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APRIL 1940

UNITED STATES  
DEPARTMENT OF THE INTERIOR  
HAROLD L. ICKES, SECRETARY

BUREAU OF MINES  
R. R. SAYERS, DIRECTOR

INFORMATION CIRCULAR

UTILIZATION OF NATURAL GAS FOR CHEMICAL PRODUCTS



BY

HAROLD M. SMITH  
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INFORMATION CIRCULAR

UNITED STATES DEPARTMENT OF THE INTERIOR - BUREAU OF MINES

UTILIZATION OF NATURAL GAS FOR CHEMICAL PRODUCTS<sup>1/</sup>

By Harold M. Smith<sup>2/</sup>

Natural gas has been used as a fuel and source of energy almost from its discovery, but its use as a chemical raw material may be said to have begun in 1918, when Brooks and Humphrey<sup>3/</sup> showed the presence of alcohols in the diluted acid oil obtained by the sulfuric acid treatment of cracked petroleum distillates. However, development of the utilization of natural gas for chemical syntheses was slow, partly because erroneous ideas existed regarding the nonreactivity of the hydrocarbons composing natural gas. Data accumulated by petroleum chemists throughout the world, particularly since about 1930, have shown that these hydrocarbons will react when activated by the effects of heat, pressure, chemical reagents, and light; also that the reactions can be made to proceed at practicable speeds and to provide good yields of useful products with moderate operating conditions, especially if catalysts are employed. As these results became known, the possibility of a synthetic organic chemical industry based upon these reactions became apparent, and today this industry is large and growing rapidly in importance.

In this paper the story of the manufacture of chemical products from natural gas is told simply in graphic form. The industry is developing so rapidly that some products may have been omitted, but every effort has been made to include all that are important or likely to become so. The difficulty of keeping information of this type up to date is shown by reference to an information circular<sup>4/</sup> on the same subject published by the Bureau of Mines in 1930, in which the important products are shown on a single chart, whereas five charts are employed for the same purpose at present.

<sup>1/</sup> The Bureau of Mines will welcome reprinting of this paper, provided the following footnote acknowledgment is used: "Reprinted from Bureau of Mines Information Circular 7108."

<sup>2/</sup> Petroleum chemist, Bureau of Mines, Bartlesville, Okla.

<sup>3/</sup> Brooks, B. T., and Humphrey, I., The Action of Concentrated Sulfuric Acid on Olefins, With Particular Reference to the Refining of Petroleum Distillates: Jour. Am. Chem. Soc., vol. 40, 1918, pp. 822-856.

<sup>4/</sup> Smith, H. M., Possible Utilization of Natural Gas for the Production of Chemical Products: Bureau of Mines Inf. Circ. 6388, 1930, 5 pp.

It would be desirable to include brief descriptions of some of the processes, but operating conditions are so varied that no simple method of explanation seems possible. The subject of catalysts also is so complex that it cannot be covered adequately in a report of this type. The nontechnical reader is interested mainly in the general picture shown by the 10 charts; the technical reader will be able to obtain from the references given such chemical and engineering information as is generally available.

#### Chart I.

Chart I shows the general composition and major uses of natural gas. The percentage of the various components in natural gas varies greatly, but "wet" gas typical of much of that produced lies within the following limits in percent by volume: Methane, 80-90 percent; ethane, 5-10 percent; propane, 3-5 percent; isobutane and butane, 1-2 percent; pentanes and hexanes, 1-2 percent. Chart I also indicates that portion of natural gas, namely, "dry" and "liquefied" gas, with which this paper deals.

#### Chart II.

The upper graph of chart II shows the consumption of natural gas in 1938 for domestic, commercial, and industrial purposes. Unfortunately, figures for the quantity of natural gas used in the manufacture of synthetic chemicals have not been segregated, but are included under "other industrial" uses. The graph at the lower left shows the great increase in production of non-coal-tar synthetic organic chemicals from 1925 to 1938. However, statistics showing the proportion of increase due to synthesis from natural gas are not available. The graph on the right shows the consumption of liquefied propane and butane; statistics of the amounts used in chemical manufacture indicate a considerable increase from 1936 to 1938. The 31 million gallons used in 1938 would represent about 1 billion cubic feet in the gaseous state.

#### Chart III.

At present there are four basic methods of converting natural-gas hydrocarbons to other products. These are named, defined, and illustrated by examples in chart III. "Dehydrogenation" is considered as one type of "decomposition" and included under that heading. A few words concerning methane may be needed. Although it is the major constituent of natural gas, it was not chosen to illustrate the reactions because in most instances it requires severe operating conditions, and the reactions are difficult to control. Methane can be decomposed by heat to give unsaturated gases and aromatic liquids, but extreme temperatures are necessary, and the processes are not economically feasible at present. Oxidation of methane is being carried out at present, and chlorination of methane is possible, but it is difficult to control the conditions so as to give a good yield of a single product rather than a mixture of three or four products.

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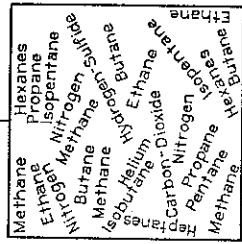
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CHART I

