combustion method has been improved also. Typical comparative data for both old and new apparatus are given with demonstration of the decreasing organic S content of gases with storage. Completely purified gas also is shown to reacquire S from distribution systems. For comparative purposes, gas samples must be identical in time, place, and other sampling conditions. Extensive bibliography of S-determination methods, grouped according to absorption agents.

2875. Roelen, O., and Heckel, H. [Most Favorable Cobalt–Kieselguhr Ratio in Cobalt Catalysts.] FIAT Reel K–29, 1938, frames 7,139–7,163; PB 70,218; TOM Reel 296.

As a result of an extensive examination and discussion, the Co-kieselguhr proportion 1:2 is indicated as virtually the most favorable under actual conditions. 6 tables and 8 diagrams.

2876. ———. [Influence of the Condition of the Kieselguhr on the Stability of the Catalyst.] FIAT Reel K–20, Sept. 12, 1939, frames 337–339; PB 70,211; TOM Reel 287.

After a discussion of the possible dependence of the catalyst stability on the condition of the kieselguhr, a method is described whereby the proportion of dust can be decreased considerably by sintering the kieselguhr with an Mg salt at 1,000°.

2877. Roelen, O., and Hintermaier, A. [Disintegration of the Catalyst in the Synthesis of Benzine.] Ges. Abhandl. Kenntnis Kohle, vol. 9, 1930, pp. 517–518; Chem. Abs., vol. 25, 1931, p. 3807.

An alkaline Cu-Fe catalyst exposed to water gas at 250° showed disintegration with increase in bulk volume. After 500 hr. its bulk density had fallen to about ¼ the original value. Thereafter it remained constant.

2878. Roelen, O., and Pflegling, —. [Synthesis of Hydrocarbons with Iron Catalysts.] FIAT Reel K–29, 1940, frames 7,240–7,241, 7,250–7,276; PB 70,218; TOM Reel 296.

Review of the development and use of Fe catalysts since 1913. Recent tests are discussed on the basis of extensive data. The output of Fe catalyst surpasses the output of Co catalyst, but more work needs to be done on its development. 16 tables.

2879. Roelen, O., and Royen, P. [Mechanism of Carbon Dioxide Formation on Catalysts of the Fischer-Tropsch Synthesis.] Erdöl u. Kohle, vol. 3, No. 1, 1950, p. 10.

Paper presented at the 1949 meeting of the die deutsche Gesellschaft für Mineraloelwissenschaft und Kohlechemie. It was already regarded in 1923, by Fischer and coworkers that CO_2 formation occurs on Fe catalysts of the hydrocarbon synthesis as a secondary reaction, which is identical with the known conversion of a mixture of CO and steam into CO_2 and H_2. Finally in 1949, H. Kölbel on the strength of newer investigations has replaced this view. According to older conceptions of Wieland in 1912, Fischer and Schrader in 1921 assumed that, by this conversion, CO and H_2O are together changed to formic acid, which then is split catalytically into CO and H_2. It is known that addition of alkali compounds, especially in the form of hydroxides and carbonates, to the Fe and Co catalysts of the Fischer synthesis intensify the conversion. Roelen and later independently Royen supposed that, in this case, a 2d mechanism is introduced consisting in an intermediate formation of potassium formate from potassium hydroxide and carbon monoxide, a reaction that technically serves for the production of formic acid. The potassium formate 1st formed is split on the catalyst by means of adsorbed water vapor hydrolytically into potassium hydroxide and free formic acid. Roelen has shown that sodium formate at 200°–230° in presence of active Fe or Co is decomposed by water vapor into CO_2 and H_2. He found that formic acid is converted by Fe catalysts and very quickly into H_2 and CO_2. In mutual tests, it was shown that these reactions occur also on alkalized Cu catalysts at 120°. It is further shown that catalysts of active C with a few % of alkali hydroxide plainly perform the conversion at 140°. By the conversion, the potassium hydroxide present on the catalyst goes over in great part into potassium formate. Catalysts which were impregnated with potassium hydroxide-potassium formate mixtures in the proportion formed by the conversion, showed by the treatment with water vapor of the same partial pressure as by the conversion tests, CO_2 and H_2 concentrations in the residual gas of the same magnitudes as in the conversion. It was shown, thus, that the formate mechanism with alkalized catalysts of the Fischer-Tropsch synthesis can supply an essential contribution to the conversion reaction. This determination is supported also by several physical-chemical observations.

