With reference to Figure VII, butane and chlorine are mixed at atmospheric pressure in the proportion of 1 to 1 and brought to a temperature of 300-350°C. The reaction takes place very rapidly in the absence of a catalyst and produces more heat than is necessary to maintain the temperature. The products are cooled to condense the chlorides and are washed with dilute hydrochloric acid to wash out the HCl. The chlorinated butanes are caustic and washed and distilled to separate the higher chlorides ("Poly"). The monochloride and dichlorides are decomposed without a catalyst at 550-600°C., and the products are worked up in the same system and together with the chlorination product.

The gaseous product, butane, butylene and butadiene, passes to an absorber where it is contacted with a copper solution. The butane-butylene stream is conducted back to the chlorinator. The butadiene is liberated from the rich absorber solution by decomposition with heat and the lean copper solution recycled.

The concentrated hydrochloric acid is electrolyzed, yielding chlorine, which is recycled, and hydrogen. The chlorine is recovered to the extent of about 90%; the remaining 10% being present in the polychlorobutane produced.

From 1000 kg. of butane and 120 kg. of chlorine, the following yields are obtained:

C_4H_6	650 kg.
H_2	65 kg.
Polychlorobutane (25-30% Cl)	400 kg.

The process has thus far been carried out only on a small scale (10 kg. per hour). It is believed it can be successfully applied to the production of butylene or to butylene and butadiene, as well as for the production of propylene from propane.

VII. MISCELLANEOUS PROCESSES AND PRODUCTS.

A. Hydrogenation of Butadiene to Butylene.

The following information on the investigation of catalysts for the hydrogenation of butadiene to butylene was obtained from Dr. Conrad.

In the catalytic dehydrogenation of normal butane, a certain percentage of the butylene is dehydrogenated to butadiene. A small percentage of butadiene is detrimental in the alkylation of butylene to iso-octane, since the consumption of sulfuric acid is greatly increased.

In the experimental plant, Op. 339, in which normal butane is dehydrogenated on a semicommercial scale by a multistage process, experiments were made to hydrogenate the butadiene with the hydrogen contained in the gas. A hydrogenating catalyst was tried which had been developed for the removal of small quantities of acetylene in the gas stream of an ethane cracking plant. It was possible to reduce the butadiene content from about 1-1.5% to 0.1% without changing the total olefin content of the gas. Since the dehydrogenation of butane as well as alkylation was interrupted by changed requirements, the investigation could not be pursued further on a commercial scale, especially the determination of the sulfuric acid consumption in the alkylation step. Further laboratory experiments, however, were made with a series of catalysts, the preliminary results of which follows:

The method of experimentation was as follows.. The gas produced in a butane dehydrogenation plant was collected in a gas holder and the butadiene content brought to 1-2% by the addition of butadiene. The mixed gas had, on the average, the following composition:-

Olefins	20-25%
Butadiene	1-2%
Hydrogen	23-28%
Butane	remainder

The gas was drawn from the gas holder at the rate of 25 liters per hour through a gas meter and a drying section, then into the catalyst chamber, which was a vertical tube of 30 mm. diameter, heated electrically. The different space velocities were obtained by altering the quantity of catalyst. The freedom of the gas from butadiene was determined by the failure of a portion of the stream to discolor 87% sulfuric acid. The butylene content was determined in the usual way by absorption in 87% sulfuric acid. The following observations were made in the series of experiments.

If the temperature of the catalyst is raised at a given space velocity of the charge gas, hydrogenation of butadiene to butylene begins at a definite minimum temperature, and with further increase of temperature, all the butadiene disappears without any hydrogenation of butylene, that is, the olefins remain unchanged. This result holds over a definite limited temperature range which is different for each catalyst. Further increase of temperature generally causes a decrease in the olefin content of the gas, since butylene is then hydrogenated to butane. The temperature range of selective hydrogenation is different for each catalyst and can change for a given catalyst in the course of continued use, an effect which can, of course, be ascribed to a change of catalyst activity. All catalysts investigated showed this behavior, with the exception of copper chromite on silica gel. With this catalyst only, selective hydrogenation was observed over a wide temperature range. Further increase of temperature resulted only in the reappearance of butadiene and no butylene was hydrogenated. A further investigation of this catalyst and other chromite catalysts is planned.

