Brief review of the status of production of fatty

HENKE, G. See abs. 164. HENSELING, F. See abs. 2219. HENSINGER, G. See abs. 1969. HERBERT, W. See abs. 137.

1402. HERBERT, W., AND RUPING, H. [Recovery With Activated Carbon of Benzine and Gas Oil From the Residual Gases From the Synthesis of Benzine by the Fischer-Tropsch-Ruhrchemie Process.] Chem. Fabrik, vol. 13, 1940, pp. 149-153; Chem. Abs., vol. 34, 1940, p. 4888.

Activated C Supersorbon absorbs 20% of benzine before permitting any loss in the exit gas from the absorber, and with proper operation, 1 lb. will produce over 1,000 lb. of product. With the plant operating for total benzine recovery the steam for regenerating is 2.5 lb. per lb. of benzine. The recovery of oil gas (3and 4-C hydrocarbons) is about 95%, at which capacity the steam consumption is 3.5-4.0 lb. per lb. product. When both products are recovered simultaneously at atmospheric pressure from a residual gas containing 35-45% CO2, the CO2 is absorbed to such an extent that it amounts to 50% of the recovered gases, and when the hydrocarbons are liquefied, it is absorbed and lowers the calorific value. The compression efficiency also is lowered. These difficulties are overcome by the fact that toward the end of charging activated C with compounds of different molecular weights there is an enrichment of the heaviest molecules at the entrance side of the apparatus and of the lightest at the exit side, so that a fractional separation can be effected during regeneration. A flowsheet of a plant is shown, with some operating directions. At present 22 plants are operating or under construction with a daily capacity of about 1,400 tons of total product. Results with activated C and with oil washing are compared.

1403. HERBST, H. [Cracking of Tar and Mineral Oil at Ordinary Pressure Without Hydrogen as Opposed to Berginization.] Petrol. Ztschr., vol. 22, 1926, pp. 947-949; Chem. Abs., vol. 21, 1927, p. 2378.

Brown-coal coke may be gasified and synthetic petroleum products obtained from it.

1404. Herbst, M. [Temperature Resistance of a New Hexagonal Iron Carbide in Catalysts for the Hydrocarbon Synthesis According to F. Fischer.] FIAT Reel R-19, 1942, frames 7,136-7,147, P. B. 73,594; TOM Reel 300.

Tests described in the report concern a new hexagonal Fe carbide (Fe.C) discovered in 1938 and found in the Fe catalysts used for Fischer gasoline synthesis. The X-ray examination showed that the new Fe carbide is an essential constituent for the activity of the Fischer catalysts. In the temperature range 290°-330°, the new Fe carbide is converted into the Fe<sub>2</sub>C described by Hägg. This conversion temperature is considerably higher when the Fe catalysts contain Cu. It was determined that with a Cu content of 2% the conversion temperature is about 350°-400° and with 7.4% of Cu. 430°-450°. It may be seen that cuprous Fe catalysts in the Fischer synthesis are less sensitive to temperature, and that a catalyst with 7% Cu tolerates a temperature 100° higher than a catalyst free of Cu. Includes 2 tables.

1405. HERINGTON, E. F. G. Ethylene and Acetylene Adsorption in Hydrogenation Catalysis. Trans. Faraday Soc., vol. 37, 1941, pp. 361-366; Chem. Abs., vol. 35, 1941, p. 7274.

Conditions of atomic separation for the chemisorption of C.H. and C.H. on the crystal facets of Ni and Co are compared. Whereas C.H. should be held on the short spacing, 2.47 A., C.H. will be held on the long,

3.50A. Adsorbed C-H, has no free valences, whereas C2H2 is potentially reactive. This is in agreement with experience, since C2H2 will polymerize in the presence of H2 and a Co catalyst, although C2H4 is merely hydrogenated to C2H4. Support for these views is found in the different behaviors of these gases in the Fischer-Tropsch synthesis: When C2H, or C2H2 is introduced in the mixture of CO and H2 used in this synthesis C2H4 is incorporated in the oil products and in addition yields liquids containing O2; on the other hand, it was found that the products from a mixture of C2H2, CO and H2 are indistinguishable from a mixture of the C2H2 plus H2 and CO plus H2 products and do not contain appreciable quantities of O-containing compounds.

. Study of the Mechanism of Polymerization Reaction by Means of Size-Distribution Curves. Trans. Faraday Soc., vol. 40, 1944, pp. 236-240; Chem. Abs., vol. 38, 1944, p. 6170.

Degree of polymerization must be known to obtain information on the mechanism. A great simplification in the theoretical treatment, together with the avoidance of many of the practical difficulties, results if the reaction is allowed to proceed to a small extent (5-10%), preferably in dilute solution. 3 types of distribution curves are distinguished: (1) The molecular yield decreases continuously as the chain length increases; this can be terminated either by monomer formation, disproportionation, or transfer in conjunction with either of these; (2) the curve rises from 0 at very small chain length, passes through a maximum, and then decreases as chain length increases, terminated by some combination of mechanisms; (3) the curve commences at real finite values, passes through a maximum and decreases; may be terminated either by (a) monomer formation, disproportionation or transfer, where velocity of termination/propagation increases with chain length, or (b) transfer and combination occurring at the same time. Distribution curves taken in conjunction with other considerations can extend knowledge of polymerization reactions

1407. HERRINGTON, E. F. G., AND RIDEAL, E. K. Poison<sup>2</sup> ing of Metallic Catalysts. Trans. Faraday Soc., volt 40, 1944, pp. 505-516; Chem. Abs., vol. 39, 1945, p.

Phenomena of poisoning are examined to determine whether they are compatible with the hypothesis that uniform crystal facets rather than active patches are the sites of catalytic activity. These considerations are restricted to the active hydrogenating catalysts, for example, Ni, Co, Pt, Pd, in the face-centered cubic form where the reaction velocity in simple hydrogenation is usually of zero order in respect to the material under going hydrogenation. It is assumed that the rate is proportional to the surface concentration of the given reactant. If after poisoning with a substance that occupies 1 active center, a fraction  $\theta$  of the active spots is bare and an isolated group of n centers is required; for reaction, then the number of unpoisoned groups is proportional to  $\theta^n$ . With this mechanism, the plot of activity against poison concentration is linear throughout the entire poison range only when N=1Much of the observed behavior during the poisoning of heterogeneous catalysts can be duplicated by the poisoning of a uniform set of sites. It is stated that an explanation of catalytic behavior requiring active spots appears in many cases to be unnecessary.

1408. HERINGTON, E. F. G., AND ROBERTSON, A. Infil. ence of Reaction Mechanism on Size Distribution in Polymers. Trans. Faraday Soc., vol. 38, 1942. pp. 490-501; Chem. Abs., vol. 37, 1943, p. 1318.

Where the polymer grows by successive addition active radicals, the distribution curves of reaction product can be derived for the general case where the ratio of termination coefficient to the propagation coefficient is considered to vary with chain length. It is assumed first that the initiation rate remains constant over the period considered. Only those polymerizations are considered in which the mean life of the active chain centers is very small compared with the half life of the total reaction, so that application of the stationary state treatment is permissible. It is most desirable to have approximate instantaneous experimental distribution curves.

1409. HERINGTON, E. F. G., AND WOODWARD, L. A. Experiments in the Fischer-Tropsch Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen. Trans. Faraday Soc., vol. 35, 1939, pp. 958-966; Brennstoff-Chem., vol. 20, 1939, pp. 319-324; Chem. Abs., vol. 33, 1939, p. 9583.

Catalyst of the following composition by weight was used throughout: Co: ThO2: kieselguhr=100:18:100. Oil synthesis can be insured by breaking in the catalyst in a suitable manner, that is, by keeping the temperature well below 150° when the synthesis gas is first admitted (following the treatment with H2), the temperature should then be raised very slowly. Under otherwise similar conditions of reaction, a high H2: CO ratio in the ingoing gas favors the formation of hydrocarbons of lower molecular weight. Most of the revivifying effect of the H2 on a used catalyst is shown to be due to chemical interaction. The addition of S compounds during the reaction at first causes an increased production of hydrocarbons of higher molecular weight. Treatment with H2 at 375° destroys the preferential S resistance of centers, so that, with a partly poisoned catalyst, an increase in poisoning may result owing to redistribution of the S.

HERRMANN, K. Sec abs. 1356.

1410. HERROUN, E. F., AND WILSON, E. Magnetic Susceptibility of Certain Natural and Artificial Oxides. Proc. Phys. Soc. (London), vol. 33, 1921, pp. 196-206; Chem. Abs., vol. 15, 1921, p. 3023.

Susceptibility of Fe<sub>2</sub>O<sub>3</sub>, as occurring in nature, varies through a wide range, but in the case of artificial preparations the range of variation seems to be much greater. The highest susceptibility exhibited by Fe2O2 occurs when either FeO or Fe<sub>3</sub>O<sub>4</sub> is oxidized at a high temperature in the anhydrous condition. From hydrated Fe.O., the susceptibility, though considerable, is much less. The lowest susceptibility is obtained from native hematites or naturally oxidized chalybite or by the ignition or precipitation of ferric salts. It appears that the passage through the stage of Fe<sub>2</sub>O, impresses more pronounced magnetic properties upon the resulting Fe<sub>2</sub>O<sub>2</sub>. The susceptibilities of a number of ferrites were measured, of which that of Cu ferrite is most conspicuous, being higher than those of Co or Ni ferrites or any similarly constituted compound except Fe.O. itself. Heating feebly magnetic Fe.O. with a basic oxide, as CaO or MgO, increases susceptibility (confirming List and others). When higher susceptibility has been produced by heating Fe<sub>2</sub>O<sub>2</sub> with a basic oxide, such as Ag-O or HgO, subsequent removal of the metal leaves the Fe<sub>2</sub>O<sub>3</sub> in a magnetic condition. The chemical compounds formed when Fe<sub>2</sub>O<sub>3</sub> is replaced by Al<sub>2</sub>O<sub>2</sub> show no definite increase in susceptibility, which is in marked contrast with the ferrites. In the cases of Co and Mn the susceptibilities of the different oxides show a steady decrease with increase of O2, and, unlike Fe, there is no increase in the susceptibility of Co2O4 and Mn2O4 corresponding with Fe2O4. Although the susceptibility of Cu is negative, that of each of its oxides is positive but small in magnitude.

HETHERINGTON, H. C. See abs. 150.

1411. HEUBLUM, R. [Synthetic Fatty Acids in the Production of Soap.] Riv. ital. essenze, profumi, piante

offic., olii vegetali, saponi, vol. 20, 1938, pp. 236-237, 304-305; Chem. Zentralb., 1939, I, p. 4133

Patent review of the synthesis of fatty acids with a discussion of their use in soapmaking.

HEWLETT, H. See abs. 45.

1412. HEYD, F. Water-Gas Generation From Coal and Coke. Gas- u. Wasserfach, vol. 75, 973-974; Chem. Abs., vol. 27, 1933, p. 827.

While Heyd agrees in general with Dolch, he stresses the effect of the ash content of cokes as an important. factor in attaining the water-gas equilibrium (abs. 407, 713, 714, 2436).

1413. Hibshman, H. J. Separation of Iso- and Normal Paraffins by Adsorption. Ind. Eng. Chem., vol. 42, 1950, pp. 1310-1314; Chem. Abs., vol. 44, 1950, p. 9143.

Activated C selectivity adsorbs n-Cs, -Ce, and -C; paraffins from iso-octane at room temperature. Based on experimental data, a flow plan for a continuous separation of iso-octane and heptane is presented by using fluidized solids technique. C introduced at the top of a column falls countercurrently to the feed and liquid reflux streams introduced at the center and bottom, respectively. The C withdrawn at the bottom contains heptane in high purity, which is removed from the C by washing with pentane, the pentane and heptane being separated by distillation. The pentane on the C need not be removed before the C is reused, since it appears in the filtrate with the iso-octane and is separable by distillation. The fil-trate is 90% pure iso-octane. The process is analogous to the conventional extraction and distillation.

1414. HIDAKA. T. Winkler Water-Gas Producer: Jour. Fuel. Soc. Japan, vol. 19, 1940, pp. 1008-1015; in English, vol. 20, pp. 1-6a; Chem. Abs., vol. 35, 1941, p. 3062.

Describes the principle of the Winkler water-gas producer. Gives method and the results of operation.

HIDETAKA, S. Sec abs. 2504. HIEBER, G. See abs. 165.

1415. HIGHTOWER, J. V. Organics From Natural Gas. Chem. Eng., vol. 56, No. 1, 1949, pp. 92-94, 132-135.

MeOH, formaldehyde, and acetaldehyde are produced by oxidation of natural gas components near Winnie, Tex., by the McCarthy Chemical Co. The rated maximum amount of feed gas processed by the chemical plant is 100,000,000 cu. ft. per day. Oz of 90-95% purity is provided by a large, low-temperature unit of Hydrocarbon Research process design. The operation is described by the aid of a flowsheet.

1416. HILBERATH, F. [Composition of Synthetic Benzine From Carbon Monoxide and Hydrogen (Kogasin) and Suitability of Its Monoolefins for Production of Lubricating Oils.] Thesis, Keil, 1940, 79 pp; Feuerungstech., vol. 29, 1941, p. 191; Chem. Abs., vol. 36, 1942, p. 4316.

Fraction boiling below 100° of a Fischer-Tropsch synthetic benzine was separated into paraffins and olefins by means of Hg acetate, and the properties of narrow fractions of each series of hydrocarbons were determined. Some hydrocarbons of high purity were: isolated. Various methods of determining the I value of olefins were compared. The Kaufmann and Gross-Getringhaus methods proved satisfactory. Monoolefins were polymerized with AlCla. n-C.Has proved a-suitable chemically indifferent solvent for this purpose. The viscous oils obtained were compared with those obtained in the same manner from known olefins. The yield, viscosity, and pole height of the lubricating oils (mostly high-grade) depend on the structure of the olefins and particularly on the position of the double linking, for example, tertiary olefins yield oils with

poor pole heights. Results are presented in tables and

See abs. 1823, 1824, 1825, 1826.

HILDITCH, T. P. See abs. 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86.

1417. HILDITCH, T. P., AND HALL, C. C. Methanol Synthesis. Catalytic Processes in Applied Chemistry, D. Van Nostrand Co., New York, 2d ed., 1937, pp. 97, 99, 115.

1418. HILES, J., AND THOMPSON, J. K. Fischer-Tropsch Process. Fuel, vol. 21, 1942, p. 115.

Editorial covering developments in the United States at Bureau of Mines.

1419. HUL, D. G., AND KISTIAKOWSKY, G. B. Hydrogenation Over Metallic Cesium. Jour. Am. Chem. Soc., vol. 52, 1930; pp. 892-894; Chem. Abs., vol. 24, 1930, p. 2663.

Catalytic combination of H2 with C2H4 or CO but not with N2 occurs appreciably over metallic Cs at room temperature, though much more rapidly at 200°. The rate of combination is much retarded by the gradual formation of cesium hydride.

1420. HILPERT, S., AND DIECKMANN, T. [Iron Carbides and Their Catalytic Action on the Decomposition of Carbon Monoxide.] Ber. deut. chem. Gesell., vol. 48, 1915, pp. 1281-1286; Chem. Abs., vol. 9, 1915, p. 2847.

According to Boudouard, the oxides of Fe, Co, and Ni are the principal factors in the decomposition of CO; according to Schenk and Zimmermann, the free metals, not the oxides, act as catalysts. In their experiments Hilpert and Dieckmann confine themselves to a study of the catalyst. In every case pure Fe<sub>2</sub>O<sub>2</sub>, which had been heated previously, was used. The CO was carefully purified and dried. At 950° the tendency of CO to separate C is very slight. In spite of this, it is surprising that at this temperature the oxide is reduced to pure Fe. After 10 hr. at this temperature a gravish metallic product was obtained, which analyzed 99.8% Fe. At 850° the formation of carbide occurs rapidly, and at the same time the separation of C occurs. Below 800° the separation of C occurs very rapidly. The evident conclusion is that not the Fe itself but a carbide hastens the reaction. The material showed no trace of magnetic properties at 200°. Since pure Fe loses its magnetic property at 750° and the carbide at 200°, only the carbide could have acted as catalyst. The mechanism of the process probably is that the apparently stable carbide Fe C is broken down by the action of CO into a series of compounds rich in C, such as Fe<sub>2</sub>C and FeC. These are very unstable and tend to form Fe<sub>2</sub>C again, with separation of C.

HINSHELWOOD, C. N. See abs. 2746, 3263, 3407. 1421. HINSHELWOOD, C. N., AND HARTLEY, H. Influence of Temperature on Two Alternative Modes of Decomposition of Formic Acid. Jour. Chem. Soc., vol. 123, 1923, pp. 1333-1338; Chem. Abs., vol. 17, 1923,

1422. HINSHELWOOD, C. N., AND TOPLEY, B. Energy of Activation in Heterogeneous Gas Reactions With Relation to the Thermal Decomposition of Formic Acid Vapor. Jour. Chem. Soc., vol. 123, 1923, pp. 1014-1025; Chem. Abs., vol. 17, 1923, p. 2810.

1423. HINSHELWOOD, C. N., HARTLEY, H., AND TOPLEY, B: Influence of Temperature on Two Alternative Modes of Decomposition of Formic Acid. Proc Roy. Soc. (London), vol. 100, A, 1922, pp. 575-581, Chem. Abs., vol. 17, 1923, p. 914.

HINTERMAIER, A. See abs. 2877.

HIRAO, T. See abs. 1930.

HIROSE, S., NOBORI, N., AND NOGUCHI, M. Manufacture of Fatty Acids by the Oxidation of Paraffin. IV. Composition of Refined Fatty Acids. See als

Manufacture of Fatty Acids by the Oxidation of Paraffin. V. Methanol-Soluble Portion of the Unsaponifiable Matter. See abs. 1685. HIROTA, K. See abs. 1756, 1757, 1758.

1423. Hirsch, E. [Conversion of Methane.] Mem. soc. ing. civils France, vol. 85, 1932, pp. 286-302; British Chem. Abs., 1932, B, p. 919; Chem. Abs., vol. 27, 1933, p. 2282.

Experimental data on the critical temperature range, rate of flow through the reaction chamber, and the optimum H2O : vapor ratio are given for the conversion of CH, in natural and coke-oven gas into H2 or H-CO mixtures suitable for synthesis purposes. The difficulty of maintaining the strongly endothermic reaction at 1,200° is met by the use of specially designed regenerative heat exchangers.

-. [Manufacture of Synthetic Gasoline by the Société Courrières-Kuhlmann-Fischer-Tropsch Process.] Mem. soc. ing. civils France, vol. 90, 1937, p. 756-767. Chem. Abs., vol. 32, 1938, p. 9463.

From 1 m. of the mixture of CO+2 H a yield of 120-130 gm, of primary products was obtained. This mixture of open-chain paraffins and olefins has the composition: Gaseous products (C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>4</sub>H<sub>6</sub>, C<sub>4</sub>H<sub>6</sub>, C<sub>4</sub>H<sub>6</sub>) 8%; primary gasoline (boiling point<200°) 60%; gas oil (b. p.>200°) 22%; solid paraffins (m. p. 20°-100°) 10%. The primary gasoline can be used after a simple treatment. The heavier liquid hydrocarbons are converted to gasoline (octane index 65) by cracking. The octane index can be raised by admixture with alcohol or benzene or addition of PbEt. Primary gasoline is recovered from the gas oil by distillation.

[Heat Removal From Exothermic Catalyst Reactions.] Chaleur et ind., vol. 19, 1938, pp. 394-398; British Chem. Abs., 1938, B, p. 1012. Methods adopted in MeOH synthesis and the production of hydrocarbons by the Fischer-Tropsch process are given.

1427 --[Manufacture of Synthetic Gasoline According to the Fischer-Tropsch Process by the Société Courrières-Kuhlmann.] Rev. Carburants France, vol. 1, No. 12, 1938, pp. 505-509.

Describes process. The yield of hydrocarbons is about 65% theoretical. The primary products consist of S% gases; propane, propylene, butane, and butylene; 60% gasoline distilling below 200° C.; 22% gas oil distilling above 200°; and 10% solid paraffins melting at 20°-100°. The gasoline fraction is cracked to raise the octane number. This yields 80% motor fuel of 65 octane number, with very high Pb susceptibility. The gas oil has a cetene number of over 100 and can be blended with heavy oils of various origins. The Courrières-Kuhlmann Co. has built a synthesis unit of 20,000 tons annual capacity.

HIRSCH, J. H. See abs. 117.

1428. HIRSCHFELDER, J. O., AND BOYD, C. A. Physical-Chemical Approach to Reaction Kinetics. Jour. Chem. Education, vol. 27, 1950, pp. 127-135; Chem. Abs., vol. 44, 1950, p. 4759.

Discussion of the principles of reaction mechanism, catalysis, and reaction rates. 14 refs.

1429. HIRSCHKIND, W., AND LOWDERMILE, F. R. Fischer-Tropsch and Allied Processes. CIOS Rept. XXVII-82, 1945, 24 pp., PB 474; British Coal Utilization and Research Assoc., Monthly Bull. 10, 1946, abs. 942; TOM Reel 239.

Report of a visit to the Kaiser Wilhelm Institute für Kohlenforschung at Mülheim. Several completeplants and pilot plants were investigated. Flow sheets

and full operating conditions are given for: (1) Manufacture of synthesis gas from purified and H2-enriched water gas (80,000 m. per hr.); (2) normal pressure synthesis (description of steel converter embodying catalyst 30% Co, 10% ThO2 per MgO, 60% kieselguhr), the product was largely straight-chain paraffins, with a large quantity of liquid and small amounts of gases and solids: (3) medium-pressure synthesis, 11 atm. pressure. With Co catalyst, 190°-200°, products were equally liquids and solids. With Fe catalyst, 225°-240°, products were largely liquids with small amounts of solids and gases and more unsaturates than with Co; (4) olefin synthesis. The synthesis gas has a  $H_2$ : CO ratio of 1:1.25. 2 trains are used: 1 at 10-12 atm.; 2 at 1 atm. for working up the residual gases from 1. Co catalysts are used for both. Yields: Train 1, 10 gm. liquefiable gas and 120 gm. liquid per m. feed gas; train 2, 30 gm. solid products and 160 gm. liquid and gaseous products per m. feed gas.; (5) aldehyde synthesis. In the Oxo process aliphatic aldehydes are formed by catalytic reaction of water gas on olefins. The aldehydes are reduced to alcohols for production of detergents by sulfonation. The olefins are Cn-Cn with the double bond at the end of the chain. The reaction was carried out batchwise at temperatures rising 125°-145° and at 150 atm. pressure using the Co catalyst. A plant costing 11,000,000 RM was built having a capacity of 10,000 tons higher aliphatic alcohols C<sub>1-</sub>C<sub>2</sub>. Estimated cost of product 0.90-0.95 RM per kg., market price 2.50 RM per kg. 1 lb. olefin was equal to about 1 lb. distilled alcohol. Raw material and power consumption were as follows: Power 1.5 million kw.-hr, per yr. at 0.025-0.03 RM; H<sub>2</sub>O 200m.3 per hr.; water gas 750 m. per hr. at 0.03-0.035 RM per m. olefins 1,250 kg. per hr. at 0.38-0.40 RM per kg.; H<sub>2</sub> 400 m. per hr. at 0.00-0.70 RM per m. ; steam 300 tons per

1430. Hirst, L. L. Methanol Synthesis From Water Gas. Chemistry of Coal Utilization, vol. 2, 1945, pp. 1846-1868.

Review. Bibliography of 230 refs. -. See abs. 155, 156, 1677a, 3211, 3212.

1431. Hirst, L. L., Dressler, R. G., and Batchelder, H. R. Bureau of Mines Completes Gas-Synthesis Plant. Valve World, vol. 48, No. 1, 1951, pp. 98-103.

Describes recently completed gas-synthesis demonstration plant at Louisiana, Mo. The sections of the plant are those for oxygen production, coal gasification, synthesis-gas purification, hydrocarbon synthesis, and distillation and product recovery.

HIRTZ, H. See abs. 2304, 2305.

1432. Hochstrasser, J. [Catalytic Synthesis of Hydrocarbons by the Fischer-Tropsch Process.] Rev. quim ind., Buenos Aires, vol. 2, No. 19, 1949, pp. 10-13, 20; British Chem. Abs., 1950, B, I, p. 484.

Summary of effects of temperature, pressure, proportions of initial constituents fed to reaction chamber, and shape of reaction chamber on the type and quantity of the finished product. Contrasts process with the high-pressure Synthol process developed by the I. G. Farbenindustrie A.-G. Discusses use of Fe and thoriated Co catalysts.

1433. Hopgins, E. Coal. I. Industrial Darkness. II. Coal Miner Speaks. III. Fuel Revolution. Fortune, vol. 35, No. 3, 1947, pp. 85-95, 221-232; No. 4, pp. 99-105, 238-254.

Discusses the economy of the coal industry and lays special emphasis on the inefficiency of the methods for mining, transporting, and consuming it. In attempting to answer the question, "What shall we do about it?", the technology of the modern developments in the processing of coal and its consumption is presented. The one imperative requirement appears to be that coal

must be gasified, and it is from this viewpoint that the subject matter of this article is developed. Various developments are discussed: Underground gasification, total gasification by producer gas methods, such as the Winkler and Lurgi processes, the Bergius process of coal hydrogenation, the Fischer-Tropsch catalytic gas-conversion process, in particular the Americanized version, the Hydrocol process, and the powergas turbine. Only coal hydrogenation and shale oil are ruled out as being uneconomical compared with other processes. The most favorable method of coal beneficiation from an economic standpoint appears to be total gasification under pressure and oxidation at the mine into a high B. t. u. (600 B. t. u. and above) gas, supplemented if desired by a phase of the Fischer-Tropsch reaction to convert part of the CO and H2 into a rich blending gas, thus producing a rich fuel gas capable of pipeline transportation in direct competition with transported coal or petroleum at the point of consumption. Alternative methods are presented such as the method planned by the Pittsburgh Consolidation Coal Co. that leads from coal to gas, gasoline, and chemicals, or the Hydrocol process or a modification thereof adapted to coal instead of natural gas. It is believed that, given consistent development of the new technology, consumption of coal would rise to an enormous extent.

185

Hoene, J. V. See abs. 3262.

1434. Hofer, L. J. E. Preparation and Properties of Metal Carbides, With Critical Comment as to Their Significance in the Fischer-Tropsch Synthesis. Bureau of Mines Rept. of Investigations 3,770, 1944, 39 pp.; Chem. Abs., vol. 38, 1944, p. 5647.

Probable physical and chemical characteristics of the Fischer-Tropsch (abs. 1026) carbides are summarized tabularly. The kinetics of the formation of carbides of Fe, Co, and Ni were studied, and the results of various authors were correlated. 3 reactions were isolated: (1) A rapid reaction proceeding on the surface before it has been covered with carbide and reaction products; (2) a slow reaction, which may take weeks for completion. At the end of this reaction, the catalyst has a definite composition, by weight of carbide, corresponding to Fe<sub>2</sub>C, Ni<sub>3</sub>C, and Co<sub>2</sub>C. Some Fe<sub>3</sub>C may be formed. This slow reaction is identified with carbide formation in the lattice; (3) if the temperature is above a characteristic value for each metal, C is formed. It continues until the Fe is diluted to 1% of the total Fe-C mass. The Fe and any metal with it is distributed through the C in a finely divided state. Above the critical temperature mixtures of Fe and C corresponding to almost any composition can be prepared. The C-forming reaction is apparently 1st order. All the carbides of Fischer-Tropsch catalysts are more unstable than the true refractory carbides. As Fe, Co, and Ni the carbides are unstable with respect to C and metal. For all known Fischer-Tropsch catalysts, the ratio of Catom radius to metal-atom radius exceeds 0.58. This seems to be a condition necessary for Fischer-Tropschactivity. The carbides are more or less distorted interstitial compounds with the C inserted into the interstices of the distorted metal lattice. The C does not exist in the ionic form. It is bound to the metal by essentially intermetallic bonds. This may be true of the surface carbide. It is inconceivable that carbide formation in the body of the catalyst will not profoundly modify the properties of the catalyst. Metalto-metal distances will change. The electrical and magnetic properties will not remain the same. H2, dissolved in the lattice, probably will not behave the same, partly because many of the interstices in the metallic lattice are filled. The absorption of reagents and desorption of the products probably are modified by the carbides. C formation, by carrying away active cen-

# 10 DESCRIPTION

ters and producing irreducible residues on the catalyst, would tend to poison it.

BIBLIOGRAPHY OF FISCHER-TROPSCH SYNTHESIS AND RELATED PROCESSES

. Introduction to the Carbides of Iron and Their Physical and Chemical Properties. Bureau of Mines Tech. Paper 718, 1949, pp. 1-15.

Introduction to the main report by Pichler and Merkel, entitled "Chemical and Thermomagnetic Studies on Iron Catalysts for the Synthesis of Hydrocarbons." Presents a comprehensive, annotated literature review with critical comments on present-day knowledge concerning Fe carbides, their types, formation, and properties, with special reference to their application to the carbide theory on the production of hydrocarbons by the hydrogenation of CO over Fe catalysts. Special consideration is given to the conditions of formation and the identification of 2 new Fe2C carbidesthe carbides (I) and (II) of Pichler and Merkel, the former having the Curie point at 265° and the latter at 380° identifiable with the hexagonal, close-packed Fe carbide of Halle and Herbst. Appendixes A-D present the evidence in the form of translations of laboratory memoranda on the discovery of the Halle and Herbst carbide. Recent investigations at the Bureau of Mines indicate that carbide (I) is identical with the Hägg carbide.

-. Scc abs. 47, 52, 54; 586, 3297, 3647.

1436. Hofer, L. J. E., and Cohn, E. M. Studies of Ferromagnetic Materials. Consolidated Eng. Corp. Recordings, vol. 4, No. 1, March 1950, p. 5.

Measurement of the magnetic properties of ferromagnetic substances is a convenient method for investigating their composition and chemical reactivity. 2 of these properties, the Curie point and the specific magnetization, can be determined from the thermomagnetic curve, which is obtained by means of the magnetic balance. Typical thermomagnetic curves are shown. The material was a mixture of 2 modifications of Fe<sub>2</sub>C, the Hägg carbide (Curie point, 250°), and the hexagonal close-packed carbide (Curie point, 380°), containing about 10-30% Higg carbide as estimated from specific magnetizations. The apparatus is illustrated and described.

-. Synthesis of Cementite. Jour. Chem. Phys., vol. 18, No. 5, 1950, pp. 766-767; Chem. Abs., vol. 44, 1950, p. 6367.

Describes new method for synthesizing cementite, which overcomes the difficulties of the presently known methods. It is based on the fact that, in partly carburized Fe containing either or both modifications of the Fe carbide, Fe.C, the carbides will begin to react with the free Fe at a relatively low temperature (above 260°) and will have reacted completely below 500° to form well-crystallized cementite. This reaction. Fe,C+Fe→Fe,C, thus requires substantially lower temperatures than any other known series of reactions producing cementite uncontaminated by free C, and the synthesis is comparatively simple to carry out. The operation is described with the aid of a thermomagnetic

1438. Thermomagnetic Determination of Hägg Carbide in Used Iron Fischer-Tropsch Catalysts. Am. Chem. Soc., 117th Meeting Abs., March-April, 1950, p. 36-J; Anal. Chem., vol. 22, 1950, pp. 907-910.

Being capable of measuring the Curie points and magnetic moments of ferromagnetic materials, the magnetic balance is suitable for relatively rapid qualitative and quantitative determination of the ferromagnetic phases in used Fe Fischer-Tropsch catalysts. Because of the nature of the samples and the method. special consideration must be given to the magnetic field strength, elastic effects, remanent force, sampling technique, shape of sample, and heating schedule. These points are discussed, and it is shown how a

composite thermomagnetic curve may be resolved into its components when their characteristic magnetic constants are known. In connection with X-ray and chemical analyses, and by means of a few simple equations, the relative abundance of ferromagnetic phases can be calculated. This procedure is illustrated for the 3-component system Fe<sub>2</sub>C-Fe<sub>2</sub>O<sub>4</sub>-a-Fe, and the significance of the magnetically nondetectable Fe is discussed.

Some Reactions in the Iron-Carbon System. Application to the Tempering of Martensite, Nature, vol. 167, 1951, pp. 977-978.

Precipitated Fe-Cu-K<sub>2</sub>O (100:10:0.32) catalyst was reduced with H, at 220° C. and carburized with CO at 188° C. to a C: Fe weight ratio of 0.06966. This preparation, consisting of metallic Fe and hexagonal close-packed Fe carbide, was used as a model for the thermomagnetic study of the reaction that occur during the tempering of carbon-martensite. The results indicate that the 1st tempering reaction (below 200° C.) may be the decomposition of martensite to hexagonal carbide and metallic Fe. and that the 2d reaction (at 200°-240° C.) is the decomposition of the retained austenite into the same products. Between 240° and 300° C., the hexagonal carbide is converted to Higg carbide (see abs. 1446) and above 300° C., Fe and Higg carbide react to form cementite (see abs. 1437). Above 470° C., the rate of decomposition of Hägg carbide into cementite and free Fe becomes appreciable (see abs. 586). Thus, the 3 stages of tempering are essentially confirmed by the reactions observed in the catalyst model, except that an intermediate reaction (formation of Higg carbide) is postulated that has not yet been observed in martensite.

1440. HOFER, L. J. E., AND PEEBLES, W. C. Preparation and X-Ray Diffraction Studies of a New Cobalt Carbide. Jour. Am. Chem. Soc., vol. 69, 1947, pp. S93-S99; Chem. Abs., vol. 41, 1947, p. 4363.

CO reacts with finely divided Co at 226°-230° to form a product of the composition corresponding to the formula Co<sub>2</sub>C (9.3% C). This product reacts completely with H<sub>2</sub> at 240°-250° to give Co metal and CH<sub>4</sub>. The carburization of Co at temperatures higher than 230° leads to C contents higher than 9.3%. However, only C up to 9.3% reacts with H2 at 240°-250° to form CH. Carbon in excess of this amount reacts with H2 only at temperatures above 350°. The paper reports the results of studies on the carburization of Co by CO at various temperatures, and the reaction of He with, and X-ray analyses of, the resulting products. The results indicate that the easily hydrogenated C produced by the action of CO on finely divided Co. metal is combined with Co to form a new crystalline species, Co.C, whose structure is distinct from either a- or β-Co. X-ray diffraction data indicate that the difficulty hydrogenated C is in the form of finely divided C crystallites. Lattice parameter measurements of a-Co. gave no evidence of any solid solution of C in a-Co in a partly carburized sample.

1441. -. X-Ray Diffraction Studies of the Action of Carbon Monoxide on Cobalt-Thoria-Kieselguhr Catalysts. I. Jour. Am. Chem. Soc., vol. 69, 1947, pp. 2497-2500; Chem. Abs., vol. 42, 1948, p. 1483.

Reduction of the Fischer-type and Hall-type Fischer-Tropsch catalysts at 400° leaves the Co in the facecentered cubic \$ form, which does not convert readily to the hexagonal close-packed a form. On carburization of the reduced catalyst, the Co is converted to the same carbide previously reported by the authors (abs. 1440). The carburization of  $\alpha$ -Co and  $\beta$ -Co as associated with kieselguhr, Tho, and MgO proceeds at nearly the same rates and results in the same crystalline carbide. Hydrogenation of the carbide forms CHi and the stable a-Co. The cycle of carbiding the Co

in the reduced catalyst and hydrogenating the carbide so formed can be repeated apparently indefinitely at

1442. HOFER, L. J. E., PEEBLES, W. C., AND BEAN, E. H. X-Ray Diffraction Studies of the Action of Carbon Monoxide on Cobalt-Thoria-Kieselguhr Catalysts. II. Jour. Am. Chem. Soc., vol. 72, 1950, pp. 2698-2701.

Below 235±10° CO reacts with finely divided Co to form only Co2C, above this temperature inert free C also is formed. The results of a study of the reactions occurring above this critical temperature are presented. Reduced Co-Th-kieselguhr catalysts produced increasing amounts of free C and decreasing amounts of Co.C on carburization with CO at increasing temperatures in the range 243°-298°. At the high temperatures, the maximum amount of carbide is formed within the 1st 5 hr. of carburization. Free C tends to make the catalyst inaccessible to further carbide formation either by poisoning or by mechanical blocking. Carbide inhibits free-C deposition. Scc abs. 1441. 1443. HOFER, L. J. E., AND PEEBLES, W. C. X-Ray Dif-

fraction Studies of the Carburization of a Cobalt-Thoria-Kieselgulir Fischer-Tropsch Catalyst. Am. Chem. Soc., 111th Meeting Abs., 1947. p. 1-E.

Catalyst containing Co-ThO2-kieselguhr (100:18 :100) was prepared essentially by the method of Fischer and Koch, reduced with H. at 400°, and then treated with CO at 210°. The reaction was followed gravimetrically in the manner of Bahr and Jessen. At 210° the weight increase owing to carburization stopped when the ratio C: Co in the catalyst was nearly the same as that in Co.C. The C deposited at 210° could be rapidly converted to CH, and traces of higher hydrocarbons by treatment with H2 at 210°. X-ray diffraction analysis showed that the ThO, and kieselguhr in the catalyst were amorphous, as was also the Co oxide before reduction. After reduction, however, the Co was in the form of cubic B-Co, which is the form stable above about 360°. No trace of any hexagonal a-Co lines could be detected. Upon carburization, lines of a new phase appeared, which previously have been identified as owing to a new Co carbide. After hydrogenation of the carburized catalyst, the lines of hexagonal a-Co appeared.

X-Ray Diffraction Patterns of Solid Aromatic Hydrocarbons. Anal. Chem., vol. 23, No. 5, 1951, pp. 690-695.

Investigations into the basic aspects of coal hydrogenation have led to the preparation of a series of highly purified solid aromatic hydrocarbons that are of interest to the coal-tar, fuel, and other industries and to the field of medicine. For the positive identification of solid crystalline aromatic hydrocarbons X-ray diffraction analysis is proposed. X-ray powder diffraction patterns of 59 hydrocarbons have been obtained using Fe-target radiation. Enough impurities to lower the melting point by as much as 15° C. do not appreciably modify the diffraction patterns. The patterns are very characteristic; those of closely related compounds and even isomers are unique and can readily be identified.

1445. HOFER, L. J. E., COHN, E. M., AND PEEBLES, W. C. Isothermal Decomposition of the Carbide in a Carburized Cobalt Fischer-Tropsch Catalyst. Jour. Phys. and Colloid Chem., vol. 53, 1949, pp. 661-669; Chem. Abs., vol. 43, 1949, p. 6064.

In a previous study of Co catalysts, a new Co carbide Co.C was prepared and identified, and the rates of formation and of hydrogenation of this carbide in the standard Co-ThO-kieselguhr Fischer-Tropsch catalyst were observed. A study now is made of the thermal stability of this Co carbide as it occurs in a carburized catalyst. The rate of isothermal decomposition was studied magnetically and chemically 300°-

360°. The Co carbide in the preparation used was either paramagnetic or very weakly ferromagnetic. In the range from about 80-25% Co carbide, the decomposition time curves were linear, and hence the reaction was of apparent zero order in that range. An empirical activation energy of 54.3 kcal. per mole was found for the range of apparent zero order. The details of a magnetic method are described, by means of which the complete course of a reaction in the solid state can be followed under certain conditions.

187

-. Modifications of the Carbide, Fe<sub>-</sub>C-Their Properties and Identification. Jour. Am. Chem. Soc., vol. 71, 1949, pp. 189-195; Chem. Abs., vol. 43, 1949, p. 3699.

Purpose of this paper is to determine the relationship between the Fe-C carbides that were reported in thermomagnetic studies and those reported in X-ray diffraction studies. The existence of 2 carbides of Fe with formula Fe<sub>2</sub>C and having Curie points at 247° and 380° has been confirmed. A hexagonal close-packed carhide of Fe has been prepared. This carbide has properties similar to those of the carbide described by Halle and Herbst. The identity of the 380° Curie-point carbide of Pichler and Merkel with the hexagonal carbide has been established. The identity of the 247° (265° according to Pichler and Merkel) Curie-noint carbide with the Higg carbide has been established. The carbides reported by Hofmann and Groll and by Tutiva seem to be the hexagonal carbide. The hexagonal carbide decomposes above about 300° to Hägg carbide, which in turn decomposes at about 550° in 1 hr. to cementite and free C.

Isothermal Decomposition of Nickel 1447. Carbide, Jour. Phys. and Colloid Chem., vol. 54, No. S, November 1950, pp. 1161-1169; Chem. Abs., vol. 45, 1951, p. 1850.

Thermal stability of Ni<sub>2</sub>C was studied magnetically and by X-ray diffraction 320°-355° on a fully carburized and on an almost fully carburized sample. An induction period precedes the decomposition. This period is analogous to that found for the decomposition of austenite. There is no detectable structural change in the carbide during the induction period. The carbide decomposed into free metal and free C without intermediate formation of a lower carbide. Shortening the induction period by temporary overheating did not affect the zero-order rate of the decomposition, except when the normal induction period was completely suppressed. In that case, the zero-order rate was approximately doubled. In the range 70-10% Ni-C, the decomposition rate was constant; hence, the reaction was of apparent zero order in that range. Empirical-activation energies were found for the induction periods and quasi-zero-order range of decomposition of both the fully carburized carbide and the almost fully carburized carbide.

HOFER, L. J. E., PEEBLES, W. C., AND BEAN, E. H. X-Ray Diffraction Studies of the Action of Carbon Monoxide on Cobalt-Thoria-Kieselguhr Catalysts. II. See abs. 1442.

1448. HOFER, L. J. E., PEEBLES, W. C., AND DIETER, W. E. Magnetic and X-Ray-Diffraction Studies of Unreduced Ferric-Oxide Fischer-Tropsch Catalysts. Jour. Am. Chem. Soc., vol. 68, 1946, pp. 1953-1956; Chem. Abs., vol. 41, 1947, p. 644.

Catalysts prepared by precipitation with K2CO3 or KOH from a solution of a ferric salt are inactive in the Fischer-Tropsch synthesis if the original solution contains chloride anion and are active if the original solution contains nitrate ion only. This difference in activity is an extremely marked one. The catalysts precipitated in the presence of chloride ion in no case produced more than 2 or 3 gm. of liquid hydrocarbons per m. of synthesis gas, while catalysts precipitated in the presence of nitrate ion, in some cases, gave yields as high as 70 gm. per m. X-ray diffraction patterns showed that all the catalysts contained identifiable crystalline constituents. In the case of active catalysts, this was a-Fe<sub>2</sub>O<sub>4</sub> (I), a-FeOOH (II), or both. In the case of the inactive catalysts, there was one exception, \(\beta\)-FeOOH (III). The magnetic susceptibility of the active catalysts was higher (100-300×10-6) than that of either (1)  $(25 \times 10^{-6})$ , (II)  $(42 \times 10^{-6})$ , (III)  $(40 \times 10^{-6})$ . The magnetic susceptibilities of the inactive catalysts were quite close to the expected 40 x 10°. It should be remembered that both (II) and (III) decompose to (I) below 200°, so that the inactivity accompanying the presence of (III) in raw catalysts is not due to the (III) itself, but to some characteristic that it transmits to the ultimate catalyst. This hypothesis is supported by a subsequent investigation of the inactive, chloride-precipitated catalyst, which contained no (III). Repetition of the procedure leading to this catalyst showed that it was formed from (III) as an intermediate and, hence, had the undesirable poisoning characteristic owing to (III). That the chloride ion is not directly responsible for the poisoning action is shown by the fact that good active catalysts can be made starting with FeCl, in which case no (III) can be formed. Catalysts prepared by precipitation of hot FeCls with K2CO2 contain B-Fe<sub>2</sub>O<sub>2</sub>·H<sub>2</sub>O when freshly precipitated, and they are inactive as Fischer-Tropsch catalysts whether or not they contain β-Fe<sub>2</sub>O<sub>2</sub>·H<sub>2</sub>O after washing and drying. Catalysts prepared by precipitation of Fe(NO2), solutions with K2CO2 or KOH contain a-Fe2O2 and in some cases a-Fe<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O and are active in the Fischer-Tropsch synthesis. The magnetic susceptibility of active raw Fe<sub>2</sub>O<sub>2</sub> catalysts was considerably greater than that of any Fe2O2 or Fe2O2 hydrate, which would be identified in the diffraction pattern of the catalysts. The magnetic susceptibility of those catalysts containing β-Fe<sub>2</sub>O<sub>2</sub>·H<sub>2</sub>O was very much lower than that of the active catalysts and did not greatly exceed that of β-Fe<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O. Several suggestions are proposed to account for the deactivation of the catalyst.