2880. Roelen, O., and Schenk, —. [Nickel-Containing Cobalt Catalysts.] FIAT Reel K–29, no date, frames 7,302–7,307; PB 70–218: TOM Reel 296.

Tests show that the partial replacement of Co by Ni in Co catalysts produces a deterioration of the grain solidity of the catalyst and that, in the synthesis, the gasification is higher, the boiling conditions easier, and the rate of saturation higher. Extending the Co stock by Ni is, therefore, of doubtful value for a large production.

2881. Rogers, B. A., Wentzel, K., and Riott, J. P. Magnetic Methods for Determining Carbon in Steel. Trans. Am. Soc. Metals, vol. 29, 1941, pp. 969–983; Chem. Abs., vol. 36, 1942, p. 720.

Magnetic saturation and C content can be correlated accurately at 0.50–1.10% C. Samples containing more than 0.40% C were quenched from above 700°; other C contents required slow cooling. When both types of heat treatment were used, samples containing 0.10–1.10% C could be tested. The apparatus is described.

2882. Rogers, L. J. Oil From Coal. Hydrogenation. Chem. Eng. and Min. Rev., vol. 23, 1931, pp. 373–380; Chem. Abs., vol. 25, 1931, p. 5272.

Brief description of the catalytic reduction of CO and the synthetic production of MeOH. The production of synthetic fuels is not recommended from an economic standpoint as an adjunct to a gas works.

2883. Rogers, W. Reduction of Mixed Oxides. Copper and Zinc Oxides. Jour. Am. Chem. Soc., vol. 49, 1927, pp. 1432–1435; Chem. Abs., vol. 21, 1927, p. 2855.

In a mixture with CuO, ZnO is completely reduced by H_2 at 300°, a temperature far below that necessary for ZnO alone. A tentative explanation is offered.

2884. Roginskiĭ, S. Z. [Theory of Preparation of Catalysts. The Role of the Free Energy of the Processes of Preparation.] Jour. Phys. Chem. (U. S. S. R.), vol. 15, 1941, pp. 708–730; Chem. Abs., vol. 37, 1943, p. 821.

Roginskiĭ continues his development of a theory of catalyst surfaces. The active points are considered as points of supersaturation with respect to free energy. 4 types of such points are considered: A definitely distinct phase, local or general structural variations of a given phase, anomalous chemical composition of a phase, and, finally, the degree of dispersion of a phase. The free energy of such active centers and of the formation of such centers are discussed essentially according to Gibbs' technique. The supersaturation with respect to free energy is shown to be not only a thermodynamic precursor of formation of any type of deviation from equilibrium in a solid phase, but assures this formation kinetically. Also, in any process of physical and chemical crystallization, along with the growth of supersaturation of the genetic reaction of a solid body, in the moment of its formation and thereafter, the content of any possible supersaturated formation in the above solid must increase constantly. This article is the introduction to a series of applications of the supersaturation theory to experimental data.

2885. ———. Theoretical Principles of the Preparation of Catalysts. I. Methods of Production and Regulation of Supersaturation. Jour. Appl. Chem. (U. S. S. R.), vol. 17, 1944, pp. 3–15 (English summary); Chem. Abs., vol. 39, 1945, p. 1350.

Theoretical discussion of physical and chemical principles that control supersaturation in the preparation and use of catalysts. Suitable selections must be made for preparation of specific catalyst masses.

2886. ———. [Theoretical Principles of the Preparation of Catalysts. II. Conditions for Utilization of Supersaturation of Reactions in the Preparation of Catalysts.] Jour. Appl. Chem. (U. S. S. R.), vol. 17, 1944, pp. 97–106; Chem. Abs., vol. 39, 1945, p. 1350.

Excess free energy, that is, supersaturation, of the reaction in the preparation of catalysts is the source of the catalytically active structures in the final product. A theoretical discussion shows that concentration and temperature are essential factors in the preparation of catalyst masses. The usual methods of catalyst preparation are classified and analyzed as to phase conditions in the course of topochemical reactions. A preliminary guide is indicated for selection of the interval during which the application of high supersaturation is most effective.