In the course of the experiments it was found necessary to remove from the gas stream the polymerization products which are always present in such dehydrogenated gases as vapor or entrained as mist. The removal is necessary to protect the catalyst from fouling. The removal was easily effected by a mist filter and an activated carbon filter. The lack of such purification was the reason that the butadiene content was not completely reduced to zero in the commercial experiment.

The principal results are summarized in the following table.

The second column shows the space velocity employed, stated in liters per hour per liter of catalyst. The third column gives the temperature range within which the catalyst hydrogenates selectively at the space velocity shown.

Catalyst	Space Velocity	Temperature range °C
$\text{Cr}_2\text{O}_3 / \text{NiO}$ (Dr. Hüber)	1000 2000	85-130° 80-138°
8376/High Pressure expts Sulfide catalyst, clay support	250 1000 4000	110-260° 130-240° 160-270°
$\text{CuO} / \text{Cr}_2\text{O}_3$ on silica gel	1000 2000 4000	140-320° 220° and higher 260° and higher
Cu On clay	1800 4500	105-150° 130-200°
Ni on clay	500	225-300°

These experiments show that the selective hydrogenation of butadiene in the presence of butylene is possible with each catalyst tried, and it is only necessary to find by experiment the particular conditions that a given catalyst requires.

In order to determine accurately the hydrogenation product, pure butadiene was hydrogenated over copper supported on clay. In this experiment, the catalyst was fully active at 75°C. The products were removed as solids by carbon dioxide. The Raman analysis gave the following results:

Trans-butene - 2	80%
Cis-butene-2	15%
Butene-1	5%

No butane and no butadiene were present. These results show that the addition of hydrogen is principally 1,4-addition.