1449. HOFER, L. J. E., PEEBLES, W. C., AND GUEST, P. G. Preparing Extruded Specimens for X-Ray Diffraction Analysis. Anal. Chem., vol. 22, No. 9, 1950, pp.

Details of the equipment and the method.

1449a. HOFER, L. J. E., ANDERSON, R. B., PEEBLES, W. C., AND STEIN, K. Chloride Poisoning of Iron-Copper Fischer-Tropsch Catalysts. Jour. Phys. and Colloid Chem., vol. 55, 1951, pp. 1,201-1,206; Chem. Abs., vol. 46, 1952, p. 233.

Catalysts prepared from ferrous, ferric, and cupric ion solutions are active only when they contain sizable amounts of Fe<sup>++</sup>. The β-Fe<sub>2</sub>O<sub>3</sub> H<sub>2</sub>O catalysts contain up to 0.92% Cl, the poisoning effect of which accounts for the inactivity of this catalyst. Activity is not affected by the presence of Cu.

HOFFMAN, D. S. See abs. 2310.

HOFFMAN, H. M. See abs. 2574.

1450. HOFMANN, F. [Oil Syntheses.] Österr, Chem.-Zfg., vol. 32, 1929, pp. 210-212; Petrol. Ztschr., vol. 26, 1930, pp. 283-284; Chem. Zentralb., 1930, I, p. 1561; Chem. Abs., vol. 24, 1930, p. 2868. Lecture.

HOFMANN, H. See abs. 3374.

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1451. HOFMANN, K. [Heterogeneous Water Vapor and Carbon Dioxide Dissociation Equilibria Over Iron and Its Oxides. I.] Ztschr. Elektrochem., vol. 31, 1925, pp. 172-176; Chem. Abs., vol. 19, 1925, p. 2293.

From data contained in the literature derived equations for the heterogeneous equilibrium of the system Fe-O-C over Fe<sub>2</sub>O<sub>4</sub>/FeO:  $\log K_{2pK} = (-1645/T) + 1.935$ ;

FeO/Fe:  $\log K_{xpK} = +(949/T) - 1.140$ ; Fe<sub>2</sub>O<sub>4</sub>/Fe:  $\log$  $K_{\rm spx} = + (261/T) - 0.325$ . For the system Fe-O-H over the same solid phases the equations are log  $K_{zpW} = -(3237/T) + 3.509$ ; log  $K_{zpW} = -(834/T) + 0.636$ ; log  $K_{zpW} = -(1482/T) + 1.411$ .  $K_{pW}$  and  $K_{pR}$ represent the constants of the homogeneous dissociation equilibrium of water vapor and CO2, respectively. From the discussion of the heterogeneous equilibrium of CO2 and H2O over Fe and its oxides from the standpoint of the phase rule Hofmann concludes that a true chemical equilibrium does not obtain in a blast furnace.

BID-OGRAPHY OF FISCHER-TROPSCH SYNTHESIS AND RELATED PROCESSES

--- Reduction Mechanism of Iron Oxides in a Gas Stream. II.] Ztschr, angew. Chem., vol. 38, 1925, pp. 715-721; Chem. Abs., vol. 19, 1925, p. 3197.

Blast-furnace process is imitated in a simplified manner, using pure H2 gas and various Fe2O2 and Fe2O4 preparations. The reaction products are analyzed, and the results are given in curves of H2 adsorption in relation to time and reduction in relation to temperature. Equilibrium reactions indicate only the tendency of the reaction, because the result is determined by the surface conditions. Fe Os shows 100% reduction at 550° and 1,000°, with minima at 750° (a) and 925° (b). Granules of 0.05-0.02 mm. diameter are best. Fe<sub>3</sub>O<sub>4</sub> exhibits the same character, but is harder to reduce (ferric ferrate). FeO was not found below 564°. Fe3O4 forms only in slow processes. The reduction minima are explained (a) by adhesion and (b) by the  $\beta-\gamma$ transformation. They can be suppressed by addition of MgO. Acid admixtures (SiO.) do the same but form irreducible slag above 700°.

1453. HOFMANN, K. A., AND GROLL, H. [Production of Ammonia and Hydrocarbons From Lignite Coke by the Action of Steam at 500°. I Ztschr, angew, Chem, vol. 40, 1927, pp. 282-287; Chem. Abs., vol. 21, 1927, p. 1880.

Although at 900° C+H2O=CO+H2, and at lower temperatures the reaction C+2H2O=CO2+2H2 is favored, at 500° both reactions are too slow to be of technical importance. By the use of catalysts, however, reactions involving the addition of H2 (obtained either from the above reactions or added as such) to the primary tar and to the N2 present are accelerated. Thus Fe induces the transformation of 15% H2 into CH4, Ni, 30%, and Mn, 45%. With Mn and Co oxides together, still higher yields are obtained. It is assumed that metallic carbides, finely divided and rich in C, are formed, and that the H. reacts with them to form the hydrocarbons. Experiments are described showing the methods used for activating the C; the effects of H2 on low temperature lignite coke at 500°, with the production of large yields of hydrocarbons and NH3; and the influence of catalysts, such as the oxides of Fe. Ni. Mn. and Mn-Co. 1454. HOFMANN, K. A., AND SCHIBSTED, H. [I. Reduci-

bility of Formic Acid. II. Preparation of Formaldehyde and Methyl Alcohol From Formates.] Ber. deut. chem. Gesell., vol. 51, 1918, pp. 1389-1398, 1398-1418; Chem. Abs., vol. 13, 1919, pp. 720-723.

It was found that the initial decomposition temperature of metallic formates increases regularly with an increase in the basic properties of the metal; for example, formate of Cu, 170°; of Pb, 195°; of Ni, 210°; of Ca, 335°; etc. At different temperatures above the initial decomposition temperature, a given formate may decompose in any of several ways; the formate of Li at temperatures 400°-500° may yield MeOH, acetone, HCOOH, CO, and H.O; of Mg above 340° MeOH, acetone, and HCHO; of Cu and Ni, MeOH; of Zn. HCHO and MeOH; of Sn, HCHO but no MeOH; of Al, neither HCHO nor MeOH. These facts may be applied to the transformation of HCOOH in the vapor phase in the presence of chemically unchanged catalysts if the catalyst and temperature are so chosen as to allow for the possibility of formate formation. Under these circumstances cyclic processes involving the synthesis and decomposition of formates may be adapted to the preparation of MeOH and HCHO. The best catalysts for the preparation of aldehyde were found to be ZnO or ThO: deposited on asbestos.

1455. HOFMANN, U. [Deposition of Carbon From Carbon Monoxide and Benzine in the Presence of Iron. I.] Ber. deut. chem. Gesell., vol. 61, B, 1928, pp. 1180-1195; Chem. Abs., vol. 22, 1928, p. 4289.

Continuation of the study of black C crystals. In previous work on thermal decompositions of hydrocarbons, temperatures under 700° could not be employed. With an Fe catalyst C separates from CO at 400°-700°, and from benzine at 700°-900°. The form or previous history of the Fe is without influence. The C samples so obtained were distinctly crystalline by X-ray analysis, the grain size increasing with temperature of deposition. Numerous density, chemical, and activity tests also depend on temperature. The fact that crystals of C can be obtained at so low a temperature indicates formations of a carbide with the Fe with subsequent decomposition. The formation of Fe<sub>3</sub>C is not proved by X-ray analysis. However, at 400° with CO and at 700° with benzine diffraction lines appear tor an unknown substance, which is called X-carbide, richer in C than Fe.C.

[Deposition of Carbon From Carbon Monoxide or Benzine in the Presence of Iron. II. Crystalline Carbon With High Adsorptive Power.] Ber. deut. chem. Gesell., vol. 61, B, 1928, pp. 2183-2194; Chem. Abs., vol. 23, 1929, p. 751.

C obtained from CO or benzine by the method previously described or precipitated in the presence of Fe(CO); although crystalline, is highly adsorptive. The adsorptive power cannot be attributed to the presence of amorphous C. It is due to a very loose, crystalline structure, presenting an enormous surface.

1457. HOFMANN, U. AND GROLL, E. [Separation of Carbon From Carbon Monoxide in Iron. III. Formation of Iron Oxides and Iron Carbides in the Solid Phase.] Ztschr. anorg. u. allgem. Chem., vol. 191, 1930, pp. 414-428; Chem. Abs., vol. 24, 1930, p.

O-free CO was passed over pure Fe, prepared from Fe(CO). The solid phase was examined with X-rays by the method of Debye-Scherrer. Up to 450°, graphite and Fe<sub>3</sub>O<sub>4</sub> were found with little Fe and Fe<sub>3</sub>C; 450°-650°, graphite and FeO and small quantities of Fe.C: 450°-650°, graphite and FeO and small quantites of Fe<sub>3</sub>C, Fe and Fe<sub>3</sub>O<sub>4</sub>: above 655°, Fe, C and Fe<sub>3</sub>C but no FeO or Fe<sub>2</sub>O<sub>4</sub>. At 320° and 275°, CO was passed over pure Fe<sub>2</sub>O<sub>3</sub>. X-ray examination showed Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>2</sub>C in the solid phase. Unknown lines were attributed to a C-rich carbide, Fe-C, which is unstable at higher temperature. Benzine vapors passed over Fe at 700°, together with O. free N., gave C, Fe, and cementite in the solid phase. The results are discussed with reference to the phase diagram of Schenck, abs. 3054. Attempts to detect oxoaustenite in the solid phase were unsuccessful. Acording to Schenck (abs. 3053), this occurs in carbonization above 575°. The CO-CO2 analyses obtained at 700° are within this field but only cementite and a Fe were found in the solid phase. The latter was cooled both in H2O and in liquid N<sub>2</sub>, but since the mass is in the form of a fine powder because of the separation of C cooling may not be rapid enough to prevent decomposition of oxoaustenite.

HOFMANN, U. See abs. 1356.

HOFMANN, U., AND GROLL, E. Separation of Carbon From Carbon Monoxide in Iron. III. Formation of Iron Oxides and Iron Carbides in the Solid Phase. See abs. 1457.

1458. HOHENADEL, H. P. Products From Synthesis of Petroleum and Natural Gas. Oil Weekly, vol. 120, No. 12, 1946, pp. 27-28; Min. and Met., vol. 26, 1945, pp. 576-578; Chem. Abs., vol. 40, 1946, p. 2964. Brief review.

1459. HOKANSON, H. [Some Observations on the Motor-Fuel Supply.] Tek. Tid. Uppl. D. Mekanik, Skeppsbyggnadskonst Flygtek. Automobil Motortek., vol. 70, No. 38, 1940, pp. 74-76; No. 42, pp. 77-84; No. 46, pp. 85-89; No. 51, pp. 98-100.

Lecture on the production of motor fuel from petroleum and coal by high- and low-temperature carbonization, hydrogenation, and gasification, as well as from gases by the Fischer-Tropsch process.

1460. HOLADAY, W. M., ALBRIGHT, R. E., UPJOHN, T. E., AND STEFFENS, L. R. Fuels-Their Present and Future Utilization. Oll Gas Jour., vol. 48, No. 27, 1949, pp. 277-304; Petrol. Processing, vol. 4, No. 11, 1949, pp. 1233-1244.

Trends in energy consumption; utilization developments; future availability of fuels are discussed in a paper presented at the annual American Petroleum Institute meeting, November 1949. Presents potential and practical possibilities for converting natural gas. coal, and oil shale into liquid fuels. Exhaustion of petroleum supplies is too remote to warrant active development of the above additional sources of liquid fuels at present. Of the 3 sources, shale oil appears to offer the best prospects.

Holden, J. H. See abs. 3306.

HOLLIMAN, W. C. See abs. 3220.

1461. HOLLING, — [Comparison of the Catalytic Cracking of Gas Oil From the Fischer-Tropsch Synthesis and From Naphtha.] FIAT Reel K-29. frames 6,603-6.615, PB 70,218; TOM Reel 296.

Tests have proved that, in catalytic cracking of gasoil from the Fischer synthesis, aviation fuels cannot be obtained as in the cracking of gas oil from naphtha under approximately the same conditions. The output of gasoline is smaller also when Fischer gas oil is used. 3 tables and 5 diagrams.

1462. Hollings, H. Removal of Sulfur Compounds From Gas. Inst. Gas Eng., Pub., No. 175/64, 1937, pp. 4-7, 51-64; Gas Jour., vol. 220, 1937, pp. 475-476, 479-485, 667; Gas World, vol. 107, 1937, pp. 379-383. 471-476, 563. Chem. Abs., vol. 32, 1938, p. 6437.

In recent years, large-scale removal of S from gas has depended upon removal of benzene. The active C process removes about 75% of total S compounds. The normal oil washing removes only about 1/2 this amount. In a modified process, gas is washed with relatively large volumes of oil to remove CS. The oil is regenerated by treatment with K.CO. solution to remove CO2 followed by alcoholic caustic soda. The K-CO3 is regenerated by heat. The reaction with alcoholic caustic soda forms Na xanthate; CS: and MeOH are recovered by acidification and distillation. This process does not remove any substantial amount of benzene as wash oil becomes saturated with hydrocarbons. A catalytic process (abs. 1258) seems best.

463. — Wintershall A.-G., Lützkendorf. CIOS. Rept. XXXII-90, 1945, 37 pp.; PB 2,233; Bureau of Mines Inf. Circ. 7369, 1946, 21 pp.; TOM Reel 197.

Report deals with the Schmalfeldt gasification plant for making synthesis gas, the Fischer-Tropsch plant, the hydrogenation plant, and the catalyst factory and includes a report on lubricating oil from Hanover and Austrian crude. The Schmalfeldt gasification process consists of gasification of brown coal in the entrained state by hot (1,000°) recycled synthesis gas. The plant was intended to supply synthesis gas for the Fischer-Tropsch plant, but later a hydrogenation plant was added and the gas requirement increased. The

original designed output per gasifier unit (2 generators in series) was 20,000 m. per hr. This was increased to 30,000 m. by the use of O. The gasification period was 4.5 sec. at 30,000 m. of gas per hr. and 6.0 sec. at 20,000 m.3 In addition to 4 gasifier units, there were 5 producer units, each making 30,000-35,000 m.\* of gas per hr. The gasification time was 11 sec. Producer gas also was made by gasification of entrained brown-coal dust, but without recycling of gas or the use of O2. A mixture of gases was used to heat the gasification units (for each unit 24,000 m. per hr., consisting of 3,000-4,000 m.3 of rest gas from the Fischer-Tropsch plant and 21,000-20,000 m. of producer gas). The composition of the synthesis gas with and without O. was, respectively: CO, 25 and 28%; H2, 50 and 56%; CO2, 18 and 10%. CH4, 3.5 and 3%, N2, 3.5 and 3%, The H, for the hydrogenation plant came from the Wintershall generators. The cost of raw water gas is given as 2.70 pf. per m. and of H<sub>2</sub>, 7.30 pf. per m. The Fischer-Tropsch plant consisted of 144 catalyst chambers, generally worked in 2 stages with a 1-stage conversion of about 50%. In 1940 and 1941 yields were 130 gm. per m. of synthesis gas by changing the catalyst every 1.5-2 mo. Total annual production was about 30,000 tons. The catalyst (Co, 100 parts; MgO. 10; ThO2. 5; with 1.7-2.3 lb. of kieselguhr per lb. of Co) was made and regenerated in an adjacent catalyst factory. Gives details of the method and of the operation of the plant, which hydrogenated the residues from the lubricating oil plant. A table showing capital costs, broken down for the various plants, is presented. - Lurgi High-Pressure Gasification. Gas Jour., vol. 248, 1946, pp. 889, 890, 895-897, 899; BIOS Final Rept. 521, 1945, 75 pp., PB 32,578; TOM Reel-

Reviews the literature on the gasification of coal with steam and O2 under pressure and describes the plant and its operation in detail. Gives flowsheets. In general, it was found that lean, hard coal could be gasified under pressure satisfactorily, while gas-flame coals usually required pretreatment to reduce the caking properties. The proportion of CH, formed on gasification increased with increasing pressure and decreases with increasing temperature. By gasification at 20 atm. it is possible to produce a gas with calorific value of 5,000 kcal. per N m. In actual practice the theoretical value is not obtained. However, the more reactive the fuel gasified, the nearer does the gas approach the ideal. Operating data, analyses and costs are tabulated. Describes operation of the A.-G. Sachsische Werke at Böhlen in detail, and covers the experiment to produce synthesis gas from hard coal in less detail.

1465. HOLLINGS, H., AND GRIFFITH, R. H. Activated Adsorption of Hydrogen. Nature, vol. 129, 1932, p. 834; Chem. Abs., vol. 26, 1982, p. 4224.

Adsorption of hydrocarbons at high temperatures (up to 450°) takes place with every metal or metallic oxide so far investigated (Cr. Ti, Fe, Cu, Mo, Zn, Cd, Ca, Zr, Mg, Sn, Co, Al, Mn, and W). The velocity and extent of adsorption vary greatly in different cases and are also considerably influenced by the presence of impurities.

1466. HOLLINGS, H., AND KING, J. G. Lurgi Gesselschaft für Wärmetechnik, Lurgi Haus, Frankfurt-am-Main. 5 and 7. High-Pressure Gasification. CIOS Rept. XXXII-91, 1945, pp. 6-7, 11; PB 1,722 and PB 4,328.

3 plants are gasifying brown coal under high pressure: Zittau, Böhlen and Brüx, the last 2 having productive capacities of 150 and 100 million cu. ft. per yr., respectively. The process had been investigated for production of synthesis gas from bituminous coal, but no plant had been installed. The process uses 0.5-0.2 m. of O., per m. of gas. The purity of the O. utilized

depends upon the reactivity of the fuel, the higher the reactivity the lower the purity. Zittau had used O<sub>2</sub> of 72-75% purity. The maximum size of the generator at present is 2.5 m. An Fe, 100; Cu, 10; Al-O<sub>2</sub>, 9; kieselguhr 120 catalyst made by Lurgi Gesellschaft is used at a temperature 70° higher than in the Fischer process. The total cost of producing O<sub>2</sub> in the standard Linde-type plant is estimated at 2.2-2.5 pf. per N m<sup>3</sup> for plants producing 1,000-2,000 N m<sup>3</sup> per hr., of which 40% is for depreciation, 40% for power, and 20% for wages, maintenance, and chemicals. For large units of 17,000 m<sup>3</sup> per hr. the cost would be 1.5 pf., of which 0.4 pf. would be for depreciation.

1467. Lurgi Gesellschaft für Würmetechnik, Lurgi Haus, Frankfurt-am-Main. 6. Lurgi and Fischer-Tropsch. CIOS Rept. XXXII-91, 1945, pp. 8-11, PB 1,722 and PB 4,328; TOM Reel 197.

Because of outstanding developments in the Fischer process, Lurgi had been granted full rights by Ruhrchemie A.-G. for constructing Fischer-Tropsch plants, with interchange of technical information. Although it is conceded that hydrogenation is more suitable for the production of high-octane fuel, nevertheless, because of its better applicability to the treatment of high-ash coals and the production of wax and other products, the Fischer-Tropsch process is of considerable potential importance from the chemical point of view. Operation under medium pressure enables the quality of the product to be rather closely controlled, Some tabulated data are given on the yields of products obtained at 7-10 atm., 190°-225° with a Co catalyst and at 20 atm., 230° and 275° with two Fe catalysts in 3. 2, and 1 stages, respectively. Yields per m.3 of high-CO: H2 ratio water gas were 160, 170, and 135 gm., respectively. The Fe catalyst developed by Lurgi is stated to work at 218°-230°, 10 atm., and He: CO ratio =2, a 2d stage of conversion being necessary. It has the composition Fe, 100; Cu, 25; Al<sub>2</sub>O<sub>3</sub>, 9; K<sub>2</sub>O, 2; SiO2, 30. It is insinuated that the double-tube, medium-pressure oven is not very satisfactory, with operation at 20 atm. pressure. Its temperature limit is 230°. The average cost per kg. of product is given as 24 pf. The average price of all products is 45 pf. Capital cost is set at S00-900 RM per yr. per ton of liquid products. A recent plant was quoted at 600 RM. 1467a. Hollings, H., Hopton, G. U., and Spiver, E.

Lurgi High-Pressure Gasification. Gas Jour, vol. 248, 1946, pp. 889, 890, 895-897, 899; BIOS Final Rept. 521, 1945, 56 pp.: TOM Reel 227; PB 32,578; Chem. Abs., vol. 41, 1947, p. 847.

Critical examination of the working results of the plants of the Lurgi Co. in Germany. The fuel is dried in the top of the generator by the hot gases in exit. The latter leave at a temperature 300°-600° and a pressure of about 20 atm. The dried fuel passes down through the generator, and is carbonized by contact with the hot gases. The yield of tar plant and its operation are described at some length. It had a capacity of 150,000,000 m. of town gas per yr. and used dried brown-coal lumps and broken briquets as fuel. A diagram is attached. The O2 consumption is 0.145 m. per m. of purified gas; steam consumption, 1.47 kg.; over-all power consumption for production of O<sub>2</sub>, 1.1-1.2 kw.-hr. per N m.<sup>2</sup>; and the cost, 2.2 pt. per m., including capital charges. The total power consumption for gas manufacture including O2 production is 0.22 kw,-hr. per N m. of purified gas. Based on costs of fuel at 6.50 RM per ton, H<sub>2</sub>O at 6 pf. per m. power at 1.1 pf. per kw.-hr., labor at 0.4 pf. per m. maintenance cost at 0.4 pf. per m3, and 0, at 2.2 pf. per m.3, the total cost of gas is 3.8 pf. per m.3 After deducting a byproduct credit of 1.4 pf. per m., the net cost is 2.4 pf. per m. The Fischer-Tropsch pilot-plant unit was originally installed by Lurgi Gesellschaft Wärmetechnik m. b. H. to study detoxification of town gas but was later turned over to the production of hydrocarbons at 18 atm. pressure, 250° and with a precipitated Fe catalyst. The unit never operated satisfactorily and made only a few short runs. The yield of liquid and solid product was only 40 gm. per m.

1468. HOLLINGS, H., HOPTON, G. U., NEWMAN, L. L., HORNE, W. A., AND SPIVEY, E. A. G. Siichsische Werke, Böhlen, Germany. CIOS Rept. XXX-13, 1945, 12 pp., PB 977; TOM Reel 197.

Deals with the low-temperature carbonization plant, the Lurgi high-pressure gasification plant, and the experimental high-pressure Fischer-Tropsch plant. The carbonizing plant is the standard Lurgi "Spulgas" design. Its primary object was to produce tar for hydrogenation in the adjoining Brabag I plant. The Lurgi high-pressure gasification is comparable to that from low-temperature carbonization. The fuel must not cake during carbonization. The carbonized fuel passes down into the combustion zone in the base of the generator where it reacts with steam and Oz. As the gases ascend through the fuel in the combustion zone, it is cooled and reactions leading to the formation of CH, occur. Analyses of the gas range 10-25% CH. All solid, noncaking fuels are suitable for pressure gasification, such as brown coal or lean hard coal. Artificial aging can be used to reduce the caking properties of coals which are unsuitable without treatment. 1469. HOLM, M. M., NAGEL, R. H., REICHL, E. H., AND

VAUGHN, W. E. Oxo Process. FIAT Final Rept. 1,000, 76 pp., PB S1,383.

Historical development of the Oxo process is outlined. and the work of the I. G. Farbenindustrie A.-G. at Leuna and the Ruhrchemie A.-G. at Oberhausen-Holten discussed. The 10,000 ton-per-day plant at Holten is the only commercial plant in existence, and it was never in actual operation. The more recent development at Ruhrchemie A.-G. considered in this report covers: Production of Oxo olefins by cracking of wax; conversion of Oxo alcohol to soaps by fusion with caustic; conversion of Oxo aldehydes to soap by the Canizzaro reaction; the manufacture of highly branched alcohols by alodol condensation of the lower aldehydes and the production and oxonation of olefins in the C<sub>20</sub> range for use in cosmetics, emulsifiers, etc. The main contribution of Leuna to the Oxo problem was the development of the original Ruhrchemie A.-G. process to a continuous operation. Also described is the modification of Dr. Reppe at Ludwigshafen in which the hydrogenation is carried out over a fixed catalyst bed consisting of Cu chromite instead of Co with Co carbonyl as the active ingredient as at Leuna and Ruhrchemie A.-G. A commercial development of the process under construction at the end of the war was the Bombrini plant in Italy for the manufacture of propionaldehyde by the oxonation of C.H. Some discussion is made of the possible mechanism of the process but without conclusion. A-bibliography of references to TOM reels is appended.

Holmes, J. See abs. 2284.

1470. HOLMES, J. AND EMMETT, P. H. Alteration of the Size and Distribution of Pores in Charcoals. Jour. Phys. and Colloid Chem., vol. 51, 1947, pp. 1276-1307; Chem. Abs., vol. 42, 1948, p. 1102.

Pore-size and surface-area, alterations produced in 4 gas-mask charcoals by various combinations of steaming, hydrogenation, oxidizing, sintering, or impregnating with NiO, CuO, MocOa, NacOa, TesOa, or Cr.Oa were studied. Adsorption isotherms for N, at —195° were used to judge the changes in pore-size distribution and surface area. The samples included 2 charcoals made by the ZnCla process, 1 steam-activated coconut shell charcoal, and 1 made from coal by a combina-

tion of calcination and steam activation. The various treating procedures are discussed in terms of 6 possible types of pore alteration that can be produced. The results can be summarized by saying that suitable combinations of the treating process seem capable of increasing the relative proportion of any particular size of pore that it is desired to produce in the charcoals.

1471. HOLROYD, R. Report on Investigations at the I. G. Farbenindustrie A.-G. Works at Ludwigshafen and Oppau. CIOS Rept. XXX-103, 1945, 69 pp., PB 23,750; Bureau of Mines Inf. Circ. 7,375, 1946, 75 pp.; TOM Reel 197.

This report contains information on the following subjects: (II) Synthesis-gas production, pressure operation of the water-gas shift, and the CH. O. process for synthesis gas and for C.H. production (costs for the latter); (IV) MeOH and higher alcohols synthesis: (V) hydrogenation and related processes, bituminous and brown coal, bituminous and brown-coal tars, 300 and 700 atm. vapor phase. Dehydrierung-Hoch-Druck process, isooctane and alkylate production, fuel for jet planes, costs of hydrogenation process 200,000 ton-peryear basis, methods of manufacture of catalysts for hydrogenation, and related processes: (VII) Fischer-Tropsch synthesis-Michael gas-recycle fixed-bed catalyst and the foam processes; (VIII) miscellaneous chemical processes; (IX) plant operation at Heydebreck, Auschwitz, and Politz-Stettin; (X) negotiations between I. G. Farbenindustrie A.G. and Japan. with flow sheets and data on hydrogenation of Utibuti coal; (XI) Wickel pressure vessels; (XII) development of high-pressure vessels; (XIII) H.-resistant steels.

472. I. G. Farbenindustrie A.-G. Works at Ludwigshafen and Oppau. II-B. Synthesis Gas Production—Pressure Operation of the Water-Gas Shift Reaction. CIOS Rept. XXX-103, 1945, pp. 2-5, PB 23,750; Bureau of Mines Inf. Circ. 7,375, 1946, pp. 2-5; TOM Reel 197.

There are 3 advantages in using the pressure process for CO conversion: (1) Compression of the gases for removal of CO2 is eliminated. The saving from this source is greater when H2 or NH2-synthesis gas is the required product than when synthesis gas for MeOH or Fischer-Tropsch is being made. (2) The equilibrium of the reaction CO+H<sub>2</sub>O=CO<sub>2</sub>+H<sub>2</sub> is unaffected, the volume of gas that can be treated is simply increased. and no change in reaction temperature or catalyst (91% Fe<sub>2</sub>O<sub>3</sub>+7% Cr<sub>2</sub>O<sub>3</sub>) is necessary. (3) The makeup steam requirement is reduced from 400 gm to 250 gm. per m. of inlet gas. The potential disadvantage is corrosion owing to an increased concentration of dissolved CO2, O2, and S gases in the water. This is combatted by using a 17% Cr steel where contact with the liquid water is made. A description of the plant with diagrams is given. A pressure of 12-30 atm. is used... With a catalyst volume of 10 m., a 25-30 atm. pressure-plant has a capacity of 25,000 m. per hr. of inlet gas, as compared with only 3,000 m. at atmospheric pressure: This increase in unit capacity may not result in any reduction in capital cost per m. of synthesis gas product because special steels are required and a larger % spare capacity has to be installed. For regular production of 100,000 m. per hr., 5 pressure units with a total capacity of 125,000 m. per hr. would have to be installed as against 11 atm. units with a total capacity of 110,000 m. per hr. Not all of the 7 plants that have. been installed have found the process satisfactory. It is said that the output of the plant has been limited, corrosion troubles have been severe, and the life of the catalyst has been shortened by deposition of scale on.it. -. I. G. Farbenindustrie A.-G. Works at

473.——. I. G. Farbenindustrie A.-G. Works at Ludwigshafen and Oppan. II-C. Methane-Oxygen Process for Synthesis-Gas Production. CIOS

Rept. XXX-103, 1945, pp. 6-9, PB 23,750; Bureau of Mines Inf. Circ. 7,375, 1946, pp. 5-9; TOM Reel 197. General description of the process, the operation, and the equipment is given for a plant treating 6,000-7,000 m. per hr. of coke-oven gas. Synthesis gas may be produced from pure gaseous hydrocarbons, coke-oven gas or purge gas from MeOH synthesis. S content must be low, the presence of even 15 mg. per m. of feed necessitates an increase in reaction temperature of about 200°. The first step of the process consists of burning the preheated hydrocarbon (650°) with O<sub>2</sub> or O<sub>2</sub>-enriched air, the amount of O<sub>2</sub> being substantially the theoretical requirement for the reaction CH.+1/2 O2= CO+2H2. The second step consists of the conversion of residual CH, by the CH, steam reaction and the attainment of the water-gas equilibrium. The composition of the final gas is CO<sub>2</sub>, 7%; CO, 23.8%, H<sub>2</sub>, 69%; and CH., 0.2%. The consumptions per m. of CH, fed are O2, 0.487 m.3; steam, 0.107 kg.; cooling water at 15°, 9.6 kg. No cost data are given.

Visit to Oil Centers in Leuna, Lutzkendorf, Zeitz, Böhlen, Stassfurt and Factories in Russian-Occupied Territories. PB Rept. 38, 1945, 6 pp. Brief account of activities at plants in Leuna, Lutzkendorf, Zeitz, Böhlen, Stassfurt, Blechhammer, Brüx, Politz, Heydebrech, Moosbierbaum, and Oppau (Ludwigshafen). The chief research and development work at Leuna has been in connection with production of high aromatic content gasoline. Synthesis gas and H. were made at Lutzkendorf by the Wintershall-Schmalfeldt process. At Blechhammer a pressure process was used for conversion of water gas to H2.

I. G. Farbenindustrie A.-G. Works at Leuna. XXVI. German Oil-Production Data-Fischer-Tropsch Plants. Scc abs. 1481.

1475. HOLROYD, R., AND OTHERS. Report on Investigations at the I. G. Farbenindustrie A.-G. Works at Leuna. CIOS Rept. XXXII-107, 1945, 135 pp., PB 6,650. Bureau of Mines Inf. Circ. 7,370, 1946, 135 pp. TOM Reel 197; Chem. Abs., vol. 40, 1946, p. 6235.

This report comprises 27 sections as follows: I. Gas production. II. Ammonia synthesis. III. Methanol and higher alcohol synthesis. IV. Hydrogenation. V. Dehydrierung-Hoch-Druck process. VI. Hydroforming process. VII. Arobin process. VIII. Catalytic cracking. IX. Dehydrogenation of butane-alkylation. X. Isomerization of normal butane. XI. Synthetic lubricating oil-Leuna. XII. Synthetic lubricating oil—Schkopau. (A) Synthetic lubricating oil—Stet-tin—Pölitz. XIII. Aviation fuel manufacture and engine testing. XIV. Oxo process. XV. Synol process. XVI. Mersol process. XVII. Methylamine. XVIII. Manufacture of carboxylic acids. XIX. Polymerization of C. and C. olefins. XX. Fertilizers and nitric acid. XXI. Synthesis of toluene from benzene and methanol. XXII. Catalyst preparation. XXIII. Metallurgy. XXIV. Blechhammer. XXV. Rrüx. XXVI. General oil production data. XXVII. Use of bottled propane and butane for road vehicles.

1476. Morley, R. J. I. G. Farbenindustrie A.-G. Works at Leuna. III. Methanol and Higher Alcohol Synthesis. CIOS Rept. XXXII-107, 1945, pp. 15-17 PB 6,650. Bureau of Mines Inf. Circ. 7,370, 1946, pp.

About 12,000 tons per mo. of MeOH was produced and used for motor fuel, CH2O manufacture and for solvents. The plant for making isobutanol (higher alcohols) was very similar to that used for MeOH synthesis as also was the synthesis gas. The catalyst was the same a for MeOH (Zn+Cr) with 2% K2O added; maximum catalyst temperature was 450°. Plant output was 12,000 tons per mo. of which 12% was isobutanol. The composition of the crude was: MeOH 50-55%:

H-O 22-25%: dimethylether 1-3%; n-propanol 1-2%; isoputanol 11-12%; alcohols, ketones, hydrocarbons, etc., C. 2%, C. and C. 2.5%, C. and C. 1-2%, C. C. 1%; yellow oil containing 70% clefins 1-2%; fractions 110°-160° and 160°-250° each 3-4%. The MeOH was separated and repassed through the converter to produce more higher alcohols. Working-up of the crude can be followed by reference to a flow sheet. The dimethylether (purified to 98%) was used for making dimethylsulfate and dimethylaniline. The purified propanol was used for cosmetics and solvents; other material was converted to propionic acid or reacted with CH2O to yield trimethylolethane which, when reacted with the oxidized acids from the 160°-200° fraction, yielded a substitute for castor oil. Some propanol was used in the production of glycerin. Isobutanol was converted to isobutylene and thence to isooctane or to Oppanol (polyisobutylene); some was used as acetates as lacquer solvents and some for making Koresin a CH2O resin; other amounts were converted to isobutylamine. Some of the fractions 110°-130° and 130°-160° were used as acetates as solvents (Intrasolvane); the fraction 110°-160° was used to make Palatinol HS, esters of phthalic acid, used as plasticizers. The fraction 200°-250° was used in the manufacture of esters, lubricants and driers. Higher fractions could not be used.

1477. Howes, D. A., Allen, J. G., and Schindler, H. I. G. Farbenindustrie A.-G. Works at Leuna. Synthetic Lubricating-Oil Manufacture at Stettin-Pölitz. CIOS Rept XXXII-107, 1945, pp. 81-83 PB 6,650. TOM Reel 197. Bureau of Mines Inf. Circ. 7370, 1946, pp. 81-83.

Under closely controlled conditions, a mixture of Fischer-Tropsch wax (maximum melting point 176° F.), and a special wax from brown coal tar distillation (made by a combination cracking-hydrogenation process) is cracked under closely controlled conditions to give 95-97% olefins. These are polymerized at atmospheric pressure in the presence of AlCl. catalyst. Ultimate yields are % by weight: Gas 27-30, lubricating oil 49-52, diesel oil 6-7, steam cylinder oil 8-11. 2 grades of lubricating oil have been made: Engler viscosity at 100° 3.0 and 5.5-5.6. Production capacity of the plant was 1,000-1,200 ton per mo.; actual production was about one-half this amount.

1478. HAENSEL, V. AND JONES, J. P. I. G. Farbenindustrie A.-G. Works at Leuna. XIV. Oxo Process. CIOS Rept. XXXII-107, 1945. pp. 87-92. PB 6.650; Bureau of Mines Inf. Circ. 7370, 1946, pp. 87-92.

Oxo process consists of the reaction of olefins with water gas in the presence of Fischer-Tropsch catalyst to give aldehydes, which are hydrogenated to alcohols in a subsequent step. The raw materials processed at Leuna were Kogasin and yellow oil, an olefinic byproduct of the higher alcohols process. The chemistry of the process is outlined and flow sheet is attached. The catalyst has the approximate composition, Co 30%, ThO, 2%, MgO 2%, kieselguhr 66%. Process conditions and operating details are given. An essential of any scheme for operating the Oxo process is that the synthesis gas rate in both the Oxo and hydrogenation stage must be sufficiently high to ensure efficient stirring and complete suspension of the catalyst. A large excess of synthesis gas is not necessary. Intead of 220-240 atm. pressure, the Oxo stage might be operated at 40-50 atm., but with a lower throughput and at a higher temperature than 150°. 1 of the difficulties sometimes encountered was that unless the conditions in the Oxo stage are carefully controlled, olefin polymerization takes place, and these polymers, after hydrogenation, are difficult to separate from the higher boiling alcohol products. In addition to Kogasin and yellow oil, Leuna had investigated the treatment of cracked petroleum oil. The crude product con-

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tained 16-17% of alcohols which may be separated from the hydrocarbons by forming boric esters. Only about 60% of the olefins were converted, of which approximately 80% were recovered as alcohol. See also abs. 1174.

1479. HAENSEL, V., JONES, J. P., AND HORNE, W. A. I. G. Farbenindustrie A.-G. Works at Leuna. XV. Synol Process. CIOS Rept. XXXII-107, 1945, pp. 93-97. PB 6,650; Bureau of Mines Inf. Circ. 7370, 1946, pp. 93-97.

Synol process consists essentially of the reaction of a CO-H2 mixture (1 CO : 0.7-0.8 H2) at 18-25 atm. and 190°-200° over a sintered-Fe catalyst such as is used for NH, synthesis. The liquid product consists principally of alcohols and hydrocarbons, the former consisting essentially of straight-chain primary alcohols. Operation was still in the pilot-plant stage; 2 plants existing, 1 a 4-stage unit with tubular reactors with capacity of 3-5 tons per month, and a recycle plant with a single plate-type reactor with a capacity of 10-15 tons per month. A 2-stage process with gas recycle was under consideration. Both processes are illustrated by flowsheets. Optimum yield of liquid products is estimated at 155–165 gm. per m. of CO+H, and appears to consist of 35–50% alcohols, 25–10% olefins and 20-35% paraffins, the alcoholic content being greatest in the temperature range 150°-200°. Neither type of reactor was satisfactory, the catalyst caked badly in both and was very difficult to remove. A new design is proposed and illustrated in a diagram. The sintered Fe catalyst, for which preparation is described, has the analysis: Fe,O, 97%, Al<sub>2</sub>O, 2.5%, K,O 0.2-0.6%, S 0.6%, C 0.03%, apparent density 2.0. Reduction takes place with pure H2, atmospheric pressure and 450°. The essential features of the reduction are: Maintenance of a high H2 rate corresponding to a minimum linear velocity of 20 cm. per sec. and a minimum space velocity of 2.000 1. per hr. per l. of catalyst, and efficient drying of H. The time required is about 50 hr. The method proposed and shown by the flowsheet for the separation of alcohols from the crude synol depends on the formation of boric acid esters. 1480. Underwood, A. J. V. I. G. Farbenindustrie A.-G.

Works at Leuna. XVI. Mersol Process. CIOS Rept. XXXII-107, 1945, pp. 101-103, PB 6,650; Bureau of Mines Inf. Circ. 770, 1946, pp. 98-99.

Mersol reaction consists in treating paraffin hydrocarbons with SO2 and Cl to produce sulfonyl chlorides which are saponified to give sodium sulfonates. The product capacity of the Leuna plant was 50,000 tons per yr. The raw material was a Kogasin fraction b. 220°-320°. Preliminary hydrogenation at 200-230 atm. with a Ni-W-S catalyst is necessary to convert olefins to saturated compounds to prevent absorption of Cl. The Mersol reaction is carried out in 12-16 hr. at ordinary temperature and pressure using ultraviolet light to catalyze the reaction. The product, Mersol D, contains about \$2% sulfonyl chlorides and 18% unreacted hydrocarbons. The reaction is not carried to completion in order to avoid the formation of higher sulfonyl chlorides which give inferior products on saponification. The soaps made therefrom, called Mersolates, are used mainly for soap powders. They are not as good as natural soaps for removing dirt, but are better grease removers and thus have the advantage for wool washing. By carrying the reaction with SO, and CI only to the extent of 30-33%, a product called Mersol 30 is obtained and is made into flakes. Mersol D can only be made from Kogasin but Mersol 30 can be made from other materials. Kogasin has the advantage that it is more transparent to ultra violet light. The paraffinic Fischer-Tropsch material is preferred as it requires a smaller hydrogenation plant and the consumption of Cl is less. This applies even more strongly to

natural petroleum fractions. With Kogasin at 30 pf. per kgm. and petroleum oil at 18 pf., there is not much difference in the final cost of the product.

1481. Holnoyd, R. I. G. Farbenindustrie A.-G. Works at Lenna. XXVI. German Oil Production Data-Fischer-Tropsch Plants. CIOS Rept. XXXII-107, 1945, pp. 132-133; TOM Reel 197; Bureau of Mines Inf. Circ. 7370, 1946, pp. 132-133; PB 6,650.

Plants:	Total gasoli tons p	ne capaci er year
1. Ruhrchemie A-G 2. Victor Rauxel. 3. Rheinpreussen 4. Krupp Benzin 5. Essener Benzin 6. Hoesch Benzin 7. Schwarzheide 8. Schafforisch 9. Lutzkendorf		40, 000 70, 000 60, 000
Total		591, 000

1 Under construction.

HOLT, A. Sec.abs, 471.

1482, HONDA, K. Double Diagram of the Iron-Carbon System, Trans. Am. Soc. Steel Treating, vol. 16. 1929, pp. 183-189; Chem. Abs., vol. 23, 1929, p. 4430. This is an argument, based principally on X-ray data, in favor of the single diagram for the Fe-C system.

1483. HONDA, K., AND MURAKAMI, T. Thermomagnetic Properties of the Carbides Found in Steels. Sci Repts. Tôhoku Imp. Univ., vol. 6, 1917, pp. 23-29 Chem. Abs., vol. 11, 1917, p. 2887.

To obtain the carbides, rods of C and W steels were annealed at 880°-920° and cooled very slowly. The rods were then polished and turned down until they were 7 mm. thick and 10 cm. long. The rods were used as anodes in dilute HCl, and by electrolysis the carbides were obtained. The Fe cementite was ob tained as a gray powder and the double carbide as a black powder. The former contained 6.08% C and 93.5% Fe; the latter 8.10% C, 31.71% Fe, and 53.70% W. The Fe cementite is ferromagnetic and in a field of 500 gauss its specific magnetization is 19.7. The critical temperature, above which the carbide is para magnetic, is 215°. In its free state the cementite i decomposed almost completely into its components by heating long enough at 900°. The double carbide found in low W-steels also is ferromagnetic, and its spec fi magnetization in a field of 500 gauss is 15.5. It critical temperature lies at 400°. It is decomposed into its components by heating it to 850°. The con clusion, however, may not apply to the double carbid as it exists in low-W steel because its boundary con dition is quite different in the steel than when existin by itself in the free state.

1484. HONDA, K., AND NISHIYAMA, Z. Nature of th Tetragonal and Cubic Martensites. Trans. Am. Soc Steel Treating, vol. 20, 1932, pp. 464–470; Sci. Repts Tohoku Imp. Univ., vol. 21, 1932, pp. 299–331; Chem Abs., vol. 27, 1933, p. 253.

X-ray analyses show martensite to be a solid solu tion of C in Fe, divided into 2 distinct kinds, a i quenched steels and  $\beta$  in quenched and tempered steels 8-Martensite is a solid solution, the C atoms bein present within the space lattice of Fe. It is ver probable that in a-martensite each of the C atom occupies 1 of the face centers of the tetragonal lattice and in  $\beta$ -martensite a position ( $\frac{1}{2}$ ,  $\frac{1}{4}$ , 0) of the cubi lattice. The mechanism for the transition austenite $\rightarrow \alpha$ -martensite $\rightarrow \beta$ -martensite.

