

usually involved as a first step hydrogenation of carbon or formation of hydrogen-carbon products similar to those already present in natural gas or easily derived from petroleum. It was soon recognized that petroleum and natural-gas hydrocarbons offer raw materials suitable in their original form, or after rearrangement to new molecular structure, for use in synthesis of chemical products. Further steps in the production of synthetic organic chemicals involve the addition or substitution of other elements such as oxygen, chlorine, nitrogen, or sulfur to the hydrocarbon structure. Typical methods for rearranging the hydrocarbon molecule and for converting it into other products are shown and defined in chart 4.

Probably the most important method used for converting petroleum hydrocarbons to other compounds is decomposition effected by pyrolysis, catalysis, or electric discharge. Decomposition as used here also includes, in many instances, subsequent recombination of primary products into new compounds. Dehydrogenation and hydrogenation, alkylation, polymerization, isomerization, desulfurization, and cyclization and aromatization all may be considered as special cases of controlled decomposition or decomposition and recombination. Some methods of oxidation, halogenation, nitration, sulfurization, and amination involve preliminary decomposition of saturated hydrocarbons to olefins and recombination with the added elements.

Decomposition, oxidation, halogenation, nitration, and sulfurization are further discussed with the charts showing products obtained by use of the respective methods. Many of the products shown on these charts are the result of a second series of reactions or conversions using the primary products as starting materials. Some typical examples of such reactions are shown in chart 4, and the following deserve special mention: Alkylation and hydrogenation have been of especial importance in the production of high anti-knock blending agents for aviation gasoline; isomerization has been used extensively to convert n-butane or n-pentane to isobutane or isopentane for use in alkylation and in aviation gasoline. Selective and non-selective polymerization is used in the manufacture of intermediates for plastics and synthetic rubbers as well as in making motor fuels and lubricants; desulfurization is often a necessary process in the production of motor fuels; dehydrogenation (and sometimes polymerization) together with cyclization and aromatization is used in the production of aromatics and cyclic compounds. The development of processes using these conversion methods received much consideration before and during the recent war, and processes developed are now being adapted to peacetime needs.

It has been mentioned already that coal, petroleum, agricultural products, and other carbonaceous materials may be used interchangeably as raw materials for hydrocarbon synthesis and manufacture of chemicals. Hydrocarbon synthesis and production of chemicals from materials other than petroleum has been used in Germany and in our own country as a wartime measure. Liquid fuels, lubricants, materials for synthetic rubber, and a large number of organic chemicals were produced in Germany from coal (or in some cases natural gas).

Among the processes using coal or coke as raw material are the production of calcium carbide for conversion into acetylene, the hydrogenation of

coal to produce gaseous and liquid hydrocarbons, and the Fischer-Tropsch synthesis, which involves a prior oxidation of coal or other carbonaceous material with oxygen or steam. Natural gas may be used in this process instead of coal, and this application has received much interest recently. It is discussed further with the chart showing products obtained by oxidation (chart 8). Similarly, acetylene is produced also by decomposition of natural gas or gas from coal hydrogenation and is discussed further with chart 7.

Chart 5

Chart 5 shows diagrammatically the production of butadiene by several possible methods using some of the possible raw materials. The chart illustrates the diverse routes by which a desired organic chemical may be obtained. Economic considerations involved usually determine the choice of raw materials and route. Butadiene for synthetic rubber was produced from coal in Germany during the war, whereas in America it was made on an extensive scale from ethyl alcohol, which was obtained from agricultural sources or from petroleum; also, directly from petroleum hydrocarbons, chiefly from butylenes and butanes. The choice of starting material in each instance was determined by the availability and need for the several types of materials. In Germany, coal was the initial raw material, but actual butadiene production was mainly from byproduct gases obtained in the hydrogenation of coal. These gases were converted into acetylene and ethylene by means of the electric arc, and the acetylene was converted to acetaldehyde and then to butadiene by the aldol route.

Chart 6

Chart 6 should be used for reference in studying charts 7 to 12, as it indicates the significance of the several "boxes," brackets, and types of lettering used in them. In chart 6 the terms used have the following meanings:

Primary product. - A product obtained directly by the application of the basic method of conversion indicated in the title of the individual chart.