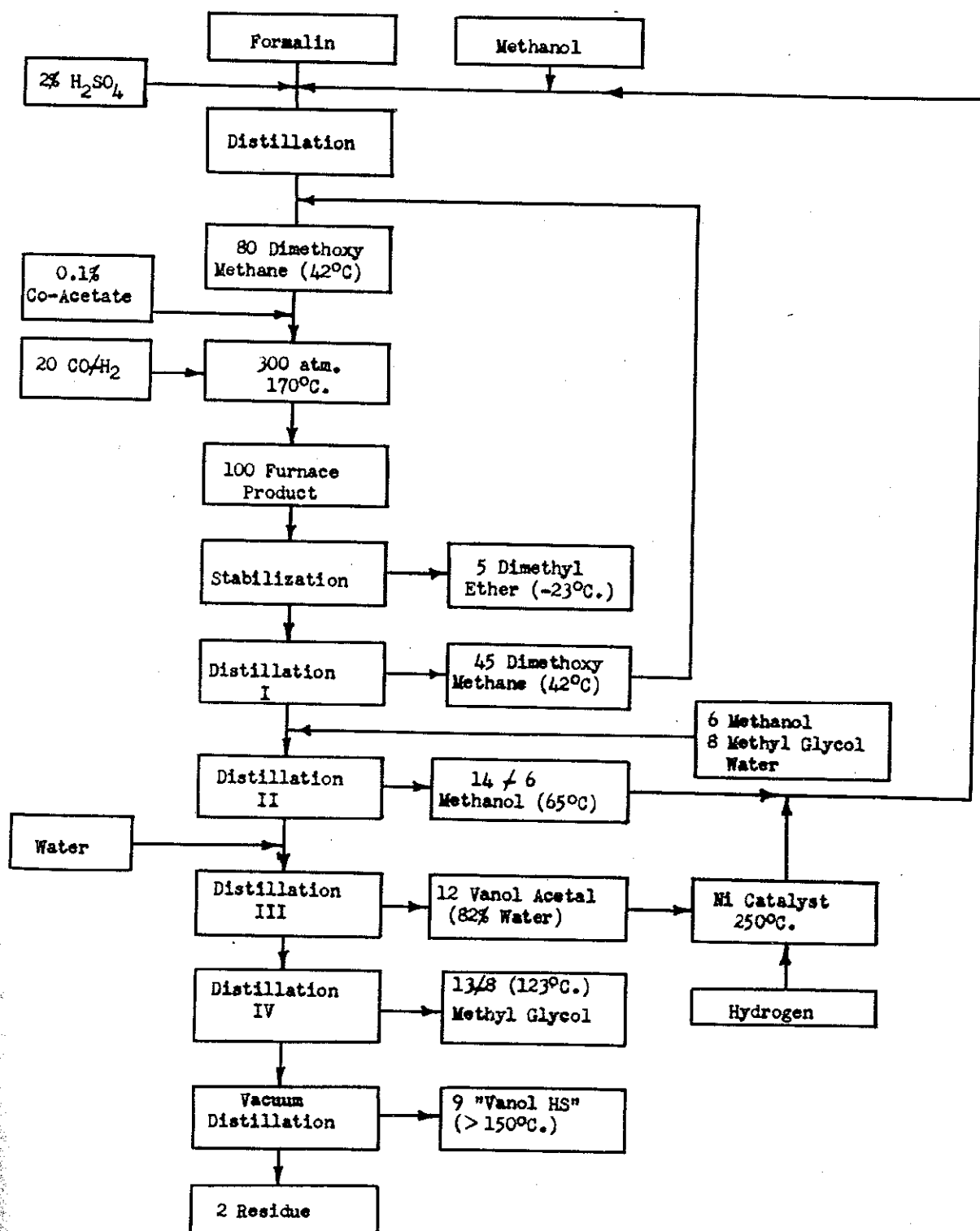


Fig. VIII FLOW SHEET FOR PRODUCTION OF VANOL

B. Kybol.

The following information concerning the manufacture of Kybol was obtained from Dr. Waldman.

Kybol (diethyl benzene) is manufactured from benzene by alkylation with ethylene, using aluminum chloride as catalyst. Ethylene and benzene (mol ratio 2:1) are reacted in a tower containing aluminum chloride at the boiling point of benzene at atmospheric pressure, vaporization removing the exothermic heat of reaction. The ethylene is nearly completely absorbed in one pass. The product is washed and distilled.

The first fraction containing benzene, as well as the third fraction containing triethyl benzene, is recycled to the alkylation towers. The middle fraction (about 30% of the mixture) represents the final product, "Kybol". There is also a residue of the higher alkylated benzenes.

From 1000 kg. of benzene and 720 kg. of ethylene, 1450 kg. of Kybol are produced with a consumption of 5-7% of aluminum chloride (based on the benzene).

Kybol was chiefly obtained as a by-product of the manufacture of ethyl benzene for styrene.

In the same manner, isopropyl benzene can be prepared from benzene and propylene.

C. Tannol.

The following brief statement on Tannol was obtained from Dr. Kuhn.

Diisobutylene and triisobutylene from polymerization are hydrogenated in the liquid phase at 200 atm. pressure and 250°C. over a tungsten-sulfide catalyst. A space velocity of 3 liters of liquid charge per liter of catalyst per hour was employed. Yield is practically 100% of Tannol (isooctane and isododecane), which is used for a gasoline blending agent.

At first, nickel on a carrier such as pumice or kieselguhr was used, but was later replaced by tungsten-sulfide pellets.

D. Vanol H.S.

The following description of the preparation of Vanol was obtained from Dr. Lorenz.

A mixture of 1 mol of formaldehyde and 2 mols of methanol with 2% H_2SO_4 as catalyst is introduced into a distillation column (see Fig. VIII). Methylal (dimethoxymethane) in an azeotrope with 8% of methanol is taken overhead.