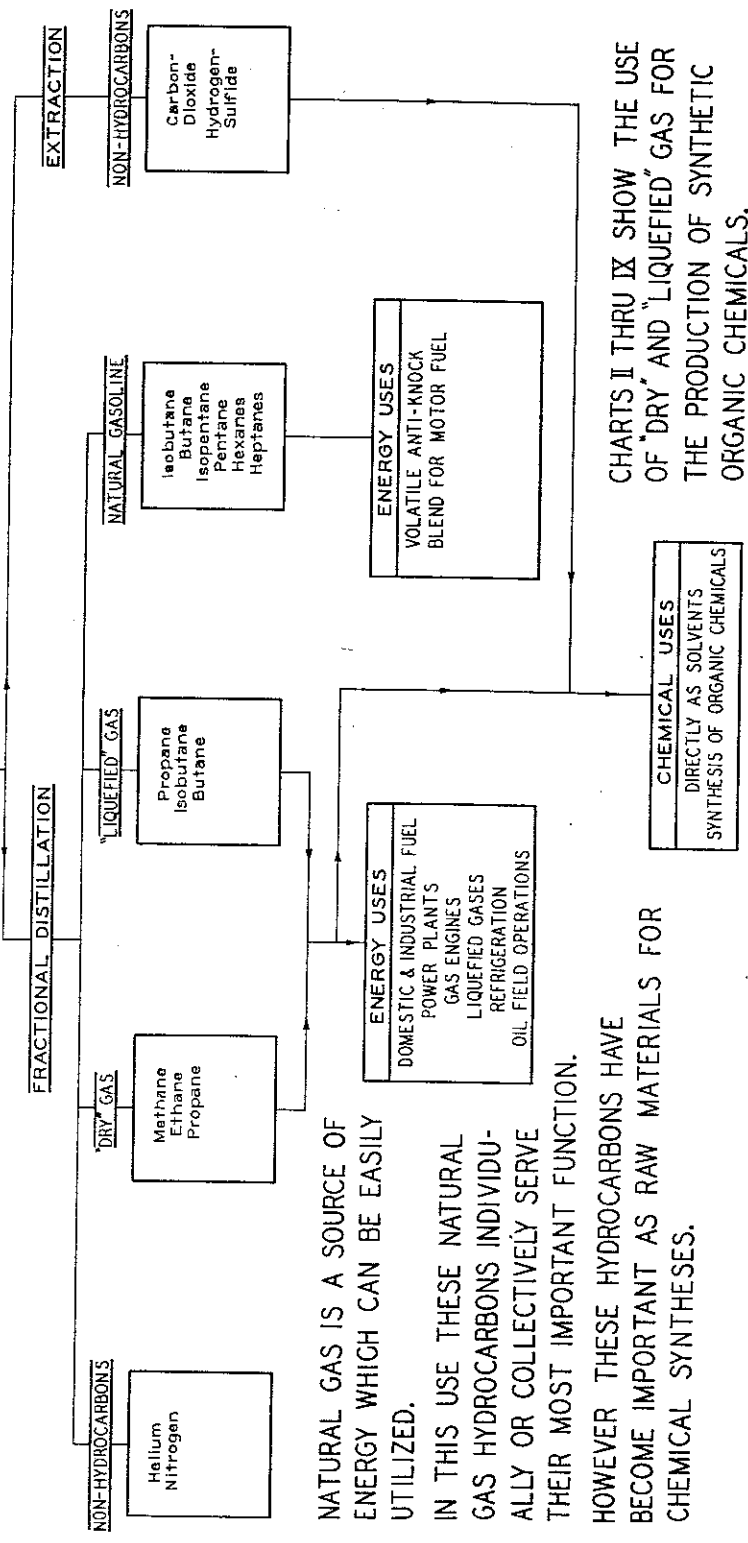
**NATURAL GAS**

NATURAL GAS IS A MIXTURE OF HYDROCARBON AND NON-HYDROCARBON GASES. THE SEVERAL HYDROCARBON COMPONENTS MAY BE SEPARATED FROM EACH OTHER BY FRACTIONAL DISTILLATION. IN THE FIRST SEPARATION THREE GROUPS OF PRODUCTS MAY BE MADE.



THERE IS SOME OVERLAPPING BETWEEN THESE GROUPS, AS SHOWN BELOW. BY FURTHER FRACTIONAL DISTILLATION THE INDIVIDUAL COMPONENTS CAN BE ISOLATED WHEN DESIRED. SOME NON-HYDROCARBON GASES ARE SEPARATED BY EXTRACTION WITH SOLVENTS.

**GROUP SEPARATION**



NATURAL GAS IS A SOURCE OF ENERGY WHICH CAN BE EASILY UTILIZED. IN THIS USE THESE NATURAL GAS HYDROCARBONS INDIVIDUALLY OR COLLECTIVELY SERVE THEIR MOST IMPORTANT FUNCTION. HOWEVER THESE HYDROCARBONS HAVE BECOME IMPORTANT AS RAW MATERIALS FOR CHEMICAL SYNTHESSES.

CHARTS II THRU IX SHOW THE USE OF "DRY" AND "LIQUEFIED" GAS FOR THE PRODUCTION OF SYNTHETIC ORGANIC CHEMICALS.