1485. HONDA, K., AND TAKAGI, H. Magnetic Transform mation of Cementite. Sci. Repts. Tohoku Imp. Univ

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vol. 4, 1915, pp. 161-168; Engineering, vol. 100, 1915, pp. 665-667; Chem. Abs., vol. 10, 1916, p. 740.

BIBLIOGRAPHY OF FISCHER-TROPSCH SYNTHESIS AND RELATED PROCESSES

By cooling, the magnetic transformation of cementite begins at 215°, and by heating it ends at the same temperature. This is the critical temperature of the cementite. In former experiments steels with a C content 0.14-1.5% showed almost the same critical temperature as the latter steels. Since the ferromagnetic compounds of Fe have critical temperatures peculiar to them it may be concluded that the carbides may have different critical temperatures. But, since the various steels, with 0.14-4.2% C, show a single transformation between room temperature and 700°, it is probable that the only carbide existing at ordinary temperature is cementite.

Hongo, M. See abs. 1911, 1912, 1913, 1914.

1486. Hood, H. Netherland Report on Additional Information on Various Catalytic Processes in Western Germany. I. BIOS Miscell. Rept. 112, 1947, 50 pp.; PB 96,550.

Report is made of a trip through the British zone in February 1947, for the purpose of collecting information supplementing previous CIOS and BIOS reports. Some of the subjects reported are: (1) Development of the Fischer-Tropsch catalyst (Co-Th-Mg-kieselguhr) by Ruhrchemie A.G.: preparation of the Fe catalyst with determination of the degree of reduction by the method Fe+2 FeCl, -3 FeCl, with titration by KMnO. Details are given by Dr. Rottig in an appendix. (2) status of the Oxo process at Sterkrade-Holten with some description of the reactors and filters and discussions of the catalysts and reaction conditions by Dr. Roelen. (3) catalytic oxidation of hydrocarbons in the liquid phase at I. G. Farbenindustrie Werke, Uerdingen. (4) catalytic hydrogenation of various products such as aldol, C.H. to C.H. at Hills, and methanization of town gas at Ruhrchemie A.-G., Sterkrade-Holten by Dr. Roelen. (5) manufacture of Fischer-Tropsch cobalt catalyst at Sterkrade-Holten. (6) compression and storage of water gas, manufacture of CO at I. G. Farbenindustrie A.-G., Leverkusen. Appendix: A new method for the determination of the metallic iron in reduced iron catalysts by Dr. Rottig of Ruhrchemie A.-G., Oberhausen-Holten. Several diagrams of apparatus are shown.

-. [Fuel Synthesis and Other Catalytic Processes in West Germany.] Chem. Weeblad, vol. 45, 1949, pp. 201-203.

Digest of a paper presented to the Netherlands Chemical Society July 1948 is given. A survey is made of processes for production of motor fuel with brief descriptions. The Oxo process is emphasized.

-. Slurry Process Versus Fixed-Catalyst-Bed Operation. Proc. 3d World Petrol, Con., The Hague, May-June 1951.

Catalyst slurry process was chosen for pilot plant development. Improvements instituted included the use of low-quartz catalyst to reduce mechanical wear; the use of short contact time and operating temperatures on the low side of the maximum range with recycling of unconverted olefins; preheating of the olefin feed and water gas to effect rapid initiation of the reaction; the use of a high-pressure cooler and cold-senarator system to reduce Co hydrocarbonyl content of recycle gas and oil contamination in recycle pumps; and a specially designed decobalting system to prevent excessive Co deposition in the preheating section for the decobalter feed and in the decobalter proper. A special feature, added to the Leuna process for producing C.-C. alcohols, was a catalytic after-hydrogenation for removing color-producing unsaturated aldehydes in refining the final alcohols.

1488. HOOVER, C. R., DORGAS, M. J., LANGLEY, W. D., AND MICKELSON, H. G. Catalytic Preparation of Unsaturated Hydrocarbons From Carbon Monoxide and Hydrogen. Jour. Am. Chem. Soc., vol. 49, 1927, pp. 796-805; Chem. Abs., vol. 21, 1927, p. 1444.

Mixture of approximate equal parts of CO and H. with a trace of O2, when passed at a space velocity of 1,500-2,000 over a Ni-Pd catalyst supported on Al or pumice stone, produced 1-3% of C.H. at temperatures in the neighborhood of 100°; the catalyst lost 0.5% of its efficiency in 30 hr. Other catalysts in order of decreasing activity were Ni-Cu-Pd, Fe-Ni-Pd, Ni-Pt, Cu-Co-Fe, Cu-Pd, Cu-Co-Ni, C-Pd, Ni-Cu, Cu-Co. While saturated hydrocarbons were not specially sought, Ni and Ni-Pd catalysts yielded from 20-25% CH, at temperatures in the neighborhood of 250°. The catalysts showed little decrease in activity after several days' use.

HOPTON, G. U. See abs. 1467a, 1468.

1489. Horiba. S., and Rr. T. Decomposition of Carbon Monoxide in the Presence of Reduced Nickel. Bull. Chem. Soc. Japan, vol. 3, 1928, pp. 18-25; Chem. Abs., vel. 22, 1928, p. 1520.

Improved apparatus for the investigation of contact catalysis has been described. The decomposition of CO in the presence of reduced Ni in the vicinity of 230° is a unimolecular reaction.

1490. Horn, -. Composition of the Reaction Products From the Fischer-Tropsch Benzine Synthesis. FIAT Reel A-26, frames, 2999-3008, Oct. 15, 1940; PB

Compilation of data collected from the literature showing the analyses of the various fractions from C.-C. to the heavy paraffins and the saturated acids. 1491. Honn, O. [Development and Present Status of

the Benzine Synthesis.] Forschungen u. Fortschr., vol. 7, 1931, p. 185; Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 693-694.

Brief review from 1925 to date.

—. See abs. 1827, 2249.

1492. Horne, W. A. Interrogation of Prof. Franz Fischer at Munich, Germany. FIAT Final Report 90, 1945, 3 pp.; PB 1,253; TOM Reel 199.

Isosynthesis process produces iso-octanes by the polymerization or alkylation of isobutylene obtained by the dehydrogenation of isobutane and isopentane produced by synthesis from CO and H2 at 300-600 atm. and 400°-500° in the presence of a Th catalyst activated with 10-20% of Al2O2. The product contains higherboiling constitutents consisting of naphthenes, arematics, ethers, and alcohols. The proportions of these and of the isoparaffins can be varied by changing the operating conditions and the catalyst: the addition of ZnO favors the formation of naphthenes and aromatics, of Al-O3, the isoparaffins. In preparing a Th-il-ZnO catalyst, its activity with respect to the formation of liquid hydrocarbons can be virtually doubled by pouring the nitrate solution into the soda solution, the reverse of normal precipitation. Attempts have been made to replace the Th in the catalyst with other ele ments but unsuccessfully; a part only (25%) can be substituted by either Al<sub>2</sub>O<sub>3</sub>, ZnO, or a mixture of both Mention is made of Fe synthesis, Ni catalysts, sus pended catalysts, and isomerization of Fischer-Tropsch products with AlCl. promoted by HCl. but no details are given.

-. Review of German Synthetic Lubricants. Ind. Eng. Chem., vol. 42, 1950, pp. 2428-2436. Brief review is presented of the processes used in Germany during World War II to manufacture syn-

thetic lubricating oils. These lubricants were of 2 general classes, hydrocarbons and nonhydrocarbons. The former consisted of ethylene polymers, polymers prepared from mixtures of higher boiling olefins produced by the vapor-phase cracking of Fischer-Tropsch wax or gas oil, and the condensation product of chlorinated paraffins and naphthalene. I. G.-Pölitz, Rhenania-Ossag (Harburg) and Ruhrchemie A.-G. (Holten) had developed methods for the polymerization of higher olefins from the Fischer-Tropsch process. These are briefly described with the aid of flow diagrams. The composition and applications of the lubricating oils produced are presented.

See abs. 872, 873, 874, 875, 876, 877, 878, 1468, 1479.

1494. HORNE, W. A., AND FARAGHER, W. F. Interrogation of Dr. Pier and Staff. I. G. Farbenindustrie A .- G. Ludwigshafen and Oppau. II. Synthesis of Hydrocarbons From Water Gas-Michael Process. FIAT Rept. 426, 1945, pp. 1-8, PB 1367 and 7745: TOM Reel 199; Bureau of Mines Inf. Circ. 7376, 1946. 27 pp.; Coke Smokeless-Fuel Age, 1946. pp. 194-

Four processes developed to the pilot plant scale by the I. G. Farbenindustrie A.-G. at Ludwigshafen under the direction of Dr. Michael are described. The fixedbed circulating-gas process uses a fixed catalyst made by pasting powdered Fe carbonyl with a concentrated borax solution equivalent to about 1% on the Fe and sintering 1 c. of the paste at 800°-850° for 4 hr. and cooling in an H2 atmosphere. The synthesis gas is recirculated over this in the ratio of 100 vol. of old gas to 1 vol. of new, having a CO: H2 ratio of 1:1 or 4:5, a S content of less than 2 mg. per m. and no CO2, so that the rise in temperature in the catalyst bed is not over 10°. The gas velocity is about 1 m. per sec. and the time of contact 0.5-1 sec. The flow must be nonturbulent. Operating pressure is 20 atm. and the temperature 300°-325°. The yield of hydrocarbons per m. of catalyst is 700-800 kgm. per day recovered in 3 stages of condensation. 1 m. of 4 CO : 5 Hz gas yields about 35 gm. of CH4 and C2H6 and 160 gm. of useful products; the gasoline having an octane number of 68-70 and the gas oil a cetene number of 45-50. In the oil-circulation process an oil fraction from the synthesis product is circulated over the catalyst to remove the heat of reaction and prevent excessive production of C and CH4. The process operates at 20-25 atm. pressure and temperatures of 260°-300° in the first stage and 280°-330° in the second. It uses the same catalyst as the first process. The gas has a CO: H. ratio of 55: 45 and the yield per liter of catalyst per hr. is 20-25 gm. of all products and per m.3 of synthesis gas 150 gm., the gasoline having an octane number of 62-65 and gas oil a cetene number of 70. Foam process has for its object the production of a higher proportion of olefins in the product. It operates in the liquid phase using a finely divided catalyst suspended by an ascending stream of gas. The catalyst is made by precipitation of Fe2O2 and is pasted into granules with a solution of K2CO3, dried, reduced by H<sub>2</sub> at 350°-450° and ground fine in a ball mill mixed with gas oil. A gas of composition CO: H2=1:1 or 4:5 is used at 20 atm. pressure and 250°. The time of reaction is 3 minutes. The temperature rise through the reaction chamber is about 10°. Conversion to useful products is about 70% and the CO, content of the exit gas is 40-45%. The yield per day per m. of reaction products is 350-450 kg. The gasoline has a 70% olefin content and the gas oil 40-50%. In tubular reactor process, the operating pressure is 20 atm. and the temperature 230°-250°. The synthesis gas has a CO: H. ratio 4:5 to 5:5. The catalyst is made by

mixing Fe<sub>2</sub>O<sub>2</sub> with 5-25% of alkali earth and 1-2% of K.CO., pelleting, heating to 850°, cooling to 350°-450° and reducing in H2. It has a high activity at 240° and below. Conversion is 70-80%, giving 0.35-0.45 kg. per liter per day of products all of high olefin

1495. Interrogation of Dr. Pier and Staff. I. G. Farbenindustrie A.-G. Ludwigshafen and Oppau. IV. Oxidation Process. Fatty Acid Production. FIAT Final Rept. 426, 1945, pp. 9-11; Bureau of Mines Inf. Circ. 7,376; PB 1,367 and 7,745; TOM

Paraffin waxes produced by the hydrogenation of brown coal, from crude petroleum oils and from the Fischer-Tropsch synthesis, have been oxidized successfully to fatty acids. The molten wax is blown with air in pure Al towers in presence of Mn compounds, such as KMnO, or Mn soaps; addition of 0.08-0.15% of Na or K carbonate improves the quality of the products. A temperature of 130°-160° is maintained until oxidation begins and is then lowered to 100°-120°. The lower the oxidation temperature, the smaller is the formation of peroxides, but the longer the reaction time. The airflow is continued for 10-30 hr. until approximately 30% of the paraffin is converted. The product has an acid number of 75 and a saponification number of 130-150. The oxidation product is saponified with aqueous NaOH (20-25% at 80°), heated in an autoclave to 130°-150° under pressure. the soap solution and the unsaponifiable product separating in layers, the former at the bottom. The upper layer is recycled to the oxidation tower, the lower heated in a pipe still to 280°-350° at 80-100 atm., the pressure being released flashing the water vapor and the remaining unsaponifiable material. The molten soap from the flash tower is dissolved in water and hydrolyzed with H2SO4. The fatty acid is washed and distilled under a vacuum of 3 mm. Based on 100 parts of paraffin the following 3 fractions are obtained: Acids C-C<sub>10</sub> boiling up to 150°, 7-15%; soap acids C-C<sub>10</sub> boiling 150°-240°, 45-55%; higher acids C16-C25 boiling 240°-300°, 2-5%; residue 5-20%. The plant at Oppau had a capacity of 20,000 ton of paraffin wax per yr.

1496. HORNE, W. A., AND JONES, J. P. Fischer-Tropsch Unit at Leipzig Gas Works. CIOS Rept. XXVII-68, Item 30, 1945, 10 pp. PB 294; TOM Rept. 11, TAC Rept. SnMc-5, TOM Reel 198; Gas Age, vol. 97, No. 3, 1946, pp. 28, 68; Chem. Abs., vol. 41, 1947, p. 1828.

Installation was for the purpose of enriching city gas. The synthesis gas, a 2: 1 mixture of water gas and coke-oven gas (CO: H==1:2), after purification, was to be passed at 1,200 mm. Hg in parallel flow into 4 units of 3 standard plate reactors operating at 185°-200° and atmospheric pressure, each reactor containing 10 m.2 of Co catalyst of 350 kg. per m.3 density. Pressure drop through the catalyst bed was expected to be 500 mm. Hg. Boiler condensate from the gas works was to be used as the heat-exchange medium. The residual gas from the reactors containing about 21.3% CO, 37.5% H2, 23.6% CH4, 8.1% CO2, and 8.5% N. was to be returned to the gas works for admixture with water and coke-oven gas and used for city gas. The expected yield of liquid hydrocarbons was about 100 gm. per m.3 of gas consisting of about 1/4 each of benzine, medium oil, and wax.

1497. Hoselitz, K. Iron-Nickel Phase Diagram by Magnetic Analysis and the Effects of Cold Work. Jour. Iron Steel Inst. (London), vol. 149, I, 1944, pp. 193P-211P; Chem. Abs., vol. 38, 1944, p. 1198.

Small prismatic samples of Fe-Ni alloys in the range 3-50 at. % Ni were heated to 1,000° for 4 hr., quenched in cold water, and cooled to  $-180^\circ$  for 48 hr. to insure a single-phase state. The magnetic saturation intensities were determined over a wide range of temperatures. It was found that annealing of cold-worked alloys gave inconclusive results. Cold work on quenched alloys produced definite changes in the alloys, notably in the range 29–35% Ni; this indicates a distinct separation into 2 phases. In alloys with less Ni the changes are small, since these samples are not far from their equilibrium state. The boundaries of the heterogeneous  $(\alpha+\gamma)$  region extended from 5% Ni to 34% Ni at 336°. Below this temperature the rates at which equilibria states are approached become extremely slow. It was estimated that the time for complete change is about 10 yr. at 325° and of the order of 40 yr. at 300°.

Hoselitz, K., and Sucksmith, W. Magnetic Study of the 2-Phase Iron-Nickel Alloy. II. See abs. 2695.

Hoshino, S. See abs. 1906a. Hot, M. See abs. 248, 249.

1498. HOUDREMONT, E., KLINGER, P., AND BLASCHCZYK, G. [New Electrolytic Isolation Procedure for Determining Iron Carbide.] Tech. Mitt. Krupp, Forschungsber., vol. 4, 1941, pp. 311-328; Arch. Eisenhüttenw., vol. 15, 1941, pp. 257-270; Chem. Zentralb., 1942, I, p. 2167; Chem. Abs., vol. 37, 1943, p. 3017.

In the electrolytic apparatus the anode compartment is separated from the cathode compartment by a diaphragm, which consists of a clay plate impregnated with agar agar. The sample of steel is made the anode in a neutral anolyte of such chemical composition that no precipitation of ferrous salt results from hydrolysis. The used analyte contains ferrous salt from the anode and is therefore heavier than the original solution, so that it falls to the bottom of the anode chamber from whence it can be withdrawn and fresh anolyte introduced through a filtering arrangement. The anolyte consists of a 15% Na citrate solution containing about 1.2% KBr and 0.1% KI. The solution is diluted with boiled water and freed from O2 before it is driven by N2 or H2 gas pressure into the anode compartment. The cathode is formed from Cu gauze dipping in 10% CuBr. solution. An ampere-hour counter, an ammeter, and a voltmeter are introduced into the electrical circuit as parts of the apparatus. To control the anode potential, which is important for the isolation of carbides, a measuring cell is introduced. which consists of a calomel cell with siphon and a Pehavi measuring instrument. For the isolation of the carbide, the apparatus is provided with a contrivance whereby the carbide can be removed while under a neutral gas atmosphere. In the experiments made with this apparatus. Fe<sub>2</sub>C was the only carbide that could be isolated from either hypocutectoidal or hypereutectoidal steel, produced under all conditions of heat-treatment. The literature often contains contrary statements, which doubtless are caused by decomposition of the very reactive lamella of carbide.

1498a. HOUGEN, O. A., AND WATSON, K. M. Solid Catalysts and Reaction Rates—General Principles. Ind. Eng. Chem., vol. 35, 1943, pp. 529-541; Chem. Abs., vol. 37, 1943; p. 4,294.

Effect of solid catalysts on the reaction rates of liquid- or gas-phase chemical reactions is discussed on the basis of the following steps: (1) The mass transfer of reactants and products to and from the gross exterior surface of the catalyst particle and the main body of the fluid, (2) the diffusional and flow transfer of reactants and products in and out of the pore structure of the catalyst particle when reaction takes place at interior interfaces, (3) the activated adsorption of reactants and activated desorption of products at the

catalytic interface, (4) the surface reaction of adsorbed reactants to form activation adsorbed products. Equations are derived for the effects of adsorption, catalyst activity, particle size, porosity, flow conditions, poisons, and diluents as well as pressure temperature and concentration. It is suggested that the constants of the rate equation be determined by experiment with a differential reactor containing a thin bed of catalyst at a uniform temperature. Methods of integrating the rate equation are given to determine the volume of reactor to produce a specified catalytic conversion.

1499. Howard, F. A. Conversion of Coal to Oil and

Gas. Oil Gas Jour., vol. 46, No. 42, 1948, p. 70; Min. and Met., vol. 29, July 1948, pp. 388-395.

Paper presented at the 166th meeting of the American Institute of Mining and Metallurgical Engineers at New York is abstracted. The development of coal liquefaction and the synthesis of liquid fuel from natural gas are traced, and some evaluation is given of the processes in comparison with the petroleum process. Whether water gas or natural gas is converted into liquid products, the process is the same and requires the same equipment and experience, the essential difference at the present time being that a more efficient method of coal gasification must be developed. In comparing the hydrocarbon synthesis process with the high-pressure hydrogenation process, the former looks the more attractive from both commercial and military standpoints in that the capital cost and steel requirement have been estimated to be as much as 50% lower. From a construction standpoint, the building of a synthetic-fuel industry does not seem to be the best solution of either the immediate shortage or the immediate military problem. It will be a slow and costly development as compared with the expansion of facilities for producing, refining, and transporting more crude oil and natural gas, and it will represent a worse drain on our economy.

In an address before the National Coal Association, the development of destructive hydrogenation and the hydrocarbon synthesis processes for producing oil from coal is traced, and the present economic status is discussed. Methods are suggested for building up a national synthetic-fuel industry in this country. A definite program should be laid out whereby industry and Government would cooperate in creating the necessary foundation. There are 3 lines of endeavor: (1) Further technical development and pilot-testing of modernized coal gasification. This should be left to private industry without Government subsidy. (2) The preparation of complete and reliable project plans for large synthesis units at fixed locations preferably capable of great expansion. The actual engineering cost would be met by Government funds under contract with the industrial units involved. (3) The collection of field engineering and geological data on location, quality, and mining conditions of coal and shale reserves suitable for conversion to permit the drafting of a master plan for a national synthetic-fuel industry. This could be contracted for and supervised by the Army engineers. 1501. Howar, D. D. Synthesis of Oils From Industrial Gases-Fischer-Tropsch and Allied Processes.

trial Gases—Fischer-Tropsch and Allied Processes. Chem. Age, vol. 44, 1941, pp. 57-60; Chem. Abs., vol. 35, 1941, p. 2302.

Review with 16 refs.

1502. — Large-Scale Production of Oxygen. Chem. Age, vol. 56, 1947, pp. 767-771, 801-805, 812, 835-837; vol. 57, 1948, pp. 81-85.

General review of the development of methods for the production of O<sub>2</sub>, touching upon the work of Ruhemann, Frankl, Linde, Kapitza, and Claude. Economic aspects are set forth.

Howe, K. E. See abs. 739.

1503. Howes, D. A. Synthesis of Methanol and Higher Alcohols From Water Gas. Sci. Petrol., vol. 4, 1938, np. 2812-2821.

This paper reviews the historical development of the process, discusses the equilibrium data, classifies and describes the catalysts for synthesizing MeOH and the higher alcohol from water gas, and explains the mechanism of formation.

1504. — Interrogation of A. Bollhorn, E. Grages and Dr. Gross of Deutsche Erdoel A.-G., Berlin. Production of Vaseline From Fischer-Tropsch Wax. BIOS Final Rept. 326, 1945, p. 17, PB 27,705, TOM Reel 227.

At the Research Station, Berlin, an inferior grade of vaseline has been made experimentally by dissolving Fischer-Tropsch wax in liquid paraffin. The wax is dissolved in ethylene dichloride and the fraction of the required melting point obtained by fractional crystallization. It is then refined by treatment with H<sub>2</sub>SO<sub>4</sub> at 160°-180° until water-white.

\_\_\_\_. Sec abs. 873, 874, 875, 876, 877, 878.

1505. Howes, D. A., and Rampton, H. C. Properties of Hydrocarbon Gas Turbine Fuels. Internat. Cong. Pure Appl. Chem., July 1947, 11th Cong., London; Jour. Inst. Petrol., vol 35, 1949, pp. 419–435; Chem. Abs., vol. 43, 1949, p. 7662.

Summary is presented on the properties of hydrocarbons boiling within the range 65°-300°, with particular reference to their use as constituents of fuels for gas turbines. These various properties, determined by chemical composition and configuration, are closely interrelated and they lie mostly between the extremes set by the paraffins and the aromatics, respectively. This means that any gas-turbine fuel comprised entirely of hydrocarbons will have properties within this range. Information is given on the hydrocarbon compositions of petroleum, Fischer-Tropsch, hydrogenation, and shale-oil fractions, and attention is drawn to the present lack of knowledge concerning hydrocarbon compositions in fractions boiling above the motor gasoline range. This is due to the considerable difficulties encountered in analysis. Methods of analysis are reviewed and the possibilities of synthetic methods for producing gas-turbine fuels of different hydrocarbon compositions are summarized. No synthetic process exists at the present time for producing fuels in the 65°-300° boiling range, which would appear to be ideally suited to the aero-gas turbine. Such processes as alkylation, polymerization, catalytic cracking, etc., are not suitable methods for producing turbine fuels, since the products contain appreciable amounts of aromatics or olefins that have not yet been found acceptable in turbine fuels. The same objection applies to the products of Fischer-Tropsch type processes. 1 of the 1st problems to be solved is how to use fuels containing olefin hydrocarbons satisfactorily in aero-gas turbines.

Howes, D.-A., Allen, J. G., and Schindler, H. I. G. Farbenindustrie A.-G. Works at Leuna. XII A. Synthetic Lubricating-Oil Manufacture at Stettin-Pölitz. See abs. 1477.

1506. Howey, J. H. Magnetic Behavior of Nickel and Iron Films Condensed in a Vacuum Upon Various Metal Backings. Physiol. Rev., vol. 34, 1929, pp. 1440– 1447; Chem. Abs., vol. 24, 1930, p. 4674.

1507. HOYT, L. F. German Chemical Developments in Synthetic Detergents and Wetting Agents. PB Rept. 3,868, 1945, 151 pp.

Detailed report on development and uses of synthetic detergents, Igepons, based on natural fats or oils or

on synthetic fatty acids, were produced to the limit of available materials. Igepals, based on ethylene oxide, provided a variety of detergents and emulsifiers for technical purposes. Higher alcohols of suitable chain length and quality were produced by the reduction of the corresponding synthetic fatty acids derived from the oxidation of paraffin. Outstanding large-scale development of synthetic detergents was based on the production of Mersols from byproducts of the Fischer-Tropsch synthesis of hydrocarbons from coal. Appendix IV has a chart showing compounds derived from some byproducts of Fischer-Tropsch process.

1507a. Hradek, V. [Conversion of Light Hydrocarbons Into Carbon Monoxide and Hydrogen.] Paliva, vol. 31, 1951, pp. 266-277; British Abs., 1952, B, I. p. 639.

Thermodynamics of all possible 20 reactions during the conversion of CH<sub>4</sub> with O<sub>5</sub>, steam and CO<sub>2</sub> are discussed. It is found that: (1) Below the minimum temperature of 920° K. a conversion of CH<sub>4</sub> by O<sub>2</sub> is not possible without liberation of C; (2) the liberated C is mainly due to the reaction CH<sub>4</sub>- $O_2$ -C+H<sub>2</sub>O; (3) the conversion of CH<sub>4</sub> by steam needs a higher temperature (1,000°); (4) the same applies for the conversion by CO (about 900°); (5) the rising of temperature favors all cases of CH<sub>4</sub> conversion, lowers the amount of steam and reduces the possibility of free C formation to compare quantitatively these facts the equilibrium constants are calculated from the free energies and the limiting conditions at which C is not liberated are determined.

1508. HSIUNG, S. Y., AND KUNG, K. M. A Study on the Synthesis of Liquid Fuels From Carbon Monoxide and Hydrogen. Jour. Chinese Chem. Soc., vol. 8, 1941, pp. 112–122; Chem. Abs., vol. 37, 1948, p. 6107.

Preliminary report on the use of Ni and Co catalyst on kieselguhr in the synthesis of liquid fuels from CO and H. A procedure is suggested for eliminating the CH. reaction, which involves the passage of CO over the catalyst before the introduction of the CO-H. mixture. A mechanism of the CO pretreatment is suggested.

Hsu, W. W. Sce abs. 468.

1509. Hubmann, O. Production of Synthesis Gas From Wyoming Subbituminous Coal. General Investigation of Methods and Flowsheet for Plant to Process Bight Million Cubic Feet per Day. Bureau of Mines Spec. Rept., Nov. 1946, 23 pp.; TOM Reel 242, Rent. 9.

To obtain general information on the advantages. and disadvantages of various methods of producing synthesis gas from a coal like the Wyoming coal, 4 methods are considered suitable for treating this coal, and calculations are made of the investment and production costs for a plant with a capacity of 100,000 N m. per hr. of synthesis gas. The high content of H2 of Wyoming coal promises very high tar content and consequently very favorable conditions for utilizing it for producing motor fuels by a combination of carbonization, byproduct gasification with the synthesis of hydrocarbons, and hydrogenation of tar. The 4 methods investigated are: Lurgi pressure gasification; combined carbonization-gasification with O, and with burning of the coke and cracking of the carbonization gas; the same with use of air in the 1st step and O. in the 2d, with burning of the carbonization gas and gasification of the coke; and the Koppers complete gasification of powdered coal. Cost of equipment is taken from figures available from German sources. Corresponding figures for the United States are calculated with the ratio of 1 RM : \$0.50 for the investment cost and 1 RM : \$1.00 for the cost of labor, with a rough adjustment for special work.

Investment costs and production figures for 100,000 N m.3/hr. of synthesis gas

	Gasification of pulverized coal (Koppers)	II Lurgi pressure gasification	Carbonization with O <sub>1</sub> , gasification with O <sub>2</sub>	IV Carbonization with air; gasifies. tion with O <sub>2</sub>
Investment cost: Million RM. Million dollars. Coal consumption, tons per year. Laborers. Wages: Wages: Wages: Willion RM. Million dollars. % of production cost. Production cost per year: Million RM. Million dollars.	740,000 420 1.05 11.0 20 9.6 5.18	54.0 945,000 27.0 600 1.5 13.5 24.5 11.14 44,200 6.13 43.5 21.6 7.2 5.40	50. 2 995,000 1. 37 12. 8 65,500 65,500 6. 58 62. 0 28. 3 4. 60 4. 70	46.6  925,000  1.13  11.5  21.5  9.79  60,500  1.51  62.0  23.5  4.24  4.25

Further calculations on 3 so-called pioneer plants A, B, and C: Carbonization gas-producer plant; Koppers pulverized-coal gasification; and Lurgi pressure gasification give production costs per 1,000 N m.3 on the basis of capacities of 8,000,000 cu. ft. of ideal gas per day and 320 operating days, respectively, of \$9.30. \$11.80, and \$11.50. Here again the combined carbonization-gasification method is found to be the most favorable one. It is proposed to erect 2 units of carbonization-gasification type with the necessary equipment for operating each of the units for the production of gas as well as for the carbonization of coal and the production of coke as this seems the safest, the cheapest, and the most flexible method with respect to the requirements of a pilotexperimental plant, which should be able to handle various types of coal from such standpoints as tar recovery and alteration of the CO: He ratio. It also might prove an economical method for the treatment of oil shales with more than 10% of oil.

1510. ——. Production Costs of CO-H. Mixtures for Different Methods of Gasification With Oxygen and Various Fuels. Bureau of Mines Spec. Rept., 1947, 35 pp.

Describes various methods of gasification and their operating principles. The technical performance and the possible improvements of these methods with some directives in the selection of the gasification method best suited for a specific purpose are presented. The many factors entering into the investment and production costs are discussed in detail and extensive calculations are made in arriving at an approximate idea of the economic advantages and disadvantages of the various processes. The most important investment and operating figures are compared and the data tabulated. They show that such costs, O2 and power costs included, are lowest with methods using a fixed fuel bed, and that a fluidized fuel bed or a powdered fuel requires additional costs for a lower efficiency and higher investment costs because of the necessity of pulverizing the coal and handling large volumes of gas with a high dust content. However, gasification of pulverized coal is the only method of utilizing caking coals for the production of synthesis gas. Therefore, it should be developed as the most important base of a large-scale industry in the eastern coal fields. Furthermore, the Winkler process (fluidized fuel bed), though slightly cheaper in operating costs, may lose its interest as soon as the pulverized-coal gasification has been developed further, especially if this latter method could be operated under several atmospheres pressure.

Huff, W. J. See abs. 738. Huffman, E. H. See abs. 1729. 1511. Huffman, J. R., and Dodge B. F. Decomposition of Methanol Over Catalysts Composed of Oxides of Zinc and Chromium. Ind. Eng. Chem., vol. 21, 1929, pp. 1056-1061; Chem. Abs., vol. 24, 1930, p. 334.

Parallelism between the decomposition and synthesis of MeOH at 350° over a series of ZnO-Cr2O, catalysts is not complete but is surprisingly good. Both results show the maximum rate for a catalyst containing 4 Zn:1 Cr. At about 60% Cr. there is a rapid decrease in the activity for decomposition. From 60-100% Cr, there is very little activity for decomposition into CO and H2, which is contrary to the results for synthesis. A steady decrease in the activity of the catalysts for the decomposition, but not for the synthesis, was observed in all cases. The decomposition over these catalysts was quite complex, the products being CO, H2, CO2, CH4, unsaturated compounds, HCO3Me, HCHO, Me2O, and small quantities of unidentified substances.

1512. Hugel, G. [Synthetic Gasoline and Its Derivatives.] Ann. combus. liquides, vol. 11, 1936, pp. 719-733: Chem. Abs., vol. 30, 1936, p. 8570.

Describes coal-hydrogenation process employed by the Compagnie de Béthune, the Fischer process and the products obtained from it.

1513. \_\_\_\_\_\_\_ [Hydrogenation in France and Foreign Countries.] Sci. et ind., Tech ind. pétrole, No. 271, 1936-1937, pp. 71-79; Chem. Abs., vol. 31, 1937, p. 5976.

Outline of the hydrogenation processes of International Hydrogenation Patents Co., Ltd., of Vallette, of Audibert and of Fischer.

HUGEL, R. See abs. 1980.

1514. Huggett, J., and Chaudron, G. [Temperatures of Magnetic Transformations in the System fron-Iron Sesquioxide.] Compt. rend., vol. 184, 1927, pp. 199-201; Chems. Abs., vol. 21, 1927, p. 1218.

System Fe<sub>-</sub>O<sub>-</sub>Fe<sub>2</sub>O<sub>4</sub> shows two points of transformation, 1 at 590°, corresponding to Fe<sub>2</sub>O<sub>4</sub>, and the other at 650°, corresponding to a solid solution of Fe<sub>2</sub>O<sub>4</sub> in Fe<sub>2</sub>O<sub>5</sub>. These transformations are rigorously reversible. The system Fe<sub>2</sub>O<sub>4</sub>-FeO has a transformation point at 570° for the Fe<sub>2</sub>O<sub>4</sub>. In the system FeO-Fe, the temperature of transformation is the same as that of Fe, or 765°.

1515. Huenl, J. T. Tonnage Oxygen for Chemical Industry. Canadian Chem. Process Ind., vol. 13, 1947, pp. 1115-1120; British Abs., 1948, B, I, 300.
Review of developments with description and flow

sheet of 100-ton-per-day Air Liquide-Frankl O. plant (Air Liquide Oxyton).

HUHN, W. See abs. 1571.

1516. Hull, A. W. Crystal Structure of Iron. Phys. Rev., vol. 9, 1917, pp. 84-87; Chem. Abs., vol. 12, 1918, p. 2064.

In the X-ray analysis of Fe a special procedure is necessary on account of the difficulty of obtaining large crystals. (The large crystals of pure ferrite, reaching a length at times of several inches, which are met with in blast-furnace "bears", are not considered.) Single crystals about 6 mm. square and 2 mm. thick were isolated from a sample of Si steel. The value of d100=1.43×10° cm. requires 2 atoms for a cube of side 2d200. A lattice having atoms at cube corners and cube centers satisfies this condition and gives the observed spacing for other planes. Pure Fe was then investigated in the form of a fine powder. A narrow beam of rays from a W target passed through the powder and formed on the plate a kind of generalized Laue photograph in which every possible plane in the crystal structure had an equal opportunity of reflecting and reflected all wave lengths present. What was actually observed was the position of the K lines, which with the tube running at 110,000 volts, stood out very clearly. Their reflection in different planes appeared as concentric, nearly circular lines whose distance from the center should be inversely proportional approximately to the spacing of the planes. On the assumption that the atoms were arranged on a centered cubic lattice, and that the scattering electrons in each atom were concentrated at its center, the calculated spacings agree remarkably well with the observed values but fail to account for the following facts: (1) That the intensity of the lines falls off continuously with increasing distance from the center; (2) that the 1st-order (100) reflection is much too weak for its position; and (3) that the 2d-order (100) reflection is entirely lacking. In calculating intensities it is assumed (1) that the rays, when they reach the crystal, consist of long trains of waves, to which the electromagnetic theory is applicable: (2) that the scattering is due entirely to the electrons in the atoms, each of which scatters independently and equally; (3) that the number of electrons in an atom is equal to its atomic number; and (4) that the electrons have fixed positions in the atom, about which they move in very small orbits.

-1517. Hume-Rothery, W., Raynor, G. V., and Little, A. T. Lattice Spacings and Crystal Structure of Cementite. Jour. Iron Steel Inst. (London). vol. 145, 1942, pp. 143P-152P; Iron and Steel (London), vol. 15, 1942, pp. 318-320; Chem. Abs., vol. 36, 1942, p. 3485.

Cementite examined by Lipson and Petch (abs. 2120) was prepared by passing CO over Fe2O2 at 550°. It evidently had been partly decomposed during annealing and had lattice spacings different from the cementite used in the present study, which was extracted from steel by electrolytic attack in HCl. The values obtained by Debye-Scherrer photographs in a 19-cm. camera are: a=4.5155 Å., b=5.0773 Å., c=6.7265 Å. at 25°. Samples from 3 steels of commercial purity gave the same results. Analysis confirmed the composition Fe<sub>2</sub>C. The structure of cementite can be derived from that of martensite by a simple shearing process. The ready formation of cementite from martensite (compared to formation from austenite) suggests that the relative positions of Fe and C atoms in martensite enable this transformation to take place with small atomic movements at a low temperature. 2 refs.

HUNSMANN, W. See abs. 853.

HUNTER, W. See abs. 409.

HUNTOON, R. T. See abs. 3262.

 HUPPERT, O. [Hydrogenation of Coal and Oil.] Petrol. Ztschr., vol. 26, 1930, pp. 1250-1251; Chem. Abs., vol. 25, 1931, p. 1359.

Coal is liquefied by hydrogenation under high temperatures and pressure with or without catalysts and indirectly by hydrogenation of CO obtained from coal. Hurn, N. L. See abs. 1105.

1519. Hurst, W. W. and Rideal, E. K. Promoting Action of Palladium on Copper. I. Catalytic Combustion. Jour. Chem. Soc., vol. 125, 1924, pp. 685-694; Chem. Abs., vol. 18, 1924, p. 1775.

Ratio CO: H<sub>2</sub> burned in a mixture of the gases containing O<sub>2</sub> at the surface of Cu, and Cu containing, admixed with it, varying quantities of Pd has been measured. A real specific promoting effect was observed and the addition of Pd to Cu definitely increased the ratio CO: H<sub>2</sub>. The promoting action of Pd on Cu is ascribed to a peculiarity of the Cu-Pd interface. The anomalous activities of molecules at interfacial boundaries and points of discontinuity are cited in favor of this view.

1520. — Promoting Action of Palladium on Copper. II. Adsorption of Hydrogen and Carbon Monoxide. Jour. Chem. Soc., vol. 125, 1924, pp. 694-705; Chem. Abs., vol. 18, 1924, p. 1775.

Adsorption of H2 and CO and of mixtures of these gases by Cu and a Pd-promoted Cu catalyst has been studied, by means of a device based on the difference in thermal conductivity of the gases. Definite proof has been obtained that in general both gases are adsorbed, and that the composition of the adsorbed gas phase is independent, not only of the composition of the gas phase, but also of the nature of the adsorbent. The addition of Pd to the Cu produces an increase in the CO adsorption and a decrease in the H. adsorption, as well as a relative increase in the CO of the adsorbed phase in the presence of both gases. Arguments are advanced for the hypothesis that polar molecules are adsorbed at low temperatures and high pressures in multimolecule layers, and nonpolar molecules in unimolecule layers.

1521. HUSMANN, W. | Effluents From Fischer-Tropsch Plants Erected Under the German 4-Year Plan.] Gesundh-Ing., vol. 62, 1939, pp. 299-304; Chem. Abs., vol. 34, 1940, p. 5624.

Phenols, S, and NHs are recovered from the effluents at hydrogenation works using the I. G. Farbenindustrie A.-G. process. The slightly acidic effluents from Fischer-Tropsch synthetic petrol works are treated by biomechanical methods. The strongly acidic effluent from synthetic fatty acid works is made harmless by separating the crude paraffin wax and neutralizing.

1522. HUTCHISON, W. K. A Plant for the Removal of Sulfur Compounds by Oil Washing. Inst. Gas Eng., Copyright Pub. 175/64, 1937, pp. 8-44, 51-64; Gas Jour., vol. 220, 1937, pp. 475-476, 479-485, 667; Gas World, vol. 107, 1937, pp. 379-383, 471-476, 563; Chem. Abs., vol. 32, 1938, p. 6437.

S was determined by drawing products of combustion of a free-burning fame of gas in purified air through an accurately neutralized solution of H<sub>2</sub>O<sub>2</sub> of about 5 vol. strength and titrating H<sub>3</sub>SO<sub>4</sub> formed with standard alkall with methyl red indicator. S compounds likely to be present in purified coal gas are CO<sub>5</sub>, COS, thiophene and its homologs, mercaptans, suffides, and disulfides, the last 3 representing less than 5% of the total S. As much as 18% of S in some coal gas is in a compound completely absorbed by alcoholic KOH, similar to CS<sub>2</sub> but more volatile, perhaps COS. Methods for determination of each are described, and analyses of 9 coal gases are tabulated. Partition factors for benzene and CS<sub>2</sub> were determined for 10

oils: this factor is largely instrumental in determining the quantity of oil to circulate. Sludge formation increased rapidly with temperature but varied widely in different oils, gas oils being most unstable. Washing with 80% H2SO4, followed with 10% NaOH and distilling greatly reduced sludge formation in gas oil. Specific gravity of oil used should be far enough from H2O to reduce likelihood of emulsion formation. Viscosity should be as low as possible; doubling viscosity will increase the size of heat exchangers one-third and increase back pressure one-half. The mean boiling point should be high and distillation range narrow. The relations between rate of oil circulation, partition factor, and the characteristics of the washing plant; the conditions governing the performance of the stripping plant; and the effect of individual efficiencies of the two parts on the performance as a whole are analyzed. Some of the features of the plant are described, including power and heat, pumps, vacuum system and heat exchangers. The process differs from others in the larger quantity of oil circulated and lower ratio of steam to oil in stripping. The most favorable stripping conditions were distillation at 80° and 200 mm. abs. pressure; exhaust steam at a m. pressure can be used at this temperature. After 7 months' operation, total S removal is 70-76%. CS2 removal is 90%.

1523. Hüttig, G. F. Course of Chemical Reactions in Which Solid Substances Are Involved. I. Historical Basis. Kolloid Ztschr., vol. 94, 1941, pp. 137-147; Chem. Abs., vol. 35, 1941, p. 3857.

"IBING, G. See abs. 1828, 1829, 1830. ICHIMARU, T. See abs. 2507.

1526. ICKES, H. L. Coal's New Horizons. Coal Age, vol. 48, 1943, pp. 54-64; Petroleum (London), vol. 6, No. 7, 1943, p. 110.

Not until 1937 did an experimental plant for producing liquid fuels by direct hydrogenation come into production. That plant, erected by the Federal Bureau of Mines at Pittsburgh, Pa., has a capacity of 100 lb. of coal per day. It is to be supplemented with another plant for the investigation of indirect hydrogenation. Direct hydrogenation gasoline has an octane rating of 70-75, which can be increased to 85-90 by adding tetraethyl lead. Gasoline made by the indirect hydrogenation has a low octane number and must be cracked to make it usable as motor fuel, but the diesel fuel made by this process is of excellent quality.

1527. I. G. FARBENINDUSTRIE A.-G. [History of Methanol Synthesis. 1 Ztschr. angew. Chem., vol. 40, 1937, p. 166; Chem. Abs., vol. 21, 1927, p. 1249.

-. Oxidation of Paraffin by Air or Oxygen for the Production of Fatty Acids. TOM Reel 54, May 1937, bag 3414, target 30/4.17, item 11.

This is a lengthy and detailed report of the experimental work by the I. G. Farbenindustrie at its experimental plant and by the Standard Oil Co. at Baton Rouge on the production of fatty acids by the oxidation of paraffin. Much is said concerning the oxidation and saponification procedures and the purification of the fatty acids, as well as their composition and analysis.

-. [Supervision of the Purity of Oxygen and Nitrogen Produced by the Liquefaction of Air.] TOM Reel 195, Part 10, Item 3, Frames 31,234-31,246,

Description of a new method, based on the heat conductivity of O2 and N2, by which impurities of even 0.1% can be detected rapidly and efficiently. Several tables and graphs are included, depicting the effect of

Review of the development of theoretical chemistry

Kinds of Chemical Reactions and Their 1524 -Systemization. II. A Comprehensive Treatise on the Course of Chemical Reactions in which Solid Materials are Involved. Kolloid Ztschr., vol. 94. 1941, pp. 258-283; Chem. Abs., vol. 35, 1941, p. 5379.