The azeotrope is mixed with 0.1% cobalt acetate (dissolved in methanol) and reacted with CO:H_2 in the ratio of 1:2 at 170°C . and 300 atm. The product is stabilized to remove dimethyl ether and methane. Methylal is taken overhead in distillation I, methanol in distillation II, and both are recycled. After adding sufficient water to form the 82% water azeotrope of vanol acetal (1,1,2 trimethoxyethane), the mixture is distilled off at 92°C . and hydrolyzed in the presence of H_2 at 300 atm. and 250°C . The products, methanol, water, and methyl glycol are charged to distillation II.

The main product, methyl glycol (2 methoxyethanol) is obtained by distillation IV, and finally in a vacuum distillation, Vanol HS is recovered, leaving a viscous residue. The vanol HS is a mixture of polyoxy compounds, partly ethers, containing acetal groups which can be hydrolyzed by hydrogenation over nickel.

The technical experimental plant for this investigation was working only partly. It was built for 50 tons per month of methylglycol in continuous operation. The methyl glycol was to be hydrolyzed to glycol but this stage had not been satisfactorily developed.

From 100 parts of reactor product, the following materials are obtained:

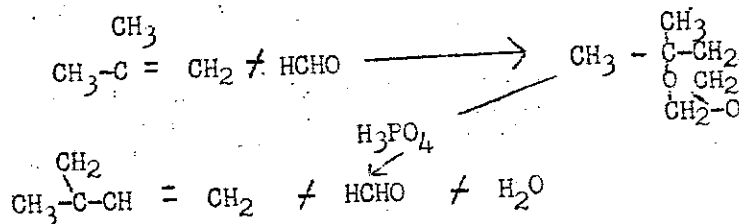
Dimethyl ether	5 parts.
Methylal	45
Methane	14
Vanol acetal	12
Methyl glycol	13
Vanol HS	9
Residue	2

E. Diolefins from Olefins and Formaldehyde.

The following brief information on the preparation of isoprene was obtained from Dr. Bueren.

The preparation of diolefins is carried out by first reacting the olefin with formaldehyde in the liquid phase at ordinary temperature in the presence of hydrogenchloride, to form a 1,3 dioxane. The dioxane is then decomposed to the diolefin by contacting with phosphoric acid catalyst at about 220°C .

This is illustrated in the following reaction:



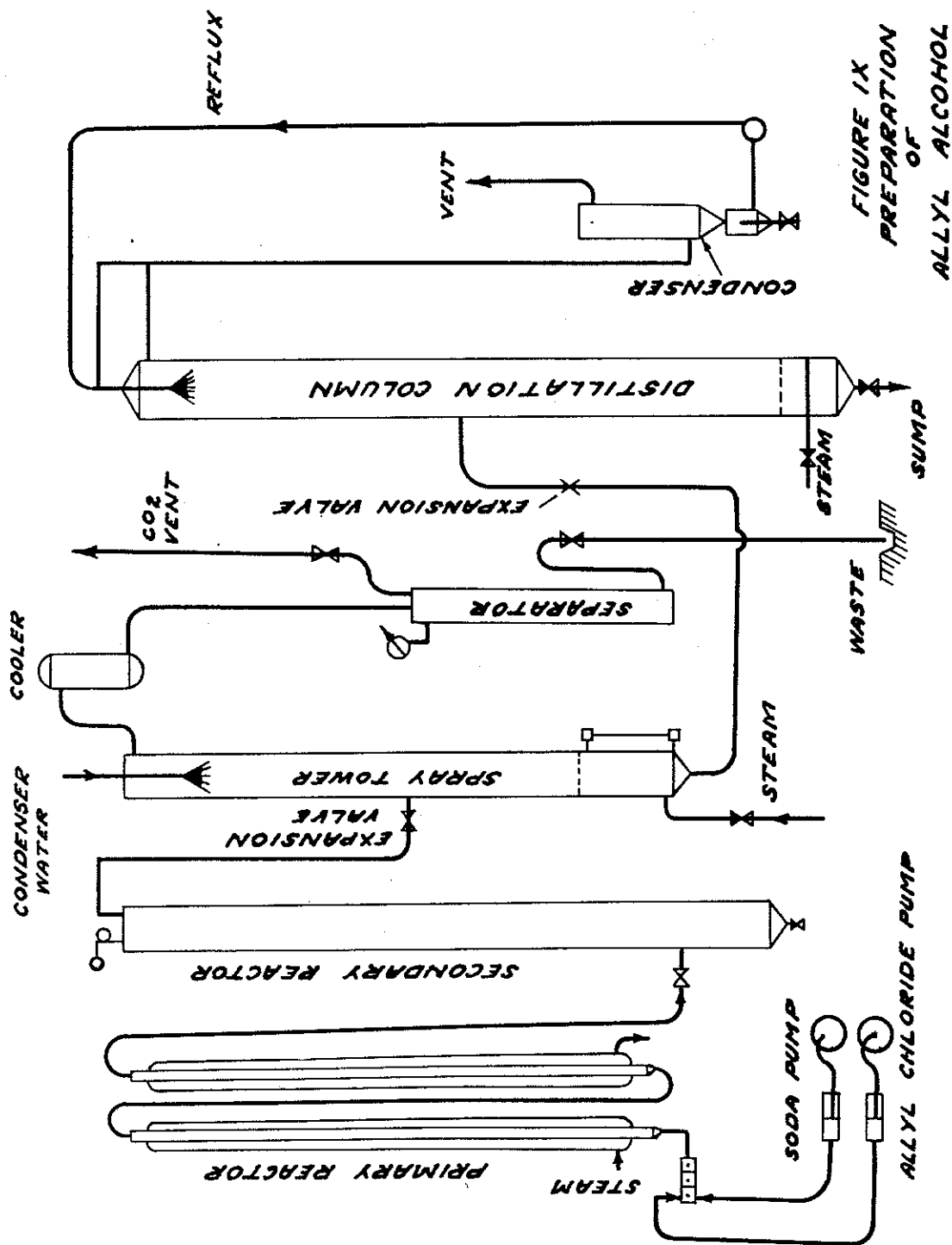


FIGURE IX
PREPARATION
OF
ALLYL ALCOHOL

When trimethyl ethylene is used, besides dimethyl butadiene, pinacol is obtained.

Further details may be obtained in DRP. IG. No. 663/43 and DRP. 610,371.

F. Preparation of Allyl Alcohol.

The following information on the preparation of allyl alcohol from allyl chloride was obtained from Dr. Klein.

Soda solution (1.25 m³/h. of 2.5 normal) is preheated to 130-140° C. and mixed with 250 liters per hour of allyl chloride. The allyl chloride contains 3-4% of isomers of lower molecular weight.

The mixture passes into a steam-jacketed reactor (see Fig. (IX) where it is maintained at 150°C, afterwards flowing into a secondary reactor. As it is unknown in which stage of the reactor the major portion of the CO₂ is liberated, the contact time cannot be calculated exactly, but it is estimated to be 20-30 minutes. Pressure in the reactor is maintained at 10-11 atm.

The reaction mixture is expanded to 8 atm. into a spray tower, in which the liquid phase separates from the CO₂. The gases pass through a cooler to a separator and are then vented.

The liquid phase from the spray tower is charged to a distillation column heated by direct injection of steam where an azeotrope (250 liters per hour) containing 30% water and 70% allyl alcohol is taken overhead. The allyl alcohol frequently contains small quantities (0.5-1.5%) of diallyl ether. The salt solution leaving the column should have a slightly alkaline reaction and contain no traces of allyl alcohol (by bromine test).

G. Methacryl Nitrile.

The following information on the preparation of methacryl nitrile was obtained from Dr. Lorenz.

Isobutyl alcohol is oxidized, through the aldehyde, to isobutyric acid. This acid with ammonia is contacted over beauxite at 500°C. to obtain isobutyronitrile in 95% yield. The isobutyronitrile is chlorinated at 65-70°C. in a quartz tube by exposure to a mercury vapor lamp, the chlorine being added in such amounts that the chlorination does not exceed 40%. The product is distilled and the first fraction containing unconverted isobutyronitrile and so-called "alpha-chloroisobutyronitrile" (BP 119°C) is recycled to the chlorinator. A second fraction (160-170°C), containing the so-called "beta-chloroisobutyronitrile" and an unknown "dichloroisobutyronitrile" is treated with 10% KOH. Approximately 5% of an unsaponifiable, highly chlorinated product is obtained as a residue.