CHART II

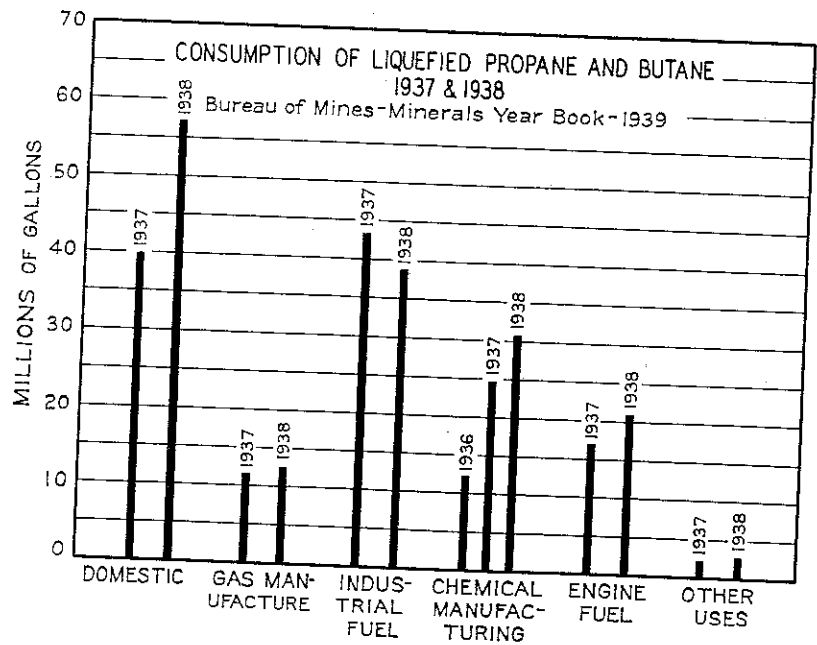
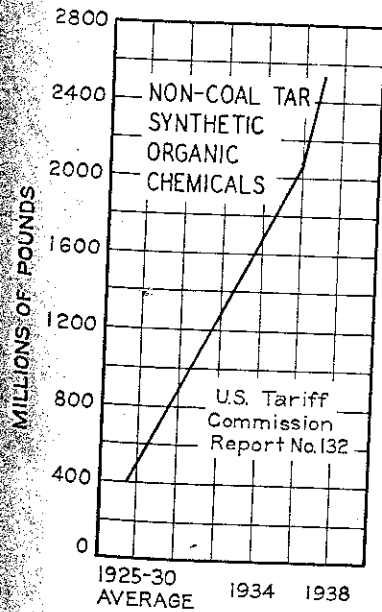
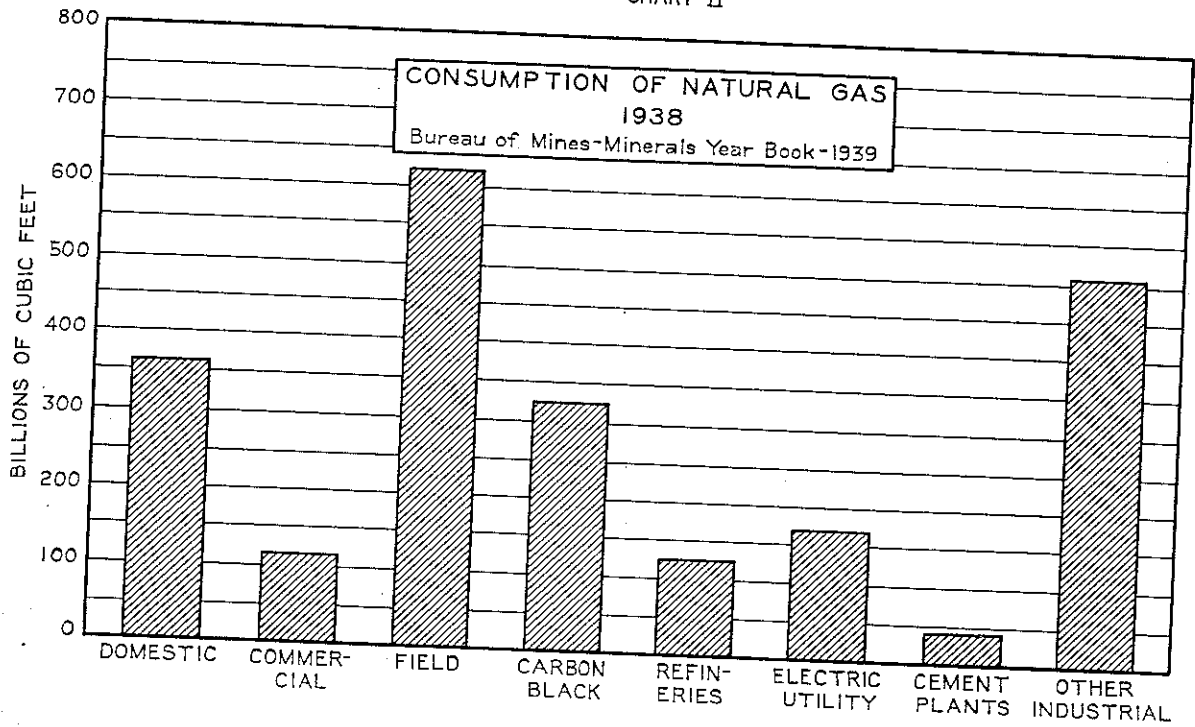
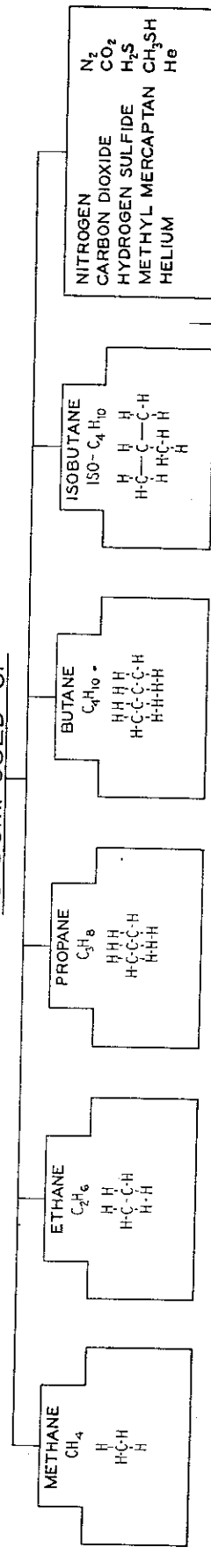


CHART III

# "DRY" AND "LIQUEFIED" NATURAL GAS IS COMPOSED OF



## THESE HYDROCARBONS MAY BE CONVERTED TO OTHER PRODUCTS BY

**DECOMPOSITION (1)**  
Splitting the hydrocarbon molecule into fragments by heat alone (pyrolysis), with the aid of catalysts, or by electric discharge, and generally including, especially in pyrolysis, the recombination of these fragments into new products.  
SEE CHART VI

**OXIDATION (2)**  
Reaction of the hydrocarbon molecule with oxygen, air, or oxygen-containing compounds activated by heat or catalysts, whereby oxygen is introduced into the hydrocarbon molecule, or the molecule is changed to carbon monoxide and hydrogen or finally carbon dioxide and water.  
SEE CHART VII