———. *See* abs. 703, 1709.

2887. Roginskiĭ, S. Z., and Tsellinskaya, T. F. Experimental Investigation of the Role of Supersaturation in the Preparation of Catalysts. Acta physicochim. U. R. S. S. vol. 19, 1944, pp. 225–247 (in English); Jour. Phys. Chem. (U. S. S. R.), vol. 18, 1944, pp. 477–492; Chem. Abs., vol. 39, 1945, p. 2447.

Pyrolytic decomposition of $NiCO_3$ is a centripetal topochemical reaction. The decomposition was affected in an apparatus in which the CO_2 pressure (pT) was controlled by freezing out CO_2 in a cryostat maintained at various temperatures. The supersaturation (A) of the genetic reaction is defined as $A=RT\ ln\ (pT/pT')$, in which pT is the equilibrium pressure of CO_2 at the surface of the solid. The decomposition of $NiCO_3$ is autocatalytic; the reaction velocity increases with increasing supersaturation. This decomposition is extremely rapid at CO_2 partial pressures of 10^{-4} to 10^{-2} mm. of Hg; near the equilibrium pressure the decomposition is slow. The rate constant varies exponently with the temperature. The apparent activation energies for the decomposition are 11,000 cal. per mol. for ΔF=constant, 17,000 for $p_{co_2}=3\times10^{-3}$ mm., 15,000 for $p=2$ mm., and 11,000 for $p=10$ mm. Up to its maximum, the reaction velocity obeys an approximate quadratic law; hence the process involves primarily the development of formerly existing initiation centers, as is true for the decomposition of Ni formate (abs. 703). The values of the reciprocals of the times needed to attain a definite degree of decomposition increase almost linearly with the supersaturation. A plot of velocity versus % of decomposition shows a maximum for each temperature and CO_2 pressure; this maximum is at 5–10% decomposition and is only slightly dependent on the experimental conditions. The H_2O content of the sample of $NiCO_3$ has a peculiar, and as yet unexplained, effect on the kinetics of the decomposition.

Roĭter, V. A. *See* abs. 1164, 1165.

2888. Roĭter, V. A., and Gaukhman, S. S. [Adsorption Properties of Differently Prepared Iron Catalysts of the Same Composition.] Ber. Pissarjewsky Inst. physik. Chem., Akad. Wiss. Ukr. S. S. R., vol. 12, 1940, pp. 3–11, in German 12–13; Chem. Abs., vol. 35, 1941, p. 2686.

Study was made of the nature of adsorption of H_2 and N_2 within the interval of −184° to +425° on 2Fe catalysts used in the synthesis of NH_3. The catalysts contained 98% Fe_2O_3 and 2% Al_2O_3. 1 of the catalysts was fused in an electric arc. 3 types of sorption of H_2 were observed; physical sorption at 184° and 2 types of activated sorption analogous to pure Fe and other promoted catalysts. With the fused catalyst there was activated sorption of N_2 at 250°–425° with measurable speed, but there was no measurable sorption of N_2 on the unfused catalyst. Measurements also were made of the kinetics of NH_3 synthesis (both catalysts were used). The catalytic activities are compared with the sorption characteristics.

2889. Roĭter, V. A., Gaukhman, S. S., and Leperson, M. [Investigation of the Adsorption of Hydrogen and Nitrogen on Iron–Molybdenum–Ammonia Catalysts.] Acta Physicochim. U. R. S. S., vol. 4, 1936, pp. 145–158; Chem. Abs., vol. 30, 1936, p. 3707.

Stable catalyst composed of 18.5% Mo, 74.1% Fe, and 7.4% Al_2O_3 was prepared by reduction at 450°. At 1 atm. its activity is the same as that of the unstable catalyst without Al_2O_3 but, at 150 atm., it is 8 times as great. At −183°, adsorption of H_2 is completely reversible. Above 0°, a slow "irreversible" adsorption begins, more marked for the still unfatigued and especially the promoted catalysts. N_2 shows only van der Waals reversible adsorption with Q=about 4,500 cal. at 25° for the unpromoted and 12,000 cal. for the Al_2O_3-promoted catalyst. The mechanism proposed by Emmett and Brunauer (abs. 823) is criticized.