Reactions of solids are divided into 5 classes on the basis of the number of components. These classes are further divided into subgroups on the basis of such considerations as the existence of polymorphic forms fusibility, volatility of reactants and products, surface effects, and homogeneity of the mixture. A bibliog raphy of 142 refs. is included.

1525. HUTTIG, G. F., AND WEISSBERGER, E. [Catalytic] Activity of Platinum Metals in the Decomposition of Methanol.] Siebert Festschr., 1931, pp. 173-178; Chem. Abs., vol. 26, 1932, p. 4233.

Catalytic activity of metals of the Pt group deposited on asbestos on the reaction of MeOH→2H2+CO is generally very erratic in the early stages of use but finally reaches a constant value that decreases in the order Pd. Os. Rh. Ru. Ir. Pt. In the 1st few hr. the activity of Os rises to more than 15 times its final constant value, then falls rapidly, whereas the values for Pd. Pt, and Rh undergo relatively little variation. The ultimate values are in all cases much higher than that of a ZnO catalyst.

HUTTON, R. S. See abs. 2752. HUZIMURA, T. Sec abs. 2506.

various phenomena encountered in the determination of impurities on the sensitivity of the measuring apparatus.

[Collection of Patents on Paraffin Oxi-1530. dation.] FIAT Reel J-281, frames 2755-2776, May 24. 1940; TOM Reel 285; PB 74,562.

Claims of 62 I. G. patents and patent applications in the field of paraffin oxidation are presented. Only 3 specific references are made to Fischer-Tropsch products. The corresponding foreign patents are listed. -. [Flowsheet of the Winkler Plant and? Miscellaneous Plant-Cost Data Sheets.] TOM Reel, 115, Item 4, 1941-1944, 28 pp.

Contribution of the Merseburg Ammonia Works, Leuna, Plant Control Department. The Winklerplant flowsheet is laid out as a schematic drawing of the installation, showing relative sizes of the various units. The plant-cost sheets include: Energy data for the overall hydrogenation process including hydroforming and hydrocarbon separation; a flowsheet for the treatment of rich and lean hydrogenation gases; graphs of output of pure hydrogenation gas as a function of CH, % in Winkler output gas; computations of the analysis of pure hydrogenation gas for various; CH. %; test analyses of hydrogenation gas output for different 24-hr. shifts; and analytical report on gasoline synthesis for a typical month.

1532. -[Hydrocarbon Synthesis From Carbon Monoxide and Hydrogen With an Iron Catalyst According to the Emulsion Method.] TOM Reel 148, Rept. LU 558, No. N-25, June 23, 1942, 2 pp.

Tabular data summarize the products obtained in a 10-week run on a 1.5 m. furnace at 250° and 20 atm. with a 55:45 mixture of CO: H2 and a daily yield of 0.3. In smaller experiments a high percentage of high-boiling products was obtained. The paraffin content was as high as 40%. . Some of the products were worked up to yield alcohols, sulfonates, fatty acids, lubricating oils, and leather oils.

-. Comparison of Products of Vapor-Phase and Foam-Phase Syntheses at Different Temperatures. Bureau of Mines Transl. T-436, January

Paper from Dr. Pier's files, high-pressure experiments, Ludwigshafen 558. Results of a few tests, and tabulated comparisons of products from the Synol process at Leuna, from the straight vapor-phase reactors, and from the gas circulation reactors. The products are expressed as free and total alcohol.

Igarashi, H. See abs. 1345.

IGAWA, S. Sec abs. 3607, 3608, 3609, 3610, 3611.

IHARA, K. See abs. 1910.

1534. IIZIMA, S. [Sorption of Hydrogen by Reduced Nickel. I. Quantities of Hydrogen Adsorbed by, and Diffused in, Pure and Contaminated Reduced Nickel, Isothermal Adsorption Lines and Heat of Adsorption.] Sci Papers Inst. Phys. Chem. Research (Tokyo), vol. 22, 1933, pp. 285-300. Chem. Abs., vol. 28, 1934, p. 2589.

Adsorption of H2 by reduced Ni is due to both adsorption and diffusion. Quantitative distinction is drawn between the amount of H2 adsorbed and the amount diffused. Isotherms showing the quantities of H, adsorbed under low pressures agree with the Freundlich equation. Heats of adsorption are calculated by means of the Clapeyron equation, and an average of 16,350 cal. per mol. is obtained. Reduced Ni that was brought into contact with air before the adsorption studies showed lower adsorptive capacity for H. The heat of adsorption in one such case was 6,479 cal. per mol.

[Sorption of Hydrogen by Reduced Nickel. II. At Low Temperatures.] Sci. Papers 1535. — Inst. Phys. Chem. Research (Tokyo), vol. 23, 1933, pp. 34-43. Chem. Abs., vol. 28, 1934, p. 2589.

Adsorption of H2 under low pressures by reduced Ni was measured at 100°, 19°, 0°, -45.2°, -78.5°, -112° and -183.5°. The results of Nikitin, see abs. 2469, at 19° were not confirmed. Ni and H2 did not form a compound at 19°. Isobars all showed maxima 0°-20°, and minima were found between -80° and -180°. The lower the equilibrium adsorption pressure the lower the temperature of the minimum. Irregularities in the isothermal at -183° are accounted for on the basis of local heating of the adsorbent due to adsorption of large quantities of H2. The isothermal is smooth when H2 is admitted slowly.

[Sorption of Hydrogen by Reduced Nickel. III. Heat Treatment of Reduced Nickel and Its Relation to the Sorption Velocity and to the Quantity of Hydrogen Sorbed.] Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 23, 1933, pp. 164-172.

Chem. Abs., vol. 28, 1934, p. 2589.

Reduced Ni was successfully heat treated in H. for 1 hr. at temperatures ranging 300°-500°. Between each heat treatment the adsorptive capacity for H. at 0° and 20.3 cm. pressure was measured. Increasing temperatures of heat treatment shortened the time necessary for adsorption to reach equilibrium and diminished the quantity of H2 adsorbed. The velocity with which A diffused into reduced Ni was unaffected by heat treatment up to 500°.

- [Sorption of Hydrogen by Reduced 1537. ---Nickel. IV. The Velocity of Sorption of Hydrogen at the Early Stage.] Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 26, 1935, pp. 45-69; Chem. Abs., vol. 29, 1935, p. 3893.

Rate of sorption of H2 by reduced Ni was measured at 0°, 10°, 21°, 30°, 40°, 50°, 60°, 70° and 100° for various pressures of H. Except for the first 15 sec. after the introduction of H, the rate of sorption was followed up to 90 min. The results indicate 3 types of sorption.

A rapid adsorption of the van der Waals type occurred during the 1st minute or 2. This was followed by a period of activated adsorption. Slow diffusion then followed and this was attributed to the diffusion of H from the surface to the interior of the metal as well as the slow distribution of H over the surface of the metal. [Adsorption of Hydrogen on Reduced

Nickel. Studies at Low Temperatures.] Rev. Phys. Chem., Japan, vol. 12, 1938, pp. 1-14; Chem. Abs.,

vol. 32, 1938, p. 6124.

Adsorption velocities were studied at 6 temperatures between -23° and -130°. The adsorption occurring 1 min. after the start consists of several activated adsorptions with markedly different velocities. The heat of activation of a particular adsorption was found to be 7,100 cal. Adsorption isotherms for some particular adsorptions were found, which gave a heat of adsorption of 10,600 cal.

-. [Adsorption of Hydrogen on Reduced 1539. -Nickel.] Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 38, No. 1006, 1941, p. 183; Rev. Phys. Chem. Japan, vol. 14, 1940, pp. 128-136; Chem. Abs.,

vol. 35, 1941, p. 3138.

Some additional facts are noted in the study of the adsorption of H2 on reduced Ni. The adsorption and desorption of H2 on reduced Ni is irreversible with change of temperature. It is difficult to desorb Ha by evacuation at low temperatures. The amount of activated adsorption decreases markedly with rise in reduction temperature used in preparing reduced Ni. The maximum and minimum points on the adsorption isobar should vary with the activity of the reduced Ni and the pressure of the gas. Van der Waals adsorption accounts for the adsorption at -183°.

IMAI, O. See abs. 1909. 1540. IMHAUSEN, A. [Coal as Raw Material for

Soaps]. Fette u. Seifen, vol. 44, 1937, pp. 411-415; Chem. Abs., vol. 32, 1938, p. 823.

Lecture is given outlining the history and chemistry of the processes for production of fatty acids by oxidation of paraffin hydrocarbons, which in turn may be synthesized by the Fischer-Tropsch contact process from water gas produced from coal.

- [Early History and Chemistry of the Industrial Synthesis of Fatty Acids.] Chem.-Ztg., vol. 62, 1938, pp. 213-215; Brennstoff-Chem., vol.

19, 1938, p. 232. Process recently developed by the I. G. Farbenindustrie for the production of fatty acids involves the catalytic oxidation of a suitable fraction of the highmolecular hydrocarbons obtained from the Fischer-Tropsch process. The reaction mechanism is not very well known. Whether the O2 molecule ruptures a C-C bond of the hydrocarbon with the formation of a dialkylperoxide or whether it becomes enclosed in a molecule of paraffin with the formation of an alkylhydroperoxide is not yet clear. The O2 could, in the primary step, unite with a molecule of paraffin with the formation of a molecular compound. The formation of an olefin by dehydrogenation, whose double bond then reacts further with O2, is conceivable. The peroxides then become further oxidized with the formation of alcohols and aldehydes from which the fatty acids arise by way of the peracids. Alcohols and aldehydes are, thus, the intermediate products of fatty acid oxidation. There is also the possibility of ester formation from 2 mol. of aldehyde. Esters could be produced also by the reaction of the intermediately formed alcohols with the fatty acids. Side reactions are favored thereby so that the fatty acids are sensitive to further oxidation and can react with O2 more easily than do the hydrocarbons. In this way undesired oxyacids are formed, which easily form lac-

203

tones with the intermolecular splitting off of H2O, and, if the oxy-group of the one acid reacts with the carboxyl-group of another, estolides are formed. Moreover, the oxyacids easily split off H2O with the formation of unsaturated acids. The oxidation also can lead to ketocarboxylic and dicarboxylic acids. It has been found possible, however, to suppress all these side reactions in favor of the desired formation of normal fatty acids so that today a large part of the soap used in Germany is made from synthetically produced fatty acids.

- [Soaps From Synthetic Fatty Acids.] Kolloid-Ztschr., vol. 85. 1938, pp. 234-246; Chem. Abs., vol. 33, 1939, p. 1979,

Manufacture of soap from synthetic fatty acids on a commercial scale is described. Hydrocarbons were produced by the reaction of CO, from coal or lignite, with H2 in the presence of a catalyst. These hydrocarbons were oxidized, by air, to fatty acids, consisting mainly of C10-C22 chains. These acids were purified by boiling to remove the low-boiling fatty acids, and saponified to soaps or esterified to fats. The soaps produced in this manner were similar to soaps from natural fatty acids in their surface tension, viscosity, foam-producing properties, gold number, turbidity formation, and detergent properties. Experiments on the production of edible fats from synthetic fatty acids were successful on a laboratory scale.

-. [Importance of Synthetic Fatty Acids for the German Fat Economy.] Kolloid-Ztschr., vol. 103, 1943, pp. 105-108; Chem. Abs., vol. 37, 1943, p. 6917.

Process for manufacturing synthetic fatty acids is described based on the oxidation of the residue obtained during the hydrogenation of CO. This residue of the synthetic-fuel plants is first fractionated then oxidized to fatty acids. The product is washed to removed the catalyst, saponified, and the unsaponifiables are steam-distilled and returned to be oxidized again. The soap is acidified, the fatty acids are distilled and fractionated. These acids have 10-20 C atoms in the chain and are similar to natural fatty acids, except that the synthetic product contains acids with both even and uneven C atoms. The product is used for soap and, after esterification with glycerol, for cooking fats and for artificial butter.

1544. IMHAUSEN, K. H. [Synthesis of Edible Fats.] Ztschr. Ver. deut. Ing., vol. 91, 1949, pp. 463-467; Chem. Abs., vol. 44, 1950, pp. 4695, 5615.

Fischer-Tropsch process yields 10-15% of paraffinic residue boiling 320°-450° (chain length,  $C_{20}$ - $C_{20}$ ) suitable for producing synthetic fatty acids. The conversion uses finely distributed air of atmospheric pressure at temperatures slightly above 100° in the presence of Mn catalyzers. The process takes 15-30 hr. in Al or special steel towers 11 m. high and 2.6 m. in diameter. Oxidation requires approximately 50 m. per hr. per ton of paraffin. The reaction is exothermic. The product is washed in towers and saponified with 30% Na.CO. and 45% NaOH at 95°. Nonsaponifiables are separated, and the soap is heated 320°-350° to remove H<sub>2</sub>O and paraffins, which are recycled along with the previously recovered nonsaponified material. The soap is dissolved and converted into fatty acid and Na, SO, by means of 75% H-SO. The crude fatty acid is fractionated under 4-10 mm. absolute pressure at 320° into Co-Co, C10-C17, C14 and higher, and residue. Yield is 70-80%

Імногг, D. H. See abs. 202. INABA, T. See abs. 1120.

· MARKET !

1545. INDUSTRIAL and Engineering Chemistry. Meth-· anol Developments. Vol. 17, 1925, pp. 772-773.

Full significance of the synthesis of MeOH and petroleumlike compounds from CO and H, has not been realized. The significant thing is not so much whether production will be undertaken in the United States or even the price at which foreign producers will demonstrate their ability to send this chemical to us. It is rather the patent situation that is causing the gravest concern in the light of the controversy taking place between Badische Anilin- und Soda-Fabrik. versus Patart. Present production in Germany is about 1,000 ton monthly; the estimated total for 1925 is 15,000 ton. Production costs are believed to be about 13% of the cost of MeOH by wood distillation. It is stated that at 1 plant the cost has been reduced to \$0.03 per kg.

BIBLIOGRAPHY OF FISCHER-TROPSCH SYNTHESIS AND RELATED PROCESSES

Synthetic Manufacture of Methanol. Vol. 17, 1925, pp. 981-982; Chem. Abs., vol. 19, 1925. p. 2928.

British Patent 229,715 is reproduced in full, together with a statement of conclusions drawn from this patent and from other literature as to proper apparatus and conditions necessary in MeOH synthesis. The essential features are as follows: (1) A gaseous mixture of CO and H2 in which there are at least 2 vol. of H2:1 of CO; (2) catalyst, a number of which are available, consists chiefly of ZnO with admixture of Cr2O2 and metallic Cu or CuO; (3) absence of alkali in the catalyst, which would cause decomposition of the MeOH produced and production of higher alcohols. H.O, and oily and tarry bodies therefrom; (4) proper apparatus made of alloy steel and lined with Cu, Al. or Zn capable of withstanding very high pressure, at least 250 atm., and containing a heating element so that the incoming gases will come in contact with the catalyst at a temperature around 250°-300° C. without coming in contact with Fe. Ni, or Co; (5) condensation of the MeOH produced, and the recirculation of the residual gases brought again to the proper concentration by the addition of H2 and CO.

- Pressure-Synthesis Operations of the DuPont Ammonia Corp. Vol. 22, 1930, pp. 433-437.

Outstanding characteristics in the pressure-synthesis industry are exemplified by a survey of the synthetic NH, plant at Belle, W. Va. Because of the extremely high capital investment necessary, a plant of 300 ton-per-day capacity is probably the minimum economic size that can be constructed if costs are low enough to make a satisfactory rate of return in this field. Furthermore, the size of such operating units as compressors and converters is increasing to such a degree that this factor of unit size controls very largely the desirable overall plant capacity. Also, the enormous research and development expense must be distributed over a fairly large output, if reasonably low expense is to be shown per unit of output. Assuming that the 300 ton-per-day plant is the smallest that should be projected, then the total capital requirement, at the commonly accepted figure of \$250-per-yr.-perton of NH3, would be about \$25,000,000.

1548 : Gasoline From Natural Gas. Vol. 37, No. 7, 1945, Adv. Sect., p. 5.

It has been reported that gasoline can be made at about \$0.05 per gal. using the Fischer-Tropsch process and natural gas (abs. 2516 and 2997). Our natural gas resources are estimated at 111 trillion cu. ft. The price ranges from \$0.015-\$0.05 per 1,000 cu. ft. It is claimed that with gas at \$0.05, it is possible to make a \$0.05 per gal. gasoline having an octane rating of 75, a diesel oil with a 90-100 diesel index, and various chemicals in the form of oxygenated compounds. Using natural gas, 440 lb. or 10,450 cu. ft. is needed to make 1 bbl. of gasoline, about 8% less than by European methods. Conversion of all available natural gas would produce 11 billion bbl. of gasoline, enough to last 18 yr. at the 1940 rate of consumption. A plant capable of making 300,000 bbl. per day, American design, would cost 660 million dollars, as com-

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pared with a plant of European design, which would cost 1.4 billion. As to costs, without depreciation, before taxes, and without profit, gasoline can be made at \$0.036 per gal. with \$0.05 natural gas. With depreciation, without taxes and profit, cost would be \$0.048 per gal. At present, refinery costs, with \$1.20 crude, are \$0.051 and \$0.053 for the same conditions.

1549. INDUSTRIAL AND ENGINEERING CHEMISTRY, NEWS EDITION. Soap Production From Paraffin to be Doubled. Vol. 16, 1938, pp. 193-194.

First experimental plant in Witten on the Ruhr. Germany, now produces 20,000 tons of fatty acids from paraffin per yr. A second plant of 20,000-ton capacity is under construction. The new soaps do not differ from the customary soaps either in odor or in characteristics in use. The paraffin is produced in the synthesis of gasoline.

Coal Hydrogenation. Japan. Vol. 19, 1941, p. 70.

In addition to coal hydrogenation, research was conducted on the synthesis of motor fuel from CO and He. The Fischer-Tropsch synthetic fuel plant of the Mitsui Mining Co. has been partly completed with test runs under way, but none of the other Mitsui plants under construction will be ready for production before 1942. The National Gas Institute of the Formosan Government-General has completed 2 pilot plants. One will produce carbon black, the other Hr-CO mixture for gasoline synthesis. MeOH is manufactured by 6 companies, with an aggregate capacity of 19,650 tons per-yr.

1551. INDUSTRIAL BULLETIN OF ARTHUR D. LITTLE, INC. Gas From Gas. No. 224, 1946.

Review of the Hydrocol development at Brownsville.

1552. INDUSTRIAL CHEMIST AND CHEMICAL MANUFAC-TURER. Oxygen in Water-Gas Manufacture. Vol. 19, 1943, pp. 13-17, 57-60.

Review of processes. Describes Winkler, Lurgi, and Thyssen-Galocsy processes briefly, with details of recent installations in Germany, particularly in combination with low-temperature carbonization plant.

1553 -Thirty Years of F. Fischer's Work. Vol. 20, 1944, pp. 257-259.

On October 1, 1943, F. Fischer handed over to Prof. Karl Ziegler the direction of the Kaiser Wilhelm Institut für Kohlenforschung in Mülheim-Ruhr. Review work by Fischer at Mülheim. Up to 1924, the institute was occupied largely with researches upon the constitution of coal; after that date, with problems of gas chemistry, leading up to full-scale application of the Fischer-Tropsch synthesis.

1554. -Operation of Two Fischer-Tropsch Plants. Vol. 22, No. 256, May 1946, pp. 253-257. Report on the operation and production of the Rheinpreussen plant at Moers-Meerbeck and the Ruhrbenzin A.-G. plant at Sterkrade-Holten.

-. Mersol and Hostapon-Manufacture of Sulfonated Detergents in Germany. Vol. 23, 1947, pp. 242-249; CIOS Rept. XXVI-2, PB 6, 684, and XXXII-107, PB 6,650; BIOS Final Rept. 805, PB

The nature, manufacture, and uses of Mersol and Hostapon are given. Mersol is a mixture of sulfochlorinated paraffins in the Cy-Cis range, made by the action of SO2 and Cl in the presence of ultraviolet light on a hydrogenated Fischer-Tropsch Kogasin distillate (Mepasin). The reaction is known as the Reed reaction. Hostapon is a mixture of alkyl sulfonic acids produced directly by the sulfo-oxidation of Mepasin, the reaction being promoted either by ultraviolet light or with acetic anhydride. The Fischer-Tropsch fraction used for starting material was the 220°-330° C. or the 230°-320° C. cut. Flowsheets, detailed descriptions of the processes, and the outputs from the plants are given.

1556 Synthetic Fatty Acids. I. II. Vol. 23, 1947, pp. 652-656, 755-763.

Information in this article is drawn mainly from BIOS final reports S6, PB 18,911; 275, PB 23,808; and 805, PB 49,196, and FIAT reports 407, PB 7,738, and 426, PB 7,745. The raw materials used by the Germans to produce synthetic fats consisted of Fischer-Tropsch wax, gatsch boiling at 320°-450°, waxes from hydrogenation of brown coal, and even petroleum derivatives of waxy character. Plants were operated by the Deutsche Fettsäurewerke at Witten-Ruhr, by the I. G. Farbenindustrie at Ludwigshafen-Oppau and Heydebreck, by Hubbe and Fahrenholtz at Magdeburg, and by Ruhrchemie in a 3-ton per month pilot plant at Sterkrade-Holten. The intake capacity of these plants was approximately 100,000 tons per year, with a rated yield of 75-80% of fatty acids. The process of Ruhrchemie developed by Velde utilized the harder, longchain waxes and produced fatty acids of high molecular weight. The raw wax was heated to 125°, treated with nitrosyl sulfuric acid for 8-12 hr., the acid was separated and the waxy product washed, dried, melted again, kneaded with caustic and, after saponification was complete, extracted with a Fischer-Tropsch motorgasoline fraction boiling at 80°-100°. The separated wax was returned to the process, while the soap was treated with dilute H-SO4, washed, and dried. The material so made was called OP32, and the yield was about 80% on the wax used. It was yellow to brown in color, hard, and solidified at 80°, its acid No. was 145-150 and its saponification No. 150-155. The I value was nearly zero

-. Synthetic Oil in Japan-an Attempt to Gain Self-Sufficiency. Vol. 23, 1947, pp. 333-340.

Complete plants at the end of the war numbered 2 for hydrogenation, 5 for Fischer-Tropsch, and 14 for low-temperature carbonization. The output of synthetic oil, excluding Manchuria, for 1944 was 113,000 kl., of which 770 kl. were hydrogenation products, 18,000 kl. Fischer-Tropsch oils, and 95,000 kl. lowtemperature carbonization oils. Outputs are discussed in detail.

1558. -. Igepon, Igepal, and Tylose. 1948, pp.

Survey of Germany's efforts to produce synthetic detergents. Fatty acids and fatty alcohols from Fischer-Tropsch waxes were a considerable source of the raw materials. The importance is drawn mainly from CIOS Reports XXVI-2, PB 6,684; XXX-10, PB 954; and BIOS Final Report 711, PB 45,243; and BIOS Miscellaneous Report 11.

1559. INSLEY, E. G. Study of Finely Divided Metals and a Method for Their Preparation. Jour. Phys. Chem., vol. 39, 1935, pp. 623-636; Chem. Abs., vol. 29, 1935, p. 5327.

Adsorption of H, C.H. and C.H. was determined at 0° and compared with the rate of hydrogenation of . C.H. and Cu, Ni, Co, and Fe catalysts prepared from both the oxides and the amalgams. Ni, Co, and Fe, but not Cu catalysts prepared from amalgams, showed hydrogenating activity as high as those prepared from the oxides. The adsorption of H2 on Ni was studied over the temperature range -80°-150°.

1560. INSTITUTE OF GAS TECHNOLOGY. Fischer-Tropsch Process. An Annotated Bibliography. Rept. for Technical Sec. Postwar Planning Cooperating Com., October 1945, 82 pp., 423 refs., 49 tables and 16 figs.

Very comprehensive review of the Fischer-Tropsch process is given. It embraces the following: Chapter I Introduction; II Historical development; III Products of the reaction, (1) nature, (2) treatment, (3) lubricating oil from primary products, (4) products of Robinson-Bindley process; IV Variables affecting the reaction, (1) catalyst, (2) pressure, (3) temperature, (4) time factor, (5) CO: H. ratio, (6) constituents other than CO and H. in the synthesis gas; V Thermodynamics of the reaction; VI Mechanism of the reaction; VII Industrial production, (1) production of CO-H. mixtures, (2) removal of S from synthesis gas, (3) contact chambers, (4) product recovery; VIII Industrial application of the Fischer-Tropsch synthesis; IX Integration of Fischer-Tropsch synthesis; IX Integration of Fischer-Tropsch synthesis; II Conversion factors. A tabulated compilation of every published type of Fischer-Tropsch catalyst, the best catalyst of each type on the basis

of yield is included. See abs. 1562, 1563, 1564, 1565, 1566.

1561. — Fischer-Tropsch Process. Rept. for Tech. Sec. Postwar Planning Cooperating Com., August 1945, pp. 19-33.

August 1940, pp. 19-33.

General review of published information with a summary of plant and operating costs taken from the Hearings before the Senate Committee on Senate Bill S-1243. Recommendations to the American gas industry as to the disposition of the process are: That no research be done on the production of liquid fuels by the Fischer-Tropsch process; that research be conducted on directing the Fischer-Tropsch synthesis to the production of gaseous hydrocarbons; and that the developments of the Fischer-Tropsch synthesis by the petroleum industry be followed closely.

1562. — Fischer-Tropsch Process, an Annotated Bibliography. Rept. for Tech. Sec., Postwar Planning Cooperating Com., October 1945, p. 19.

Compilation of every published type of Fischer-Tropsch nickel catalyst

Composition	Ratio of constituents, wt. basis	Reac- tion temp.,	Yield of pri- mary product, liquid, and solid hydrocarbons, gal./1,000 ft.3	Remarks
Do. Do. Do. N-Mn-Cr-kguhr Do. N-Mn-Ou-kguhr N-Mn-Oul-kguhr N-Mn-Holler's earth-kguhr N-Mn-K-OD-kguhr N-Mn-K-OD-kguhr N-Mn-K-MP-Kguhr N-Mn-K-MP-Kguhr N-Mn-Mn-K-MP-Kguhr N-Mn-Mn-K-N-Kguhr N-Mn-Mn-CO-kguhr N-Mn-Mn-CO-kguhr N-Mn-Mn-CO-kguhr N-Mn-Mn-Ky-CO-kguhr N-Mn-Mn-Ky-CO-kguhr N-Mn-Starch-kguhr N-Mn-Starch-kguhr	100:8:125 100:18:125 100:18:125 100:18:125 100:18:125 100:18:100 1	440 -446 446 379 409 389 389 389 387 401 401 401 401 401 403 401 403 401 403 401 403 401 403 401 403 401 403 401 403 403 403 403 403 403 403 403 403 403	gal,/1,000 ft.s'  0. 03  277 777 16 90 937 78 174 183 1.93 90 90 90 90 90 90 90 90 90 90 90 90 90	Also when prepared by ignition.  Space velocity, 130.
N-Entr-040-Figuir NI-Mn-W-Iguir NI-Co-Mn-Ab0-Figuir NI-Co-Mn-Th0-Figuir NI-Co-Mn-Th0-Figuir NI-Mn-U-00-Ab0-Figuir NI-Mn-U-00-Th0-Figuir NI-Mn-U-00-Th0-Figuir NI-Mn-U-00-Th0-Figuir	100:12:3:125 100:12:3:125 100:50:12:4:125 100:50:12:3:125 100:50:12:3:100 100:20:8:4:125 100:20:8:4:125	401 401 374 374 374 392 392 392	.70 .68 .88 .93 .1.02 1.14 1.16	

<sup>1</sup> At 5 atm. pressure.

1563. ——. Fischer-Tropsch Process, an Annotated Bibliography. Rept. for Tech. Sec., Postwar Plan-

ning Cooperating Com., October 1945, p. 23.

Compilation of every published type of Fischer-Tropsch cobalt catalyst

Composition	Ratio of constituents. wt. basis	Reaction temp., e. F., F., F., F., Yield of primary product, liquid and soll hydrocarbons, gal./1,000 ft.3	i Pamerke
Co-Co-Co-Co-Co-Co-Co-Co-Co-Co-Co-Co-Co-C	 100 100:20 100:20 100:20 100:20 100:21 100:18 100:20 100:33:15	410 0.33 419 .07 419 10 419 34 419 47 392 10 419 31	

## Compilation of every published type of Fischer-Tropsch cobalt catalyst-Continued

Composition	Ratio of constituents, wt. basis	Resc- tion temp.	Yield of pri- mary product, liquid, and solid hydrocarbons, gal./1,000 ft.3	Remarks
Co-Cu-ThO <sub>2</sub> Co <sub>0</sub> O <sub>2</sub> -MnO <sub>2</sub> -CuO Co <sub>0</sub> O <sub>2</sub> -MnO <sub>2</sub> -CuO Co-Mn-kguhr Co-ThO <sub>2</sub> -kguhr Co-ThO <sub>2</sub> -kguhr Co-Cu-MgO-sugar-char Co-Cu-MgO-pumice Co-Mn-Ai-kguhr Co-Mn-Ai-kguhr Co-Cu-MgO-ThO <sub>2</sub> -kguhr Co-Cu-MgO-ThO <sub>2</sub> -Kguhr Co-Cu-ThO <sub>2</sub> -ThO <sub>3</sub> -Kguhr Co-Cu-ThO <sub>2</sub> -ThO <sub>3</sub> -Kguhr	100:18:100 100:18:100 100:18:100 100:35:15:- 100:35:15:-	397 523 392 374 392 473 473 419 401 365-410	1 6.20 .03 .90 .97 1 6.97 17.56 .33 .50 .57 .81 1.11	Middle pressure. See footnote 1. See footnote 2. Ignition of nitrates gave slightly
Co-Cu-Th-starch-kguhr. Co-Cu-Th-U-kguhr. Co-Cu-Th-U-kguhr. Co-Cu-Th-U-kguhr. Co-Mg-Cu-Cu-Cu-Cu-Cu-Cu-Cu-Cu-Cu-Cu-Cu-Cu-Cu-	100;12.5:1.88:1.88:1.28 100;12.5:1.76:130:130 100;25:12.5:12.5:- 100;25:12.5:5:75 100;25:12.5:5:5:75 100;25:12.5:5:12.5:- 100;25:12.5:5:12.5:- 100;25:12.5:12.5:- 100;25:12.5:12.5:- 100;25:12.5:5:12.5:- 100;25:12.5:5:12.5:- 100;25:12.5:5:12.5:- 100;25:12.5:5:12.5:- 100;25:12.5:5:12.5:- 100;25:12.5:5:12.5:- 100;25:12.5:12.5:12.5:- 100;25:12.5:12.5:12.5:- 100;25:12.5:12.5:12.5:- 100;25:12.5:12.5:12.5:- 100;25:12.5:12.5:12.5:- 100;25:12.5:12.5:12.5:- 100;25:12.5:12.5:12.5:- 100;25:12.5:12.5:12.5:- 100;25:12.5:12.5:12.5:- 100;25:12.5:12.5:12.5:- 125.	410 410 410 414 410 410 455 410 410 410 471 410 455 392	. 87 . 39 . 35 . 42 . 54 . 56 . 44 . 40 . 97	higher yield.  CO:H;=1:1. CO:H;=1:1. CO:H;=1:1. CO:H;=2:3.  Naphthene production (?)

<sup>1</sup> Lb. per 1,000 cu. ft. <sup>2</sup> Reference gives yield ten times larger. A source of error has been assumed

1564. —— Fischer-Tropsch Process, an Annotated Planning Cooperating Com., October 1945, p. 27. Bibliography. Rept. for Tech. Sec., Postwar

Compilation of every published type of Fischer-Tropsch nickel-coball (1:1) mixed catalyst

Composition	Ratio of constituents, wt.	Reaction temp., ° F.	Yield of pri- mary product, liquid and, solid hydro- carbons gal./ 1,000 cu. ft.	Remarks
(Ni-Co)-Mn-Al-Or-kguhr. (Ni-Co)-Mn-Cr-Or-kguhr. (Ni-Co)-Mn-Cr-Or-kguhr. (Ni-Co)-Mn-Un-kguhr. (Ni-Co)-Mn-Un-kguhr. (Ni-Co)-Mn-Un-kguhr. (Ni-Co)-Mn-Un-kguhr. (Ni-Co)-Mn-Un-kguhr.	(100):15:5:125 (100):15:5:125 (100):15:5:125 (100):15:5:125 (100):19:5:125 (100):20:20:125 (100):19:5:19.5:- (100):15:5:3:125	410 410 410 392 383 374	0.71 .70 .89 .96 1.20 1.14	Variation of N1:Co ratio from 30:70 to 70:30 has no effect.

1565. — Fischer-Tropsch Process, an Annotated Bibliography. Rept. for Technical Sec. Postwar

Planning Cooperating Com., October 1945, p. 28.

Compilation of every published type of Fischer-Tropsch iron catalyst

Composition	Ratio of constituents, wt. basis	Reaction tem- perature, ° F.	Yield of pri- mary product, liquid and, solid hydro- carbons gal. per 1,000 ft.*	Remarks
-Cu-kguhr Do. Do. Do. Do. Do.	100:20:- 100:25:- 100:25:- 100:25:- 100:20:- 100:100:-	518 518 518 518 518 527 527	0.17 11.63 12.18 12.18 17	Electrolytic washing.  From 0.005-0.2 mol. Na <sub>2</sub> CO <sub>2</sub>
Do Cu-MgO Cu-NaiOi Cu-NaiOi Cu-Co-kguhr - Cu-KiOCi-kguhr - Cu-MgO-NaiOi Cu-Ni-adsestos.	100:35:125 100:100:15 100:100:- 100:25:5:125 100:25:3:125 100:100:105:25	495 518 518 482 495 500-536	. 45 .06 .17 .54 .54	has no effect on yield.  CO:H; ratio.
On-Ni-asbestos On-Ni-kguhr On-Ki-Op-kguhr On-Ki-Op-kguhr On-Ki-Op-kguhr Do Cu-Ki-Op-Ci-IOp-kguhr See foothote at end of table.	100:25:2.8:- 100:25:5:125 100:25:2:125 100:25:2:2125 100:25:2:2:125 100:25:5:2:125	509 482 482 482 495 495	.31 .54 .23 .54 .28 .09	

## Compilation of every published type of Fischer-Tropsch iron catalyst-Continued

Composition	Ratio of constituents, wt. basis	Reaction tem- perature, ° F.	liquid and	Remarks
Fe-Cu-K <sub>2</sub> CO <sub>7</sub> -MgO-kguhr Do.  Fe-Cu-K <sub>3</sub> CO <sub>7</sub> -MnO <sub>7</sub> -kguhr Do.  Fe-Cu-Mn-KOH-kguhr Fe-Cu-Mn-KOH-kguhr Fe-Cu-Mn-KOH-kguhr Fe-Cu-Mn-KOH-kguhr Fe-Cu-Zn-K <sub>3</sub> CO <sub>7</sub> -kguhr Fe-Cu-Zn-K <sub>3</sub> CO <sub>7</sub> -kguhr Fe-Cu-Mn-My-ThO-kguhr Fe-Cu-Mn-Ny-ThO-kguhr Fe-Cu-Mn-Ny-ThO-kguhr Fe-Cu-Ny-ThO-Kguhr Fe-Cu-Ny-ThO-Kguhr Fe-Cu-Ny-ThO-Kguhr Fe-Cu-Ny-ThO-Kguhr Fe-Cu-Ny-ThO-Kguhr	100:25:2:2:125 100:35:2:2:125 100:35:2:2:125 100:25:2:2:125 100:25:2:2:125 100:25:2:2:125 100:25:2:2:125 100:25:2:2:125 100:25:2:2:125 100:25:3:2:125 100:25:3:2:126 100:25:3:2:126 100:25:3:2:126 100:25:3:0:74:0.10:- 100:25:5:5:74:6	495 482 495 482 495 482 495 495 495 509 495	.61 .31 .61 .54 .59 .47 .45 .64 .17 .65	Yield of gaseous.

<sup>1</sup> Lb. per 1,000 cu. it.

-. Fischer-Tropsch Process, an Annotated Bibliography. Rept. for Tech. Sec., Postwar Planning Cooperating Com., October 1945, p. 29.

## Compilation of every published type of Fischer-Tropsch alloy catalyst

		Composition		Ratio of constituents, weight basis	Reaction tempera- ture, °F.	Yield of pri- mary product, liquid and solid hydrocarbons, gal. per 1,000 cu. ft.	Remarks
Co-Al. Co-Si. Do. Do. Ni-Al. Do. Do.				? ? 100:100 100:100 100:100 100:100	392 428 401 446 348 383	1, 20 -75 -47 -55 1, 15 -52	Increase in Al or temperature decreased yield.
Do. Do. Ni-Fe-	\1Si			100:100 100:100:200 100:100:200 100:100:200 100:100:200 100:20:100 100:20:200	401 383 396 388 446 410 419	. 47 . 90 . 58 79 . 66 . 32 . 36 . 80	Yield varied with diameter of reaction tube.

-. Utilization of Off-Peak Gas Capacity. Rept. for Tech. Sec., Postwar Planning Cooperating Com., August 1945, pp. 35-47.

Discusses the possibilities of utilizing spare watergas equipment for producing synthesis gas for making synthetic MeOH or synthetic gasoline by the Fischer-Tropsch process. The conclusion is that the utilization of spare water-gas capacity during off-peak periods for the above purpose is not economically feasible. It is proposed, however, that the feasibility of producing lamp black or carbon black be investigated, as this proposition is economically possible.

1568. IPATIEFF, V. N. [Pyrogenic Contact Reactions of Organic Compounds. I, II, III.] Ber. deut. chem. Gesell., vol. 34, 1901, pp. 596-600, 3579-3589; vol. 35, 1902, pp. 1047-1057, 1057-1064; Jour. Chem. Soc., --1901, I, p. 248; 1902, I, p. 4; 1902, II, p. 335.

MeOH is decomposed by heat into trioxymethylene, a decomposition facilitated by Zn, but Fe causes a further decomposition into H2 and CO. In presence of graphite, MeOH yields considerable quantities of CH4. When MeOH is passed through a red-hot Fe tube, considerable quantities of HCHO are produced together with combustible gases and about 3% of C. The oxides of Zn, Fe and Cr are classified as dehydrogenation catalysts.

-. [Pyrogenetic Contact Reactions of Organic Compounds. IV. A New Method of Preparing Olefins. J Ber. deut. chem. Gesell., vol. 36, 1903, pp. 1990-2003; Jour. Chem. Soc., 1903, I, p. 593.

- [Pyrogenetic Contact Reactions of Organic Compounds. V. Contact Isomerism.] Ber. deut. chem. Gesell., vol. 36, 1903, pp. 2003-2013; Jour. Chem. Soc., 1903, I, p. 594.

1571. IPATIEFF, V. N., and HUHN, W. [Pyrogenetic Contact Reactions of Organic Compounds. VI. Contact Isomerism.] Ber. deut. chem. Gesell., vol. 36, 1903, pp. 2014-2016; Jour. Chem. Soc., 1903, I, p.

1572. IPATIEFF, V. N., and LEONTOWITSCH, W. [Pyrogenetic Contact Reactions of Organic Compounds VII. Contact Metamerism.] Ber. deut. chem. Gesell., vol. 36, 1903, pp. 2016–2019; Jour. Chem. Soc. 1903, I, p. 598.

1573. IPATIEFF, V. N. [Catalytic Reactions at High Temperatures and Pressures. VIII, IX.] Jour-Russian Phys.-Chem. Soc., vol. 36, 1904, pp. 786-813, 813-835; Ber. deut. chem. Gesell., vol. 37, 1904, pp. 2961-3005; Jour Chem. Soc., vol. 2, 1904, pp. 644-645.

Investigation of the decomposition of alcohols at high temperatures and pressures in presence of Fe catalyst leads to the conclusion that increase of pressure diminishes the decomposability of alcohols, and

although the course of the reaction is the same as under ordinary pressure, yet the products of the reaction, especially the gases formed, differ in composition from those obtained under atmospheric pressure. The decomposition of primary, secondary, and tertiary alcohols differs as regards both the products formed and the velocity which may be taken as approximately proportional to the rate of increase of pressure. Investigation of the decomposition in presence of alumina as catalyst of alcohols in closed vessels under high pressures and at definite temperatures shows that the alcohols undergo decomposition into olefins and H2O just as is the case under ordinary pressure. The temperatures at which the catalytic decompositions occur are, however, higher than under atmospheric pressure. But it is found that at temperatures lower than those at which the olefins are formed from primary alcohols, 1 mol. of H2O is given up by 2 mol of alcohol, an ether being formed. This reaction is reversible, the ether again yielding the alcohol under the influence of alumina. At higher temperatures the ether undergoes further decomposition into olefins and H.O. At still higher temperatures the olefins and also the aldehyde formed by the hydration of the ether are decomposed, yielding gaseous products partially similar to those formed during catalysis by Fe.

1574. -[Catalytic Synthesis of Methane.] Jour. prakt. Chem., vol. 87, 1913, pp. 479-487; Jour. Russian Phys.-Chem. Soc. vol. 45, 1913, pp. 433-442; Chem. Zentralb., 1913, II, p. 234; Chem. Abs., vol. 7, 1913, p. 3126.

It has been assumed that the catalytic synthesis of CH, from C and H: in presence of reduced Ni is facilitated by the formation of hydrides of the metal. Ipatieff ascribes catalysis to the presence of metallic oxides, which may serve both as oxidizing and reducing agents. In this case the scheme is as follows: Actor H-NiO catalyzer; Actor H-C acceptor. The NiO oxidizes the C to CO2, and the latter is reduced by the H. according to the reversible reaction: CO.+4H.= CH4+2H2O. As the H2O produced is decomposed by the metal with regeneration of metallic oxide, the process is continuous, a small amount of the latter being enough for synthesizing a considerable amount of CH. The correctness of this view is supported by the fact that at least a small amount of H2O is necessary in this, as in many other reactions and that the reaction represented by the above equation is reversible. This is proved by numerous experiments made at different. temperatures and pressures, and with different concentrates of the gases. The results of these experiments are summarized as follows: The reduction of CO2 by H2 does not go to completion, whether the H2 or the CO2 is in excess; when a large excess of CO. is used, the relative amount of H. left unchanged decrease with an increase in the original concentrate of the CO2; both NiO and reduced Ni catalyze the reduction, while CuO is considerably less effective; with theoretical amounts of the 2 gases the reaction of reduction tends to reach a certain limit. Several tables illustrate the results.

1575. [Displacement of Metals and Their Oxides by Hydrogen Under Pressure at High Temperatures.] Chim. et ind., Spec. No., April 1928, pp. 411-414; Chem. Abs., vol. 22, 1928, p. 4287.

Effects of CO on CuSO, solutions at 160°-220° and 20-100 atm. for 16 hr. were studied. It was found that H.O and CO reacted to give HCOOH, which decomposed to give 2H2 and CO2.

-. Hydrogenation Developments in Russia. Nat. Petrol. News, vol. 23, No. 25, 1931, pp. 61-64; Chem. Abs., vol. 26, 1932, p. 1424.

Decomposition and synthesis investigations of organic compounds were made possible with the development of high-pressure and high temperature methods. The reduction of CO by H2 at atmospheric pressure with catalysts produces liquid and solid homologs of CH. The formation of metal carbides appears to be an intermediate stage of the reactions involved. A gasoline produced similarly from water gas was shown to be highly unsaturated, and several 02 compounds were isolated.

577. \_\_\_\_\_\_ Mixed Catalysts. Nat. Petrol. News, vol. 32, No. 32, 1940, pp. R-280-282; Petrol. Refiner, vol. 19, 1940, pp. 250-255; Science, vol. 91, 1940, pp. 605-608; Chem. Abs, vol. 34, 1940, p. 6512.

According to a theory formulated by Ipatieff, increased activity is not explained satisfactorily as a purely physical effect of the promoters resulting in arrested recrystallization and preservation of the surface. Experiments with promoted catalysts led this author to conclude that a new source of energy contributes to catalysis. He assumes that contact of the metallic promoter with the basic catalyst produces electric energy. Ipatieff believes that the metallic oxide promoters participate in the reaction according to their chemical nature, thus assisting the catalyst in utilizing the reaction energy. This would mean, for instance, that ThO<sub>2</sub> in a Co-ThO<sub>2</sub>-kieselguhr catalyst acts not only by its stabilizing influence on the specific structure of the catalyst but actually takes part in the reaction as a dehydrating agent. An activating agent may thus operate by physical, chemical, or physicochemical means.