**HALOGENATION (3)**  
Reaction of the hydrocarbon molecule with a halogen, generally chlorine, activated by heat, light or catalysts, whereby one or more halogen atoms are introduced into the hydrocarbon molecule by replacing an equivalent number of hydrogen atoms.  
SEE CHART VIII

**NITRATION (4)**  
Reaction of the hydrocarbon molecule with nitric acid in the vapor phase, activated by heat, whereby a nitro group, NO<sub>2</sub>, is introduced into the hydrocarbon molecule by replacing a hydrogen atom.  
SEE CHART IX

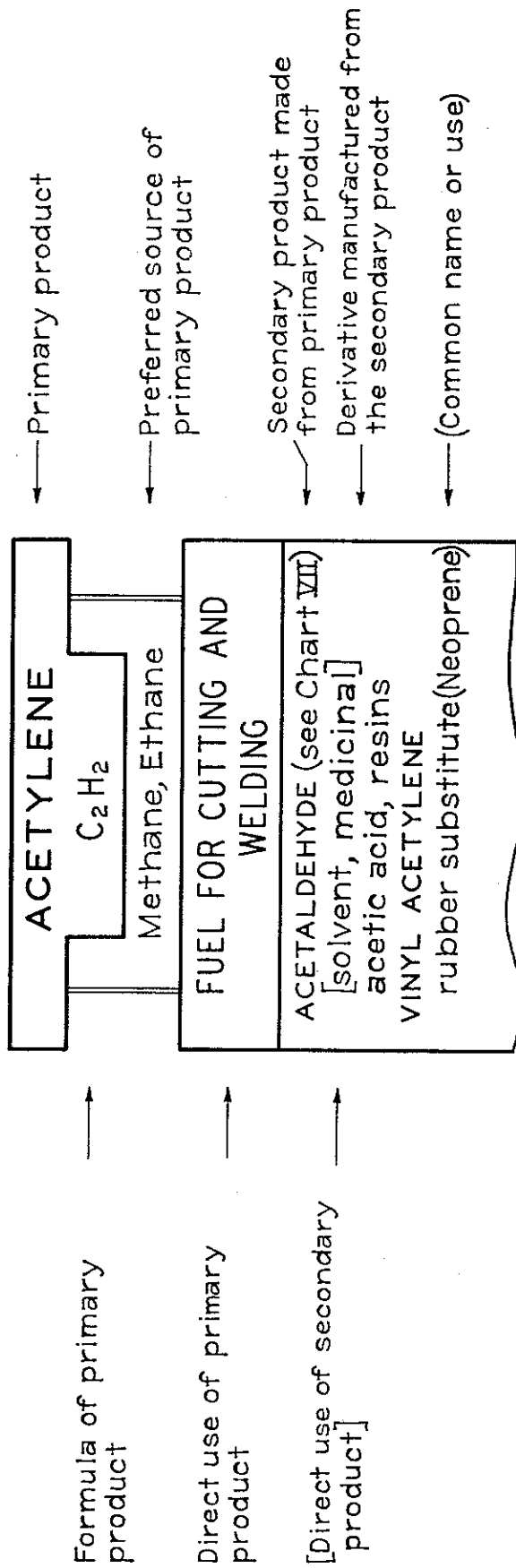
These usually minor constituents may be commercially important when present in sufficient quantities. Modern solvent extraction methods have made the utilization of hydrogen sulfide of industrial interest, and the Government has extracted helium from natural gas for inflation of lighter-than-air craft and for other uses for more than 20 years.  
SEE CHART X

## EXAMPLES OF THESE REACTIONS WITH ETHANE ARE

- (1)  $C_2H_6 \xrightarrow{\text{Heat, Catalysts}} H_2 + C_2H_4$
  - (2)  $2C_2H_6 + O_2 \xrightarrow[\text{Catalysts}]{\text{Heat, Pressure}} 2C_2H_5OH$
  - (2)  $C_2H_6 + H_2O \xrightarrow{\text{Heat, Catalysts}} 5H_2 + C_2H_4$
  - (3)  $C_2H_6 + Cl_2 \xrightarrow[\text{Catalysts}]{\text{Heat, Light}} C_2H_5Cl + HCl$
  - (4)  $C_2H_6 + HNO_3 \xrightarrow{\text{Heat}} C_2H_5NO_2 + H_2O$
- $C_2H_6 + O_2 \xrightarrow[\text{Catalysts}]{\text{Heat, Pressure}} 2C_2H_5OH$   
 Ethane + Oxygen → Ethyl alcohol  
 $C_2H_6 + 2H_2O \xrightarrow{\text{Heat, Catalysts}} 5H_2 + C_2H_4$   
 Ethane + Steam → Hydrogen + Carbon monoxide  
 $C_2H_6 + Cl_2 \xrightarrow[\text{Catalysts}]{\text{Heat, Light}} C_2H_5Cl + HCl$   
 Ethane + Chlorine → Ethyl chloride + Hydrogen chloride  
 $C_2H_6 + HNO_3 \xrightarrow{\text{Heat}} C_2H_5NO_2 + H_2O$   
 Ethane + Nitric acid → Nitroethane + Water



CHART V





Nitration of methane is possible if operating conditions are drastic enough. Thus, methane, the most prevalent of all hydrocarbon gases, is more resistant to chemical treatment than the others, and its reactions are less typical as is often true for first members of an homologous series of compounds. The utilization of methane other than as a gaseous fuel is still a problem awaiting solution.

This brief discussion regarding methane also brings out the fact that for each hydrocarbon there is one set of operating conditions - temperature, pressure, and contact time - that will provide optimum yields. For this reason it is often desirable to segregate the hydrocarbons as individuals or small groups. For example, if it is desired to decompose propane thermally to produce propylene, then any butane, pentane, or other higher-molecular-weight hydrocarbons should be removed. These heavier compounds react to produce undesirable products under conditions suitable for propane. On the other hand, methane and ethane would react very little, and would serve largely as diluents to decrease the extent of the propane decomposition.