By the KOH hydrolysis, the beta-chloroisobutyronitrile splits off HCl yielding methacrylnitrile I which is separated by distillation. The dichloride residue is passed over TiO₂ at 420°C., yielding methacrylnitrile II, which is less pure. The yield of methacrylnitrile is about 75% based on the butyric acid.

This investigation had not proceeded beyond the experimental stage, and the preparation for pilot-plant construction.

VIII. SPECTROGRAPHIC STUDIES.

A. Research

The following information was obtained from Dr. Fromherz. As other investigators were covering this subject thoroughly, only a brief summary of the conclusions was obtained.

Experiments were performed by Dr. Fromherz together with Dr. Luft (of Oppau Manufacturing Control Dept.) on the use of the infrared spectrum of hydrocarbons for qualitative and quantitative analysis of hydrocarbon mixtures, and to prove the advantages and disadvantages of infrared analysis as compared with Raman analysis. The studies led to the following conclusions:

1. The infrared fundamental oscillations between 3 μ and 12 μ are very characteristic for the individual hydrocarbons; they give sufficiently intensive absorption bands and permit a good qualitative analysis of mixtures with not more than three components, and a quantitative analysis with a precision up to 0.5 per cent.

2. A comparison of infrared analysis with the Raman analysis shows that the Raman analysis is in general preferable for qualitative investigations, because the characteristic Raman lines of different hydrocarbons can be observed lying adjacent to each other, while infrared absorption bands for different hydrocarbons are overlapping. Therefore, the individual hydrocarbon in a mixture can be identified more easily by the Raman spectr, and mixtures of more than three components can be qualitatively analyzed satisfactorily.

3. For quantitative analysis, the infrared method is generally better, because the intensity of absorbed light can be measured easily with great accuracy. In quantitative Raman analysis, it is necessary to measure photometrically the blackness of photographic plates, which is difficult, not too accurate and subject to many errors. If special precautions are not taken, the accuracy may not exceed 5%. Further, the results are not expressed in absolute concentration, but only in relative ratios.

4. The latter fact leads to a further advantage of infrared analysis. If, in Raman analysis, one component is missed because of its very weak Raman line, the remaining components (by ratios) will still add up to give a total of 100 per cent for the analysis. If the same mixture is analyzed by infrared rays, it can be determined if the sum is actually 100 per cent, or if it is less than 100 percent (beyond the limits of errors.). If the latter condition is found, some component has escaped Raman analysis, and the infrared analysis will give the quantity of this component by difference from 100%, and possibly from some disagreement in the infrared spectra, a clue to the identity of the missing component may be gained.

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B. Equipment.

The information given below was obtained from Dr. Luft.

In Oppau, two infrared spectorgraphs were developed; one registers the course of the energy, the other gives directly the spectral course of the absorption relation (ratio ?) of the substance being examined. The spectral range of the first apparatus extends from 1 to 8; that of the second from 1 to 14. Both instruments have rock-salt prisms. In the last few years, these apparatus have been used to investigate the infrared absorption of a number of substances (including paraffinic and aromatic hydrocarbons).

Both of these apparatus were described in the "Zeitschrift für technische Physik". In addition, a recording apparatus was developed for plant analysis using a summing up (integrating) method of infrared absorption. This apparatus serves to record continually the analysis of CO, methane, etc. (Infrared absorption recorder).

Both spectographs are in the Lenard Institute at Heidelberg. Spectra, calibrating curves, etc. are partly in the Lenard Institute and partly in the salt mine at Heilbronn. Both places are under control of the American authorities.

The standard samples had mostly remained in Oppau, Building OP. 567, where they were partly destroyed in the air raid in December 1944. The others were stored in the basement of building Op. 567. A few samples were stored in the Lenard Institute in Heldeberg. Infrared absorption recorders are in place in various parts of the Oppau and Ludwigshafen plants.