-. Sec abs. 3091a.

1578. IPATIEFF, V. N., AND DOLGOV, B. N. [Study of Catalysts for the Synthesis of Methanol.] Jour. Chem. Ind. (U. S. S. R.), vol. 8, 1931, pp. 825-829; Chem. Abs., vol. 26, 1932, p. 80.

Decomposition of MeOH over various catalysts was studied as a guide to the discovery of the catalyst most active for the MeOH synthesis. Zn-Cr catalysts are best, though Zn and ZnO also may be used. Asbestos forms a better support than pumice. For best results the Zn-Cr nitrates are precipitated from dilute solution by dilute alkaline carbonates, which produce a more active catalyst than the hydroxides on the asbestos at 60°-80°. The density of the catalyst on the support should be high. The catalyst is then reduced by H. or MeOH vapors. In catalysts are less easily poisoned by PH, than those of Cu. Nitrates of Ce, Th. and UO: serve as activators in small amounts, but in larger quantities they reduce the catalytic activity. On standing, the activity of all the catalysts decreases.

IPATIEFF, V. N., AND HUHN, W. [Pyrogenetic Contact Reactions of Organic Compounds. VI. Contact Isomerism.] See abs. 1571.

IPATIEFF, V. N., AND LEONTOWITSOH, W. [Pyrogenetic Contact Reactions of Organic Compounds. VII. Contact Metamerism.] See abs. 1572.

1579. IPATIEFF, V. N., AND MONROE, G. S. Synthesis of Methanol From CO2 and H2 Over Copper-Alumina Catalysts. Mechanism of Reaction. Jour. Am. Chem. Soc., vol. 67, 1945, pp. 2168-2171; Chem. Abs., vol. 40, 1946, p. 1140.

Synthesis of MeOH from CO2 and H2 over Cu-Al2O2 catalysts was investigated over a catalyst temperature range of 282°-487° and a pressure range of 117-410 atm. Cu alone and Al-O. alone had no catalytic effect. The most active catalyst had a Cu content of 8-28%, giving conversions of 94% at 410 atm. and catalyst temperature of 285°. Similar experiments with CO and H. gave conversions of 39-43%, with as much as 15 and 41% of the CO charge reacting to give CH<sub>2</sub> and dimethyl ether, respectively. When CO<sub>2</sub> was added to the CO (mol. ratio CO: CO<sub>2</sub>=3.1:1.0) the MeOH conversion was raised to 64%, and the formation of dimethyl ether was reduced to about 1%. Results

obtained with aqueous CH<sub>2</sub>O solutions indicate that the formation of MeOH from CO<sub>2</sub> and H<sub>2</sub> under pressure may proceed along 2 paths. After reduction of the CO<sub>2</sub> to the CH<sub>2</sub>O stage, part of the MeOH is formed by direct hydrogenation of the CH<sub>2</sub>O and part by the Cannizzaro reaction.

1579a. IPATIEFF, V. N., AND SCHMERLING, L. Alkylation of Isoparaffins. Advances in Catalysis, Academic Press, Inc., New York, 1948, vol. I, pp. 27-64. Critical discussion of catalytic alkylation of isoparaffins with special emphasis on catalysis and reaction mechanism. 43 refs. listed.

1579b. IPATIEFF, V. N. MONROE. G. S., AND FISCHER, L. E. Low-Temperature Hydrogen Production. Ind. Eng. Chem., vol. 42, 1950, pp. 92-94; Chem. Abs., vol. 44, 1950, p. 3,221.

Experiments were conducted on the direct catalytic conversion of CH, and H<sub>2</sub>O to H<sub>2</sub> and CO<sub>2</sub> at about 500°-800° and at atm. and at 250 p. s. i. pressure. Space velocities of CH<sub>2</sub> of about 120 per hr. and mole ratios of H<sub>2</sub>O: CH<sub>2</sub> of about 5 at atm. pressure and 32 at high pressure were used. The most effective catalysts were NiO or NiO and CuO on kieselguhr and the optimum concentrations about 7% CuO, 70% NiO, and 23% kieselguhr. This gave 55–92% conversion of CH<sub>2</sub>. Increase of temperature increased H<sub>2</sub> yield and formation of CO. Increase of pressure decreased CO formation and H<sub>2</sub> yield, but the latter effect was nullified by increasing the H<sub>2</sub>O: CH<sub>4</sub> mole ratio.

1580. IREDALE, T., AND LYONS, L. E. Influence of Inert Gases on the Photodecomposition of Gaseous Acetone. Jour. Chem. Soc., November, 1944, pp. 585-590; Chem. Abs., vol. 39, 1945, p. 3735.

A study was made on the influence of CO<sub>2</sub> and N<sub>2</sub> at about atmospheric pressure on the photodecomposition of gaseous acetone at room temperature in light of wave length 2,400-3,100 A. The yield of CO was increased, no detectable amounts of biacetyl were formed, and the ratio C<sub>2</sub>H<sub>2</sub>: CO approached unity. The results are attributed to increased dissociation of acetyl radicals on collision into CO and methyl and/or to hindering diffusion of acetyl to the walls, where it associates to give biacetyl.

1581. IRON AND COAL TRADES REVIEW. Hydrocarbons From Water Gas. Germany. Vol. 129, 1934, p. 542.

Fischer experimental plant for the manufacture of synthetic benzine from coal, which is being erected by the Ruhrchemie A.-G., of Oberhausen-Holten, will probably be completed at the end of this year. The cost will be approximately RM 1,000,000. The Fischer process operates at normal pressure and commences with water gas made directly from coke; thus, it is not based on coal byproducts but on the raw fuel itself. The collieries in the Ruhr, which are associated with the I. G. Farbenindustrie in the development of coal hydrogenation, are awaiting the results of the plant erected at Oppau by the I. G., which operates on the modified Bergius process and is claimed to have a much greater output than that adopted by the Ruhrchemie. The full-scale plant to be erected at Scholven will probably be on this process. It remains to be seen whether, following the successful outcome of the I. G. trials, the Ruhr collieries will come to a general agreement with the I. G., especially if the expectations regarding the Fischer process are fulfilled.

IRSA, A. P. See abs. 3395, 3395a, 3501.

Ізнівавні, Т. Sec abs. 3315, 3316, 3317.

1582. ISHIGAKI, T. Determination of the Density of Cementite. Sci. Repts. Tohoku Imp. Univ., vol. 16, 1927, pp. 295-302; Chem. Abs., vol. 21, 1927, p. 2643.

Results of all previous investigations are listed; they differ considerably. Ishigaki redetermines the

density by extrapolating the density-concentration curves of annealed C steels and cast irons to the concentration of cementite. Hot-forged and annealed samples were used to eliminate minute intercrystalline cracks and gas enclosures. The density measurements are made with an accuracy of  $\pm 0.0003~\rm gm$ , by an application of Archimedes' principle. The density of cementite is 7.662, in satisfactory agreement with 7.68 found by Westgren and Phragmen by means of X-ray analysis. A table showing the influence of common impurities, other than C, upon the density of Fe is given.

ISHIKAWA, H. Sec abs. 1802, 1803. ISHIKAWA, S. Scc abs. 1867.

Iro. S. Sec abs. 1918, 1919, 1920, 1921, 1922, 1923, 1924, 1925, 1926.

1583. IURA, T. Synthetic Motor Fuels. Wisconsin Eng., vol. 49. No. 3, 1944, pp. 9. 29. Review.

IVANNIKOV, P. Y. See abs. 1107.

1584. IVANNIKOV, P. Y., FROST, A. V., AND SHAPIRO, M. I. [Effect of Ignition Temperature on the Catalytic Activity of Zinc Oxide.] Compt. rend., acad. sci. U. R. S. S., 1933, pp. 124-126; Chem. Abs., vol. 28, 1934, p. 1595.

Activity of ZnO as catalyst for the decomposition of MeOH vapor decreased sharply with rise in ignition temperature of the hydrate from which the ZnO was formed. The hexagonal lattice remained unchanged between  $110^{\circ}-1,300^{\circ}$  and had the following parameters:  $a=3.248\pm0.002$  Å. U.;  $c/a=1.602\pm0.002$ . The size of the crystallites remained unchanged  $100^{\circ}-500^{\circ}$ ; à rapid increase began at  $770^{\circ}$ . A comparison of the changes in activity and crystal size showed that the decrease in activity began sooner and proceeded more rapidly than the decrease in surface caused by sintering.

1585. IVANOFF, N. [Esterification of Fatty Acids With Glycerol.] Bull. mat. grasses inst. colonial Marseille, vol. 29, Nos. 1-2, 13-19, 1945; Chim. et ind., vol. 53, No. 1, 1945, p. 41; Chem. and Met. Eng., vol. 53, No. 3, 1946, p. 270.

Work done on the rate of esterification of fatty acids with glycerol showed what quantities of catalyst and glycerol should be used, as well as the most favorable temperatures in regard to rate of reaction and preparation of undecomposed products. It was found that the catalytic action of benzene-sulfonic acid and p-toluenesulfonic acid is practically the same. At 175°-185° and in presence of 0.22% catalyst, the reaction is virtually in equilibrium after 8 hr. of heating, the yield being 82%. With 0.5% catalyst the yield is still 82%, and the reaction stops after 5 hr. of heating. When the temperature is raised to 250°-260°, the reaction is rapid and the yield is 96-97%, but the product is partly carbonized at the end of 3 hr. The rate of esterification and the yield of esterified fatty acids increases very rapidly when the quantities of glycerol used are greater than those indicated in the theoretical formula for triglycerides, but then there is a distinct predominance of diglycerides. p-toluenesulfonic acid was found to be more advantageous than benezenesulfonic acid.

1586. IVANOV, K. I., AND GUSEV, V. I. [Properties of Zinc-Chromium Catalysts for the Synthesis of Methanol.] Jour. Chem. Ind. (U. S. S. R.), vol. 12, 1935, pp. 1143-1146. Chem. Abs., vol. 30, 1936, P. 1525.

When a catalyst of 8ZnO . 1.5Cr<sub>2</sub>O, is first used, it is most efficient at 370°, but as its use is continued, the optimum temperature rises slowly to 400°. Very high rates of passing the gas over it favor MeOH formation, while low rates of passing the gas, or temperatures above 400°, begin to favor OH, formation.

1587. IVANOV, K. N. [Properties and Structure of the Copper-Methanol Catalysts.] Acta Physicochim., U. R. S. S., vol. 1, 1934, pp. 493-502; Chem. Abs., vol. 29, 1935, p. 6711.

Addition of ZnO increases somewhat, and of Cr<sub>2</sub>O<sub>2</sub> very strongly, the activity of the catalyst. Very active catalysts, 5 times as active as any previously reported, were prepared, for example: Cu, 82; ZnO, 16; Cr<sub>2</sub>O<sub>3</sub>, 2; and Cu, 60; ZnO, 35.6; Cr<sub>2</sub>O<sub>3</sub>, 44. High ZnO (more than 30%) and low Cr<sub>2</sub>O<sub>3</sub> (less than 2%) lead to rapid aging of the catalyst. Reduction of the dried mixed precipitate takes place in a H. stream at 200°-220°. X-ray studies indicate that the function of Cr<sub>2</sub>O<sub>3</sub> is to preserve a small amount of CuO, and that the real active centers are the Cu-CuO interfaces. During use, ZnO with Cu forms a-brass, with an increase in lattice constant of Cu and a decreased catalytic activity.

1588. — [X-Ray Examination of Copper Methyl Alcohol Catalysts.] Mem. Inst. Chem. All-Ukrain. Acad. Sci. vol. 1, 1934. pp. 49-55 (in German, pp. 56-57); Chem. Abs., vol. 29, 1935, p. 7169.

Activation of CO and H<sub>2</sub> molecules by Cu–ZnO–Cr<sub>2</sub>O<sub>4</sub> catalysts (I) is due to active Cu and CuO molecules, the dispersion of which is increased by the ZnO. Cr<sub>2</sub>O<sub>2</sub> acts as a promoter forming solid solutions with CO. Inactivation of (I) is due to diminution in the dispersion of Cu, to reduction of active CuO, and to increase in the parameters of the Cu lattice consequent on conversion into α-brass.

------. Sce abs. 893, 2710, 2711, 2712, 2713, 2716,

1589. IVANOV, K. N., AND KOZLOV, L. I. [Corrosion of Alloy Steels Under the Conditions of Methanol Synthesis.] Khim. Mashinostroenie, vol. 5, No. 6, 1936, pp. 36-39; Chim. et ind., vol. 38, 1939, p. 923; Chem. Abs., vol. 32, 1938, p. 2496.

Corrosion of steel during the synthesis of MeOH results mainly in the production of Fe carbonyl. The metals alloyed with the steel can reduce corrosion, but not suppress it completely. The most resistant steels are those with high Cr content (13-15%); their corrosion is practically nil up to 100° and above 300° Cr-V steel, on the other hand, is unsuitable. To secure practically absolute resistance, the steel should be covered with a protective lining such as a surface layer of a high=Cr, Fe-Cr alloy.

1590. IVANOV, K. N., KOZLOV, L. I., AND SOFER, M. A. [Properties of Zinc-Chromium Catalyst for the Synthesis of Methanol.] Jour. Chem. Ind. (U. S. S. R.), vol. 13, 1936, pp. 406-408; Chem. Abs. 30, 1936, p. 4630.

Presence of Pb and Cu in the catalyst lowers its productivity somewhat. More than 1% of sulfide or sulfate S lowers the productivity and increases the amount of esters in the MeOH. Above 400°, this effect is not so important. The presence of even 0.1% of Fe is very harmful, though FeO does not shows this effect.

1591. IVANOVSKII, F. P., AND BRAUDE, G. E. [Low-Temperature Catalysts for the Conversion of Carbon Monoxide.] Jour. Chem. Ind. (U. S. S. R.), vol. 15, No. 1, 1937, pp. 14-19; Chem. Abs., vol. 32, 1938, p. 3100.

Catalysts deposited on grog are not strong enough for industrial use. The best catalysts are mixtures of about 35% CuO and 65% CoO containing some  $K_0C_{10}O_{10}$ , fused and reduced with  $H_2$  at 300°. Such catalysts are poisoned by  $H_2S$ .

1592. IVANOVSKIT, F. P., BRAUDE, G. E., AND PANINA, A. M. [New Catalysts for the Conversion of Carbon Monoxide.] Jour. Chem. Ind. (U. S. S. R.), vol. 10, No. 2, 1934, pp. 37-44; Chem. Abs., vol. 28, 1934, p. 3845.

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Fe catalysts should be heated for 2 hr. at 700° before use to give them the greatest stability. Cocatalysts are very active but are mechanically weak. Addition of MgO strengthens them but lowers their activity. Siderite is a good catalyst, but it loses its activity on prolonged use. The loss may be prevented by addition of 0.7% by wt. of K.Cr.O. to siderite that has been heated for 6 hr. at 500°-525°. Such a catalyst gives 94-96% conversion. Addition of too much K.Cr.O. weakens the catalyst. H.S lowers its activity. Titanomagnetite, Fe chromite, and bauxite are unsatisfactory as catalysts.

1593. IVANOVSZKY, L. Natural Gas; Possibilities of Exploitation in Great Britain. Petroleum, vol. 5, 1942, pp. 133-134; Chem. Abs., vol. 37, 1943, p. 1030.

Possibility of using CH, from natural gas as starting material and possibly fuel in the Fischer-Tropsch and Bergius processes for the production of motor fuel in Great Britain is briefly discussed. Reports of a 1938 drilling campaign indicate that a group of Scottisli gas wells could supply more than 10,000,000 cu. ft. per day, while by horizontal drilling and vacuum extraction from coal seams, 1,000 cu. ft. (equivalent to 7 gal. of gasoline) could be extracted per ton of coal—or a total of 1,400 million gal. of gasoline per yr. based on a production of 200,000,000 ton per yr.

1594. — . [Synthetic Waxes—Attempted Classification and Definition.] Chim. et ind., vol. 63, 1950, pp. 239–245; Chem. Age, vol. 62, 1950, p. 610.

Waxes may be classified as (a) natural-animal, vegetable, mineral, (b) refined (natural), (c) chemically modified, (d) synthetic, (e) compound. The term "synthetic" should be restricted to waxes that differ essentially from the raw materials used and result from chemical processes, which are often complicated. From the strictly scientific point of view, they are to be regarded as products of important chemical changes and partial synthesis. There are 3 synthetic processes: Hydrogenation of CO (Fischer-Tropsch waxes); low-temperature hydrogenation of C (T. T. H. waxes); and ethylenic polymerization (alkathenes, polythenes). Conversion of these hydrocarbon waxes into those of fatty acids, alcoholic or ketonic waxes, or of esters or other condensation waxes, leads to a series of purely synthetic waxes, if the hydroxylated consituents used are themselves synthetic, but the conception of true or purely synthetic has only theoretical interest. It is more important to inquire if the synthetic waxes are true replicas of the corresponding natural substances. In some cases this is so, as with the hydrocarbon waxes, which are similar to paraffin wax; and in some other cases there are analogies or similarities. In such instances the synthetic product may be superior or inferior to its natural analog, but in any case offers greater variety of properties. The difference between the natural ester waxes and the synthetic residues is that the latter contain various glycols, etc., but do not contain fatty alcohols of high molecular weight in appreciable quantities. Some, therefore, are completely saponifiable, while others (pseudo-esters) are virtually unsaponifiable.

IWAMOTE, T. See abs. 3199. IWAMURA, E. See abs. 2205. IWAO, M. See abs. 1927, 1928, 1929.

1594a. IYENGAR, I. M. S. Fluidization. Jour. Sci. Ind. Research (India), vol. 9A, 1950, pp. 314–322; Fuel Abs., vol. 11, No. 7, 1952, abs. 677.

Fluidization technique is described and its application to the production of water gas from coal, catalytic cracking of petroleum oils, Fischer-Tropsch synthesis of liquid fuels, oxidation of naphthalene, washing of coal, and removal of S from town's gas is discussed.

1595. JACK K. H. Iron-Nitrogen, Iron-Carbon, and Iron-Carbon-Nitrogen Interstitial Alloys: Their Occurrence in Tempered Martensite. Nature, vol. 158, 1946, pp. 60-61; Chem. Abs., vol. 40, 1946, p. 6392.

Prolonged reaction of CO with Fe nitrides below 500° eliminates N, forming Fe percarbide (C, 30.5-32.1 atomic %). The unit cell is orthorhombic; it contains 4 Fe2.C, molecules. Above 500° the product of the same reaction is cementite. Both of these Fe carbides are metastable; Fe percarbide decomposes in vacuo to C+cementite; cementite to a -Fe+C. The rate of decomposition is negligible below 350°.

 Binary and Ternary Interstitial Alloys. I. Iron-Nitrogen System: The Structures of Fean and Fe.N. Proc. Roy. Soc. (London), vol. 195, A, 1948, pp. 34-40; Chem. Abs., vol. 43, 1949, p. 3765.

ζ-Fe<sub>2</sub>N phase is prepared by passing NH<sub>2</sub> over Fe at temperatures not exceeding 450°. The positions of N in y (Fe,N) and in 5-phases are determined. Both are fully ordered interstitial alloys. In & the Fe atoms are in approximately hexagonal close-packed array. In each layer plane of octahedral interstices one-half of their number is occupied such that each N atom is allowed to have unoccupied holes above and below it in adjacent planes.

-. Binary and Ternary Interstitial Alloys. II. Iron-Carbon-Nitrogen System. Proc. Roy. Soc. (London), vol. 195, A, 1948, pp. 41-55; Chem. Abs., vol. 43, 1949, p. 3765.

Reaction of CO with nitrides of Fe and of NH, with carbides of Fe gave new Fe carbonitrides, a series of new ternary interstitial alloys. Carbonitrides with structures similar to corresponding Fe nitrides extend from Fe,N, to Fe,C,N. The latter is isomorphous with Fe.N. Phase fields are described. Prolonged reaction of CO with nitrides of Fe leads to elimination of the N. Below 500° the product is Fe percarbide; above this temperature it is cementite.

-. Binary and Ternary Interstitial Alloys. III. Iron-Carbon System: The Characterization of a New Iron Carbide. Proc. Roy. Soc. (London), vol. 195, A, 1948, pp. 56-61; Chem. Abs., vol. 43, 1949,

Fe percarbide has a narrow range of composition and is identical with a carbide previously assumed to be an Fe.C. The unit cell is either orthorhombic or hexagonal, the former having approximately 80 Fe atoms. An empirical formula Fe<sub>2</sub>C, is proposed. Fe<sub>2</sub>C has probably not yet been prepared. Cementite and the percarbide are both metastable. Fe percarbide decomposes giving cementite and C while cementite gives a -Fe and C. The rates of decomposition of the 2 carbides are negligible below 350°.

[Results of Further X-Ray Structural Investigations of the Iron-Carbon and Iron-Nitrogen Systems and of Related Interstitial Alloys.] Acta cryst., vol. 3, 1950, pp. 392-394; Chem. Abs., vol. 44, 1950, p. 10641.

Tempering of C-martensite, the structure of Naustenite, N-martensite, and the tempering of N-martensite, the structure of e-Fe and the  $\epsilon \rightarrow \zeta$  transition, and the hexagonal Ni, Ni nitride, and Ni carbonitrides

1600. -. [X-Ray Structural Investigations of the Iron-Carbon and Iron-Nitrogen Systems and of Related Interstitial Alloys.] Acta cryst., vol. 3, 1950, pp. 392-393; British Abs., 1951, I, A, p. 41.

Three tempering stages of C martensite are discussed. The loss of tetragonality of martensite during the 1st tempering stage is due to the precipitation

of a close-packed hexagonal Fe carbide, structurally similar to e-Fe3N. The unit-cell dimensions are a 2.73 Å, c 4.33 Å. The behavior of N martensite on tempering is quite different from that of the corresponding C alloys. At temperature <250° a new phase, a", is formed as an intermediate in the decomposition a'-\gamma'. This a" phase is relatively stable, with a 5.72Å, c 6.29 Å. The structures of  $\epsilon$ -Fe nitrides and the c-f transition are discussed. The bexagonal structure of Ni2N is confirmed, the unit-cell dimensions being a 2.6677  $ilde{\mathrm{A}} \pm 0.0005$   $ilde{\mathrm{A}}$ , c 4.3122 ű0.0005 Å. There appears to be no evidence as yet for the existence of a hexagonal allotrope of Ni.

- Sec abs. 578a, 1218.

JACOB, K. See abs. 2434. JACOBS. J. See abs. 1255.

1601. JACOBSON, B., AND WESTGREN, A. [Nickel Carbide and Its Relation to the Other Carbides of the Series of Elements Scandium-Nickel.] Ztschr. physik. Chem., vol. 20, B, 1933, pp. 361-367; Chem. Abs., vol. 27, 1933, p. 2860

X-ray analysis was made of Ni<sub>2</sub>C. The elementary cell has dimensions a=2.646 Å. U. c=4.329 Å. U. and c: a=1.636. The results do not agree with the rule of Hägg for the structure of hydrides, borides, carbides, and nitrides of the transition elements.

JACOBUS, G. See abs. 385.

JACORY, J. See abs. 2219.

1602. JACQUÉ, L. [Action of Hydrogen on Carbides of Iron and Chromium.] Compt. rend. vol. 206, 1938, pp. 1900-1902; Chem. Abs. vol. 32, 1938, p. 6170.

H, at a pressure of 100 kg. per cm. at 550° in 50 hr. entirely decomposes cementife, prepared by the action of KCN or NaCN on Fe at 650°. At lower temperature and pressure the removal of C was less complete, thus under 50 kg. per cm.2 at 500° the amount of C remaining was 2.5-3.5%, at 550°, 1.6-2.3. Treated similarly, H2 had no appreciable effect on Cr carbides, whether Cr.C., Cr.C., or Cr.C.

-. [Thermodynamics and Catalysis in the Synthesis of Fuels Under Pressure.] Centre de perfectionnement technique, Cours confs., No. 1318, February 1945, 31 pp.; Chim. et ind., vol. 55, 1946,

Application of thermodynamics to the study of reactions permits a formula being established giving as a function of temperature and pressure the equilibrium concentrations of the constituents of the reaction. It has been established that the paraffins and the polymethylenes are relatively the most stable hydrocarbons at low temperature (below 500°), while the aromatics and olefins are the most stable at high temperature. Except for C2H2, no hydrocarbon is thermodynamically stable compared with its elements above 577°. In most reactions for synthesis of motor fuels, equilibrium is not attained in practice. It is often necessary to operate at a velocity high enough to avoid side reactions. A study of the kinetics of the reactions enables suitable reaction conditions to be selected, especially from the point of view of the dissipation of the heat of reaction.

- See abs. 3723.

1604. JACQUE, L., GIVAUDON, J., SCHMITT, P., AND DELION, R. [Preparation of Pure Paraffin Hydrocarbons by the Superfractionation of Synthetic Gasoline.] Rev. Inst. franc. petrol. et Ann. combustliquides, vol. 1, December 1946, pp. 137-140; Chem. Abs., vol. 42, 1948, p. 4325.

By superfractionating a hydrogenated synthetic Fischer gasoline, the authors have prepared fractions of pentane, hexane, heptane, octane, and nonane, which analyze 8-9%, 22-23%, 20-25%, 20-22%, 10-15% of gasoline, respectively. The utilization of hexane for precipitating the asphaltic substances of lubricating oils and that of heptane as standard motor fuel for determining the octane numbers with the Cooperative Fuel Research motor is shown.

JAECKEL, B. Sce abs. 2139.

1605, JAEGER, A. [Reduction of Carbon Monoxide to Formaldehyde and Methanol at Ordinary Pressure.1 Ges. Abhandl. Kenntnis Kohle vol. 7, 1926, pp. 51-54; Chem. Zentralb. 1926, I, p. 3393; Chem. Abs., vol. 21, 1927, p. 3531.

Survey of literature.

--- Sec abs. 982.

1606. JAEGER, A., AND WINKELMANN, H. [Reduction of Carbon Monoxide Under Ordinary Pressure.] Ges. Abhandl. Kenntnis Kohle. vol. 7, 1925, pp. 55-62; Chem. Abs., vol. 21, 1927, p. 2550.

Yields of CH, and of mixed oxides of C obtained by passing a mixture of 26% of CO and 67% of H2 over a Ni pumice catalyst are, respectively, 12 and 12% at 220°, 54 and 7% at 245°, and 66 and 6% at 250°. The optimum temperature for CH, formation lies in a narrow zone at 250°. A mixed Cu-Ni catalyst yielded only 6% of CH4; no C2H4 could be detected when a Pd catalyst was used. Contrary to the results of French Patent 519,649, no CH<sub>2</sub>O is formed when a mixture of CO, HCl, and H<sub>2</sub> is passed over CuCl, Cu, Fe, or Ni at 200°-300°; it is produced in considerable amounts, however, when formic acid vapor mixed with H2 is passed over metals at lower temperatures, over indifferent substances at higher temperatures, or through an empty glass tube at 700°-750°. CO and steam yield small quantities of formic acid when passed over hydrated SiOz at 320°; at 450° in a quartz tube about 1.5% of the CO is converted into CH2O. This yield decreases with rising temperature and increasing streaming velocities (100 cm. per min.), and no CH<sub>2</sub>O is formed at all when Cu or Ni pumice catalysts are used or when the steam is replaced by H2. H2 free from H.S or prepared by dehydrogenation of tetralin (tetrahydronaphthalene) does not reduce CO to CH2O at 400°. CH<sub>2</sub>O likewise is not obtained by reducing the compound KaFe (CN) aCO with Ha.

1607. JAHN, H. [Studies on the Decomposition of Simple, Organic Compounds by Zinc Dust.] Ber. deut. chem. Gesell., vol. 13, 1880, pp. 983-990.

By passing MeOH over a heated mixture of Zn and ZnO, decomposition takes place giving a gas containing 30% CO, the rest being H2 containing a trace of CH. 1608. JAHN, K. [Formaldehyde From Water Gas.]

Ber. deut. chem. Gesell., vol. 22, 1889, p. 989. CH<sub>2</sub>O was produced by passing CO+H<sub>2</sub> over a

catalyst of Pd sponge.

1608a. Jain, B. C. Synthetic Liquid Fuel. Trans. Indian Inst. Chem. Engr., vol. 3, 1949-1950, pp. 79-104; Chem. Abs., vol. 46, 1952, p. 5,819.

Review of various processes for the synthesis of liquid fuels from coal and account of current economics of the processes. Among the techniques discussed are coal hydrogenation and Fischer-Tropsch. German and American work is cited. Excellent summaries are given of catalyst, operating conditions and yields for all modifications of the basic processes.

1609. JÄNECKE, E. [System: Fe-C-O.] anorg. Chem. vol. 204, 1932, pp. 257-290; Chem. Abs. vol. 26, 1932, p. 5530.

Comprehensive survey of recent work, with extensive bibliography. Jänecke's diagram has been somewhat modified, and the equilibria at various pressures

and temperatures have been calculated. The heat of formation of cementite is -6.5 kcal, and that of pearlite -2.77 kcal. Contrary to previous views, there is a maximum pressure in the univariant system: Fe-austenite-FeO-gas at 820°. The equilibria in the Fe-C-O system between 500° and 1,000° and 0.2 and 5 atm. are represented by a 3-dimensional model.

1610. JANTZEN, E., RHEINHEIMER, W., AND ASCHE, W. [Composition of a Fatty Acid Mixture Obtained by the Oxidation of Synthetic Paraffin.] Fette u. Seifen, vol. 45, 1938, pp. 388-393, 613-615; Chem.

Abs., vol. 33, 1939, p. 1527.

Paraffin produced by the Fischer-Tropsch process was oxidized in the presence of H.O, the H.O was removed, and the neutral oil was separated from the soap solution. After the fatty acids were liberated with acid, they were steam distilled, neutralized, and the lactones were extracted with petroleum ether. After the purified mixed fatty acids were liberated with acid, their constants were determined to be: Average molecular weight 229.8, I No. 486, OH No. 3.7, and solidifying point 26.2°. The fatty acids were converted to the Me esters and carefully fractionally distilled. The Me esters of all the fatty acids and. after saponification, all the fatty acids within the range Cs-Cir were isolated in pure form. The largest fraction (16.0%) was myristic acid, while acids above Car amounted to 13.29%. Small amounts of unsaturated acids and acids containing OH or CO groups introduced slight irregularities into the curves showing boiling point, melting point and nos as a function of the amount of fatty material distilled over. It is concluded, as regards the mechanism of oxidation, that all the CH groups are equally susceptible to oxidation. 1611. JAPPELT, A., AND STEINMANN, A. [Production of

Synthesis Gas in the Technical Research Plant "Reiche Zeche," Freiberg I. Sa.] Braunkohle, vol. 35, 1936, pp. 353-357, 372-377; Chem. Abs., vol. 30, 1936, p. 5757.

Describes process (abs. 3101) from operating standpoint with heat and material diagrams,

1612. JARZYNSKI, A. [Synthesis of Liquid Fuels.] Przemysl Chem., vol. 26, 1947, pp. 164-175; Chem. Abs., vol. 43, 1949, p. 5570.

Reviews catalytic hydrogenation of coal and O oxides. Describes discovery, mechanism, and development of the Fischer-Tropsch synthesis to large-scale operation in Germany. Reviews other German catalytic processes developed during World War II, such as the production of synthetic lubricants, toluene, and higher alcohols. Discusses German commercial utilization of Fischer-Tropsch waxes.

[Synthetic Liquid Fuels.] Nafta, vol. 3, 1947, pp. 245-248; Chem. Abs., vol. 43, 1949, p.

Review of the manufacture of gasoline by hydrogenation of coal or from CO+H and synthesis of CH is presented.

1614. JASPER, T. M. Building of Containers for Severe Service. Ind. Eng. Chem., vol. 20, 1928, pp. 466-470. Precautions are outlined to be observed in designing containers to operate under high pressure and

temperature. 1615. -. Building Vessels for High-Pressure and High-Temperature Service. Mech. Eng., vol. 52, 1930, pp. 193-200.

Discusses research work on vessels that has been carried to the point of practical application by pointing the way to correct design and fabrication in the production of containers for high-pressure and hightemperature service.

JEFFERSON, M. E. See abs. 390.

JELLINEK, E. See abs. 2935.

1616. JELLINEK, K., AND DIETHELM, A. [Producer-Gas Equilibrium at High Pressures.] Ztschr. anorg. Chem., vol. 124, 1922, pp. 203-229; Chem. Abs., vol. 17, 1923, p. 461.

Equilibria in the reaction C+CO==2CO were investigated for temperatures between 800° and 1,000° and for pressures up to 50 atm. for the so-called amorphous coals. The apparatus used for the determination was a specially constructed electric furnace (described in detail) for determinations up to 150 atm. and 1.300°. The equilibria for both amorphous coals and graphite agree very closely. Complete agreement also was found, up to the temperatures investigated, between the producer-gas equilibria and the law of mass action. It is true probably at still higher pressures. Primarily the generator reaction is probably a heterogeneous gas reaction, by which the validity of the law of mass action at high pressures is established. The integration constant of the isochor reaction in the producer gas equilibria agrees fully with that calculated from the chemical constants in Nernst's heat theory. It follows from the producer-gas equilibrium and the CO2 dissociation equilibrium that, with virtually approachable temperatures and pressures, the maximum work performed by the reaction C+O2=CO2 is equal to the heat tone in case the initial O2 pressure and the final CO2 pressure are alike and the reaction takes place isothermally and reversibly.

1617. JELLINEK, M. H., AND FANKUCHEN, I. Application of X-Ray Diffraction to the Study of Solid Catalysts. Advances in Catalysis, Academic Press, Inc., New York, 1948, vol. I, pp. 257-289.

General discussion is presented of the techniques of X-ray diffraction applicable to the study of catalysis with a few specific applications.

1618. JELLINEK, O. [Conversion of Coal Into Oil.] Umschau, vol. 30, 1926, pp. 533-538; Chem. Zentralb., 1926, II, p. 1481.

Describes Bergius process and the Fischer synthesis. JENCKEL, E. See abs. 3062.

JENNINGS, W. H. See abs. 368.

1619. JENNY, F. J., AND CONWAY, M. J. Equipment for Low-Cost Oxygen Production. Oil Gas Jour., vol. 45, No. 23, 1946, p. 91.

Digest of a paper presented at the 1946 national conference on petroleum mechanical engineering, American Society of Mechanical Engineers. Describes production of O2 by the liquefaction and fractionation of air as practiced on a pilot-plant scale. The unit operations involved consist essentially of compression, heat exchange, refrigeration, and fractionation. The first of 2 large plants is now under construction at Brownsville, Tex. It will operate in connection with Hydrocol process for the treatment of natural gas to produce motor fuel, diesel fuel, and crude alcohols. A second unit, to be built for a major oil company, also will supply O, for a Hydrocol plant similar in size and operation to the Brownsville plant. These 2 plants will compress approximately 250,000,000 cu. ft. of air per day to 75-85 p. s. i. g.

1620. JENSON, O. Carbonization by Electricity. Gas Jour., vol. 261, 1950, pp. 270-271,

Abstract of a paper presented at the United Nations Scientific Conference on the Conservation and Utilization of Resources, Lake Success, N. Y., is reviewed. A new electric process is described for the carbonization of noncoking bituminous coal, Spitzbergen. Carbonized briquets made from the crushed coal are charged into the top of the vertical shaft and preheated by hot gases. A diagram of this operation is shown. At the lower end of the shaft is an electric furnace containing 2 sets of 3-phase electrodes. The

carbonized and conductive briquets form the rest element, which provides the heat for the pro-Cold gas, introduced at the base of the furnace; the hot coke and is preheated. The gas is heated ther to 1,000° in the electric furnace and reacts the hot C, forming CO and H<sub>2</sub>. As the hot gas in the furnace, its sensible heat serves to carbonize coal briquets. One short ton of coal yields 1.250lb. coke briquets, 20-25 gal. low-temperature tar, 24,000 cu. ft. of gas. Power consumption is about H.: CO ratio of 2.6, and to produce synthesis H: CO 22, it is only necessary to add blue water for example, by adding steam to the circulating A plant for the synthesis of gasoline capable of verting 1.5 million short tons of Spitzbergen cont. nually will yield about 700,000 tons of low-ash! briquets, 750,000 bbl. of low-temperature coal tar, 2 million bbl. of gasoline and diesel fuel. The po requirements would be about 300,000 kw. Estimat production cost for the gasoline will be about \$0.20/2

JERDAN, D. S. See abs. 296. JESSEN, V. See abs. 133, 134. JINKINGS, A. J. Sce abs. 326. JINTA, T. See abs. 1119, 1120.

LIOGRAPHY OF FISCHER-TROPSCH SYNTHESIS AND RELATED PROCESSES

1621. JOCHUM, P. [Enrichment of the Methane of tent of Technical Gases, and the Production of a G. bon Monoxide-Free Illuminating Gas.] Journ beleucht., vol. 57, 1914, pp. 73-80, 103-111, 124-1 149-151; Chem. Abs., vol. 8, 1914, p. 1660.

Previous attempts to form CH, from the CO and of illuminating gas by the catalytic action of Nith met with difficulty, owing to the poisonous effection compounds or the fouling of the catalyzer by tark deposited C. The optimum conditions for the reach are determined, using synthetic mixtures of CO and in the ratios 1:1, 1:3, 1:5, these being the proportion named in the 3 most-important patents. The laft also approximates ordinary coal gas and is the subs of the patents of the Cedford process, the most near successful of all. The main reaction goes readily low temperatures and CO2 also is reduced easily. with high concentrates of CO or high temperatures! reaction 2 CO=CO+C makes its appearance. This partly counteracted by C+2 H=CH. The experience ments were carried out with Ni reduced from the trate on unglazed porcelain. The analyses of the fi gas were calculated back and checked very closely with the original mixtures, showing the accuracy of manif lation and absence of serious side reactions. 1:1 mixtures, the CH, could not be carried above and at this point much CO2 was formed from the secon reaction above. With 1:3 mixtures, the yield 50-65% and some CO, was formed; but with 1:1 trace of CO. appeared, though the CH. could no raised above 35%. However, in this latter gas contraction owing to the reaction was less, so that net yield of CH, was greater than where the cond tration of CH, was higher. Most of these experime were run at the rate of 8 cc./min. in a tube 16 min diameter, though it was found that up to 200 celful no CO, appeared. The optimum temperature for mixtures is 280°. With mixtures of C.H. and H. io. theoretical amounts for C2H4+H2=CH4 no diffici was met and a gas of 80% C.H. with virtually no could be obtained at 150°. As the temperature of the reaction C.H.=CH.+H.+C appeared, and at 150°. a gas of 90% CH, with no H, and only traces of CE was obtained. This decomposition is at decide lower temperatures than noted by Sabatier, probate owing to a better catalyzer. With synthetic illumining gas (9% CO, 50% H<sub>2</sub>, 38% CH<sub>4</sub>) no difficulty. found in preparing a gas of 85% CH., no trace of and less than 1% of CO. This was at 300° and the

relocity was increased to 90 cc./minute without CO pearing in the end products. With actual city gas, prified from S, after 24 hr. CO began to appear. This sis due to tarry materials collecting on the catalyzer; for when the gas was passed through CO. snow and ther on its way to the catalyzer, a gas of 85% CH., sholly free from CO, and with only traces of CO, was fill obtained after 62 hr. Though this process as apled to commercial illuminating gas means a loss of heat (with CO: H2=1:5 a net loss of 14% and with miniminating gas a loss of 11%), the resulting gas has much higher heating value/m. and as such is more valuable. The main disadvantage is the cost of purifieation by freezing, which will be partly offset by the enzene recovered. As a process for the manufacturing of CH, as a material for chemical industries, it could hardly compete with natural gas. Reviews mostimportant patents in this field.

1622. Johansson, A., and von Seth, R. Carburization and Decarburization of Iron. Surface Decarburization of Steel. Jour. Iron Steel Inst. (London), vol. 114, 1926, pp. 295-358; Engineering, vol. 122, 1926, pp. 460-464; Chem. Abs., vol. 20, 1926, p. 3429.

In an atmosphere of CO-CO the main course of the reaction is 3Fe+2CO=Fe<sub>2</sub>C+CO<sub>2</sub>. The theoretical considerations involved are discussed and experiments are described, which were to determine the equilibrium the reaction and establish isotherms at 1,100°, 2000, 900°, 800°, 750°, and 710° on steels in which ges from 0.03 to 2.32%. The equilibrium Fe.C+ 3Fe+CH. is also studied.

1423, JOHANSSON, A., VON SETH, R., AND ELFSTROM, N. Investigations on the Surface Decarburization of Steel.] Jernkontorets Ann., vol. 116, 1932, pp. 565-655; Chem. Abs., vol. 27, 1933, p. 3429.

Equilibrium isotherms have been determined for the Titlems, 3Fe+2CO→Fe<sub>2</sub>C+CO<sub>2</sub> (1) and 3Fe+CH→ 15C+2H<sub>2</sub> (II) between 680° and 1,100°. The isoth increasing C content, a result which is incontent with the assumption that C is insoluble in e below the Ac. point. Above 900°, FeO cannot diced to metallic Fe free from C. At 680° the n proceeded too slowly for establishing equilibit a mutual solubility of cementite and ferrite idicated. From 900°-1,100° the activity coeffiof C was found to be nearly unity in cementite Mn steels. By varying the CO :: CO ratio in uretted gas, either carburizing or decarburizing tions may be established. At 1,250° and 1,320 ubility of C in molten Fe was 4.4 and 4.56%, ectively. In (II) the rate of reaction was found maximum at 950° but was noticeable at 600°, Olling again above 1,000°. Ni, Mn, W, and Cr gave about the same rate as unalloyed steel. No minrization was found with N2 and none with air 710°, or 650°, probably because a protective ever prevents diffusion of gas to the Fe surface.

OHNSON, A. F., AND GRAYSON-SMITH, H. Mag-Susceptibilities of Iron-Group Salts at Low aperatures. Canadian Jour. Research, vol. 28 A, pp. 229-241; Chem. Abs., vol. 44, 1950, p. 8178. thetic balance of the Sucksmith-ring type is deeden This apparatus is used to measure the susbilities of hydrated and anhydrous CR. (SO.): the mitrates of Cr, Co, and Ni. The presence of amounts of ferromagnetic impurity is corrected making measurements at several values of the reciprocal susceptibility  $1/\chi$  is against the absolute temperature to evaluate Yelss constant o.

1625. JOHNSON, C. A., BUSCHOW, H. F., AND CARLSMITH L. E. Gasification of Coal. FIAT Final Rept. 938, April 22, 1947, 34 pp.; PB 80330.

Of the various processes proposed by the Germans for converting coal into synthesis gas by continuous gasification with O2, 2 of the more recently developed processes are of interest for possibly providing gas for Fischer-Tropsch liquid-fuel plants. These are the Lurgi high-pressure and the Thyssen-Galocsy processes, both of which use O2. The Koppers combination low-temperature carbonization and gasification process, which has been used for producing synthesis gas on a large scale, also is studied. The Lurgi process operates at a high pressure (20 atm.), assuring low velocities (small equipment), eliminating the necessity of compressing the gas ahead of the Fischer-Tropsch units, simplifying recovery of condensables in the gas, and providing another variable (pressure) for control of gas composition. This process will utilize a wide variety of coal. The Thyssen-Galocsy process operates at a temperature high enough to melt the ash, which is withdrawn as a fluid, thereby eliminating the frequently encountered problem of clogging of the generator by sintering of low-melting-point ash coals. Furthermore, the equipment is unusually simple. The Koppers process operates at atmospheric pressure and does not use O2. It consists in distilling coal briquets, followed by partial gasification of the semicoke with hot steam lower in the retort, finally cooling and removing the coke and gasifying it in conventional gas producers. The producer gas is burned in regenerators and used to superheat steam. (1,300°), which is reacted with the semicoke to form the synthesis gas. Several diagrams of the 3 processes are reproduced. A summary also is given of the status of the Fischer-Tropsch process.

Johnson, H. H. See abs. 3146.

1625a. Johnson, M. F. L. and Ries, H. E. Structure of Cobalt Catalysts Supported on Diatomaceous Earth. Am. Chem. Soc., 121st Meeting Abs., March-April, 1952, p. 12-M.