2890. Roĭter, V. A., Gaukhman, S. S., Pisarzhevskaya, N. P., and Gvaliya, T. M. [Kinetics and Mechanism of Catalytic Conversion of Carbon Monoxide.] Jour. Appl. Chem., U. S. S. R., vol. 18, 1945, pp. 439–449; U. O. P. Co. Survey Foreign Petroleum Literature Index May 31–June 7, 1946, pp. 3–8; Chem. Abs., vol. 40, 1946, p. 4593.

Reaction $CO+H_2O\rightleftharpoons CO_2+H_2+9.6$ kcal. was studied in the presence of K_2CO_3 on activated C and on technical Fe oxide catalyst of the type known as nitrogene. Data are reported on the effects of the space velocity, total pressure, and partial pressures of the components, and the kinetics and the mechanism of the process are discussed. The surface of the catalyst was determine by the method of Gaukhman and Roĭter (abs. 1164). The results are explained by a new theory for the K carbon catalyst in which the following scheme of reactions is proposed: $2KOH+CO=K_2CO_3+H_2$; $K_2CO_3+H_2O=2KOH+CO_2$, with summary result: $CO+H_2O=H_2+CO_2$. In case of the Fe catalysts there is evidence for considerable effect of the following reaction sequence: $2CO=CO_2+C$; $C+2H_2O=CO_2+2H_2$.

Rollefson, G. K. *See* abs. 1050.

2891. Rollefson, G. K., and Garrison, W. Iodine-Sensitized Decomposition of Methyl Alcohol. Jour. Am. Chem. Soc., vol. 62, 1940, pp. 588–590; Chem. Abs., vol. 34, 1940, p. 2784.

I-sensitized decomposition of MeOH has been studied at 325°. The net over-all reaction may be represented by the equation $3MeOH=2CH_4+CO+2H_2O$. This is the result of 2 parallel reactions, one an oxidation of the alcohol by I to CO, the other a reduction by HI to CH_4. These reactions are represented by equations $MeOH+2I=CO+4\ HI$ and $MeOH+2HI=CH_4+I_2+H_2O$. Tables are given for the distribution of I and for the amounts of CH_4 and CO present during the reaction.

2892. Roquet, J. [Magnetic Properties of Magnetic Ferric Oxide.] Compt. rend., vol. 222, 1946, pp. 727–729; British Abs., 1946, I, A, p. 274.

Fe_2O_3 was heated to 700° and cooled in a magnetic field. Its specific permanent magnetization, σ, was measured. The Fe_2O_3 was heated again to 700°, which demagnetized it, and it was allowed to cool again in the same field. There was an increase in σ after each heating and cooling. The curve of σ against time t (the sum of the individual times during which the Fe_2O_3 was heated to 700°) tends toward a limit, σ_s; for t amounting to several days. X-ray analysis reveals no change in the crystalline structure. σ_s and the time required to attain it vary considerably from one sample to another. The susceptibility of the unheated Fe_2O_3 is 100×10^{-6}—200×10^{-6}. If X_t is the susceptibility after a short period of heating and X_s is that after heating long enough for the magnetization to reach the limit, X_t does not differ from X_s for a given sample by more than the experimental error and lies between 25×10^{-6} and 32×10^{-6}.

2893. Rose, H. J. Secrets of German Fuel Technology. Min. and Met., vol. 27, 1946, pp. 106–108.

Brief review of German technical progress, as investigated by the Technical Industrial Intelligence Committee (TIIC), on coal treatment and synthetic fuel production.

2894. ———. New Chemical Processes Based on Coal and Their Significance. Crucible, vol. 32, October 1947, pp. 244, 246.