Preferred source. - Not necessarily the only source, but the material reacting most easily or with the best yields relative to other natural-gas hydrocarbons (see remarks under "Charts 7 to 11 - General").

Direct use. - A use (a) in which no chemical change occurs in the substance, as when it is used as a solvent or anesthetic, or (b) when the substance is completely destroyed, as when used for fuel. The direct uses of secondary products are indicated in brackets.

Secondary product. - A product made from the primary product. Common names of secondary products and their derivatives are indicated in parenthesis. Direct uses are shown in brackets.

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CHART 5

SEVERAL POSSIBLE METHODS BY WHICH BUTADIENE MAY BE PRODUCED

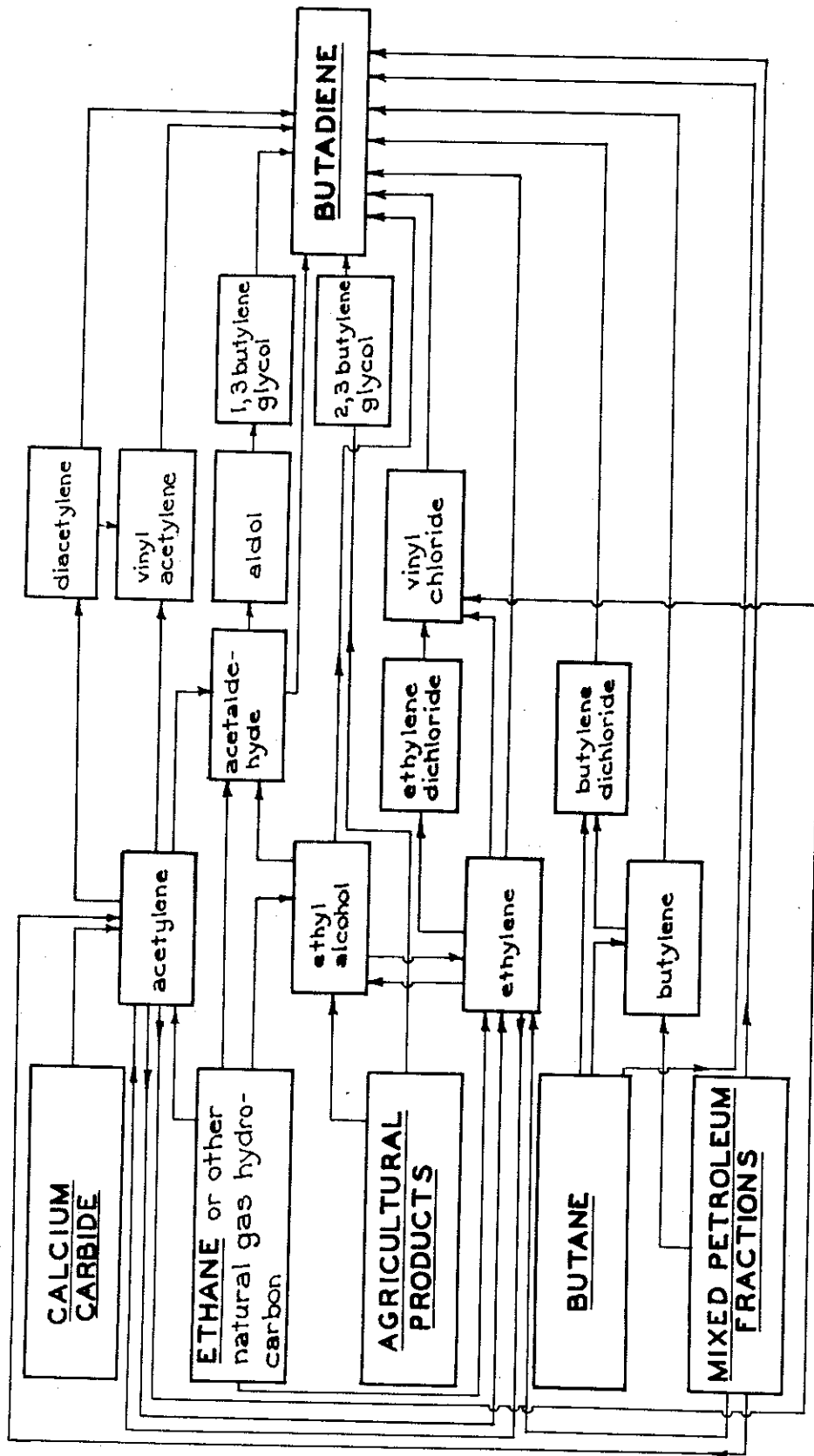


CHART 6

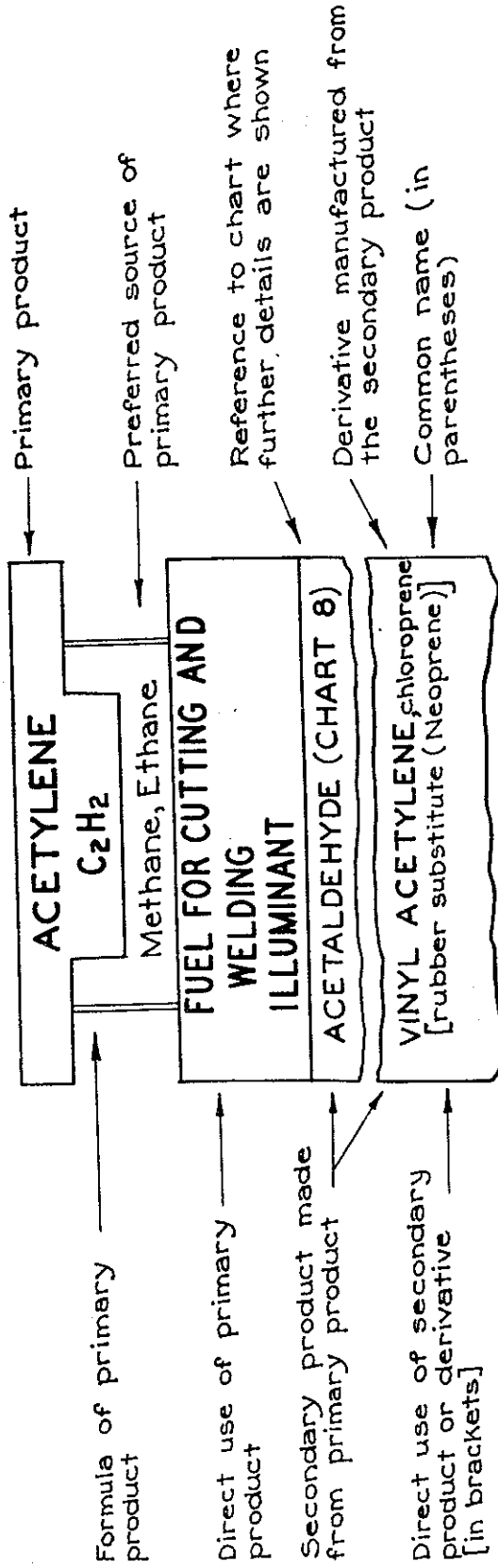


CHART 7

PRODUCTS OBTAINABLE FROM NATURAL GAS BY DECOMPOSITION
THERMAL-CATALYTIC-ELECTRIC

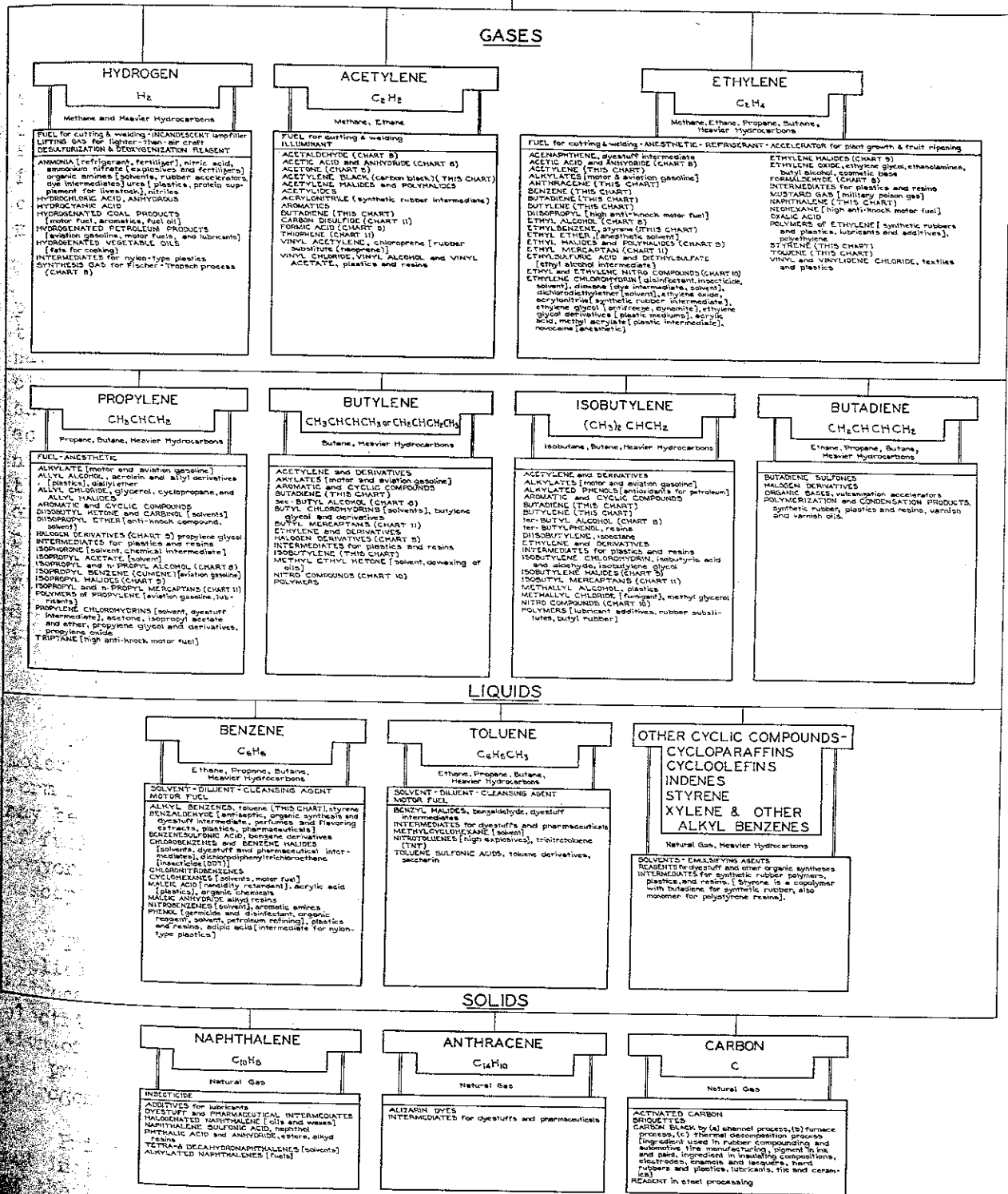


Chart 7 to 11 (General)