Various points are presented as evidence for the existence of catalyst-support interaction in the case of Co oxide precipitated in the presence of a diatomaceous earth support. These include measurements of adsorption isotherms, the degree of reduction to Co metal, and the use of area-temperature sintering curves to characterize gels. The adsorption isotherms for this type of catalyst all have the same characteristics: A nearly asymptotic approach to Po, representing interparticle condensation, plus a sharp break at 0.5 relative pressure and a volume adsorbed corresponding to the volume of small pores.

1626. Johnson, R. C. Anthracite as Fuel for Synthesis-Gas Production. Trans. 7th Ann. Anthracite Conf., Lehigh Univ., May 1949, pp. 69-82; Fuel Abs., 1950, Abs. 140.

American anthracite industry has in store and is producing many million tons of 2 low-cost byproduct fuels suitable for manufacture of synthesis gas: (a) Silt, a mixture of coal, bone, and slate with basically the same composition as commercial anthracite at the mine at which it is produced, except that the ash content is higher; and (b) bone coal, anthracite interspersed with small slate bands; its ash content varies 25-30% and is governed by the gravity at which it is separated from rock and other refuse. Investigations of different processes for gasification of these fuels are in progress. The Anthracite Institute has been operating a fluidized-bed gas-producer pilot plant. using silt; results are encouraging. There has been no trouble with the fluidization of the bed, but it has been difficult to obtain the desired bed temperatures for production of the best quality gas. The silt can be used in conventional gas generators if it is briquetted.

JOHNSON, R. T. See abs. 2128a.

JOHNSTON, H. L. See abs. 654a. JOHNSTONE, H. F. See abs. 424a.

1627. JOKLIK, A. [Methane Cracking and Carbon Monoxide Conversion in Gas Works.] Gas, Wasser, Wärme, vol. 4, 1950, pp. 247-258; Fuel Abs., vol. 9, No. 3, 1951, abs. 1625.

Reforming of gases of all kinds that contain CH<sub>4</sub> (natural gas, residual gases from benzine synthesis plants ond oil refineries, and sewage gas) can be used to supplement the production of town gas. This can be achieved by a combination of CH<sub>4</sub> cracking with CO conversion. The combined process also can be used in the manufacture of town's gas from coal gas. An account is given of the properties of various mixing gases and town's gases and of the suitability of CH<sub>4</sub>, cracked gases, and partly converted cracked gases for town gas production.

Jolley, L. J. See abs. 304, 1328, 3699.

1628. JOLLEY, L. J., AND BOOTH, N. Underground Gasification of Coal. Gas Research Board Inf. Circ. 2, Pub. 22: Gas World, vol. 128, 1948, pp. 588-595; Fuel, vol. 24, May-June 1945, No. 2, pp. 31-37; No. 3, pp. 73-79.

Bibliography of 123 refs. (see abs. 3698). Extensive review of the literature on underground gasification, particularly of Russian sources, appears. The average output/man employed was increased from 30 tons of coal/month by mining methods to the thermal equivalent of 100-120 tons by underground gasification; in large installations it might reach 500-600 tons. The cost of standard coal in Russia in 1939 was 22-30 rubles (18-25 s.)/metric ton. The cost of production of 1,000 kcal, of gas of low calorific value (100-150 B. t. u./cu. ft.) is stated to be 0.15-0.20 kopek (0.375-0.5 d.) and that of high-calorific-value gas to be 0.4 kopek (1.0 d./therm). (The above figures do not appear to include labor costs.) The cost of low-calorific-value gas is about 1/3 that of producer gas. The net cost (exclusive of capital charges) of gas from normal producer installations is 0.74-1.21 kopeks/1,000 kcal. (1.84-3.0 d./therm), while that of gas from underground installations is 0.27-0.68 kopek/1,000 kcal. (0.7-1.7 d./therm). The capital cost of underground gasification plant is stated to be 60-70% of that of a plant employing an above-ground producer. In the Stream method 80-90% of the capital cost represents surface work and 14-15%, the preparation of panels. The percolation method is stated to reduce capital investment by 15-20%. For a combined underground gas-electric power generating station the capital cost is 1,500 rubles/kw. installed power and the prime cost of power, 4-6 kopeks/kw.-hr. The cost of an O. plant is estimated to amount to 70% of the total outlay cost and the cost of gas made with an O2 blast 3 times that made with an air blast.

1629. JOLLEY, L. J., AND MORCOM, A. R. Ruhrchemie A.-G., Sterkrade-Holten. BIOS Final Rept. 1038, December 1946, 15 pp., PB 75,817.

This report presents additional details on: (1) The pelleting and grading of precipitated catalysts on kieselgular by 4 improved methods, (2) organic S removal, and (3) the production of CHz and cyanides from CHz and natural gas. A flowsheet of the scrubing process for CHz production is included. (See abs. 873, 874, 875, 876, 877, 878, 1327.)

Jonakin, J. Sec abs. 810a.

1630. JONES, A. L. Liquid Thermal Diffusion—a Continuous Separation Process. Petrol. Processing, vol. 6, No. 2, 1951, pp. 131–135.

Liquid thermal diffusion is a process in which a mixture of liquids is passed through the slit formed by 2 smooth, parallel surfaces in close proximity of about 1/32 or 1/16 in. One of the surfaces is heated, and the other is cooled so that a temperature gradient exists across the slit. Because of the temperature gradient. and the thermal convection currents set up in the liquid, some types of molecules preferentially concentrate near the hot wall and are moved to the top of the slit while other types concentrate near the cold wall and are moved to the bottom of the slit. The exact mechanism is not known as yet. It appears, however, that the direction and degree of concentration are dependent upon the relative shapes of the molecules present in the mixtures. Separations can be made of compounds having the same molecular weights or identical boiling points. Even isomers have been separated. The effects of variables such as column height, slit width, and temperature are discussed. The process is covered by United States Patents 2,541,069, 2.541.070. and 2,541.071.

Jones, H. O. See abs. 700.

Jones, H. R. See abs. 15a.

1631. JONES, I. H. Gasification of Brown-Coal Briquets in Pintsch-Hillebrand Water-Gas Generators at Wesseling. Germany. FIAT Final Rept. No. 425, November 1945, 12 pp. PB 22,441.

Report on generators that were developed especially for employing brown-coal briquets formed from brown coals that have an ash that will not exhibit incipient fusion below about 1,290°-1,300°. Detailed information on the technical and constructional features is supplemented by a list of refractories and their properties.

-. Sec abs. 451, 452, 453.

1632. JONES, J. P. Some German Solvent Extraction Developments. I. Nat. Petrol. News. Tech. Sec., vol. 38, No. 6, 1946, pp. R83-88. CIOS Rept XXXI-85, 1945, 73 pp., PB 1850.

Series of papers based on interviews with the Edeleanu G. m. b. H. describing the methods developed and used by it for the solvent extraction of low-temperature carbonization tar for the production of fuels and waxes. Of special interest is a paper presented by E. Terres, general manager, before the Deutschen Braunkohlen-Industrie Verein on The Use of Selective Solvents to Extract Fractions from Synthetic Oil from Coal (translated and introduced by Jones). This paper reviews the development of refinery methods using selective solvents, discusses the mechanism of selective solvent extraction and describes the procedure for the treatment of mineral oils, shale oil and tar. The selective treatment of the low-temperature carbonization tar includes 3 principal stages: (1) Extraction of wax-containing fraction with SO:; (2) extraction of the resulting SO: extract with naphtha after addition of the waxfree fraction; and (3) fractional separation of hard and soft wax with dichlog roethane from the SO: raffinate after removal of SO -. Some Solvent-Extraction Developments

in Germany. II. Nat. Petrol. News, Tech. Section 28, 1946, pp. R181, 182, 184. CIOS Rept. XXXI-85, 1945, 73 pp. PB 1850.

Second part of this report discusses the separation of low-temperature carbonization tar distillate into raffinate and extract by means of SO<sub>2</sub> and the use of naphtha to separate the extract. Also described is the use of triangular coordinate graphs to supply data on the relationship between solvent, raffinate and extract phases necessary for commercial operations.

in Germany. III. Commercial Methods for Manufacturing Wax in Germany. Nat, Petrol. News

Tech. Sec., vol. 38, No. 14, 1946, pp. R273, 274, 276, 278-279, 282; CIOS Rept. XXXI-85, 1945, 73 pp., PB 1850.

Both hard and soft wax were made by solvent extraction with SO<sub>2</sub> from tar distillate obtained by the low-temperature carbonization of brown coal and, to a limited extent, from shale oil. Centrifuging was used followed by 2-stage extraction also with SO<sub>2</sub>. Dichloroethane was used in the dewaxing step. The extract solution from the tar distillate was processed into diesel fuel. A study was made of wax properties.

1635. — Some Solvent-Extraction Developments in Germany. IV. Continuous Band Filter to Produce an Oil-Free Hard Wax. Nat. Petrol. News, Tech. Sec., vol. 35, No. 18, 1946, pp. R344-340, R348; CIOS Rept. XXXXI-85, 1945, 73 pp., PB 1850.

Description with drawings is given of an entirely new type of commercial wax filter. This continuous band filter was developed by the GERMAN EDELEANU COMPANY to meet the wartime need for a commercial grade of hard wax substantially free from oil. The wax slurry was treated with one or more portions of solvent, the liquid being removed by suction from the bottom of moving pans. The entire filter was en-closed in a pressure shell. Also described is a supplementary straight-line graph method for recording and evaluating data from the solvent extraction of oils. This method was found to supply information on raffinate and extract solutions not obtainable through the more familiar triangular coordinate system discussed previously. A method was also developed and described in this article for determining the wax content of a wax-oil mixture by measuring the amount of polarized light which will pass through a thin layer of the mixture. The method is based on the fact that wax crystals are doubly refractive while oil is not.

——. See abs. 1478, 1479, 1496.

1636. Jones, N. C. Activation of Halogen and Carbon Monoxide. Jour. Phys. Chem., vol. 33, 1929, pp. 1415-1427; Chem. Abs., vol. 24, 1930, p. 275.

Charcoal activates Cl and Br but does not activate CO, H2, or O2 to any appreciable extent. HBr was made rapidly by passing a current of H, containing Br over charcoal (99.3% conversion at 200°). In the COCl. synthesis over charcoal Cl is activated, but CO is not, since neither H-CO nor MeOH could be synthesized from CO and H2 over charcoal, nor could CO2 be made from CO and O. over charcoal. Hopcalite activates O2 but does not activate either CO or H2. No reaction between CO and H. could be observed but CO, H, and benzene are easily burned with air over hopcalite. Although benzene seldom burns until the temperature attains 490°, over hopcalite benzene vapor burns completely to CO2 and H2O at 78°. Evidence is presented that CO is a better reducing agent than H, by a margin of 30°-50°. Neither Fe nor Ni activates CO at a point where it reacts with molecular H. CO must be essentially electropositive in character, since it reacts much more readily with O2 and Cl than it does with H2, even when all 3 of the latter gases are activated. CO reacts only with activated monatomic H and not with molecular H2. CO does not react with electronegative H: at a temperature lower than 500°. With CaH2 at this temperature CO gives the same reaction that is produced by CO2. This work supports the theory of Fischer and Tropsch (abs. 1018 gand abs. 1021) for the mechanism of the hydrogenation of CO at ordinary pressure.

JONNARD, A. See abs. 619a.

1637. JORDAN, R. E. Gas Liquefaction and Synthesis Under Pressure. Synthesis of Ammonia and Methanol. Proc. World Eng. Cong., Tokyo, 1929, vol. 31, 1931, pp. 139-152; Chem. Abs., vol. 25, 1931, p. 5253.

Claude process for the purification of coke-oven  $H_2$  and synthesis of  $NH_2$  and  $CH_2OH$  are described.

1638. JORGENSEN, S. M. Pressure-Vessel-Design Calculations. Petrol. Refiner, vol. 24, No. 10, 1945, pp. 381-384; Chem. Abs., vol. 40, 1946, p. 3.

Numerous equations and formulas are listed for calculating combined loads on pressure vessels.

1639. JORIS, G. G., AND TAYLOR, H. S. Exchange Reactions of Nitrogen Isotopes on Iron and Tungsten Surfaces. Jour. Chem. Phys., vol. 7, 1939, pp. 893-898; Chem. Abs., vol. 33, 1939, p. 9128.

Activities of Fe synthetic-NH<sub>1</sub> catalysts and of W filaments in promoting the reaction between N215 and N2 were studied from room temperature to 725° with Fe and to 900° on W. In contrast to the exchange reaction of molecular H-isotopes, the exchange reaction of No molecules is very slow, being first measurable above 450°. The exchange is accelerated by the presence of H2. The exchange involves, as the slow process. either the rupture of valence bonds of adsorbed molecular N2 on the surface or migration of N atoms over the surface, and that He accelerates such processes. The temperature coefficient of exchange in a N2 : 3 H2 mixture is about 50 kcal. The data suggest that measurements of the velocity of N adsorption at about 400° on synthetic-NH, catalysts are measurements of true activated adsorption.

Joseph, T. L. See abs. 3370.

JOUBERT, D. B. Sec abs. 1743.

1640. JOURNAL of the Fuel Society of Japan. Synthetic Benzine. Vol. 13, 1934, pp. 3-4; Brennstoff-Chem., vol. 15, 1934, p. 132.

Survey of Japanese work on benzine synthesis from CO and H. at ordinary pressure. Especially considered is the work of Fujimura and Tsuneoka who have obtained with a Ni-Mn-Th catalyst a maximum yield of 137 cc. of liquid products per m. of mischgas. Tsutsum was able with a catalyst (no specifications given) to increase the yield to 155 cc. per m.

1641. ——. Production of Gasoline by the Fischer Process. Vol. 15, 1936, p. 89.

Mitsui Trading Co. and the Mitsui Mining Co. will erect a plant of 10,000,000 gal. annual capacity in the spring of 1937 at the Mitke colliery for producing gasoline by the Fischer process. On completion of this plant, a large-scale plant will be constructed in Hokkaido.

1642. — Japanese Plant. Vol. 16, 1937, p. 49.

Mitsui Trading & Mining Co. will erect new Fischer-Tropsch synthesis plants in Manchukuo and North China in addition to the one at Milki. An annual production is planned of 85,800,000 gal. of motor fuel and 250,600,000 gal. of heavier oils by the Fischer-Tropsch process.

1643. — Studies on Gasoline Synthesis. Vol. 16, 1937, pp. 10-11; vol. 17, 1938, p. 29.

Review touching upon the research on catalysts and the influence of reaction conditions on the yield and composition of the oils obtained in the Fischer-Tropsch process.

1644. ——. Production of Synthetic Petroleum From Coke-Oven Gas. Vol. 17, 1938, p. 74.

Showa Steel Co. has decided to produce petroleum from coke-oven gas by the Fischer process. A production of 200,000 tons per year is contemplated.

1645. ——. Oil in Japan. Vol. 18, 1939, p. 7; Fuel, vol. 19, 1939, p. 99.

Synthetic-oil industry is expanding radiply. 2 plants employing the Fischer process are nearing com-

pletion at Milke and Chinchou. Their combined output will be 60,000 tons of synthetic gasoline per year. The Hokkaido Artificial Petroleum Co. will construct a plant with an annual production of 140,000 tons of synthetic oil. This is to be completed by the end of 1940. Research is in progress, and it is stated that satisfactory yields of hydrocarbons, free from O2 compounds, have been obtained at initial pressures of 40 atm., using a catalyst of Co-ThO-kieselguhr.

1646. JOURNAL OF THE SOCIETY OF CHEMICAL INDUSTRY (JAPAN). Synthetic Petroleum Industry in Japan and Manchoukuo. Vol. 43, 1940, suppl., pp. 265-266. Patents of the Fischer-Tropsch process were bought

through the Mitsui Trading Co. in 1936, and a full-size pilot plant situated at Milke started operation in June of this year. 3 larger plants are now under construction at Hokkaido, Amagasoki, and Chinchow.

Jovitschitsch, M. Z. See abs. 2142.

1647. JULIARD, A., RAYET, R., AND LUDE. A. Kinetic Study of the Dissociation of Carbon Monoxide Accompanying the Reduction of Metallic Oxides. Disc., Faraday Soc., 1948, No. 4, pp. 193-196; British Abs., 1950, B, I, p. 415.

Kinetics of the reduction of NiO and Fe2O3 by CO have been examined by simultaneously measuring, as functions of time, the rates of oxide reduction and of CO dissociation. Absolutely pure Ni does not catalyze CO dissociation. Ni charged with H2 catalyzes the dissociation probably on account of C nuclei formed by reduction of CO by traces of active H adsorbed on Ni crystallites. In the Fe system the Boudouard reaction does not occur under conditions unfavorable to the formation of metallic Fe. CO dissociation apparently requires the presence of an interfacelike Ni or NiO or Fe-Fe<sub>2</sub>C or the prior formation of C nuclei.

Junge, C. H. Sec abs. 3146.

JUNGERS, J. C. Sce abs. 695, 2153, 2460, 2461,

1648. JUNGERS, J. C., AND COUSSEMANT, F. [Effect of Adsorption on the Course of Catalytic Reaction.1 Jour. chim. phys., vol. 47, 1950, pp. 139-144; Chem. Abs., vol. 44, 1950, p. 10,441.

Kinetics of gas-phase and liquid-phase catalytic reactions are interpreted in terms of the relative adsorptions of reactants and products. Reactions discussed include the hydrogenation of CO and CO2 to CH. over Ni (abs. 2153, 2460), of C.H. to cyclohexane in the presence of CO2 (abs. 2461), of acetone to isopropyl alcohol; C.H. to C.H. (abs. 695), and the dehydrogenation of a secondary alcohol to a ketone (abs. 3398). The hydrogenation of PhOH to cyclohexanol takes place through the intermediate formation of cyclohexanone. A quantitative evaluation of the adsorption coefficients and the several reaction velocity constants is made. Similarly, the hydrogenation of naphthalene to decahydronaphthalene takes place through the formation of 1,2,3,4-tetrahydronaphthalene. Intermediates in the hydrogenation of CoHe to cyclohexane are not detected. The possible use of C2H2, CO2, or other compounds as acceptors for H2 in dehydrogenation catalysis is discussed.

JÜNGLING, K. See abs. 207.

JUSTICE, J. L. See abs. 3240.

JUZA, R. See abs. 1948, 2483.

1648a. Juza, R., AND PUFF, H. [Crystal Structure of Cobalt Carbide.] Naturwissenschaften, vol. 38, 1951, pp. 331-332; Chem. Abs., vol. 46, 1952, p. 2,870. Co<sub>2</sub>C crystallizes in the rhombic system; a=2.885,

b=4.454, c=4.360 A; 2 CO<sub>2</sub>C in the unit cell, d,=7.76;

space group  $D \stackrel{2^{14}}{\circ}$ ; 4 Co in 4 cOy 1/4 with y=0.158. The structure is a rhombically deformed dense hexagonal packing. Close agreement with these results is obtained by recalculation of data of Hofer and Peebles (abs. 1440).

BIBLIOGRAPHY OF FISCHER-TROPSCH SYNTHESIS AND RELATED PROCESSES

1649. JUZA, R., AND SACHSZE, W. [Metal Amides and Metal Nitrides. XII. The System Nickel-Nitrogen. Ztschr. anorg. Chem., vol. 251, 1943, pp. 201-212; Chem. Abs., vol. 37, 1943, p. 6175.

Nickel nitride, Ni.N, theoretical N content 7.37%, was prepared by passing a rapid stream of NH, over 10-20 mg. of Ni powder, prepared from Ni (CO), at 445° for 3 hr. It was also prepared from NiF.2 NH.F and NiBr. but there is no particular advantage in using the halides. The nitride is tested for metallic Ni contamination by testing in a magnetic field of 11,000 gausses strength. Ni<sub>2</sub>N is a black-gray material, easily ground in an agate mortar, and is stable to O2 and moisture. NaOH solution has no action either hot or cold. Acid solutions and acids react slowly to explosively, depending on concentration and temperature. The density at 25° was 7.66 which is lower than the calculated density of 7.91 from x-ray data. X-rays showed hexagonal close packing of the Ni atoms, with lattice constants, a 2.664, c 4.298, and c a 1.613. The structure agrees with the  $\epsilon$ -phase of Fe2N. The N atoms are located at the center of an octahedron of Ni atoms, at a distance of 1.877 from the Ni atoms, and 3.423 from the other N atoms. The N atoms are interstitial and the structure differs completely from that of Cu.N. From an x-ray study it is estimated that the solubility of N. in Ni does not exceed 0.07% by weight.

1650. HAHN, H., AND MUHLBERG, H. [Metal Amides and Metal Nitrides. XX. The System Iron-Nickel-Nitrogen.] Ztschr. anorg. Chem., vol. 259, 1949, pp. 121-134; Chem. Abs., vol. 44, 1950, p. 992.

Alloys of Fe and Ni containing 10, 20, 30, 40, 50, 60, 70, 80, 90, and 95 at. % Fe were nitrided at 300°-1,000° in a stream of NH3. The optimum temperature range for uptake of N was 350°-600°. The weight % N in the nitrided alloys varies linearly with the atomic % Fe. The uptake of N can be increased further by pretreatment of the alloy with NH, at 600°-800°, quenching to room temperature, and finally prolonged nitriding at 400°-500°. For alloys treated this way which contain 50% Fe or more, the % N again varies linearly with the % Fe; with alloys containing less; Fe, the % N approximates that for Fe.N. Debye-Scherrer diagrams were made of the pure and nitrided alloys. There were 2 alloy and 2 nitride phases found. A cubic face-centered alloy (I) occurs in alloys containing 10-70% Fe and is the only phase if the % N is below 5. This phase resembles γ-Fe in dissolving N with an increase in the lattice constant a. A cubic body-centered allor phase (II) is stable for Fe above. 70%, N up to 3%, and at nitriding temperatures up to 450°; above 450° it changes to (I) with a greatly enlarged lattice. Like a-Fe, (II) takes up only very little N in solid solution. A cubic face-centered nitride phase (III) is stable up to 70% Fe, while above this a hexagonal nitride phase (IV) also occurs. (III) corresponds to Fe N with some of the Fe replaced by Ni. The constant a increases with % N and its increase with the % Fe parallels that for the pure alloys. (IV) resembles Fe,N except that a little of the Fe is replaced by Ni. The decomposition temperatures? of the nitrided alloys are low, ranging 360°-500° with increase in the % Fe.

KADOTA, N. See abs. 2205.

1651. KAFUKU, K., AND OGURA. T. Reaction Between Methane and Water Vapor. Jour. Chem. Soc. Japan, vol. 56, 1935, pp. 1145-1159; Chem. Abs., vol. 30, 1936, p. 1542.

Yield of H2 and CO from CH4 and H2O vapor was best by using Ni as catalyst with low pressure and high temperature, 5 mm. and 1,000°. Use of Ni with AlaOa, MgO, or pumice was more effective.

1652. KAGAN, G. B., AND LITVIN, M. Z. [Gasification of Low-Grade Fuels with a Steam-Oxygen Mixture Under Pressure.] Khim. Tverdogo Topliva, vol. 8, 1937, pp. 1155-1165; Chem. Abs., vol. 32, 1938, p. 4309.

Lurgi process for gasification of Aleksandriiskii brown coal, peat, and anthracite was investigated. The steam-O2 mixture should contain 75% steam for brown coal and peat and 85-90% for anthracite. A gas of calorific value 4,500 cal. per m.3 can be obtained. The cracking of tar formed in the low temperature carbonization zone affected the composition of the gas. The gas with highest calorific value was obtained in the gasification of bituminous fuel. The fuel containing ash up to 30% and moisture 25-30% can be used for the gasification. 12 refs.

1653. KAGAN, M. Y., MOROZOV, N. M., AND PODUROVS-KAYA, O. M. [Sorptive Properties of Mixed Catalysts. I. Sorption of Ammonia on Synthetic-Ammonia Catalysts in Connection with the Function of Promoters.] Jour. Phys. Chem. (U. S. S. R.), vol. 8, 1936, pp. 677-688; Chem. Abs., vol. 31, 1937, p. 2078.

Pure Al.O. has a high adsorptive capacity for NH3up to 600°-700°, with a heat of adsorption of 30 cal. per mol. for 2 cm.2 per gm. Al2O2, or 18 cal. for 6 cm.2 per gm. of Al<sub>2</sub>O<sub>3</sub>. In the adsorption layer at 500°, NH, breaks up into H and a surface-bound radical. Addition of K2O to the Al2O3 decreases the sorptive capacity and the heat of adsorption to about %. Fe additions also decrease adsorption to about 1/3, with a smaller effect at higher temperatures.

KAGAN, Y. B. Sec abs. 152, 152a.

KAGANOVA, E. M. See abs. 2714.

1654. KAINER, F. Di5. Kohlenwasserstoff-Synthese nach Fischer-Tropsch. Springer-Verlag, Berlin, Germany, 1950, 322 pp.; rev. in Chem. and Eng. News, vol. 29, No. 28, 1951, pp. 2860, 2862.

This book is based to a great extent on patents and patent applications issued during the development of the hydrocarbon synthesis. The value of these patent references could be increased, however, by mentioning their dates of application and publication. No attempt is made to compare, critically, results of research work done by different researchers or to contribute substantially to the theories or to explain the mechanism of the involved reaction. Any revision of this book should contain more data regarding the basic facts of the synthesis and fewer data on the preparation of specific, and for a great part on relatively unimportant, catalysts (45 pp. are given over to kieselguhr catalysts). The section (73 pp.) on synthesis products presents considerable useful information on the different methods used in Germany for recovering and refining the synthesis products and further shows that hydrocarbon synthesis is not only of importance for the manufacture of liquid fuels but for the production of raw materials for many other industrial

1655. KAISER WILHELM INSTITUT FÜR KOHLENFOR-SCHUNG. [Report of the Middle-Pressure Synthesis With Iron.] June 1940, 75 pp.; OTS Bib. Tech. Rept., vol. 12, No. 6, 1949, p. 228; PB 98,743.

Survey is made of work carried out on the middlepressure synthesis with Fe catalysts. Precipitation, alkalization, induction, synthesis-gas production, apparatus, pelleting of catalyst, and further processing of primary products are discussed. This report appears to be the same as H. Pichier, TOM Reel 49, frames 541–662, June 1940, Bureau of Mines Transl. T–424, December 1947, and TOM Reel 101, first 48 pp., trans. by M. Leva.

217

1656 [Direct Synthesis of Isoparaffins From CO and H2.] TOM Reel 134, Item IV-3, December 1942; TOM Reel 259, Item 20, frames 1055-1071.

It was discovered that catalysts based on Th are particularly well suited for the synthesis of branched hydrocarbons from CO and H2. The best Th catalysts are produced by precipitation of Th salt solutions, generally by precipitation of the basic carbonate by Na<sub>2</sub>CO<sub>2</sub>. from the nitrate solutions. The lifetime of the Th catalyst is very long under the conditions of isosynthesis and can easily be regenerated. A water gas of CO: H2 ratio of 1:1-1.2:1 is used for the synthesis. The type of reaction products obtained is dependent on certain conditions such as composition and method of production of the catalyst, the temperature and pressure, the residence time of the gas in the catalyst space, operation in 1 or more stages, the material of the reaction tubes, etc. With a pressure of 150 atm. and a flow rate of the gases corresponding to 10 l. final gas per hr. per 28 gm. catalyst, the amount of alcohol and other Orcontaining compounds, which prevail below 375°, decreases rapidly with rising temperature. Mostly liquid branched aliphatic hydrocarbons are formed, 375°-425°. With rising temperature, the amount of naphthenes gradually increases, reaching 50% at 450°-460°. Between 450° and 500° aromatics are identified. The amount of gaseous products increases from less than 10% at 375° to 50% at 440°, with isobutane the highest, and at 450°-460° 1/3 of the total products consists of this hydrocarbon. Unbranched aliphatic hydrocarbons appear in only very small amounts. N-butane results in amounts of about 10% of the isobutane. With a constant temperature of 450°, the reaction begins at 6 atm. pressure and at 30 atm. a 22% conversion of the CO takes place with a production of 5.1 gm. C<sub>3</sub>+n-C<sub>4</sub>, 5.4 gm. iso-C<sub>4</sub> and 16.1 gm. liquid hydrocarbons/N-m. entering gas. The amount of products from a single operation increases with rising pressure, reaching at 500 atm. 46.5 gm. iso-C, and 40.5 gm. gasoline plus oil. The yield of liquid hydrocarbons was greater with V2A stainlesssteel pipes than with Cu pipes. The conversion of CO increases with rising pressure in a single operation, likewise at 50-100 atm., providing several operations instead of 1 are performed. Graphical and tabular data show the influence of temperature and pressure on the type and yield of products, as well as their distillation range and the composition of the various fractions. The composition of the reaction products can be varied within rather wide limits by choosing the synthesis conditions. The gasoline obtained at 450° and 150 atm. and hydrogenated had an octane number, after adding 0.08 vol. % of Pb, of 95; at 370° and 150 atm. 89.6%.

Kallenberg, S. See abs. 2336.

KALLENBERGER, R. H. See abs. 576.

1657. KALLING, B. Use of Oxygen in Metallurgical and Other Thermochemical Processes. Iva, vol. 19, 1948, pp. 44-59; Chem. Abs., vol. 42, 1948, p. 6291.

Reviews cost of production of O2 and its uses in metallurgy and in production of synthesis gas.

Kalyanasundaram, A. See abs. 3013.

KAMIIKE, O. Sce abs. 2414, 2415, 2416, 2417, 2418, 2419, 2421, 2422, 2423, 2424, 2425, 2426.

KAMHKE, O., KATAOKA, S., NIBAYASHI, M., AND NEGISHI, R. Hydrocarbons From Carbide. II. Noncatalytic Polymerization Under Ordinary Pressure-Analysis and Liquid Products. See abs. 2420.

1658. KAMURA, H. Reduction of Ferric Oxide and Iron Ores by Hydrogen. Jour. Iron Steel Inst., vol. 112, II, 1925, pp. 279-298; Chem. Abs., vol. 19, 1925,

Samples of pure Fe2O2 and of hematite were heated to 500°-800° in a combustion tube, and H, was passed over them, the volume of gas used and the % of reduction to Fe being recorded at definite time intervals. At 500° the time required for 90% reduction of the hematite was 78 min.; at 600°, 46 min.; at 700°, 39 min.; and at 800°, 30 min. The volume of H2 used also decreased with rise of temperature. At about 570° the velocity of reduction increased rapidly and the volume of H2 decreased suddenly, probably because reduction below this temperature was from Fe=O4 to Fe and above it from FeaO, to FeO and FeO to Fe. As velocity of reduction increases slowly above 600°, this would be the most economical reduction tempera-

1659. KAMZOLKIN, V. P., AND LIVSHITZ, V. D. [New Method for Obtaining Ammonia Catalysts From Natural Ural Magnetite.] Jour. Chem. Ind. (U. S. S. R.), vol. 13, 1936, pp. 398-401; Chem. Abs., vol. 30, 1936, p. 4630.

Ore is fused with Al-O, and excess KNO, ground, and separated magnetically. Enough Fe is added to form Fe<sub>3</sub>O<sub>4</sub>, and the mixture is fused and separated as before. This treatment reduces the amount of SiO: to

1660. -. Effect of Different Conditions of Reduction on the Activity and Structure of Iron Ammonia Catalysts. Jour. Chem. Ind. (U. S. S. R.), vol. 14, 1937, pp. 93-98; Chem. Abs., vol. 31, 1937,

Time required for reduction is very important. A natural magnetite should be reduced for 46 hr., an artificial one for 32 hr. These reductions are best run at 400°, 150 atm. and not too high a rate of gas flow. -. [Poisoning Action of Water Vapor on Iron Catalysts for the Synthesis of Ammonia.] Jour. Chem. Ind. (U. S. S. R.), vol. 14, 1937, pp. 244-249; Chem. Abs., vol. 31, 1937, p. 4777.

H<sub>2</sub>O poisons all Fe catalysts, but its action is stronger on less active catalysts. Poisoning is greater at higher pressures and lower temperatures. It is due to destruction of active centers on the catalyst surface. 1662. KAMZOLKIN, S. P., LIVSHITZ, V. D., and Koz-

HENOVA, K. T. [Reduction of Catalysts for the Synthesis of Ammonia.] Jour. Chem. Ind. (U. S. S. R.), vol. 12, 1935, pp. 687-690; Chem. Abs., vol. 29, 1935, p. 8244.

If the reduction is run at a temperature and pressure as low as possible, a more efficient catalyst is obtained. KAN-KOGAN, K. I. See abs. 282.

1663. KANTOROVICH, B. V. [Effect of Gas Pressure and Concentration on the Length of the Reaction Zone in Heterogeneous Processes.] Doklady Akad. Nauk S. S. S. R., vol. 71, 1950, pp. 315-318; Chem. Abs., vol. 44, 1950, p. 9220.

Mathematical equations are derived for several reaction conditions involving layers of solid particles or materials suspended in flames of reacting gases. Conclusions are: (1) For first-order reaction in a layer of solid particles, x, the length of the reaction zone, is independent of pressure in the kinetic region but directly proportional to pressure in the diffusion region; in either region, x is independent of the relative weight

concentration of gas. (2) For first-order reaction in a stream of powdered material, x is inversely proportional to pressure in the kinetic region but independent of pressure in the diffusion region; in either region, a is inversely proportional to the relative weight concentration of reactive gas. (3) In reactions accompanied by a volume increase occurring in a layer of solid particles. w is independent of pressure in the kinetic region but is directly proportional to pressure in the diffusion region; a increases with increasing initial volume concentration. (4) In reactions accompanied by a volume increase occurring in a stream of powdered material, x is inversely proportional to pressure in the Kinetic region but independent of pressure in the diffusion region; x decreases with increasing initial volume concentration.

KAPPELMACHER, E. Sec abs. 2620a.

GRAPHY OF FISCHER-TROPSCH SYNTHESIS AND RELATED PROCESSES

1664. KAPUSTINSKII. A. F., AND GOFMAN, E. [Equilibrium in the Reduction of Cobalt Oxide by Carbon Monoxide.] Jour. Phys. Chem. (U. S. S. R.), vol. 9, 1937, pp. 713-715; Acta Physicochim. U. R. S. S., vol. 6, 1937, pp. 487-490; Chem. Abs., vol. 31, 1937, p. 8329.

Over the range 993°-1.393° abs., the equilibrium is given by  $\log K = -(1/R) [(-17.005/T) - 8.06 \log T +$ 0.00254 T = 0.063  $T^2 + (38.100/T^2) + 31.78$ . The value of the free energy from the experimental data was Δ F<sub>298</sub>=11,400 cal., as compared to the value 10,918 cal. calculated from data given by Emmett and Shultz (abs. 833).

KARPINSKII, M. N. See abs. 726, 727, 729, 1796. 1665. KARPOV, A. Z. [Synthesis of Methanol From Carbon Dioxide and Hydrogen.] Org. Chem. Ind. (U. S. S. R.), vol. 6, 1939, pp. 574-577; Chem. Abs., vol. 34, 1940, pp. 5047, 6929.

MeOH is obtained in good yield by passing CO.-H. mixture over a Zn-Cr-Ni catalyst at 370°. The gas from COMe-BuOH fermentation contains traces of S compounds, which inactivate the catalyst; such gases may be purified by passing over active C.

-. See abs. 724, 728, 3557.

1666. KARZHAVIN, V. A. [Low-Temperature Conversion of Methane.] Jour. Chem. Ind. (U. S. S. R.), vol. 10, No. 2, 1934, pp. 31-33; British Chem. Abs., 1934, B, p. 611; Chem. Abs., vol. 28, 1934, p. 3873.

Complete conversion of CH4 and H2O into CO2 and H2 at 500°-600° is possible only when the CO2 produced is immediately removed from the reaction gases by CaO. The reaction is catalyzed by Ni, which is, however, rapidly inactivated by traces of S in the gas.

-. Natural Gas. Conversion to Carbon Monoxide and Hydrogen. Ind. Eng. Chem., vol. 28, 1936, pp. 1042-1044; Chem. Abs., vol. 30, 1936, p. 6923.

Process of converting natural gas to CO and H2 by the use of steam is tested on a commercial scale by heating natural-gas-steam mixtures in regenerative apparatus packed with grog, then passing over a Ni catalyst. The CH, content of the resultant gas was 0.8%. For conversion, 1.9 m. of steam is added to 1 m. of natural gas, producing 3.3 m. of gas, containing H. 64 and CO 22%, respectively. Total consumption of natural gas per m. of pure N.-H. mixture is 0.44 m., including gas used for conversion and for heating. 1 m. of reaction chamber space gives 24 m. of converted gas per hr.

[Catalytic Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] Uspekhi Khim., vol. 15, No. 3, 1947, pp. 327-352; Chem. Eng., vol. 55, No. 7, 1947, pp. 276-277.

Critical review, with 59 refs.

1669. ——. [Heat Transfer in Apparatus for Catalytic Synthesis of Hydrocarbons and Water Gas.] Khim. Prom., 1947, No. 5, pp. 14-19; Chem. Abs., vol. 43, 1949, p. 2343.

Method for calculating the heat transfer in catalytic synthesis of hydrocarbons from CO and Hr. This method is applicable to both tubular and plate reactors. The temperature varies considerably along the catalyst, and for best results, the cooling should be adjusted to the conditions of each particular sector of the catalyst.

1670. KARSHAVIN, V. A., AND LEIBUSH, A.-G. [Continuous Process for Conversion of Gases Containing Methane and Other Hydrocarbons.] Jour. Chem. Ind. (U. S. S. R.), vol. 10, No. 1, 1934, pp. 34-38; U. O. P. Co. Surrey Foreign Petroleum Literature, Transl. S-396, 1946; British Chem. Abs., 1934, B, p. 611.

Hydrocarbon constituents are converted into CO and H, by passing the gas, mixed with air, over Ni at 1,000°-1,100°; at lower temperature the Ni is inactivated by 0.2-0.25% of S in the reaction gases.

1671. KARSHAVIN, V. A., BOGUSLAVSKI, I. M., AND SMIRNOVA, Z. M. [Catalysts for Methane Conversion.] Jour. Chem. Ind. (U. S. S. R.), vol. 10, No. 8, pp. 31-40, 1933; U. O. P. Co. Survey Foreign Petroleum Literature Transl. S-394-A; British Chem. Abs., 1934, B, p. 82.

Process of conversion of CH.-H2O mixtures into CO and H2 is best catalyzed by fireclay containing 6.4% of reduced Ni at 1,000°. The activity of the catalyst is increased by up to 1% MgO and diminished by more than 1% MgO. Loss of Ni as Ni (CO), and inactivation by formation of carbide are virtually negligible. Has and organic S compounds, initially, slightly depress the activity, which then remains constant. Deposition of soot takes place to an extent, increasing with the content of higher hydrocarbons in the mixture.

1672. KARZHAVINA, N. A. [Catalytic Formation of Methane From Carbon Monoxide in Industrial Gases.] Jour. Chem. Ind. (U. S. S. R.), vol. 13, 1936, pp. 598-602; Chem. Abs., vol. 30, 1936, p. 6534.

CH, cannot be profitably produced from ordinary blast-furnace gas, but if the gas has been produced by blowing O2 into the furnace, a gas can then be obtained containing up to 60.6% CH4, after adsorption of CO2. The best catalyst for the conversion with steam consists of 84% Ni and 16% Al-O3, at about 400°. 1673. KARZHEV, V. I., AND SEVER'YANOVA, M. G. [Cat-

alytic Cracking of the Synthin Fraction.] Khim. Tverdogo Topliva, vol. 9, 1938, pp. 71-76; Chem. Abs., vol. 32, 1938, p. 9436.

Synthin fractions boiling at 80°-150°, 150°-200°, and 200°-250° were introduced from burettes by drops into a quartz tube placed in an electric furnace. The catalysts were placed in the tube in a 25-cm. layer in that portion of the tube that had a constant tempera-The product was passed through with a constant velocity of 5 m.3/hr. The temperature of experiments was varied within the range 475°-550°. The following catalysts were used: Cr-Cu-P, H2PO4, activated coal as a carrier, Cr-Cu and Cr prepared by special method (not disclosed) the best being the last catalyst. The catalytic cracking of various fractions of synthin over the above catalyst at 475°-525° at atmospheric pressure yielded about 85-90% of liquid products and 10-15% of gaseous products. The practical formation of coke was not observed. The composition of the products obtained justifies the assumption that they have a high octane number.

KASAI, K. See abs. 1904.

1674. KASE, T. Equilibrium Diagram of the Iron-Carbon-Nickel System. Sci. Repts. Tôhoku Imp. Univ.,

vol. 14, 1925, pp. 173-217; Chem. Abs., vol. 20, 1926, p. 570.

Thermal and magnetic analyses, hardness tests, and microscopic examinations are reported for the Fe-Ni system, and the binary equilibrium diagram is concluded to be of the solid-solution type. The As change falls steadily with increasing Ni content down to -190° at 35% Ni and occurs in a temperature interval rather than at a point. Ni dissolves C up to 0.55%, forming a eutectic with C at 1318° and 2.22% C. Ni<sub>s</sub>C is very unstable and cannot be detected with the microscope. The ternary diagram was worked out and is described and illustrated by a sketch of a model. Photomicrographs of typical structures also are shown. For etching specimens with over 25% Ni either strong HNO, or hot HCl was used. No ternary entectic was found. A binary eutectic contains 4.3% C with no Ni and decreasing C down to 0.3% with increasing Ni up to 30%. Cementite occurs in the ternary alloys with 0 to about 30% Ni, with over 0.1% C. With increasing Ni. the A. transformation is lowered and is difficult to detect with over 10% Ni, but is almost independent of the C content. With increasing Ni, the A2 and A3 points are rapidly lowered, and the C content at the eutectoid point decreases down to 0.3% at about 35% Ni. 6 plates of curves accompany this paper.

1675. KASHIMA, S. Synthetic Methanol as a Fuel Substitute. Jour. Fuel Soc. Japan, vol. 15, 1936, pp. 57-

From the results of practical tests it is concluded that it is possible to use MeOH as a fuel for gasoline engines if the fuel: air ratio is increased. Since MeOH has a low calorific value, best results in lowering the fuel consumption are obtained by blending about 50% of benzol or gasoline with it. Compared with gasoline, the merits of MeOH are its high antiknock property and low freezing point, and its disadvantages are its high heat of vaporization and low calorific value.

1676. KASSEL, L. S. Limiting High-Temperature Rotational Partition Function of Nonrigid Molecules. VI. Methanol Equilibrium. Jour. Chem. Phys., vol. 4, 1936, p. 493-496; Chem. Abs., vol. 30, 1936, p. 6250.

Entropy of MeOH and the equilibrium constant for MeOH synthesis are calculated for 2 mol. models: 1 rotates freely and the other has a torsional oscillation about the CO bond.

KASSLER, R. Sec abs. 3187, 3188, 3457.

1677. KASTENS, M. L., DUDLEY, J. F., AND TROELTZSCH. J. Synthetic Methanol Production. Ind. Eng. Chem., vol. 40, No. 12, 1948, pp. 2230-2240.

History of synthetic methanol both here and abroad is sketched, figures on the production and price since 1898 are presented, and present producers are listed. The main emphasis is placed on a description of the Sterlington, La., plant of the Commercial Solvent Corp., which uses natural gas catalytically reformed into synthesis gas with the addition of some CO2 as the raw material. The plant operates at about 5,000 p. s. i. g. and 400°, as compared with current practice of 2,200-14,700 p. s. i. g. and 250°-400°.

1677a. KASTENS, M. L., HIRST, L. L., and DRESSLER, R. G. An American Fischer-Tropsch Plant. Ind. Eng. Chem., vol. 44, 1952, pp. 450-466.

Gives construction and operation details of the gas synthesis demonstration plant at Louisiana, Missouri. Pulverized coal is gasified with steam and oxygen to produce a synthesis gas which reacts in an agitating bed catalytic reactor cooled by concurrent flow of heavy oil. Capacity of the plant is 50-80 bbl. per day of liquid products with a conversion efficiency of about 80%. The hydrocarbon products consist of 70% gasoline, 10% Diesel oil, 10% heavy distillate, and 10% waxes. Oxygenated compounds made up about 10%

of the total product. The following subjects are discussed: Gasification, slagging type vertical gasifier, the Koppers horizontal gasifier and the Kerpely generator; gas purification; Linde-Frankl oxygen plant; gas synthesis; Fe catalyst production; operating performance; materials of construction; possibilities of pressure gasification; and utility requirements.