Paper read before the Pittsburgh section of the American Chemical Society. Approximately ½ of the world's coal reserves are in the United States and about 40% of the United States production has been in Pennsylvania. Coal constitutes 98.8% of the proved fuel reserves of the United States. It is, therefore, natural that coal should become the raw material for the production of gaseous and liquid fuels as well as chemicals. Some information was given on the Fischer-Tropsch and the Bergius processes for the production of gaseous and liquid fuels, and several new processes were briefly discussed for the production of chemicals from coal, such as acetylene chemistry, synthetic rubber, organic acids from coal oxidation, chemical methods for ash reduction, active C, ion-exchange mediums, waxes, and resins.

2895. Rosendahl, F. [Chemical Utilization of Coal.] Metallbörse, vol. 19, 1929, pp. 397–398, 455–456, 510–512, 622–624, 678–680, 733–735; Chem. Abs., vol. 23, 1929, p. 3557.

An attempt to cover in 1 article (1) the constitution of coal; (2) low- and high-temperature distillation of coal; (3) application of the gases for the synthesis of hydrocarbons and fertilizers; (4) liquid fuels: Benzene, alcohol, hydronaphthalene; (5) production of oils without coking. Conclusion: The direct utilization of coal for the production of valuable products is still an unsolved problem, but the new processes for combining CO, CO_2, and H_2 obtained from coal, low-temperature distillation, high-temperature distillation, and the indirect treatment of coal and its products by catalysts have already proved their worth.

2896. ———. [Carbon Monoxide and Hydrogen.] Montan. Rundschau, vol. 25, 1933, pp. 1–14; Petrol. Ztschr., vol. 29, No. 6, 1933, pp. 1–14; Chem. Abs., vol. 27, 1933, p. 1861.

Detailed historical review of the catalytic preparation of MeOH, hydrocarbons, etc., from CO and H_2 under high temperature and pressure.

2897. ———. [Manufacture of Hydrocarbons From Carbon Monoxide and Hydrogen.] Oel u. Kohle, vol. 36, 1940, pp. 340–349; Chem. Abs., vol. 35, 1941, p. 8251.

Review.

2898. ———. [Liquid Fuels From Coal.] Mineralöle, vol. 15, 1942, pp. 23, 61, 143.

Production of motor fuels by various processes of carbonization and by solvent extraction and hydrogenation is briefly described. The author then deals in greater detail with the processes for making Fischer-Tropsch synthesis gas (Koppers, Pintsch-Hillebrand, Wintershall-Schmalfeldt, Didier-Bubiag, Lurgi, and the reforming of waste synthesis gases either by cracking or by partial combustion). The paper concludes with a discussion of the Fischer-Tropsch process, with particular reference to the products and their treatment by dehydrogenation and polymerization along the lines adopted in the oil industry.

2899. ———. [Obtaining Fuel From Coal.] Allgem. Oel- u. Fett-Ztg., vol. 39, 1942, pp. 23–27, 61–65, 143–147; Asphalt Teer Strassenbautech., vol. 42, 1942, pp. 254–257, 288–292; Chem. Abs., vol. 37, 1943, p. 5219.

Review of synthesis processes. The subject is reviewed under the following headings: Coking, low-temperature carbonization, extraction of coal, hydrogenation and synthesis of hydrocarbons. The various processes used for synthesis of hydrocarbons are reviewed thoroughly.

2900. ———. [Production of Aviation Gasoline, With Particular Reference to American Processes.] Teer u. Bitumen, vol. 40, 1942, pp. 191–202; Chem. Abs., vol. 37, 1943, p. 6861.

Processes covering S-removal, production of isooctane and other antiknock constituents, isomerization, reforming, aromatization, polymerization, cracking and catalytic cracking, the Fischer-Tropsch and other syntheses are described briefly with some flow sheets and 27 refs. It is believed better from economic and practical standpoints to produce a motor operating on all fuels, even though it is now possible to make any desired fuel for any motor.

2901. ———. [Production of Synthetic Gas by Gaseous Transformation.] Ztschr. kompr. flüss. Gase, vol. 37, 1942, 117–122, 130–134; Chem. Zentralb., 1943, I, p. 1635; Chem. Abs., vol. 39, 1945, pp. 1280–1281.

Brief description of the various processes for the production of synthetic gas by the transformation of gaseous hydrocarbons and the production of high grade H_2 by the removal of CO from water gas.