In preparing charts 7 to 11, products shown as derivatives of a particular hydrocarbon are not necessarily produced in commercial practice from that hydrocarbon or from a hydrocarbon as the original raw material. They are included, however, as they could be produced as shown if desirable to do so.

Examples of compounds of this type are the "Freons," which are shown as secondary products obtainable from natural-gas hydrocarbons by halogenation. These refrigerants are produced commercially, according to best available information, from carbon tetrachloride or other compounds derived from nonhydrocarbon raw materials. Data on raw materials actually used in commercial production of synthetic chemicals are not revealed by many manufacturers.

Space does not permit naming all possible derivatives or secondary products. For example, one company lists 85 organic chemicals, of which they say: "In producing all these chemicals, olefins derived by processing natural gas are used either directly or indirectly as raw material." Disclosure of scientific information from enemy sources since the recent war show that German technicians produced 37 or more chemical products from acetylene. An American company manufacturing nitration products from natural-gas hydrocarbons lists 54 derivatives as an incomplete list of those that can be made available. A handbook showing uses and applications of chemicals shows butyl alcohol as a reagent in making 132 different compounds. These data show the impracticability of listing all products and indicate the possibilities of chemical production with natural gas as a raw material. The use of heavier petroleum hydrocarbons, which are non-gaseous under ordinary conditions, as initial materials for chemical production also should be considered.

Chart 7

The decomposition of natural-gas hydrocarbons into smaller reactive molecules (primary products), which may recombine during the operation to form larger hydrocarbon molecules, either aliphatic or cyclic, or which may be separated and utilized as intermediate products in the production of fuels and chemicals, is perhaps the most important of the processes for conversion of these hydrocarbons. These primary products usually are more susceptible to chemical manipulation than the original molecules.