KATAOKA, S. Sec abs. 2419, 2420, 2422. KATAYAMA, I. Sec abs. 1880, 1881.

KATAYAMA, I., MURATA, Y., KOIDE, H., AND TSU-NEOKA, S. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XLI. Activation of Catalysts by Slow Oxidation With Atmospheric Oxygen. See abs. 1877.

Като, J. See abs. 1930.

1678. KATTWINKEL, R. [Determination of Aromatic and Unsaturated Hydrocarbons in Benzine by Means of Sulfuric Acid.] Brennstoff-Chem., vol. 8, 1927. pp. 353-358; Chem. Abs., vol. 22, 1928, p. 3039.

Previous methods based on the solvent action of \$H\_\$SO\_4\$ for aromatics and unsaturates are discussed. Kattwinkel determines aromatics+unsaturates in a 10 cc. sample by shaking with 30 cc. of a mixture of 30 gm. P\_O\_4 in 100 cc. H\_\$SO\_4\$ (d. 1.840). Unsaturates alone are determined by shaking the sample with a mixture of 5 gm. boric acid in 100 cc. H\_\$CO\_4\$ (d. 1.840). The boric acid mixture does not dissolve aromatics; P\_O\_4\$ in H\_\$CO\_4\$ (atalyzes sulfonation and thus aids solution of aromatics.

1679. KAUFMANN, H. P. Effecting Separation by Adsorption in the Field of Fats. I. Experiments With Mixtures of Fatty Acids. Fette u. Seifen, vol. 46, 1939, pp. 268-273; Chem. Abs., vol. 33, 1939, p. 6073.

On passing solutions containing 2 or more fatty acids through columns of adsorptive materials, for example, Al-O<sub>4</sub> or silica gel, certain fatty acids are more strongly adsorbed; this makes possible a partial, or under suitable conditions, a complete separation. Applications of such adsorption methods being developed include: Analysis of fatty acid mixtures, isolation of naturally occurring, sensitive fatty acids and commercial processing of fatty acid mixtures to isolate more valuable fractions.

KAULAKIS, A. F. See abs. 2347. KAUPP, E. See abs. 805, 806. KAVERIN, I. B. See abs. 1806.

1680. KAWAI, S. Synthetic Fatty Acid Industry. Chem. Rev. (Japan), vol. 7, 1941, pp. 117-120; Chem. Abs., vol. 35, 1941, p. 7744.

Oxidation of Paraffin VI. Treatment of Paraffin With Aqueous Alcohol and Its Influence on Oxidation. See abs. 1886.

Manufacture of Fatty Acids by the Oxidation of Paraffin. XX. Example of an Oxidation Experiment. See abs. 1693.

Oxidation of Paraffin. XXII. Thermal Decomposition of Oxidation Products and Crude Fatty Acids. See abs. 1695.

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1681. KAWAI, S. and MORITA, K. Manufacture of Fatty Acids by the Oxidation of Paraffin. I. Jour. Soc. Chem. Ind. (Japan), vol. 44, 1941, p. 619; Chem. Abs., vol. 43, 1949, p. 9029.

Manufacture of Fatty Acids by the Oxidation of Paraffin. II. Jour. Soc. Chem. Ind. (Japan), vol. 44, 1941, pp. 702-704; Chem. Abs., vol. 43, 1949, p. 9029.

Oxidation product of Fushun oil-shale paraffin treated 3 hours with concentrated NaOH solution in

an autoclave at 260°-310° under 60-120 atm. yielded crude fatty acids of very low ester value and low OH value. These values decreased with increasing reaction temperature and pressure.

1683. Kawai, S. and Nobori, H. Manufacture of Fatty Acids by the Oxidation of Paraffin. III. Jour. Soc. Chem. Ind. (Japan), vol. 44, 1941, pp. 803–806; Chem. Abs., vol. 43, 1949, p. 9029.

Oxidation product of Fushun oil-shale paraffin was analyzed; the amount of each of the fatty acids from C<sub>7</sub> to C<sub>25</sub>, the total acids over C<sub>25</sub>, and the amount of alcohol-soluble unsaponifiable matter were determined.

1684. Hirose, S., Noborl H., and Noguchi M. Manufacture of Fatty Acids by the Oxidation of Paraffin IV. Composition of Refined Fatty Acids. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, pp. 541-544; Chem. Abs., vol. 43, 1949, p. 9029.

Refined fatty acids were prepared as follows: Oxidized paraffin was saponified and the unchanged paraffin was removed. The saponified product was treated at high temperature and the unsaponified matter was extracted with CaHa. The crude fatty acids were then distilled under reduced pressure. Properties of the distillates are tabulated.

1685. — Manufacture of Fatty Acids by the Oxidation of Paraffin. V. Methanol-Soluble Portion of the Unsaponifiable Matter. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, pp. 544-545; Chem. Abs., vol. 43, 1949, p. 9029.

Saponification of the oxidized product was carried out in the presence of MeOH at high temperature and pressure. The MeOH soluble portion of the unsaponifiable matter contained most of the infermediate oxidation products. Unchanged paraffins were insoluble in MeOH.

1686. Kawai, S. Manufacture of Fatty Acids by the Oxidation of Paraffin. VI. Treatment of Paraffin with Aqueous Alcohol and Its Influence on Oxidation. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, Pp. 834–836; Chem. Abs., vol. 43, 1949, p. 9029.

Shale-oil paraffin was soluble in 95% alcohol to the extent of 2.6%. The iodine value of the alcohol-soluble portion was greater than that of the original paraffin. When the paraffin was distilled, the solubilities in 95% alcohol and iodine values of the lower bolling fractions were greater than those of the higher fractions. The oxidation velocity of paraffins, from which the alcohol-soluble portion was removed, was greater than that of untreated paraffins.

1687. Kawai, S. and Nobori, H. Manufacture of Fatty Acids by the Oxidation of Paraffin. VII. Oxidation of Fractions Obtained by Distillation of Paraffin. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, pp. 986-987; Chem. Abs., vol. 43, 1949, p. 9029.

Shale-oil paraffin, melting 47.5° and I value 9.1, was fractionated into 3 portions: b. below 190°, b.-3 190°–240°, and the residue. 50 gm. of each fraction was oxidized at 130° by passing 21. per min. of air for 20 hr. The middle fraction gave a product with an acid value of 95, while the other fractions were much more difficult to oxidize. The acids obtained from the middle fraction were best for practical applications.

1688. KAWAI, S., NOBORI, H. AND NOGUCHI, M. Manufacture of Fatty Acids by the Oxidation of Paraffin. VIII. Composition of Fatty Acids From Oxidation of the Middle Fraction of Paraffin. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, pp. 1084-1085; Chem. Abs., vol. 43, 1949, p. 9029.

Fatty acids obtained by oxidation of the middle fraction of shale-oil paraffin acid separation by distillation as Me esters included acids from caprylic to arachidic. The yield of acids was 74-78%, mostly in the C<sub>4</sub>-C<sub>4</sub> range.

1689. KAWAI, S. AND NOBORI, H. Manufacture of Fatty Acids by the Oxidation of Paraffin. IX. Oxidation of Paraffins of High Boiling Points. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, pp. 1175-1176. Chem. Abs., vol. 43, 1949, p. 9029.

Paraffins of high boiling points in shale oil from Bojun, Manchuria, were oxidized with air. The crude fatty acids were separated from the unsaponitiable portion, and their properties and compositions were determined.

1690. Manufacture of Fatty Acids by the Oxidation of Paraffin. X. Oxidation of the Mixture of Paraffins and Fatty Acids. Jour. Soc. Chem. Ind. (Japan), vol. 46, 1943, pp. 167-170; Chem. Abs., vol. 43, 1949, p. 9029.

Shale oil, melting 45.5° and I value 11.1, from Bujun, Manchuria, was mixed with various fatty acids, such as captylic or stearic acid, and air was passed at 110°. Comparatively small amounts of the acids were oxidized. If oxidation was carried out at 130°, lauric acid and stearic acid were oxidized.

dation of Paraffin. XI. Oxidation of Crude Fatty Acids. XII. New Method for Acceleration of the Oxidation. XIII. Oxidation of Unchanged Paraffins and the Properties of the Fatty Acids Produced. XIV. Properties of the Unsuponifiable Compounds Formed by Oxidation of Unchanged Paraffins. XV. Oxidation of a Mixture of Paraffins and Fatty Acids. Jour. Soc. Chem. Ind. (Japan), vol. 46, 1943, pp. 372-386; Chem. Abs., vol. 43, 1949, p. 9030.

Crude fatty acids separated from the oxidation product of shale-oil paraffin from Bujun, Manchuria, were oxidized. When the crude acid was heated at 130°-140°, its acid value increased, and OH value and the content of oxidized acid decreased. When it was heated at 140°-150°, the color changed to dark brown. When the crude fatty acid was oxidized at 120°-130° by air in the presence of 0.1% KMnO4, its acid value decreased, saponification value increased, OH value decreased, and oxidized acid disappeared. At the same time the color turned to orange-yellow. When the oxidation product of the crude fatty acid was treated with alcohol, the portion with low acid value, low saponification value, and large OH value was insoluble and was thus separated. The free fatty acid obtainable from this portion by saponification contained a large amount of oxidized acid.

1692. Manufacture of Fatty Acids by the Oxidation of Paraffin. NVI-NIX. Jour. Soc. Chem. Ind. (Japan), vol. 46, 1943, pp. 636-645; Chem. Abs., vol. 43, 1949, p. 9030.

XVI. Oxidation of tricosane. Tricosane obtained by hydrogenating laurone was oxidized by air at 120° in the presence of Mn soap. The product contained all the fatty acids from hendecanoic acid to arachidic acid with some hydroxy acids. The unsaponifiable portion of the product contained about 20% MeOH soluble material which consisted mostly of alcohols. XVII. Oxidation of hentriacontane. Hentriacontane obtained by the hydrogenation of palmitone was oxidized by air at 110° with Mn soap as catalyst. The fatty acids obtained consisted of all the acids from undecanoic to tricosanoic. The unsaponifiable portion contained about 6% MeOH soluble material consisting of alcohols, carbonyl compounds, etc. The MeOH insoluble fraction was more easily oxidized than triacontane. XVIII. Oxidation of the methanol-insoluble fraction. of the unsaponifiable portion. The MeOH insoluble fraction of the unsaponifiable matter obtained on 3 successive oxidations of Fushun shale-oil paraffin described in part XIV (abs. 1691) was oxidized by air

at 130°-160° with the addition of 0.1% KMnO4. These fractions were easier to oxidize than the original paraffin. Crude fatty acids containing no hydroxy acids. were obtained. XIX. Treatment of raw fatty acid with solvents. Crude fatty acid obtained from the oxidation of Fushun shale-oil paraffin was separated into petroleum ether-insoluble and ether-soluble portions. The soluble portion was further separated into portions insoluble and soluble in 85% alcohol. The petroleum ether-insoluble portion was converted to the Me esters, and 37% was distilled. The distillate was was assumed to consist of Me esters of hydroxy acids having similar numbers of C atoms. The S5% alcoholinsoluble portion consisted of higher saturated fatty acids. From the portion soluble in 85% alcohol no lactones, lactides or similar compounds could be obtained by distillation,

1693. Kawai, S. Manufacture of Fatty Acids by the Oxidation of Paraffin. XX. Example of an Oxidation Experiment. Jour. Soc. Chem. Ind. (Japan), vol. 46, 1943, pp. 762-764; Chem. Abs., vol. 43, 1949, p. 9030.

Distillate, b. 200°-250°, from shale-oil paraffin was oxidized 22.5 hr. by 41./min. of air/800 gm. paraffin at 110°-120° to yield 22.2% crude fatty acids. Of the crude fatty acids, 8% are insoluble in petroleum ether. 69% are soluble in petroleum ether. 89% are soluble in 85% alcohol. The distillation test on the fatty acids soluble in alcohol was carried out, and the properties of the distillates were examined.

1694. KAWAI, S. AND NOBORI, H. Manufacture of Fatty Acids by the Oxidation of Paraffin. XXI. Oxidation of High-Boiling Fractions of Paraffin (Suppl.) Jour. Soc. Chem. Ind (Japan), vol. 46. 1943, pp. 764-765; Chem. Abs., vol. 43, 1949, p. 9030.

High-boiling fraction of shale-oil paraffin, melting 47.6° and I value 9.2, was oxidized by air, 21/min./50 gm, at 150°. The acid value did not increase after 10 hours. The formation of oxidized acids and lower acids occurred some time after the high-boiling fraction of paraffin was oxidized.

1695. KAWAI, S. Manufacture of Fatty Acids by the Oxidation of Paraffin. XXII. Thermal Decomposition of Oxidation Products and Crude Fatty Acids. Jour. Soc. Chem. Ind. (Japan), vol. 46, 1943, pp. 1058-1062; Chem. Abs., vol. 43, 1949, p. 9030.

Three oxidation products of shale-oil paraffin of different degrees of oxidation and the 3 crude mixtures of fatty acids obtained from them were, respectively, heated in a retort with or without the addition of acid clay, etc., and the properties of the distilled oils were examined and compared. The highly oxidized product and the crude fatty acids obtained therefrom yielded a smaller amount of distilled oil than the other products. The amount of acid clay added had a great effect on the yield and properties of the distilled oil. With increasing amounts of acid clay, the specific gravity of the distilled oil diminished, and the yield decreased. An increase in I value and a decrease in OH value were also noticed. The yield of olefinic material was greatest when the medium-oxidized product, that is, paraffin oxidized 20 hours at 120°-130° was slowly heated with the addition of 10% acid clay.

1696. NOBORI, H., AND KAWAI, S. Manufacture of Fatty Acids by the Oxidation of Paraffin. XXIII. Oxidation of High-Melting Faraffins. Jour. Soc. Chem. Ind. (Japan), vol. 46, 1943, pp. 1211-1212; Chem. Abs., vol. 43, 1949, p. 9031.

Paraffin, melting 59.4°, I value 3.22, from Bujun, Manchuria, was oxidized by air at 120°. The oxidation products contained  $C_{10}$ — $C_{10}$  fatty acids. The paraffins were most easily oxidized in the middle of the chain.

KAWAI, S., AND NOBORI, H. Manufacture of Fatty Acids by the Oxidation of Paraffin. VII. Oxidation of Fractions Obtained by Distillation of Paraffin. See abs. 1687.

——. Manufacture of Fatty Acids by the Oxidation of Paraffin. IX. Oxidation of Paraffins of High Boiling Points. Sec abs. 1689.

——. Manufacture of Fatty Acids by the Oxidation of Paraffin. X. Oxidation of the Mixture of Paraffins and Fatty Acids. See abs. 1690.

. Manufacture of Fatty Acids by the Oxidation of Paraffin. XI. Oxidation of Crude Fatty Acids. XII. New Method for Acceleration of the Oxidation. XIII. Oxidation of Unchanged Paraffins and the Properties of the Fatty Acids Produced. XIV. Properties of the Unsaponifiable Compounds Formed by Oxidation of Unchanged Paraffins. XV. Oxidation of a Mixture of Paraffins and Fatty Acids. See abs. 1691.

Manufacture of Fatty Acids by the Oxidation of Paraffin. XVI-XIX. See abs. 1692.

Manufacture of Fatty Acids by the Oxidation of Paraffin, XXI. Oxidation of High-Boiling Fractions of Paraffin (supplement). See abs. 1694.

KAWAI, S., NOBORI, H., AND NOGUCHI, M. Manufacture of Fatty Acids by the Oxidation of Paraffin. VIII. Composition of Fatty Acids From Oxidation of the Middle Fraction of Paraffin. See abs. 1688. 1697. KAWAKITA, K. Chemisorption of Carbon Dioxide by Reduced Iron. I. Interaction of Carbon Monoxide and Carbon Dioxide With the Reduced Iron. Rev. Phys. Chem. Japan. vol. 8, 1934, pp. 89-116: vol. 11, 1937, pp. 39-53; Chem. Abs., vol. 31, 1937. p. 3759; vol. 32, 1938, p. 403.

In chemisorption of CO: by reduced Fe an irreversible sorption always takes place in the normal state of the activity of the catalyst, the amount of the sorption being proportional to the square root of time in the intermediate state of the sorption. The final pressure of CO2 always approaches zero. Some selectivity of catalytic action was found with catalysts of various activities and mixtures of CO and CO2. Sieverts' law, that the amount of sorption is proportional to the square root of the pressure, seems to hold. It is suggested the chain reaction is Fe+(CO2)ods.=Fe,Oy+ (CO) ads.; COads.=1/2C+1/2(CO2) ads.. Facts indicating these reactions are: (a) The catalyst, saturated with CO2, recovers its activity, forming water, by its re-reduction with H2; (b) the formation of free C was observed; (c) the sorption is irreversible and has some self-poisoning. The activity of the catalyst may be accomplished by saturating it with CO2, by poisoning and by sintering.

1698. — Chemisorption of Carbon Dioxide by Reduced Iron. II. The Effect of Chemisorption on van der Waals Adsorption of Carbon Dioxide at 0°. Rev. Phys. Chem. Japan, vol. 12, 1938, pp. 105–114; Chem. Abs., vol. 33, 1939, p. 1568.

was studied by measurement of its van der Waals adsorption at 0°. The following 3 types of surfaces, obtained by pretreatment, were studied: (A) Fresh surface without chemisorption, (B) when reaction vessel is evacuated at 300° 400° after chemisorption and (C) when the reaction vessel is not evacuated or evacuated at 0° after chemisorption. The van der Waals adsorption was greater on surface (B) and less on surface (C) than on surface (A). The fraction of the surface covered with the adsorbed molecules and the total number of the elementary spaces in van der Waals adsorption at 0° were calculated. The relation between the fraction of surface covered with the ad-

sorbed molecules and the whole surface was found to be (B) = (A) > (C). The relation between the total number of elementary spaces and the surfaces was (B) > (A) > (C). Increase in van der Waals adsorption due to the chemical treatment at high temperature in the case of (B) is ascribed to increase in the total number of elementary spaces.

1699. — Chemisorption of Carbon Dioxide by Reduced Iron. III. Thermodynamic Consideration of the Chemisorption. Rev. Phys. Chem. Japan, vol. 13, 1939, pp. 87-95; Chem. Abs., vol. 33, 1939, p. 9084.

Free-energy equations are derived for the possible reactions in the chemisorption of CO<sub>2</sub> by reduced Fe, and the free-energy values are calculated for 360°. CO as an intermediate product is identified by its reduction of PdCL<sub>2</sub> solution. Fe<sub>3</sub>O<sub>4</sub> is identified as a product. These facts and the free-energy values suggest that the chemisorption consists of the following reactions: Fe+CO=FeO+CO, 3FeO+CO. The apparent reaction of the system becomes 3Fe+2CO<sub>2</sub>=Fe<sub>3</sub>O<sub>4</sub>+4CO,2CO=C+CO<sub>3</sub>.

1700. — Chemisorption of Carbon Dioxide by Reduced Iron. IV. Kinetics of the Chemisorption. Rev. Phys. Chem. Japan. vol. 14, 1940, pp. 1–10; Chem. Abs., vol. 34, 1940, p. 3717.

Kinetics of the chemisorption of CO<sub>2</sub> by reduced Fe are studied. There appear to be active centers of different character on the surface of the catalyst, some of which adsorb CO<sub>2</sub> and some CO. The apparent heat of activation is 37 kcal. per mol.

1701. — Chemisorption of Carbon Dioxide by Reduced Iron. Effect of the Chemisorption on van der Waals' Adsorption of Carbon Dioxide at 0°: Proc. Imper. Acad. (Tokyo), vol. 12, 1936, pp. 61-63; Chem. Abs., vol. 30, 1936, p. 7008.

Van der Waals' isotherms for the adsorption of CO. by reduced Fe at 0° are reproducible, equilibrium being attained within 1 min. The effect of the previous treatment of the reduced Fe (previous cycles, temperature of evacuation) and the pressure (0-20 cm. Hg) on the adsorption of CO. are shown graphically. 1702. — [Kinetics of the Reduction of Ferric Oxide.] Rev. Phys. Chem. Japan, vol. 14, 1940, pp. 79-85; Chem. Abs., vol. 35, 1941, p. 961.

Rate of reduction of Fe.O. by H., dx/dt, measured in a static system, equals  $kx^n(a-x)$ , where x is the amount of H. reacted, a is the initial H. concentration, k is the rate constant, and n is a topochemical factor related to the number of reaction nuclei and to their rate of propagation. At 500° and 600°, many nuclei are formed at the start of the reaction and n=0, and the reaction is approximately 1st order. At 205° very few nuclei are formed initially and n=1, giving a maximum rate when x=a/2. n decreases as k increases. As the temperature increases above 265° the maximum rate is larger and appears earlier.

KAWAMICHI, K. See abs. 1854.

1703. KAZANSKII, B. A. [Synthesis of Liquid Fuel From Carbon Monoxide and Hydrogen.] Gosudar stvennoe Nauchno-Tekhnicheskoe Izdateľstvo U. S. S. R. 1940.

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1704. KAZANSKII, B. A., SERGIENKO, S. R., AND ZEL-INSKII, N. D. Contact Cyclization of Paraffinic Hydrocarbons. Compt. rend. acad. sci. U. R. S. S., vol. 27, 1940, pp. 664-669 (in English); Chem. Abs., vol. 35, 1941, p. 1387.

Fraction of synthin, boiling at 83°-138°, containing 11.84% unsaturates and having 66.0 aniline point and 10 octane number, was passed over catalysts at 425°-500°, giving condensates having the following values

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for % unsaturates, % aromatics, aniline point (maximum), and octane number: 90% silica gel and 10% Cr.O. (preheated in H. to 450°) at 450°, 5.30, 11.37, -; 1:1 mixture of silica gel-Cr.O. (reduced in H<sub>2</sub> at 450°) at 425°-450°, 5.60, 14.5, 58.0, 22; 91.5% Cr<sub>2</sub>O<sub>3</sub> and 8.5% NiO at 450°, 6.03, 16.38, 48.4, —; 85% Al<sub>2</sub>O<sub>2</sub> and 15% UO<sub>3</sub> (preheated in N<sub>2</sub> to 450°) at 500°, 11.26, 11.40, 56.2, 26; 62% Al<sub>2</sub>O<sub>3</sub>, 24% Cr<sub>2</sub>O<sub>3</sub>, and 14% UO<sub>2</sub> (preheated in N<sub>2</sub> at 475°) at 475°, 9.78, 26.42, 32.3, -: 80% Al-O. and 20% MoO. (preheated in N. to 450°) at 450°, 6.03, 15.74, 52.8, 24; and Zn chromate at 475°, 20.84, 1, 58.9, -. Platinized charcoal (containing 23% Pt and prepared by impregnating activated charcoal with H-PtCl, solution and heating in H. at 300°-310°) at 300°-356° did not aromatize the synthin fraction. After removal of unsaturated hydrocarbons from the synthin fraction by means of Kattwinkel mixture (see abs. 1678) the platinized charcoal at 350° aromatized the remaining hydrocarbons to approximately the same degree as with octane. Air blowing has no effect on the activity of Zn chromate catalyst.

1705. KAZANSKIĬ, B. A., PLATÉ, A. F. BULANOVA, T. F., AND ZELINSKIĬ, N. D. [Contact Cyclization of Paraffinic Hydrocarbons. Catalysts Containing Vanadium Pentoxide and Thorium Dioxide.] Compt. rend. acad. sci. U. R. S. S., vol. 27, 1940, pp. 658-663; Chem. Abs., vol. 35, 1941, p. 1386.

When a synthin fraction, boiling at 83°-138°, was passed over V2Os at approximately 500°, NH4VOs (preliminary heating to 500° in N2 at 500° or Al2O3 at 450°-555°, there was virtually no formation of aromatic hydrocarbons. Alumina with 5-10% of V2Os at 475°-500° catalyzes the formation of aromatic hydrocarbons from synthin fractions, which boil at 83°-138° and 162°-205°, respectively, but gradually loses its activity, becoming covered with C. The catalyst readily regains its original activity by heating in a current of air. Cr2O2 with 10% V2O3 at 450°-470° showed considerable catalytic activity but rapidly lost its activity. Parby kieselguhr with 10% V2Os did not catalyze the formation of aromatic hydrocarbons from a synthin fraction boiling 83°-138°. Alumina with 10% ThO2 catalyzed the formation of aromatic hydrocarbons from the same synthin fraction. The catalytic activity of alumina with 10% ThO2 at 500° for the formation of aromatic hydrocarbons from the same synthin fraction increased slowly and then slowly decreased; the catalyst can be regenerated by heating with air. Alumina with 10% V<sub>2</sub>O<sub>5</sub> and 2% ThO<sub>2</sub> at 475°-500° acted in the same manner as alumina with 10% V2Os. Activated charcoal with 10% ThO2 at 450°-470° catalyzed considerably the formation of aromatic hydrocarbons from the synthin fraction, but the catalyst declined somewhat rapidly in activity and was not satisfactorily regenerated with

1706. KAZANSKIÍ, B. A., LIBERMAN, A. L., PLATÉ, A. F., ROZENGART, M. I., AND STERLIGOV, O. D. [Laboratory Method for Rapid Hydrogenation of Olefins at Atmospheric Pressure.] Doklady Akad. Nauk S. S. S. R., vol. 71, 1950, pp. 477-480; Chem. Abs., vol. 44, 1950, p. 8313.

Platinized C activated by a small amount of PdCl<sub>2</sub> or H\_PtCl<sub>8</sub> is a very active, rapidly acting catalyst for atmospheric pressure hydrogenation of olefins even without added solvents. A considerable economy in the amounts of catalysts needed is one of the results. Sample reductions were performed in a rocking flask with 50-200 ml. charges and platinized charcoal containing 0.01-0.05 gm. Pt to which was added 1-2.85 ml. of the activator solution (either 0.03 gm. Pt/ml. of H\_PtCl<sub>8</sub>, or 0.018 gm. Pd/ml. of PdCl<sub>2</sub> solution); the reductions were complete in 3-8 hr. (usually 97%), and after filtration the products were distilled.

1707. Kaz'min, S. [Utilization of Cheremkhov Coals.] Planovoe Khoz., 1939, No. 11, pp. 131-134; Khim. Referat. Zhur., 1940, No. 7, p. 85; Chem. Abs., vol. 36, 1942, p. 5631.

Fine coal can be utilized by semicoking after briquetting. The heat capacity of semicoke is equal to that of the initial coal. The least expensive method for producing liquid fuel is by semicoking the coal and distilling the tar: the yield is 12%. The other methods used are hydrogenation of the coal, and synthesis from water gas produced from the coal.

1708. Kehde, H., Fairfield, R. G., Frank, J. C., and Zahnstecher, L. W. Ethylene Recovery. Commercial Hypersorption Operation. Chem. Eng. Progress, vol. 44. No. 8, 1948, pp. 575-582; Chem. Abs., vol. 42, 1948, p. 8149.

Describes hypersorption process for the continuous separation of gases by selective adsorption on a moving bed of activated C; also operation and performance of the first full-scale commercial hypersorber built for the Dow Chemical Co. to recover small concentrations of C-H, from a H-CH, stream at 75 p. s. i. g. From a feed gas containing 4.5-6.0 vol. % C-H, a C-H, product is obtained of 92-93% parity and 0.1% maximum CH, contamination. The H-CH, overhead stream contains less than 0.1% C-H.

1709. Keler, N. P., and Roginskii, S. Z. [Investigation of the Heterogeneity of Active Surfaces by the Differential Isotopic Method. I. The Active Surface of Metallic Nickel and of Zine Oxide.] Izvest. Akad. Nauk S. S. S. R., Otdel. Khim. Nauk, 1950, pp. 27–38; Chem. Abs., vol. 44, 1950, pp. 5690–5691.

Heterogeneity of the surface of an active Ni-catalyst, prepared by compression of Ni grains of 1.0-2.0 mm, diam, (by reduction of NiO in a stream of Ha at 280°), specific surface area 1.5-2 m.3/gm., was demonstrated by experiments of consecutive adsorption, at room temperature, of H2 and of D2, or 1st of D2, then of H2, and thermal conductivity analysis of the gas given up in fractions on desorption at increasing temperatures. Before the adsorption experiments, 1.05gm. samples of the catalyst were outgassed at up to 450° under 10-5 mm. Hg, reduced once more with H₂ at 450° and again outgassed at 530°. Between the 2 adsorptions, the catalyst was evacuated 1.5 min. to 10-3 mm. Hg, then the 2d gas was admitted. Data for a typical run are: 1st adsorption, D: under 1.48 mm. Hg, amount adsorbed in 9 min. at room temperature, 0.095 cc. (S. T. P.); after short evacuation, 2d adsorption. H. under 3.08 mm. Hg, amount adsorbed in 9 min. at room temperature, 0.04 cc., followed by 1.5 min. evacuation, the % of D<sub>2</sub> and of H<sub>2</sub>, respectively, in the gas desorbed; at room temperature, 5 and 95; at 2°-65°, 0 and 100; at 170°-220°, 0 and 100; at 300°-320°, 40 and 60; at 420°-470°, 95 and 5; at 520°, 100 and 0; at 530°, 100 and 0. Consequently, the isotope adsorbed first is desorbed last. The same is observed in analogous runs with the order of the 2 adsorptions reversed; namely, 1st H2, then D2. In these experiments, the surface coverage is of the order of 5-10% of the total surface area. No specific effects owing to the chemical difference between H. and D. are observed. The conclusion is that active spots on the surface of Ni differ in their heats of adsorption and activation energies, and that there is no mixing of the molecules adsorbed on the surface. A gas of mixed composition is obtained only in desorption in an intermediate temperature range, which indicates limited mobility of the molecules in the adsorbed layer. On the basis of this finding, the exponential kinetic law established by Elovich and Zhabrova (abs. 814 and 815) for the rate of adsorption of H2 is rooted not in repulsive interaction between the adsorbed molecules but solely in

the heterogeneity of the adsorbing surface. Analogous

experiments were made with ZnO, prepared by oxidation of Zn in the electric arc, and outgassable at up to 500° without decomposition; decomposition is noticeable only above 600°. On adsorption of H2, the gas liberated in desorption at up to 500° is pure H2; reaction between H2 and ZnO takes place only above 500°, and then even under a pressure as low as 0.5 x 10- mm. Hg. If the 2 consecutive adsorptions are accomplished above 100°, only the gas adsorbed last is given up on heating; the isotope adsorbed first appears to have been spent. In room temperature adsorption, the 2d adsorbed gas is bound very weakly. and most of it is desorbed in the 1.5 min. evacuation at room temperature, which precedes the high-temperature desorption. Consequently, only the isotope adsorbed first is found in the gas desorbed on heating. This indicates that, under these conditions, only a very minor fraction of all active points has a high binding power for the adsorbed molecules, and these points are completely filled by the gas adsorbed first. This situation is changed when the 1st adsorption is done at 200°. Thus, with D2 adsorbed first under 6.15 mm. Hg, 50 min. at 200° followed by slow 16 hr. cooling to room temperature, the amount of D2 adsorbed was 0.2 cc. (S. T. P.); after short evacuation. H2 was adsorbed under 6.65 mm. Hg, 34 min. at 115°, amount adsorbed 0.028 cc.; the composition of the gas given up on subsequent desorption at 170°-285°, 300°-325° 395°-450°, 487°-495°, was (% D2 and H2), 15 and 85, 25 and 75, 20 and 80, 75 and 25%. Under these conditions, the gas adsorbed last is given up first, as in the case of Ni.

Kell, W. Fat Acids With Odd Number of Carbon Atoms. V. Behavior of Branched Fat Acids in the Body. See abs. 1714.

bers of Carbon Atoms. III. Sec abs. 1712.

. Fats from Fatty Acids With Odd Numbers of Carbon Atoms. VI. See abs. 1716.

\_\_\_\_. See abs. 1711, 1713, 1717.

Kell, W., AND SCHILLER, G. Fats From Fatty Acids With Odd Numbers of Carbon Atoms. Addendum to III, IV, and V. See abs. 1715.

1710. KEIL, W., APPEL, H. AND BERGER, G. [Fats From Fat Acids With Uneven Numbers of Carbon Atoms, I. Preliminary.] Ztschr. physiol. Chem., vol. 257, 1939, pp. 1–3; Chem. Abs., vol. 33, 1939, p. 3193.

1711. APPEL, H., BERGER, G., BÖHM, H., KEIL, W. AND SCHILLER, G. [Fats From Fat Acids With Uneven Numbers of Carbon Atoms. II.] Ztschr. physiol. Chem., vol. 266, 1940, pp. 158-173; Chem. Abs., vol. 35, 1941, p. 2582.

Cacao butterfat acids were reduced to the alcohols, converted to bromides with HBr and these to nitriles with CaCN and these hydrolyzed to fat acids with uneven numbers of C atoms. These, as well as the original fat acids, were resynthesized to "uneven" cacao fat and even" cacao fat and compared with natural cacao fat and with each other. The synthetic fats were completely hydrogenated. The fats were fed at 5, 10 and 20% levels to rats. No significant differences in body weight, deposition of fat, residual fats after starvation, their I numbers, extent of resorption or dicarboxylic aciduria were observed. The resorption of the 3 fats is virtually equal in man.

1712. KEIL, W. [Fat From Fatty Acids With Odd Numbers of Carbon Atoms. III.] Ztschr. physiol. Chem., vol. 274, 1942, pp. 175–185. Chem. Abs., vol. 37, 1943, p. 5943.

Ether-soluble acids were determined in the urine of dogs on basal diet supplemented with different kinds of natural fat. 0.1-0.4 gm. were recovered/100 gm. fat fed daily for 3 days. Similar results were obtained

with fats containing only odd number, straight-chain fatty acids. Triglycerides of synthetic branched-chain fatty acids gave an increased Et-O-soluble fraction in the urine. Et branched-chain fatty acids are inefficiently attacked in the body and are eliminated, whereas 2-, 3- and 5-methyldodecanoic acids are not excreted significantly. A number of branched-chain fatty acids were synthesized.

1713. Appel, H., Böhm, H., Keil, W. and Schiller, G. [Fat From Fatty Acids With Odd Numbers of Carbon Atoms. IV.] Ztschr. physiol. Chem., vol. 274, 1942, pp. 186-205; Chem. Abs., vol. 37, 1948, p. 6718.

Growth and development of young male goats were the same when fed coconut oil or butterfat or a synthetic fat mixture (1) consisting of straight-chain odd- and even-numbered fatty acids. After prolonged feeding the resorption of I was 79%, of coconut oil 91 and of butterfat 92%. Body and depot fat of rats and goats fed saturated fats contained more than 60% saturated acids. Feeding I containing C<sub>10</sub>-C<sub>22</sub> fatty acids led to C<sub>11</sub>-C<sub>11</sub> fatty acids in depot fat, and odd-numbered C-chain fatty acids amounted to 33% of the total depot fatty acids. With I. C<sub>13</sub> acids are the smallest to appear in depot fat, with coconut oil C<sub>22</sub>, and with butterfat C<sub>34</sub>.

1714. Kell, W. [Fat Acids With Odd Number of Carbon Atoms. V. Behavior of Branched Fat Acids in the Body.] Zischr. physiol. Chem. vol. 276, 1942, pp. 26-32; Chem. Abs., vol. 37, 1943, p. 6728.

Feeding to dogs of triglycerides of branched fat acids (I) with even or odd numbers of C atoms causes an increase in the amount of acid metabolic products in the urine.

1715. Kell, W. And Schiller, G. [Fats From Fatty Acids With Odd Numbers of Carbon Atoms. Addendum to III, IV, and V.] Zischr. physiol. Chem., vol. 282, 1947, pp. 135-136; Chem. Abs., vol. 43, 1949, p. 6164.

Fats from fatty acids with odd numbers of C atoms whose metabolic fate in dogs has been reported, abs. 1714, were prepared by esterification with glycerol of the fatty acids resulting from air oxidation at 100°-150° of various paraffin preparations in the presence of suitable catalysts. The crude fatty acids were removed by extraction with aqueous alkali, reprecipitated by addition of mineral acid, distilled, and the fraction of chain-length C10-C23 esterified. The resulting triglycerides were purified in the usual way. The acids prepared from Riebeck-paraffin fatty acids contained higher oxidation products (I), especially dibasic acids (II) (3-4%), HO, and Keto acids. The color of the resulting fats, G138/140, was improved by hydrogenation. The acids prepared from Fischerparaffin fatty acids, containing (1), gave the fat G137, which was hydrogenated before use. The acids prepared from a paraffin resulting from the high temperature hydrogenation of lignite or lignite tar gave, without further purification, G284 on esterification. G301 was prepared from the same material as G284, after careful separation of the fatty acids from (1), especially (II), by chromatography on silica gel, and improvement of the triglyceride color by hydrogenation. G236 was prepared from the same starting material as G137, but with purification of the acids by chromatography as for G301. Prior crystallization of the lignite paraffin and chromatography of the crude acids gave, on esterification, G405, a product free of (II), and branched-chain acids (III). The fatty acids resulting from oxidation of pure eicosane contained no (III), and chromatography removed (II); on esterification, G273a resulted, but omission of chromatographic treatment gave G289 which contained some (II). G118/119 are comparable to G138/140 and were

prepared from the acids from oxidation of Riebeck paraffin.

1716. Kell, W. [Fats From Fatty Acids With Odd Numbers of Carbon Atoms. VI.] Ztschr. physiol. Chem., vol. 282, 1947, pp. 137-142; Chem. Abs., vol. 43, 1949, p. 6165.

1717. APPEL, H., BÖHM, H., KEIL, W., AND SCHILLER, G. [Fats From Fatty Acids With Odd Numbers of Carbon. VII. Preliminary Communication Concerning Properties, Stability, Physiology, and Toxicology of Synthetic Fats From Paraffin Fat Acids.] Ztschr. physiol. Chem., vol. 282, 1947, pp. 220–244; Chem. Abs., vol. 43, 1949, p. 9487.

Synthetic fats prepared from glycerol and fat acids obtained by oxidation of paraffin from various sources are more resistant to oxidation and become rancid more slowly than natural fats. Of the fat acids not occurring in natural fats odd-numbered ones, approximately 48% in the synthetic fat, are metabolized by animals and man like natural fat. After feeding oddnumbered saturated acids with C21-C29, 9-10 unsaturated acids are found in depot fat. Branched-chain acids, approximately 15% of the synthetic fat and removable by recrystallization of the paraffin or the fat acids, when fed are mostly excreted in the urine as low-molecular branched acids, dicarboxylic acids, and unidentified acid products. Only a very small amount appears in depot fat. A diet high in branchedchain fats inhibits growth in rats and is toxic. Dicarboxylic acids from Co-C15, 3-4% of the synthetic fat and removable with alkali or by absorption, are excreted in the urine as degraded dicarboxylic acids from Ce-C... Unsaturated acids with double bonds mainly in 2-3 and 4-5 positions and with transconfiguration are present only in very small amounts. The unsaponified fraction consisting of paraffin, alcohols, and ketones is nontoxic in the low concentration, less than 1%, present in synthetic fat.

Kerlig, F. See abs. 2932, 2934.

1718. Keith, P. C. Gasoline From Natural Gas. Gas, vol. 22, No. 6, 1946, pp. 21–26; Nat. Petrol. News, vol. 38, No. 27, 1946, pp. R-506-511; Am. Gas Jour., vol. 164, No. 6, 1946, pp. 11–15; Oil Gas Jour., vol. 45, No. 6, 1946, pp. 102, 105, 107, 108, 111, 112; Am. Gas Assoc. Monthly, vol. 28, 1946, pp. 253–257, 296–297.

This is a discussion of the Hydrocol process developed by Hydrocarbon Research, Inc., studied in a 10-bbl. per-day pilot plant at Olean, N. Y., and to be put into commercial production by Carthage Hydrocol, Inc., at Brownsville, Tex., for converting CO and H2, from the partial combustion of natural gas with O2, to gasoline. A cheap, rugged, Fe-base catalyst giving high conversion has been developed. It operates by the fluid-catalyst technique. This catalyst, the cheap production of O2, and a method for the almost total recovery of the exothermic heat, make it possible to synthesize gasoline that can compete with that from natural crude. The plant will include the largest O. plant in existence and will produce 40,000,000 cu. ft. of O, per day for use in the partial combustion of the natural gas. The synthesis process will effect a 90% conversion of synthesis gas to produce 5,800 bbl. of 88-90 octane no. gasoline per day in addition to 1,200 bbl. of 45-50 cetane no. diesel fuel and 150,000 lb. of mixed alcohols. Allowing \$0.035 per gal. for the diesel fuel and \$0.005 per lb. for the crude alcohols, gasoline will be produced at a cost of \$0.0525 per gal. One of the important features in maintaining this cost level is the heat recovery through which 750,000 lb. of high pressure steam per hr. will be produced. Based on estimated gas reserves of 175 billion cu. ft., a synthetic crude supply is potentially available equivalent to the present crude petroleum reserves. Another important possibility is the use of waste refinery gases,

which could yield as much as 7-8% of the country's present crude production. Furthermore, present developments indicate that the production of gasoline from coal might not be much more difficult with complete gasification of coal offering gas reserves of astronomical proportions.

1719. ——. Synthetic Fuels Promise to Bolster Petroleum Reserves. Chem. Eng., vol. 53, No. 12, 1946, pp. 101-103; Coal Age, vol. 51, No. 11, 1946, p. 134; Combustion, vol. 18, No. 6, 1946, pp. 55-57. Lecture before the Princeton Bicentennial Confer-

ence. The successful conclusion of the coal-to-oil development will increase our potential oil resources materially. With the economic equivalence of gas-tooil well on its way to being established, the indications are that the economic equivalence of coal-to-oil will follow shortly. German developments have greatly increased the efficiency of coal gasification, and it is reasonable to expect that, since American engineering has improved and lowered the cost of the synthetic oil processes, it can also greatly improve and lower the cost of coal gasification. The present German Largi process utilizes a highly reactive, noncaking brown coal, but there appears to be no basic reason why a relatively inactive, highly caking bituminous coal could not be similarly gasified to yield a 900-950-B. t. u. gas with a thermal efficiency or 80% plus. Development work is under way, and the indications are that it will be successful. The economic equivalence of brown coal to town gas having been demonstrated, the same for bituminous coal to town gas and pipeline gas should follow. Fuel transportation is an important factor in this respect. If coal can be economically transformed into gas and oil, it will be interesting to compare the cost of transporting energy as coal with cost of transporting it as gas and oil. The relative costs of transporting equivalent amounts of energy in the form of coal, oil and gas from West Virginia to New York are shown to be as follows: Coal \$3.35, oil \$0.73, gas \$1.92. The transformation of coal into gas at 80% thermal efficiency appears economically superior to its transformation into oil. Operating cost for the former is estimated at about \$1.00 per ton of coal, exclusive of all fuel charges; therefore, with coal worth \$2.50 per ton in West Virginia the transportation of gas looks very attractive, especially gas of 1,000 B. t. u., the production of which seems feasible. The figures for the transportation of coal as oil do not look so attractive. Again, excluding fuel cost, the present predicted cost of transforming a high B. t. u., lowmoisture, low-ash coal into oil is about \$5.00 per tonor \$1.93 per bbl. Until the capital and operating costs of converting coal to oil can be decreased, oil from coal will not compete with coal as an industrial fuel.

1720. ——. Expansion in Natural-Gas Synthesis. Oil Gas Jour., vol. 46, No. 31, 1947, p. 130.

Abstract of a paper presented before the Petroleum Engineers' Club of Dallas. It is estimated that within the next decade 10 Hydrocol plants may be built to meet the anticipated demand for liquid fuels. Natural gas however, should not increase greatly in price as coal conversion, which lurks in the background, would automatically place a competitive limit to natural-gas prices. The probable economic sequence of alternative future sources for petroleum products is outlined as follows: (1) Gasoline from gas, now commercially feasible with Hydrocol plants under construction at Brownsville and Hugoton; (2) gasoline from coal, with a plant under construction at Pittsburgh; (3) oil from coal, an economic probability in 8-10 yr. The relatively fixed market for chemical products of the type produced by the Hydrocol process incidentally, will increase the commercial success of the process. Development of the method of producing cheap O2 is given recognition for the commercial success of the Hydrocol process.