2902. ———. [Manufacture of Fat Acids for Soap by Oxidation of High-Molecular Hydrocarbons.] Ztschr. kompr. flüss. Gase, vol. 38, 1943, pp. 25–30, 37–43, 49–57; Chem. Zentralb., 1944, I, p. 1149; Chem. Abs., vol. 39, 1945, p. 3445.

Oxidation of paraffins is discussed from the standpoint of basis for the process, raw materials, pretreatment of raw materials, oxidation with air and other oxidizing gases, equipment, removal of unsaponifiable (according to the patent literature), use of the fat acids in the soap industry, and for the manufacture of glycerides and fat alcohols.

Rosenfeld, L. *See* abs. 873, 874, 875, 876, 877, 878.

2903. Rosenthal, H. [Manufacture of City Gas From Water Gas.] Gas- u. Wasserfach, vol. 78, 1935, pp. 436–438; Chem. Abs., vol. 29, 1935, p. 6397.

One m.³ of water gas containing CO, 39; H_2, 51; CO_2+H_2S 6 and N_2 4% can be converted into 0.56 m.³ of city gas, analyzing CO, 16; CH_4, 25; H_2, 46.2; CO_2, 5.5; and N_2, 7.3% by catalytic conversion with H_2O and methanation. Half of the water gas is mixed with steam, the CO_2 converted into CO and H_2 at approximately 500°, and the gas cooled in a waste-heat boiler and direct cooler to 50°, at which temperature H_2S is removed. Organic S is removed at about 180°, and partial methanation, conversion of about 60% of the CO with 3 times as much H_2, is carried out at 380° with a Ni catalyst. Cost data are given for the various steps and over-all costs based on the use of blue gas from peat or brown coal.

2904. ———. [What Can the Gas Industry Contribute to the Four-Year Plan?] Gas-u. Wasserfach, vol. 80, 1937, pp. 103–106.

Discussion of the economic possibilities of utilizing the excess production capacity of German gas plants for the manufacture of liquid fuels by the Fischer-Tropsch process. It is calculated that the 80 largest gas plants, which ordinarily produce 90% of the fuel gas requirements, could gasify an extra 6,000,000 tons of coal and could thus supply the raw material for 1,000,000 tons of liquid fuel. The cost would be high until the Fischer-Tropsch installations could be written off in about 3 years, when the cost would then compete fairly well with world markets.

Ross, J. F. *See* abs. 424.

2905. Rossi, G. [Methyl Alcohol.] Riv. catasto servizi tecn. erar, vol. 9, 1942, pp. 459–471; Chem. Zentralb., 1943, I, p. 2242; Chem. Abs., vol. 38, 1944, p. 4410.

Production of MeOH by the dry distillation of wood and its synthetic production from CO and H_2 are described. Properties and uses discussed.

2906. Rossini, F. D. Heat of Combustion of Methanol. Proc. Nat. Acad. Sci., United States, vol. 17, 1931, pp. 343–347; Chem. Abs., vol. 25, 1931, p. 4773.

With the same calorimetric apparatus and procedure that was used for H_2, CH_4, and CO, the heat of the reaction $CH_3OH\ (g)+3/2\ O_2\ (g)=CO_2\ (g)+2H_2O\ (l)$ was found to be 763.77±0.20 internat. kilojoules/mol. at 25°. By combining with this value the data of Fiock, Ginnings, and Holton on the heat of vaporization of CH_3OH, the heat of combustion of $CH_3OH\ (l)$ is computed to be 726.34±0.20 internat. kilojoules/mol. at 25°, or, with the factor 1.0004/4.185. 173.63±0.05 kg.-cal_{15}. The value obtained by Richards and Davis is about 1.5% lower than this, while that of Thomsen agrees with it within the assigned limits of error. In the present experiments CH_3OH was vaporized by a stream of dry air and burned in an excess of O_2. Tests were made to determine the purity of the reaction. No CO was found, and only negligible amounts of N oxides and HCHO.

2907. ———. Heats of Combustion of Methanol and Ethyl Alcohol. Bureau Standards Jour. Research, vol. 8, 1932, pp. 119–139; Chem. Abs., vol. 26, 1932, p. 2109.