Thermal (pyrolytic), thermal catalytic, and electrical methods are applied successfully to the decomposition of petroleum and natural-gas hydrocarbons. The first two of these have found greatest application. The electric arc has been reported to have been used successfully for decomposition of natural-gas hydrocarbons; it was used in Germany during the war for the production of acetylene from natural gas or from byproduct gas from coal hydrogenation.

Primary products from natural-gas decomposition shown in chart 7 do not include aliphatic hydrocarbons containing more than four carbon atoms or the less common homologues of acetylene or butadiene that may be formed.

Because of the attention given to some of these primary products in recent years, more individual mention is deserved than can be given in the chart.

Hydrogen is produced from natural gas by thermal decomposition with concurrent production of carbon black. Another process for production of hydrogen from natural gas (by reaction with steam) is shown in the next chart (chart 8) and discussed in the accompanying discussion. Both of these methods are used extensively for the production of hydrogen for use in the hydrogenation of oils, in the manufacture of ammonia, and for other uses.

The production and chemistry of acetylene received much attention long before methods were evolved for its production from natural-gas hydrocarbons. Although acetylene presents some mechanical difficulty in handling because of its tendency to explode under pressure, its use in chemical synthesis has attained a position of importance in American synthetic processes. It is used as the basis for the manufacture of a number of commercial products and was used widely in Germany for production of chemicals needed throughout the war. Ordinarily, acetylene is produced for commercial use from nonhydrocarbon materials, but has been obtained from natural-gas hydrocarbons by thermal decomposition or by use of electric-arc cracking.

Ethylene is an important constituent in refinery gas produced in the manufacture of gasoline from nongaseous petroleum hydrocarbons. It is readily produced by pyrolysis of natural gas. Propylene, butylene, and iso-butylene are produced similarly. These unsaturated hydrocarbons are of the type known as olefins and form the basis for the manufacture of a broad series of organic chemicals. Ethylene, which has been termed a "building block" for organic synthesis, is the starting point for the commercial production of more than 50 products. A correspondingly large number of products is obtained from propylene, butylene, and isobutylene. In the manufacture of aviation fuels and alkylates, these olefins are of prime importance. The production of butadiene has been discussed previously (chart 5).

Besides heavier aliphatic hydrocarbons, not included separately in the chart, that may be formed as the result of decomposition of natural-gas hydrocarbons, a group of cyclic compounds may be formed, which include benzene, toluene, xylene, and other aromatic compounds. However, selected cuts of heavier hydrocarbons from petroleum used as feed stock in catalytic aromatization gives high yields of benzene or toluene, and much of the toluene needed for wartime demands was obtained by this method.

The use of natural gas for the production of carbon black was one of its first non-energy uses. Three methods, known as the channel, thermal decomposition, and furnace processes, are used for the production of carbon black. Each process yields a product of different type especially suited for specific uses. Carbon black is an essential ingredient in the manufacture of automobile tires and other rubber goods and in the production of paints, inks, and other materials. A type of carbon black known as "acetylene black" is produced by the electrical decomposition of acetylene.

PRODUCTS OBTAINABLE FROM NATURAL GAS HYDROCARBONS BY HALOGENATION

THERMAL-CATALYTIC - PHOTOLYTIC

Natural gas hydrocarbons can undergo direct fluorination, chlorination, bromination, and iodination when reacted under proper conditions with halogens or halogen-containing compounds. Direct fluorination is said to be violent and difficult to control but is reported as accomplished with methane, ethane, and other hydrocarbons. Iodination is a reversible reaction. Bromination and chlorination are effected most easily. Olefin hydrocarbons generally react easily with halogens, forming addition compounds; substitutive halogenation takes place under certain conditions, forming allylic halides (Chart 7).

Halogen atoms in aliphatic halides may be replaced by halogens preceding in the atomic series. Fluoro- or fluorochlorohydrocarbons usually are obtained by replacement of chlorine with fluorine in chlorohydrocarbons. Products of chlorination only are shown in this chart as representative of products obtained by halogenation of natural gas hydrocarbons, as the greatest laboratory and commercial attention has been given to chlorination.