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Hydrocol Process Development. Petrol. Refiner, vol. 26, No. 4, 1947, pp. 171-172; Nat. Petrol. News, vol. 39, No. 14, 1947, p. 9; Chem. Eng. News, vol. 25, 1947, p. 1044; Petrol. Processing, vol. 2, 1947,

Abstract of a paper presented at the 35th meeting of the Western Petroleum Refiners Association. By means of the Hydrocol process, a gasoline of 78-80 octane no., Cooperative Fuel Research Motor method, or 90-92, Research method, can be made from natural gas, plus a 39-40 gravity, A. P. I., diesel fuel of 50-75 cetane no. and a large amount of oxygenated compounds, such as alcohols. HCHO, acetone, etc. By using coal as a raw material, these same products are derived at a somewhat higher price. Thus the synthetic process, using coal, natural gas, or even refinery waste gas, has the 2-fold effect of (1) putting a definite ceiling on the price of natural gas and crude, and (2) setting at rest fears for what we shall use for fuel when and if reserves of crude and gas are exhausted. The possibility of using coal, supplies of which are sufficient to last 1.000 yr., puts a ceiling of not more than \$0.10-0.12 per 1,000 cu. ft. on natural gas and permits only a corresponding increase in the price of crude. The Hydrocol process also is of interest to the refiner, because it is the only other process, with the exception of polymerization and alkylation, by which the quality of the product can be enhanced without a corresponding decrease in quantity. It also may become a strong competitor of catalytic cracking and has the additional advantage of simultaneously utilizing both gases and refinery wastes. It is thought that by 1955 gasoline will be produced synthetically from synthesis gas made by coal gasification. It is estimated that a Hydrocol plant of 3,500-bbl -per-day capacity would be practical.

-. Current Status of Synthetic Fuels. Oil Gas Jour., vol. 47, No. 25, 1948, pp. 56-57.

Abstract of a paper presented at the annual meeting of the Texas Mid-Continent Oil and Gas Association. The manufacture of gas from coal and oil from gas will be the dominating synthesis processes used to supplement United States crude supplies. Processes used for synthesizng oil from coal, gas from coal, oil from shale, and oil from gas are reviewed. The lowpressure process of converting coal to oil is uneconomical at present, as gasoline produced in this manner would cost about \$0.165 per gal., using coal worth \$3.00 per ton. Processes for synthesizing gas from coal will soon be commercialized, as gas with a B. t. u. content equivalent to that of natural gas can be manufactured and transported about 150 miles for approximately \$0.136 per 1,000 cu. ft. Because of the huge cash outlay involved, utilization of our shale deposits will not be immediate, although technically sound processes have been developed. In order for the process to be economical, plants of 100,000 bbl. capacity or large involving a capital outlay of some \$500,000,000.00 will be required. Processing the shale oil would require a capital outlay of \$8,500.00 per bbl. of gasoline. At this time the only commercially feasible method is the synthesis of oil from gas. Such plants as those using Hydrocol process can be built for about \$3,800.00 per bbl. per day capacity. Allowing credit for byproducts, and a 10% amortization plus a 10% return on 50% of the capital and 4% on the remainder, gasoline can be produced at a cost of \$0.0833 per gal, from gas worth \$0.083 per 1,000 cu. ft. For gas worth \$0.163 the cost is about \$0.0993. There are 3 reasons why the oil industry has been slow in entering the gas-to-oil synthesis field: Newness of the process; lack of funds due to expansion of present equipment; and the tax position. There appears to be, however, no reason why the Government should assume control of the synthetic-oil industry.

1723. KEITH, P. C., AND WILSON, D. W. Manufacture of Low-Cost Oxygen. Blast Furnace, Coke Oven and Raw Materials. Am. Inst. Min. and Met. Eng. Proc., vol. 6, 1947, pp. 55-63.

Brief history of the development of modern O2 plants is given, with a description of the principles involved in plants of the type now being built. It is estimated that the approximate capital cost of a plant producing 100 ton or 2,400,000 cu. ft. of 90-96% O. per day would be \$940,000.00 and for a 400-ton or 9,600,000-cu. ft. plant, \$1,900,000.

1724. KELLER, K., AND KLEMPT, W. [Catalytic Conversion of Gases Containing Methane Into Carbon Monoxide and Hydrogen.] Ber. Gesell. Kohlentech., vol. 3, 1930, pp. 230-261; British Chem. Abs., 1931, B.

Reaction studied were (1) CH.+H-O=CO+3H. and (2) CH4+0=CO+2H2. The composition of the gas used was approximately 2% CO2, 2% CnHm, 0.5% O2, 6% CO, 26% CH. 55% H2, and 8% N2. Poisoning of the catalyst by S compounds present in the gas appears to be due to the formation of NiS, which, at suitable temperatures, can be decomposed by oxidation with steam and, thus, prevented from deactivating the catalyst completely. Since reaction (1) is endothermic, considerable difficulty was experienced in maintaining the catalyst at the high temperature required when pure steam was used. In the large-scale experiments, a study was made of the best method of combining reactions (1) and (2) to prepare a H-N-CO mixture in proportion suitable for the subsequent production of a H.-N. mixture in the proportions of 3:1. A vertical furnace of alloy steel packed with catalyst was heated externally by gas, and the gas mixture with regulated volumes of steam and air was passed in at the base of the catalyst. With this furnace, which had a layer of catalyst 94 cm. long by 12 cm. in diameter, 6 m. of gas, 3 kg. of steam, and 3 m. of air per hr. produced a gas containing (%) CO2, 2; CO. 17; H2, 56.5; N2, 24.5; CH4, traces. The highest temperature in the tube was 1,050°. In the absence of air it was only possible to convert 3.5 m.3 of gas per hr. into a CH-free mixture. Increase in the amount of steam does not in all cases increase the CH, conversion. In experiments on the carrying out of the reaction in two stages, the catalyst was divided into 2 separate portions. Gas and steam were passed through the first lower-temperature portion and air was added at suitable intervals along the second length of the catalyst. In this way the CH, content could be reduced to 0.03-0.09% when a 3:1 H-N2 mixture was required.

1725. Kelley, K. K. Thermodynamic Consideration of the Synthetic Methanol Process. Ind. Eng. Chem., vol. 18, 1926, p. 78; Chem. Abs., vol. 20, 1926, p. 538.

Free energy and equilibrium constant of the reaction CO+2H2=CH4OH(g) are calculated at various temperatures.  $\Delta F^{\circ}_{288} = -10.950$ ,  $\Delta F^{\circ}_{522} = 0$ , the working limit of the process at 100 atm. is 700° abs. The method of calculation is that of Lewis and Randall. Park's value for the entropy of liquid CH,OH is as-

1726. Heat Capacity of Methanol From 16° K. to 298° K. and the Corresponding Entropy and Free Energy. Jour. Am. Chem. Soc., vol. 51, 1928, pp. 180-187; Chem. Abs., vol. 23, 1929, p. 1344.

Heat of transition was found to be about 154 cal. per mol. and the entropy of liquid MeOH, based on specific heat measurements to 16° K, is 30.3±0.2 E. U. per mol. at 157.4° K.

Thermodynamic Consideration of the Snythetic Methanol Process. Ind. Eng. Chem., vol. 21, 1929, pp. 353-354; Chem. Abs., vol. 23, 1929, p.

From new data the following free-energy values for the reaction:  $CO(y) + 2H_2(y) = CH_2OH(y)$  are obtained:  $\Delta F^{\circ}_{==}=-9.640$  cal., and  $\Delta H_{==}=-25.150$  cal.  $\Delta F^{\circ}=-20.740+4500T\log 10T-0.01586T^2+IT$  where I=

-.. Data on Theoretical Metallurgy. VIII. 1728. -Thermodynamic Properties of Metal Carbides and Nitrides. Bureau of Mines Bull. 407, 1937, 66 pp.; Chem. Abs., vol. 32, 1938, p. 2821.

Thermodynamic data relating to metal carbides and nitrides are collected and discussed with the view of obtaining usable heat and free energy of formation relations. Pertinent data are difficult to obtain experimentally and are rare; this fact necessitates frequent use of approximations and assumptions. CH. and NH, also are included because some of the reactions considered involve these substances. The carbides considered are those of Al, Ca, Cr, Co, Fe, Mn, Mo, Ni, Si, Na. Th, Ti, W, U. V and Zr. The nitrides include those of Al, Ba, Be, B, Ca, Ce, Cr. Fe, La, Li, Mg, Mn. Mo, Si, Sr, Ta, Th, Ti, U, V and Zr. The data are applied in a discussion of the following: (1) Carburization of Fe by CH., (2) debismuthizing of Pb by Ca through the medium of CaC<sub>2</sub>. (3) partition of C between Mn and Fe in the  $\gamma$  range. (4) possibility of producing NH, direct from natural gas, (5) decarburization of Cr and (6) possibility of producing cyanides from CO and NH<sub>2</sub>. Bibliography of 108 refs.

1729. KELLEY, K. K., BOERICKE, F. S., MOORE, G. E., HUFFMAN, E. H., AND BANGERT, W. M. Thermodynamic Properties of Carbides of Chromium. Bureau of Mines Tech. Paper. vol. 662, 1944, 43 pp.; Chem.

Abs., vol. 38, 1944, p. 6183.

Describes preparation of carbides of Cr, and records some observations of the general properties of the carbides. Reports low-temperature specific-heat measurements in the temperature range 51°-298° K. for the carbides that are true compounds (Cr2C2, Cr.C3, and Cr.C) and for the mixed carbide Cr.C. The corresponding entropies are computed. High-temperature heat-content measurements from room temperature up to the limiting temperatures of available containers are reported for Cr.C., Cr.C., Cr.C, and Cr.O.. Analytical representations of the results are given. C reduction of solid Cr.O. takes place in four distinct, reversible reaction steps in which Cr.C., Cr.C., and Cr.C are the intermediate compounds. Results of the equilibrium measurements obtained with described apparatus and methods are reported for each reaction step. The various data are correlated satisfactorily and thermodynamic values and functions are derived for the Cr carbides. Each carbide of Cr at temperatures below its melting point is stable with respect to decomposition into (1) the elements, (2) any lower carbide and C, and (3) any higher carbide and Cr. The intermediate carbide, Cr.C., is stable with respect to decomposition into Cr.C. and Cr.C.

1730. Kelling, -. [Production of Branched-Chain Gas Oils and Aviation Gasoline From Fischer-Tropsch Synthesis Products.] TOM Reel 138, Doc. 22 (no date), 28 pp.

Comparison of the products obtained by subjecting Ruhrchemie Diesel oil to thermal cracking, Dubbs process, and to catalytic cracking, and an East Texas gas oil, 220°-350°, to catalytic cracking by the Houdry process. A flow sheet is given of the Ruhrchemie catalytic cracking process based upon the recovery of the exothermic heat developed during the catalystregeneration period for supplying heat to the catalytic cracking converters during the endothermic cracking period. The chief difficulty lies in regulating the amount of C deposited upon the fixed-bed catalyst during the endothermic cracking period.

KELLY, R. Sec abs. 53.

1731. KEMMER, H. [Removal of CO From Illuminating Gas.] Gas- u. Wasserfach, vol. 72, 1929, pp. 744-751; Chem. Abs., vol. 23, 1929, p. 4799.

Catalytic processes may be used, such as the hydrogenation of the CO by passing the gas over a catalyst composed of active C impregnated with Ni containing about 18% ThO2. A CO: He ratio of 1:5 is required for quantitative conversion to CH. The Ni catalyst is strongly activated by the ThO: so that the reaction temperature can be kept low. The optimum temperature for CH, formation lies between 180°-190°. It is mentioned that with these catalysts in addition to CH. quite small amounts of heavy hydrocarbons would be

[Gas Improvement by Refrigeration and Catalysis.] Gas u. Wasserfach, vol. 75, 1932, pp. 269-273; Chem. Abs., vol. 26, 1932, p. 3649.

Gas is cooled by the usual water cooler, and then passed through an electric tar precipitator, after which it is cooled to 0° by NH2 liquor to remove NH2 and part of the naphthalene, light oil, etc., while the remainder of the naphthalene and light oil is removed by oil scrubbing at -10°-15°. The gas is then further purified in the usual wet or dry S purifier. A 2-stage Altenkirch-Borsig absorption refrigeration system is used to cool the NH<sub>2</sub> liquor and oil; the operation of this apparatus is described. Flue gases supply the necessary heat for this refrigeration system. The gases may then be purified from remaining S by Lauta mass at 250°-300°, which removes the S to about 1-2 gm. per 100 m. After saturation the Lauta mass may be regenerated. The best catalyst for removing CO was found to be one consisting of Fe 75, Ni 23 and Cr 2 parts, on active charcoal, or one of Ni and Al-O, on pumice, said to be very insensitive to catalyst poisons. These catalysts permitted a 1-stage conversion of the CO to CH, and CO2 at about 360° and with the gas saturated with moisture at 60°-70°. Energy losses on catalysts are said to be 0-2%. Costs of operation are given for German conditions.

[Gas Industry and German Motor-Fuel Economics.] Gas- u. Wasserfach, vol. 77, 1934, pp. 877-883; Chem. Abs., vol. 29, 1935, p. 1609.

German requirements for motor fuel are discussed, together with the need of greater and more efficient benzene recovery, and means of increasing benzene yield, as by suction of distillation products from the interior of the coal charge. The relative advantages of the active C and wash-oil recovery processes for light oil are compared. Other sources of motor fuel are low-temperature carbonization of brown and bituminous coal and motor-fuel synthesis by the Fischer process; the suitability of the process for gasworks use is discussed. The use of compressed gas for motor fuel also is reviewed and costs are considered, as well as special equipment required for using gas with automotive equipment.

[Removal of Carbon Monoxide From City Gas.] Angew. Chem., vol. 49, 1936, pp. 133-137; Chem. Abs., vol. 30, 1936, p. 3204.

This is a description of a 2-stage process whereby a partial oxidation of the CO with steam over a Cr catalyst takes place, followed by a hydrogenation of the remaining 4-5% of CO to CH. This last reduction proceeds virtually quantitatively at 200°-250° over a Ni-Th catalyst by utilizing the H. formed in the first step. The 2-stage process should not cost more than 0.5 pf. per m. To eliminate the existing difficulties of gas purification and to lower the working costs, it is proposed to combine the process with the synthetic production of fuel by the Fischer-Tropsch process

KEMPKENS, J. See abs. 1988, 1989.

1735. Kenyon, R. L. Alcoholic Cousin—the Oxyl Process. Ind. Eng. Chem., vol. 42, No. 6, 1950, pp. 10-A, 12-A.

German associates of the Blaw-Knox Co. have developed a process for the production of alcohols from synthesis gas, and the Blaw-Knox Co. is prepared to build plants to produce them. Assurance is given that all but the lowest of these alcohols can be made and marketed in this country on a sound economic basis from natural or other synthesis gases. The Oxyl process, by means of a catalytic reaction within pressure and temperature ranges comparable to those of the Fischer-Tropsch, converts synthesis gas into a mixture of alcohols, C1-C26, saturated and unsaturated hydrocarbons. Conversion of the raw materials to alcohols is 80% or better, with the remainder of the product in hydrocarbons. One of the most important advances in the development of this process is an effective method of separation of the components of the reaction mixture. The individual alcohols can be isolated in a purity of 95% or better. The catalyst for the process is now available from Germany, but it will be prepared here when a plant using the Oxyl process is built and operated in the United States. For a small plant the cost of the catalyst will be high, but preparation in large quantities will bring the unit cost down considerably. It is estimated that plants for the Oxyl process can be built and operated economically in the United States under present conditions and prices at production capacities of 5-8 million lb. per yr. It is assumed that the plant will amortize itself in 3-5 yr.

1736. KEPPELER, G. [Gas for Syntheses From Peat. A Plant Trial in the Tiefstack Plant of the Hamburg Gas Works.] Chem. Fabrik, vol. 12, 1939, pp. 457-462; Chem. Abs., vol. 34, 1940, p. 609.

Pintsch-Hillebrand process for producing water gas is discussed, and a vertical section through the producer, a flow-sheet, and an elevation of the plant are shown. The apparatus was used on ordinary raw peat containing 28-30% H<sub>2</sub>O, which was charged just after using lignite briquets, the experiments beginning about 70 hr. after starting to charge the peat, with temperatures of 1,200° and 1,300°. Data are given on heat balance, peat consumption, gas yields, and analyses, the latter averaging about 15, 27, 54, 2.5 and 1.8% CO<sub>3</sub>, CO, H<sub>3</sub>, CH, and N<sub>3</sub>, respectively. States estimated plant and production costs based on Pintsch data, and it is concluded that a synthetic-gas plant is feasible in peat regions. Gives 5 refs.'

1737. KEPPLER, W. [Fatty Acids.] Vierjahresplan, vol. 1, 1937, pp. 269-271; Chem. Zentralb., 1937, II, p. 1913.

Production of fatty acids from Fischer-Tropsch paraffin waxes and their application in the soap industry.

Kerlogue, R. H. See abs. 404.

1738. Kershaw, J. B. C. World's Future Supply of Liquid Fuels. Engineer, vol. 143, 1927, pp. 244-245, 261-263; Chem. Abs., vol. 21, 1927, p. 1532.

Kesting, W. See abs. 3052, 3053.

1739. KEULEMANS, A. I. M., KWANTES, A., AND VAN BAYEL, T. [Structure of Formylation (Oxo) Products Obtained From Olefins and Water Gas.] Rec. trav.chim., vol. 67, 1948, pp. 298-308; British Abs., 1949, A. II, p. 2; Chem. Abs., vol. 42, 1948, p. 8152.

Formylation of olefins by means of CO and H<sub>2</sub> at 120°-160° and 100-200 atm. in presence of the Fischer-Tropsch Co catalyst is studied with 16 alkenes containing 3-8 C, cyclopentene, and cyclohexene. The aldehydes formed are immediately hydrogenated in the same autoclave with pure H<sub>2</sub> to alcohols. Analysis of

the products of reaction is simplified if the alcohols are dehydrated by pyrolysis of their stearates, and the olefins obtained are hydrogenated to alkanes.

Keunecke, E. See abs. 2295.

1740. KEUNTZEL, W. E. Preferential Catalytic Oxidation of Carbon Monoxide in the Presence of Hydrogen. I. Activity of Two Water-Gas Conversion Catalysts. of Copper Oxide, of Manganese Dioxide, and of a Mixture of These Oxides. Jour. Am. Chem. Soc., vol. 52, 1930, pp. 437-441; Chem. Abs., vol. 24, 1930, pp. 2367.

Preferential oxidation of CO by  $O_2$  in the presence of  $H_3$ ,  $CO_2$ , a large excess of steam and various catalysts has been studied. An efficiency of 96% for 37 hr. was obtained with a 2-component hopcalite. Promoted Fe oxide and Co oxide governed only the water-gas reaction  $CO+H_2O\rightleftharpoons CO_2+H_2$ . CuO,  $MnO_2$ , and a 5-component hopcalite were catalytically active but suffered reduction and loss of activity.

741. Preferential Catalytic Oxidation of Carbon Monoxide in the Presence of Hydrogen. II. Activity of 2-Component Hopcalites. Jour. Am. Chem. Soc., vol. 52, 1930, pp. 445–455; Chem. Abs., vol. 24, 1930, p. 2367.

Of the influent CO 97-99% was oxidized by free Oxwith a commercial hopcalite as catalyst in a temperature range of 160°-196°. The composition of the converted water gas used was: CO, 1.3; Ox. 1.5; COz. 28.0; Hz, 49.0; and Nz, 20.2% in the presence of 3 vol. of steam. The catalyst suffered a loss of O and of activity. The rapid dissipation of the heat of reaction was of importance. The steam acts to dissipate this heat and to inhibit the reduction of the catalyst.

1742: KEY. A., AND EASTWOOD, A. H. Removal of Sulfur Compounds From Coal Gas and Synthesis Gas at Atmospheric Pressure. 45th Rept. Joint Research Com., Gas Research Board, and University of Leeds. Gas Research Board Com. 14, 1945, 36 pp.; Fuel Abs., vol. 3, No. 2, abs. 442.

Most active catalysts for the synthesis of CH, and other hydrocarbons from CO and Ha are poisoned by traces of S compounds, such as are present in gases resulting from the carbonization and gasification of carbonaceous fuels. Most attention has been given to processes involving the catalytic reduction of organic S. It was found that certain metallic sulfides have great activity in this direction at temperatures as low as 250° when supported on carriers, such as active C and activated Al.O., which have high specific surface area and absorptive capacity. The catalyst that would give the most efficient organic S conversion in a normal coal gas is the Cu2S-Cr2O2 preparation, but it is poisoned unless the acetylenic bodies in the coal gas are first removed by a pretreatment. On the other hand, Mo sulfide, which is not normally poisoned by coal gas, effects a rather smaller degree of conversion. A combination of the 2, however, the Mo preceding the Cu-Cr, overcame both these difficulties, and is the system that should be adopted to secure maximum conversion. It is problematical whether the employment of this combined system can be justified if the aim is merely to reduce the S content of a gas to 2-3 grains/100 cu. ft. 1743. KEYES, F. G., SMITH, L. B., AND JOUBERT, D. B.

1743. KEYES, F. G., SMITH, L. B., AND JOUBERT, D. B. Equation of State for Methane-Gas Phase. Jour. Math. Phys., Massachusetts Inst. Tech., vol. 1, 1922, pp. 191–210; Chem. Abs., vol. 17, 1923, p. 668.

1744. KEYES, F. G., TAYLOR, R. S., AND SMITH, L. B. Thermodynamic Properties of Methane. Jour. Math. Phys., Massachusetts Inst. Technol., vol. 1, 1922, pp. 211–242; Chem. Abs., vol. 17, 1923, p. 668.

From the experimental values of the vapor points and densities of liquid CH4, determined over the entire liq-

nid phase region by precision methods described in detail, a number of equations and thermodynamic constants are derived.

KHAIKOVA, N. A. See abs. 891.

1745. KHARKHOV, N. V. [Gasification of Finely Ground Coal in a Boiling Layer Using Steam-Oxygen Blast.] Kislorod (Oxygen), 1944, No. 2, pp. 12-21; U. O. P. Co. Survey Foreign Petroleum Literature Index, Aug. 2-9, 1946, pp. 22-23.

Pilot-plant work was begun in 1935 with a unit of capacity of 2,000-3,000 m. per hr. on the preparation of an NH, synthesis-gas mixture. Fuel of grain size, 10 mm. and less, was used. The blast passing through the 0.3-1.5-m. bed at a velocity of 2-3 m. per sec. brings the bed into a condition resembling boiling. The Ozenriched air and steam are continuously charged both below and above the fuel bed. The O2 content of the blast was 53-55%: in mixture with steam 23-24% when the steam amounted to 56-58%. The temperature of 850°-900° in the generator is enough to crack all volatile matter, and the resulting gas contains no tar or heavy hydrocarbons and but little CH. The lowest calorific value of the gas was 1,800 kcal. per cu. m.; this is raised to 2,200-2,300 kcal. per m. when pure steam-O<sub>2</sub> is charged. The gas has the composition, in vol. %: CO<sub>2</sub>, 17.6; CO, 34.0; H<sub>2</sub>, 29.2; N<sub>2</sub>, 19.1: H2S, 0.1; no CH4, O2, or olefins. Production of 1,000 cu. m. gas requires about 0.5 ton coal of 10% moisture, 180-190 cu. m. O2 of 98% purity, 230 m. air, 280-300 kg. steam, but 500-550 kg. steam also is generated. Young fuels such as lignites are most suitable for the process. The size of the unit is virtually unlimited. In the N: industry, gas generators are being built of 15,000-20,000 m. per hr. capacity using waste O<sub>2</sub>. The extent to which the method will find practical application will depend chiefly upon the supply of cheap O2.

KHAZANOVA, N. E. Sce abs. 1985, 1986.

1746. KHITAROV, P. I. [Study of Double Carbides of Manganese and Iron.] Vsesoyuz. Nauch.-Issledovatel. Inst. Metrol., Kratkii Obzor Vazhneishikh Nauch.-Issledovatel. Rabot Lab., VNIIM, 1940, pp. 54-55; Chem. Abs., vol. 35, 1941, p. 5075.

By dissolving Fe-Mn of different compositions in dlute acids and salt solutions in the absence of air, it was possible to separate the double carbides corresponding by composition to xMn<sub>2</sub>C<sub>1</sub>Fe<sub>2</sub>C. Data on chemical and X-ray analysis and phase diagram of Fe-Mn-C show that these carbides are solid solutions and not double carbides. The carbides of Fe and Mn also form solid solutions in Fe-Mn.

1747. [Double Carbides of Iron and Manganese.] Vsesoyuz, Nauch. Issledovatel. Inst. Metrol., Sbornik Trudov, 1941, No. 3 (No. 48), pp. 35-64; Chem. Abs., vol. 39, 1945, p. 5232.

Double carbides of Fe and Mn having the typical formula of aFe<sub>2</sub>C<sub>2</sub>Mm<sub>10</sub>C were obtained as residues after acid (or other) attack on ferromanganese (20–80% Mn, 5-8% C) in an atmosphere of N<sub>2</sub> or CO<sub>2</sub>. By X-ray and phase studies these materials were shown to be solid solutions. Mn<sub>2</sub>C (used for reference in the X-ray work) was made by heating a 4:1 mixture of Mn<sub>2</sub>O<sub>4</sub> and lampblack for 10–15 min. at 1,300°–1,400°. By longer heating, homogeneous products were obtained with 7.3–7.6% C to which the empirical formulas Mn<sub>2</sub>C<sub>4</sub> and Mn<sub>2</sub>C<sub>5</sub> were assigned. 49 refs.

1748. Khodschaian, S. [Technically Important Gas Equilibria at Low Pressures.] Feuerungstech., vol. 26, 1938, pp. 109-112; British Chem. Abs., 1938, B, p. 1005; Chem. Abs., vol. 33, 1939, p. 4496.

Calculations show the position of equilibrium in various gas reactions, for example, dissociation of  $\mathbf{H}_2$ , and

in the water-gas reaction at elevated temperature and pressure up to 1 atm.

Кномулкоу, К. G. Sec abs. 3758a.

1749. KHRIZMAN, I. A. [Catalytic Decomposition of Ammonia.] Acta Physicochim. U. R. S. S., vol. 4, 1936, pp. 899-910; Chem. Abs., vol. 30, 1936, p. 7987.

Kinetics of the decomposition of NH, on promoted Fe catalysts of the Fe-AlO-K,O type were investigated over the temperature range 300°-450°. Two values for the energy of activaton were found, 12.4 kcal. per mol. for temperature 300°-350°, and 39.7 kcal. per mol. above 350°. The 2 values were explained on theoretical grounds by assuming several surface reactions with different reaction rates. 13 refs.

1750. — . [Stablization of Reduced Catalyst for Ammonia Synthesis.] Ber. Pissarjewsky Inst. physik. Chem., Akad. Wiss. Ukr. S. S. R., vol. 12, 1940, pp. 15-20; Chem. Abs., vol. 35, 1941, p. 2685.

NH, catalyst of the type Fe-Al<sub>2</sub>-K<sub>2</sub>O was 1st reduced with a dry mixture of H<sub>2</sub> and N<sub>2</sub> and then nirtided with dry NH. The temperature interval for reduction and nitriding was 350°-475°. The nitrided catalyst was cooled in a stream of NH, and tested for stability (reaction with moisture, CO<sub>2</sub> and O<sub>2</sub>). The tests indicate that the stabilized catalyst may be transported from the place of manufacture to the NH, synthesis plant without loss of activity.

1751. Khrizman, I. A., and Korniichuk, G. P. [Role of Iron Nitride in the Catalysis of Ammonia.] Ber. Inst. physik. Chem., Akad. Wiss. Ukr. S. S. R., vol. 6, 1936, pp. 95-101; Chem. Abs., vol. 31, 1937, p. 0831.

NH, was decomposed catalytically in the interval 250°-470°, the catalyst being the nitride of activated Fe of the type Fe-Al<sub>2</sub>O<sub>-</sub>K<sub>2</sub>O<sub>-</sub> At 410° and higher, a stoichiometric mixture of N<sub>2</sub> and H<sub>2</sub> was obtained, at 410°-350° the products abounded in N<sub>3</sub>, and at 350° and lower, the chief product was N<sub>2</sub> with traces of H<sub>3</sub>. By comparing these results with those obtained when ordinary Fe was used, it becomes evident that the nitride hinders the decomposition of NH<sub>3</sub> and that Fe, and not the nitride, is the catalyst in the production of NH<sub>3</sub>.

KHULLAR, M. L. See abs. 810a.

1752. Khvatov, A. D. [Dependence of the Energy of Activation on the Activity of the Gatalyst.] Jour. Gen. Chem. (U. S. S. R.), vol. 9, 1939, pp. 819-824; Chem. Abs., vol. 33, 1939, p. 7653.

Surface of catalysts is not homogeneous. The mostactive regions of the surface are first acted upon by chemical reagents, which decrease the activity of the catalyst almost 50%. In the experiments, the surface structure of Ni was changed by the reaction of Ni(CO), formation, formed when a stream of CO is passed at 100°-150° over Ni, and again decomposed into Ni and CO at 300°-400° by passing definite amounts of CO and by determining the activation energy of CH3CHO decomposition from the reaction CH.CHO→CH.+CO. The reaction velocity was determined by passing 11. of CO in 1 hr. over the catalyst at 100°. The Ni(CO), formed was passed into a U tube heated to 350° where it was decomposed into metallic Ni and CO. The deposited Ni was dissolved in HNO: and its amount determined by the method of Chugaev as Ni dimethylglyoxime. This experiment was repeated until the activity of the catalyst (measured by the reaction velocity) remained constant or changed only slightly. The reactions were performed in a quartz tube, 500 mm. long, 18 mm. diam., with 2 gm. of the catalyst, 2 cm. long. After the 1st action of CO a very sharp drop of the decomposition velocity was observed (26.6-47%). After the 2d CO action a smaller drop occurred at 250°-260°, and only a very small drop after the 3d CO action at 260°. It was found that a minimum of Ni formation corresponded to the maximum activity drop of the catalyst. This verifies the hypothesis that the number of active regions on the surface of the catalyst can be very small. From the experimental data, the energies of activation for the different steps of the chemical action of CO on Ni were calculated from the equation of Arrhenius, and they were found to be the same in all cases (9,000±300 cal.). This shows that the energy of activation does not depend on the activity of the catalyst. Gives 6 diagrams. 7 tables, and 17 refs.

1752a. Kippoo, G. Petrochemical Processes. Chem. Eng., vol. 59, No. 9, 1952, pp. 149-168; Chem. Abs., vol. 47, 1953, p. 298.

This report is a comprehensive review of the technology of the major processes used to make industrial chemicals from petroleum and natural gas hydrocarbons. It includes: Synthesis gas and H2 from natural gas, aldehydes and alcohols by the Oxo process. HCN from natural gas and NH3. chlorination of CH4 and C2H4, C2H2 by cracking of hydrocarbons, C2H4 and C3H6 by thermal cracking, polymerization and alkylation processes, alcohols from olefins, ethylene and propylene oxides and glycols, ketones by dehydrogenation of alcohols, synthetic glycerol from CaHe. aldehydes and alcohols by hydrocarbon oxidation, butylenes and butadiene, aromatic hydrocarbons by catalytic reforming and oxidation of xylenes.

KIEHL, J. P. Scc abs. 1056, 1057.

KIENITZ, H. Sec abs. 3011.

1753, KILLIFFER, D. H. A Year's Progress in Chemistry. Ind. Eng. Chem., vol. 19, 1927, pp. 1077-1082; Chem. Abs., vol. 21, 1927. p. 3289.

Review. Among the subjects treated are liquid fuels from coal and synthesis of hydrocarbons.

KILPATRICK, J. E. Sec abs. 3589.

1754. KIMPFLIN, G. [Work of the School of Louvain on Synthetic Motor Fuels.] Génie civil, vol. 119, 1942, pp. 279-281; Chem. Zentralb., 1943, I, p. 1237; Chem. Abs., vol. 38, 1944, p. 3443.

In the investigation of catalysts for the production of benzine from CO and H2, Co from Katanga (98.57% Co; 0.24 Ni; 0.13 Fe; 0.32 CaO; 0.03 S; and 0.07 Mn activated with 18% ThO:) yields 123.8 cc. benzine per m. of gas and under the same conditions a Co-Ni catalyst precipitated on kieselguhr with K<sub>2</sub>CO<sub>2</sub> (Co. 3.6; Ni. 3.6; Mn. 1.4; M<sub>2</sub>O<sub>4</sub>, 1.4) yields 166 cc. benzine. The benzines contain, respectively, 12.6 and 9% olefins, 0.84 and 1.0% aromatic compounds, 18.8 and 24.6% naphthenes, and the remainder paraffinic hydrocarbons. Best results are obtained by maintaining the temperature constant by surrounding the contact oven with boiling aniline. A short description of the production of alcohols from CO and Ha is given as well as the equilibrium value of CH3OH and propanol at 25°, 300°, and 400°.

KIMUMAKI, J. See abs. 3176, 3177.

KIMUMAKI, J., SHIRAI, S., AND FUJISARI, T. Iron Catalyst for Synthetic Petroleum, III. Influence of Barium Nitrate on Iron Catalyst. See abs.

1754a. Kimumaki, J., Shirai, S., and Ogawa, T. Iron Catalyst for the Benzene Synthesis. Jour. Soc. Chem. Ind. (Japan), vol. 46, 1943, suppl. bind. pp. 80-83; Chem. Abs., vol. 46, 1952, p. 1,186.

For the preparation of better Fe catalysts for the synthesis of benzene from gas mixtures of CO and H2, it is important to consider the state of division of the alkali to be added, the effect of the duration, and of the degree of heating. In order to improve the state of division of the alkali, it is recommended to replace the alkali carbonates, which were used in most cases with alkali nitrate which is easily formed at

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the precipitation of the metal hydroxides by K-CO. The alkali nitrate was left in suitable quantity in the precipitate by properly regulating its washing. This alkali nitrate is always converted at the reduction process into alkali carbonate, which causes a homogeneous distribution of the alkali on the surface of the diatomaceous earth. Superheating the catalyst often impairs the synthesis of benzene. The reduction with H. will, therefore, be avoided as much as possible, because higher temperatures are always needed for this purpose. It is concluded, that for the synthesis of benzene from natural gases, the selective adsorption of the alkali among the catalyst metals and the diatomaceous earth is of great importance.

KIMURA, K. See abs. 1927, 1928, 1929.

1755. KIMURA, O. Hydrogenation and Polymerization Reaction of Acetylene. I. Reaction in Liquid Phase and the Effect of High-Tension Discharge. Bull. Chem. Soc. Japan, vol. 18, 1943, pp. 1-12. Chem. Abs., vol. 41, 1947, p. 4436.

Polymerization and hydrogenation reactions of C2H2 were studied in liquid paraffin in the presence of such catalysts as Ni. Co. Pd, and Ca. The polymerization reaction occurs more easily than hydrogenation. To avoid this defect in the process of obtaining liquid fuel from C.H., high-tension discharge was applied to activate the H2; the products were mainly liquid hydrocarbons.

See abs. 2414.

BIBLIOGRAPHY OF FISCHER-TROPSCH SYNTHESIS AND RELATED PROCESSES

1756. KIMURA, O., AND HIROTA, K. Hydrogenation and Polymerization Reaction of Acetylene. II. Polymerization Reaction by Use of the Thermal Diffusion Column. Bull. Chem. Soc. Japan, vol. 18, 1943, pp. 13-21; Chem. Abs., vol. 41, 1947, p. 4436.

Applying the thermal separation column of heated W wire at 700°-1,000°, C.H. was converted into liquid hydrocarbons almost perfectly.

-. Hydrogenation and Polymerization Reaction of Acetylene. III. Kinetics of Polymerization by Use of Thermal Separation. Bull. Chem. Soc. Japan, vol. 18, 1943, pp. 45-53; Chem. Abs., vol. 41, 1947, p. 4436.

By using the thermal separation column with W wire as a reaction vessel, the reaction was found to be of the 2d order and the activation energy 44.8 kg.-

-. Hydrogenation and Polymerization Reaction of Acetylene. IV. Kinetics of Polymerization by Use of Thermal Separation Column. Bull. Chem. Soc. Japan, vol. 18, 1943, pp. 273-277; Chem. Abs., vol. 41, 1947, p. 4436.

From the equation derived by the authors, the velocity constant K and the activation energy Q of C2H2 in the thermal separation column of Clusius and Dickel were computed: K=8.7 atm. sec. at 720° and

KING, G. W. See abs. 2174.

1759. King, J. G. Production of Liquid Fuels From Coal. Jour. Soc. Chem. Ind., vol. 46, 1927, pp. 181-186T; Gas Jour., vol. 177, 1927, pp. 391-392; Age, vol. 16, 1927, p. 86; British Chem. Abs., 1927, B, p. 641; Chem. Abs., vol. 21, 1927, p. 2546.

Three main lines along which the problem of oil production from coal is being attacked are described and the latest results reviewed. The effect of temperature of carbonization on the constitution of lowtemperature tar is illustrated by experiments carried out at the Fuel Research Station. There are indications that 550°-600° is a critical temperature so far as the tar is concerned when external heating is used. At 600° only 8.8% of the tar is saturated. On a large scale the yields of tar are not much greater, than 16.5 gal. per ton of coal, and if 50,000,000 tons

of coal was carbonized only 150,000,000 gal. of motor spirit and 550,000,000 gal. of tar oils would be available—much less than the country's requirements. The Bergius process offers technically 100-130 gal. of oil per ton of coal or up to 60% by weight of suitable coals. The plant is described and yields are quoted. The catalytic production of alcohols and hydrocarbons from CO is showing considerable promise for the future, but so far results are only experimental. The recent work of Fischer and Tropsch in producing petroleumlike hydrocarbons shows particular promise. The catalysts used and the nature of the end products are described.

 Complete Gasification of Coal and Meth-1760. ane Synthesis. Inst. Gas Eng., Pub., 197/80, 29 pp.; Gas Jour., vol. 224, 1938, pp. 457-460, 637: Gas World, vol. 109, 1938, pp. 372, 410-411; Chem. Abs., vol. 33, 1939, p. 6562.

Sized semianthracite coals of low caking power can be gasified successfully in a water-gas plant to yield 67,000 cu. ft. or 205 therms of gas per ton of coal. Rate of output of gas is similar to that obtained from sized coke. High-volatile coals of low or medium caking power can be gasified by using a recuperator and introducing a backrun into a cycle. The yield of gas is about 45,000 cu. ft. or 141 therms per ton of coal. Rate of output of the generator is 15-25% less than when sized coke is used in the same plant. A small proportion of the tar (about 2.5 gal. per ton of coal) escapes cracking and means must be provided for its recovery. By modifying cycles of operation, coal can be gasified to give a gas having a high ratio of H.: C. Such a gas would be of value in connection with processes for catalytic synthesis of hydrocarbons. Mo catalysts were not entirely satisfactory for synthesis of CH, from coal gas. Activity of a ThO-promoted Co catalyst was unaffected by S, but decreased with time. The Fuel Research Station vortex burner was modified to gasify pulverized coal with steam and O: at atmospheric pressure.

Oil and Coal After the War. Petroleum (London), vol. 6, No. 12, 1948, pp. 180-181, 188.

Since the oils produced in the Fischer-Tropsch synthesis are mainly straight chain in character, the process has special significance in that the diesel-oil fraction has a high cetane value (120) and the oils are most amenable to cracking and chemical reconstruction. The significance of this process in postwar planning is, however, only partly in the field of fuel and is perhaps mainly centered in its value as a means of producing those olefins that are the starting point in the manufacture of so many of the new raw materials wanted in the chemical industry. It is, moreover, the only process from which satisfactory lubricating oil can be synthesized.

-. Research and the Gas Industry. Gas Jour., vol. 241, 1943, pp. 796, 799, 800, 805.

Lines of research commented on are: The utilization of 2d and 3d quality gas coals, complete gasification both by the Lurgi and the Leeds processes, CH, synthesis and liquid CH, the Fischer-Tropsch process, complete removal of S from town gas and high-pressure gas-distribution systems.

. Better Utilization of Coal for the Production of Oil and Petrol. I. A Survey of the Proa duction of Tars and Oils From Coal. Jour. Junior 1. Inst. Eng. (London), vol. 54, 1944, pp. 225-244; Jour. Inst. Fuel, vol. 17, 1944, pp. 192-196; Engineering, vol. 158, 1944, pp. 236, 318-320, 337-338; Chem. Abs., vol. 38, 1944, p. 5381.

This is a discussion of carbonization industries (creosote-pitch fuel, pulverized pitch, tar diesel oil, motor benzene); coal-oil suspensions (colloidal fuel), the hydrogenation of coal (catalysts, products, devel-

opment, hydrogenation of tars and tar oils), indirect production of oil from coal (processes, efficiency and yields, lubricating oils), new processes (C.H. and C2H4, CH, from coal measures and sewage, CaC2, cannel tar), and direct replacement of oils in motor fuels.

. Work of the Gas Research Board. Re-1764. port of the Director. Synthesis of Methane. Gas Research Board Pub. S: Gas Jour., 1944, pp. 623-624, 660-661, 689, 691; Gas World, vol. 120, 1944, p. 6245; vol. 121, 1944, p. 18; Chem. Abs., vol. 38, 1944, p. 4775.

In experiments on the synthesis of CH4, with a granular Ni catalyst and with passage of the gas at atmospheric pressure, a low reaction temperature (350°-500°) led to loss of catalyst activity and deposition of C, as the result of the development of a high surface temperature where the reaction gases first come into contact with the catalyst. The rate of loss of activity is increased by a decrease in the ratio H2: CO; in practice, it may be necessary to employ a ratio above 1.2. The addition of steam counteracts the tendency to form C from the CO and also under certain circumstances prevents the loss of catalyst activity caused by sintering. The surface temperature also can be controlled by recirculation and by use of a shaped or rod catalyst arranged to lose heat rapidly by radiation. By use of these expedients it is possible to operate the simple Ni catalyst at any temperature within the range 350°-800° and at any pressure within the range 1-50 atm. In the synthesis from water gas with high Hz: CO ratios the most suitable catalyst for work at a relatively low temperature is Ni promoted by ThO2 and supported on kieselguhr. The S in the gas is kept helow 0.1 grain per 100 cu. ft. by using an Fe oxide-Na.CO, contact material at 180°-230°. With purified water gas, the catalyst life was 77 days, during which time the CH, content of the CO. free gas varied from 80 down to 30% with an average of 65%. In order to prevent undue deposition of C, the H2: CO ratio must be kept above 1.5. Other factors affecting the formation of C are the rise in temperature of the catalyst, its size, and a rise in pressure above atmospheric. The gas should be passed downward through the catalyst. Under these conditions and with an exit temperature of 350°, the process gas can be treated at the rate of 3,700 vol. per vol. of catalyst per hr. Difficulties were encountered in developing these results to a semiscale apparatus possessing 5,000 cu. ft. of gas per day. . Better Utilization of Coal for the Production of Oil and Petrol. Gas and Oil Power, vol. 40, March 1945, pp. 99-101; Gas Abs., Inst. Gas

Technol., vol. 1, No. 4, July 1945, pp. 6-7. Brief review of modern methods for converting coal both directly and indirectly, into motor fuels, oils, and other products is given. In the Fischer-Tropsch process the purified gases from the gasification of coal or coke are passed through Ni and Co oxide catalysts at atmospheric pressure and about 400° F. High-quality lubricating oils may be made from the primary product by the thermal cracking of the middle oil and polymerization of the olefinic products with AlCla catalyst. Yields of about 35%, by weight, have been claimed, although these may be considerably higher if Fischer's claims are justified for the direct production of unsaturated oils by the use of an Fe catalyst at 15-20 atm. pressure.

Considerations. Gas World, vol. 122, 1945, pp. 220-226; Gas Jour., vol. 245, 1945, pp. 342, 344; Am. Gas Jour., vol. 163, No. 3, 1945, pp. 16-20, 60; Chem. Abs., vol. 39, 1945, p. 2191.

Discusses outstanding processes, with special reference to those conditions that affect thermal efficiency. The over-all thermal efficiency of a process is defined as the % that the thermal value of the products bear

98 98 W