Complete information as to apparatus and procedure is given. The heats of combustion of gaseous MeOH and EtOH, at saturation pressure, from their mixture with air, under a constant total pressure of 1 atm. to form gaseous CO_2 and liquid H_2O were found to be 763.68±0.20 for MeOH at 25° and 1407.50±0.40 for EtOH at 32.50°, in internat. kilojoules/mol. By combining with these data the heats of vaporization and correcting the data for EtOH to 25°, the heats of combustion of the alcohols, in the liquid state are, at 25° and a constant pressure of 1 atm., respectively: 726.25±0.20 and 1,366.31±0.40 internat. kilojoules, or 173.61±0.05 and 326.61±0.10 kg.-cal_{15}./mol.

———. *See* abs. 3589.

2908. Roth, W. A. [Thermochemistry of Iron, Manganese, and Nickel.] Ztschr. angew. Chem., vol. 42, 1929, pp. 981–984; Arch. Eisenhüttenw., vol. 3, 1929, pp. 339–346; Chem. Abs., vol. 24, 1930, p. 291.

Heats of formation were determined with a calorimetric bomb, paraffin being used to start the reactions. The reaction products were carefully analyzed. Values found (in general slightly higher than those previously accepted) are given in calories: MnO 96.2; Mn_3O_4, 343.8; $MnCO_3$, 218.2; $MnO+CO_2$, 27.7; Mn_3C, 23; FeO, 64.0; Fe_3O_4, 265.7; Fe_2O_3, 197.6; $FeCO_3$, 171.7; $FeO+CO_2$, 13.4; Fe_3C, —5.4; $Fe(CO)_5$, 54.4; NiO, 58.6; Ni_3C, —9.2, all at constant volume. Values at constant pressure, also given, are similar but not identical.

2909. Roth, W. A., and Wienert, F. [Thermochemistry of Iron.] Arch. Eisenhüttenw., vol. 7, 1934, pp. 455–460; Chem. Abs., vol. 28, 1934, p. 2604.

Heats of formation of the Fe oxides were redetermined from pure synthetic materials; methods are described in detail. The heats of reaction, at 20.7°, were found to be: $Fe+\frac{1}{2}\ O_2=FeO+64.6_5\pm0.1_2$ kcal.; $3Fe+2\ O_2=Fe_3O_4+266.7_6\pm0.2_6$ kcal.; $2Fe+1\frac{1}{2}\ O_2=Fe_2O_3+195.1_0\pm0.2_5$ kcal.; $FeO+Fe_2O_3=Fe_3O_4+6.9_4\pm0.3_3$ kcal.; $Fe+1\frac{1}{2}\ Cl_2=FeCl_3+93.5_6\pm0.2_3$ kcal.; $Fe_2O_3+3Cl_2=2FeCl_3+1\frac{1}{2}O_2+8:07\pm0.4_4$ kcal. A comparison with older values is added.

2910. Röttig, —. [Aromatization of Straight-Chain Aliphatic Hydrocarbons From the Fischer-Tropsch Synthesis.] TOM Reel 138, Doc. 28, 13 pp.

Some reference is made to the ability of Cr_2O_3 to convert napthenic and aliphatic hydrocarbons into aromatics and to the possibility of depositing these catalysts on active C, pumice, Al_2O_3, and silica gel. Such metals as Ni, Co, Fe, Ta, etc., are mentioned as promoters. Preliminary treatment of the catalysts with CO_2, H_2S, PH_3 is said to increase their activity. Reference is made to the work of Huppke-Frey and Moldavskii-Kamuscher with multiple component catalysts. Calcined magnesite is stated to increase catalyst activity. It is possible by means of efficient fractionation columns to isolate C_5, C_6, C_7, and C_8 hydrocarbons from Fischer-Tropsch gasoline fractions. A flow sheet of a cyclization is shown. The economics of the process is discussed.

2911. ———. [New Experiences With Iron Catalysts for the Normal Pressure Synthesis.] Erdöl u. Kohle, vol. 3, No. 1, 1950, p. 10.