#### Chart IV.

Chart IV gives in some detail the relationship between various reactions that may be applied to ethane. No attempt is made to show the mechanism of the reactions indicated - simply the over-all results. The (+) sign before a product name means that the product is added, and the (-) sign means that the product is removed. Text books on organic chemistry describe the conditions under which such reactions will occur. The chart is by no means complete and is presented only to illustrate the types of reaction possible in the synthesis of products from gaseous hydrocarbons.

#### Chart V.

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

Primary product.- A product obtained directly by the application of one of the four basic methods of conversion given in chart III.

Preferred source.- Not necessarily the only source, but the material reacting most easily or with the best yields.

Direct use.- A use, (1) in which no chemical change occurs in the substance, as when it is used as a solvent or anesthetic; or, (2) 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 and uses of secondary products and their derivatives are indicated in parentheses.

Charts VI - IX.

Charts VI, VII, VIII, and IX show the development of chemical syntheses from the primary products obtained by the application of the four methods of hydrocarbon conversion shown in chart III. Space does not permit naming all secondary products. For example, one company lists about 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 materials and in most cases as the most important raw material." Williams<sup>5/</sup> shows a chart of 71 products that can be made, beginning with just one olefin, isobutylene. A company manufacturing nitration products lists 54 derivatives as an incomplete list of those that can be made available easily. These data show the impracticability of listing all the products, and indicate the magnitude of the industry being built with natural gas as a raw material. It should be mentioned that a well-established group of organic compounds also is being prepared from the pentanes, which are not constituents of "dry" or "liquefied" natural gas. They are present, however, in natural gasoline.

Chart X.

Certain constituents of natural gas are not hydrocarbons and usually are present in relatively small amounts. Some of these materials, such as helium, are valuable even when present only to the extent of a few percent. Others, such as hydrogen sulfide, are a source of trouble and must be removed even when they are present in small quantities. Hydrogen sulfide is an example of one of the generally objectionable nonhydrocarbon gases, which may become valuable when it is removed from the other components of natural gas and converted into useful products.

Some natural gases have a composition of nearly 100 percent carbon dioxide. Carbon dioxide from this source may be of value if the wells from which it is produced are geographically situated so that the gas may be utilized economically. So far, no economic use for nitrogen in natural gas has been developed.

ACKNOWLEDGMENTS

Collection and arrangement of the information presented in this paper were carried out under the general supervision of R. A. Cattell, chief engineer, Petroleum and Natural Gas Division, Bureau of Mines, Washington, D. C., and N. A. C. Smith, supervising engineer, Petroleum Experiment Station, Bartlesville, Okla.

5/ Williams, E. C., *Creating Industries, 1919-1939* — Petroleum: Chem. Ind., vol. 44, May 1939, p. 495.

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CHART VI. PRODUCTS OBTAINABLE FROM NATURAL GAS HYDROCARBONS BY DECOMPOSITION  
THERMAL-CATALYTIC-ELECTRIC

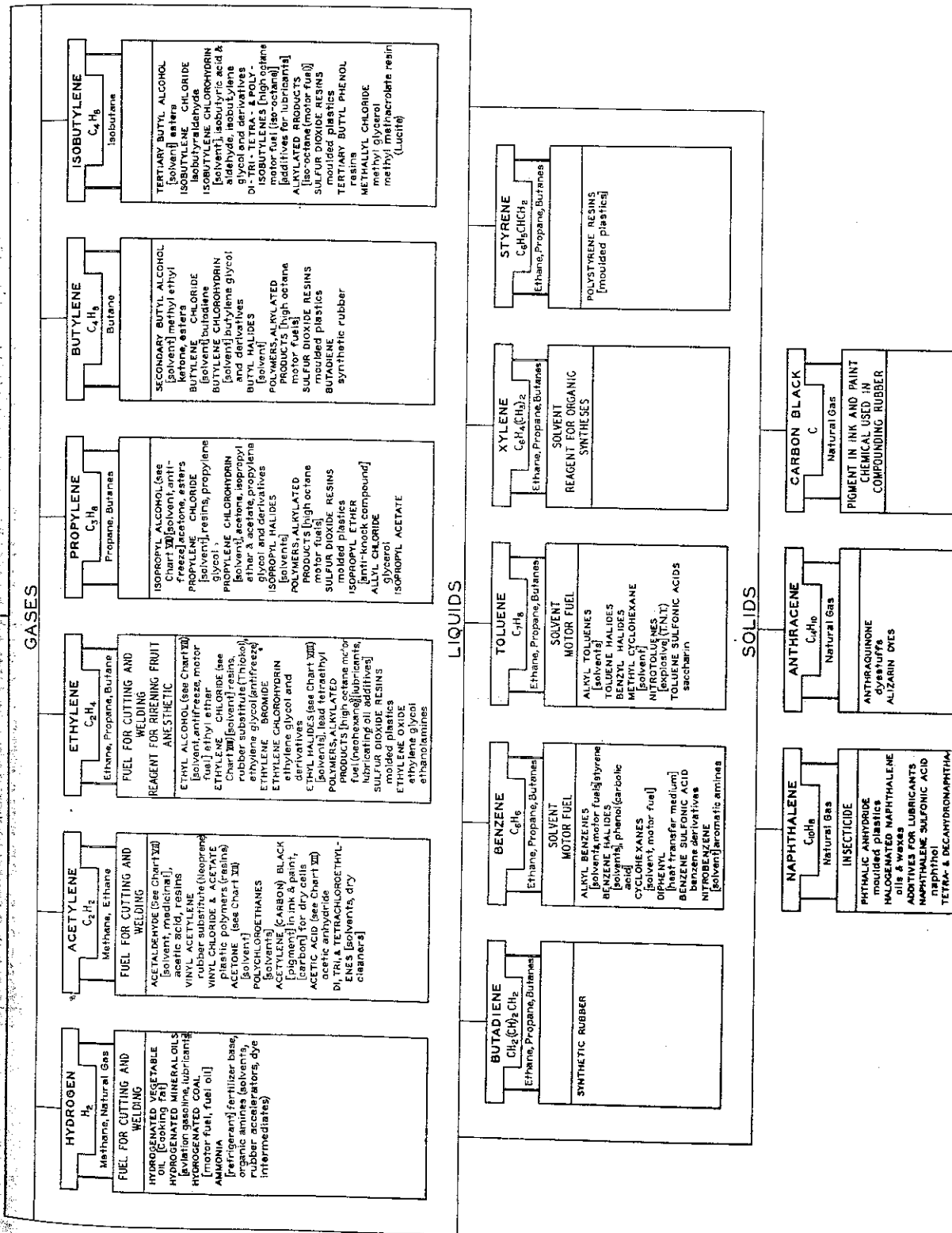


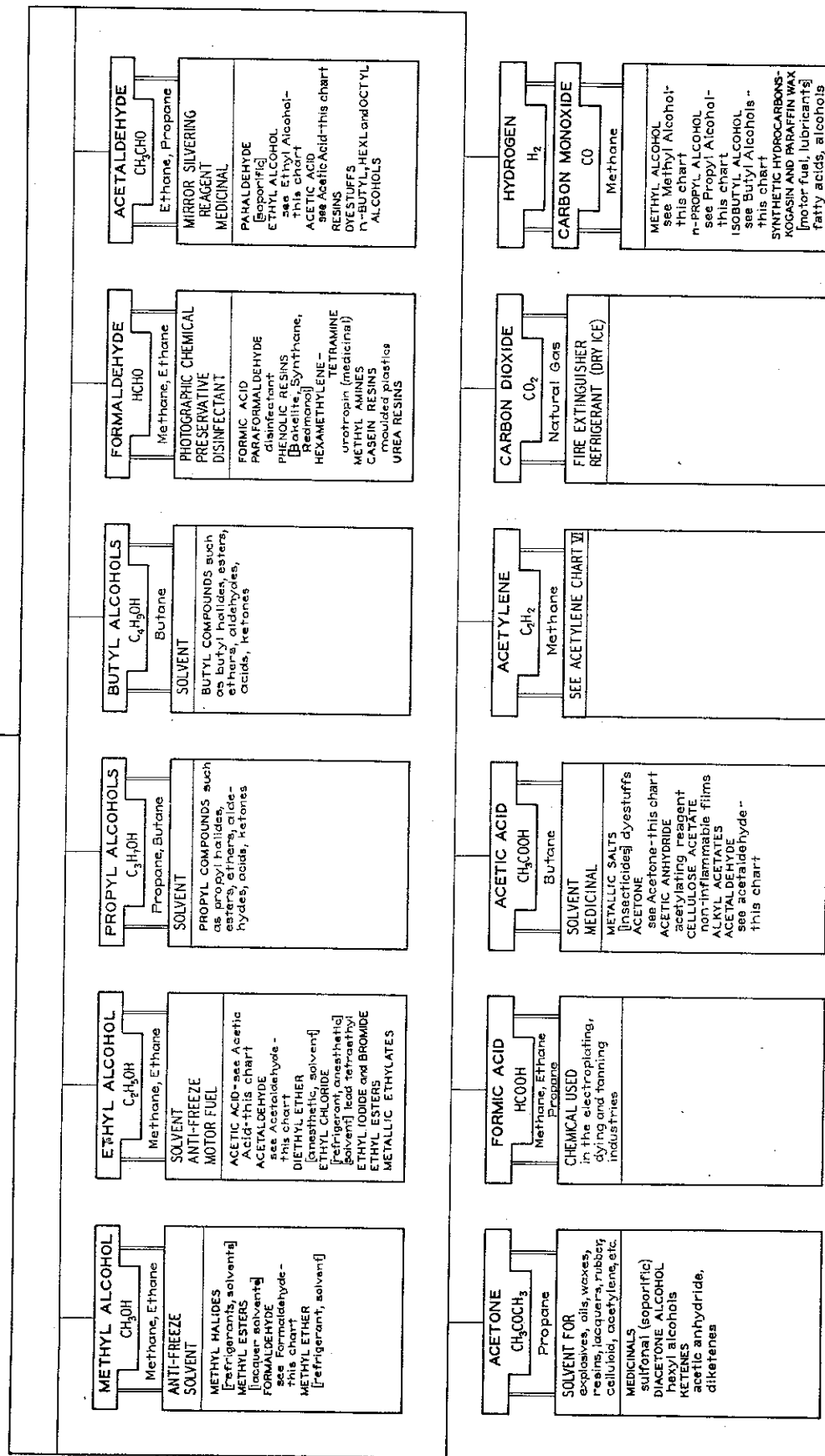
CHART VII

PRODUCTS OBTAINABLE FROM NATURAL GAS HYDROCARBONS

BY

OXIDATION

THERMAL-CATALYTIC-PRESSURE



# PRODUCTS OBTAINABLE FROM NATURAL GAS HYDROCARBONS

CHART VIII

BY

## HALOGENATION

THERMAL - CATALYTIC - PHOTOSYNTHETIC

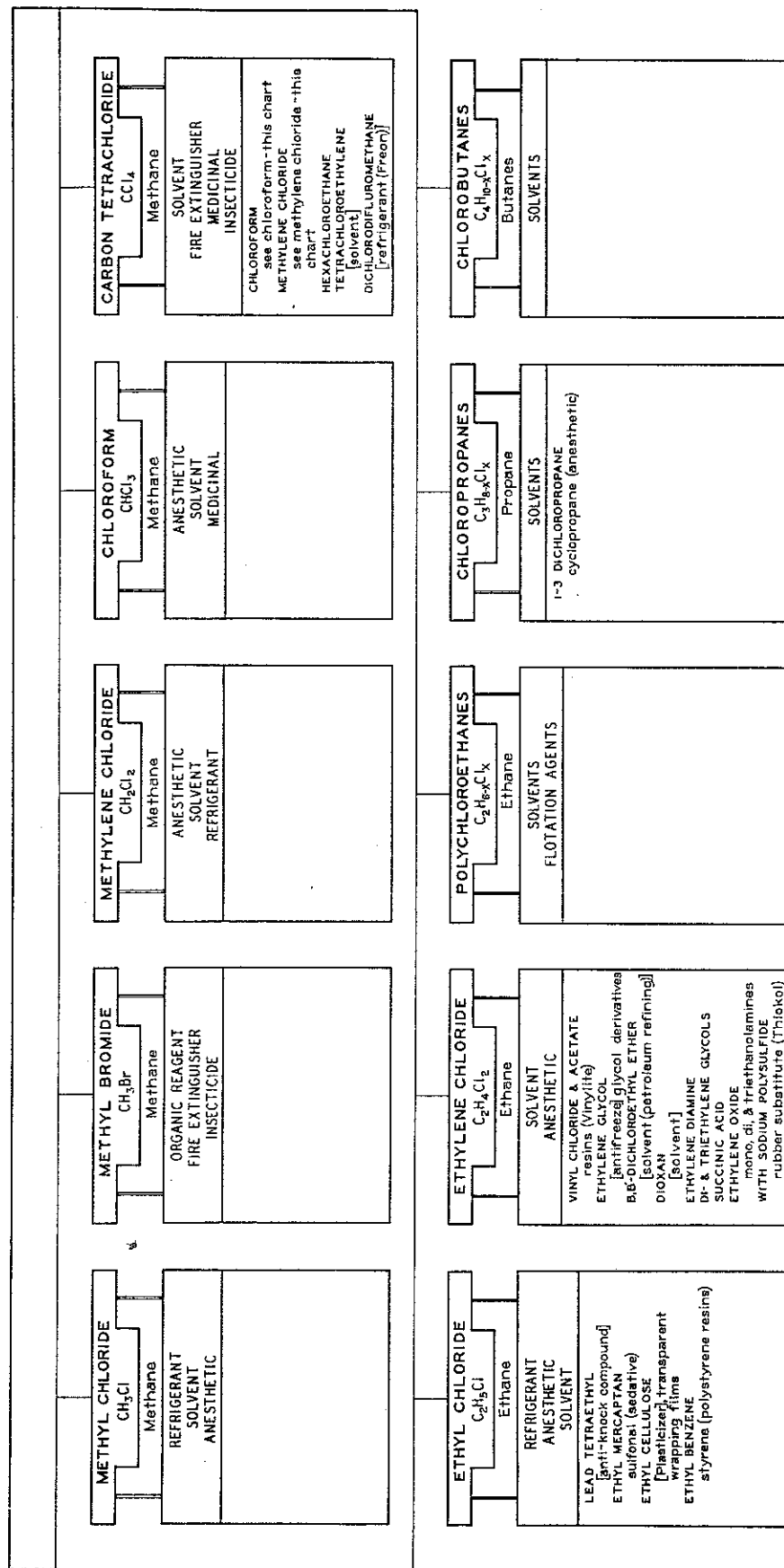
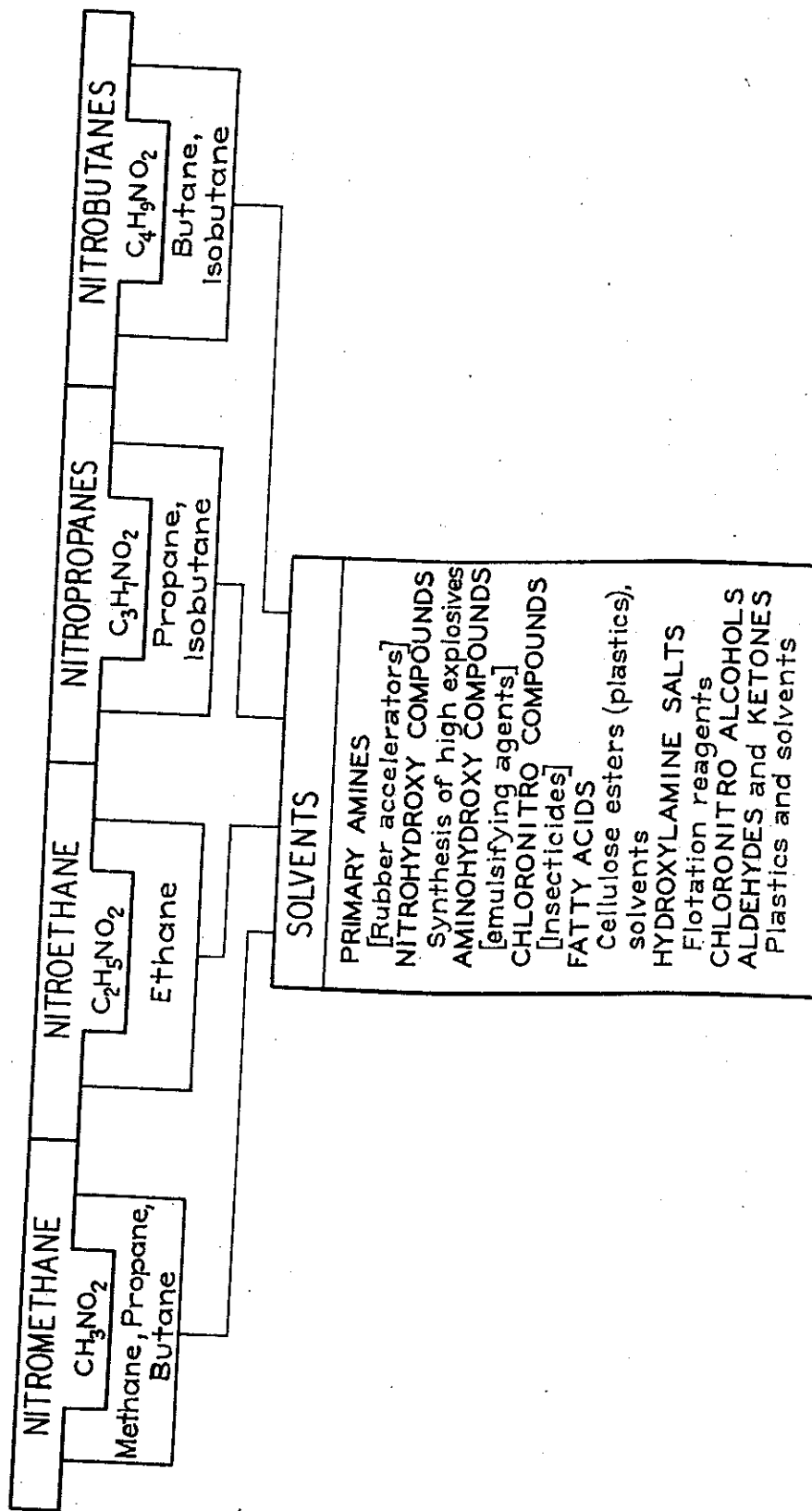


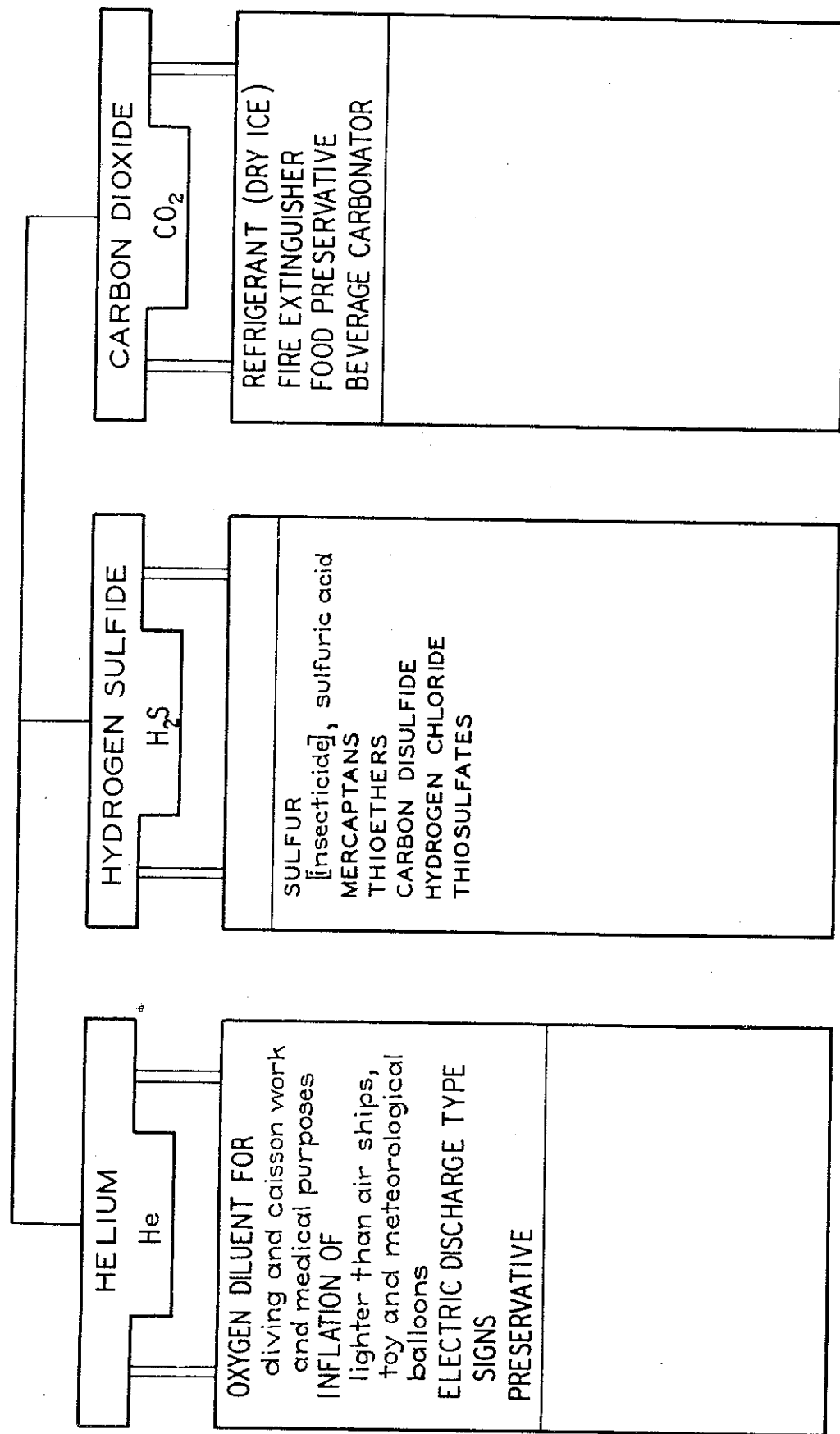
CHART IX  
 PRODUCTS OBTAINABLE FROM NATURAL GAS HYDROCARBONS  
 BY

NITRATION  
 THERMAL



# USES OF NON-HYDROCARBON NATURAL GAS CONSTITUENTS

CHART X



Much of the information contained in this circular was obtained directly from companies in the petroleum and chemical industries in reply to requests for data relating to hydrocarbon utilization. The response to these requests was gratifying, and the writer is pleased to acknowledge his indebtedness to all who contributed.

The writer is also particularly appreciative of the criticisms of the paper by members of the Petroleum Division both at Bartlesville and the other stations and field offices, by members of petroleum company laboratories, by Dr. H. B. Hass, head of the Department of Chemistry at Purdue University, Lafayette, Ind., and J. C. Walker, general superintendent, Chemical Division, Cities Service Oil Co., Bartlesville, Okla. The charts were drawn by Ralph Wright and Russell Himmelright of the Bartlesville Station.

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