Paper presented at the 1949 meeting of Die deutsche Gesellschaft für Mineraloelwissenschaft und Kohlechemie. By using nonsupported Fe catalysts, it is possible in a straight 1-stage passage at temperatures of about 200° to attain a $CO+H_2$ conversion of 65–70%, corresponding to CO conversion of 85–95%. The gas charge per hr. amounts to 100 l. per vol. of catalyst. Water gas is the best gas to use, although the use of H_2-rich gas is possible. Especially favorable is the use of CO-rich gas. The catalysts must be extracted initially in periods of 4–6 days at the reaction temperature considered. Several new experiences in the extractions are presented. The operating time of such Fe catalysts is very high; at almost constant reaction temperature a life of 10,000–11,000 hr. is attained and this can be extended considerably by raising the temperature. CH_4 formation is essentially less than with Co catalysts. The proportion of hydrocarbons boiling above 320°, calculated on the total liquid yield, is 25–30% by weight as the average of a long operating period.

2912. Röttig, E. [New Substances With Spinel Structure.] Angew. Chem., vol. 62, 1950, p. 87.

$CuFe_5O_8$, analogous to $LiAl_5O_8$ and $LiFe_5O_8$, was made at 1,200° C. Its $\Theta=390°$ and $a=8.389\pm0.003$ Å. This is a spinel. $CuFe_2O_4$, made at 600°, has $\Theta=490°$ and is psuedo-tetragonal with $a=8.4_1$ Å, $c/a=0.97_5$. Mixtures of $CuFe_2O_4$ and $\frac{Cu+Fe}{2}Fe_2O_4$ have $\Theta=440°$ and a spinel structure with $a=8.377\pm0.003$ Å. $CuAl_2O_4$ is not quite cubic. $CuAl_2O_4$ and $CuCr_2O_4$ are not cubic, contrary to the literature. Li^{+}, Cu^{+}, or Ti^{++} spinels could not be obtained. $LiFeTiO_4$ and $LiCrTiO_4$ are spinels. $LiAlTiO_4$ is not cubic. $LiFeTiO_4$ is ferromagnetic with $\Theta=130°$.

Roudebush, B. *See* abs. 626.

2912a. Rousseau, P. E. South Africa's Oil-From-Coal Project. South African Min. and Eng. Jour., vol. 62, 1951, pp. 207–211, 255–259; Chem. Age, vol. 66, 1952, pp. 129–130.

An outline of the development work being planned and carried out in the production of oil from coal and of chemical byproducts by the South African Coal, Oil & Gas Corp. ("Sasol" project). The process to be employed, and found most suitable for South African low-grade coals, is a combination of American and German developments of the original Fischer-Tropsch method.

Royen, P. *See* abs. 2879.

Rozengart, M. I. *See* abs. 1706.

Rozhdestvenskaya, I. D. *See* abs. 3179.

Rubanik, M. Y. *See* abs. 932.

2913. Rubanik, M. Y., Zabolotskiĭ, T. V., and Rusov, M. T. [Iron-Molybdenum Catalysts for the Synthesis of Ammonia.] Jour. Chem. Ind. (U. S. S. R.), vol. 14, 1937, pp. 484–485; Ber. Inst. physik. Chem., Akad. Wiss. Ukr. S. S. R., vol. 6, 1936, pp. 77–82; Chem. Abs., vol. 31, 1937, p. 5519.

Fe–Mo–Al_2O_3 catalysts are less active than Fe–Al_2O_3 ones. Addition of Al_2O_3 to Fe–Mo catalyst causes them to retain their activity longer.

2914. Rubinfeld, J. [Liquefaction of Coal.] Allgem. österr. chem. u. tech.-Ztg., vol. 43, 1925, p. 151; Chem. Abs., vol. 20, 1926, p. 1313.

Brief discussion of 4 methods by which motor fuel can be produced: Low- and high-temperature carbonization of coal, Synthol process, Bergius process, and Badische process.

2915. Rubinshtein, A. M. [Catalytic Hydrogenation in the Vapor Phase in Connection With the Degree of Dispersion of the Catalysts.] Bull. acad. sci. U. R. S. S., Classe sci. chim., 1940, No. 1, pp. 144–150 (in German, pp. 150–151); Chem. Abs., vol. 35, 1941, p. 3512.

Hydrogenation of C_6H_6 and CO in the presence of a Ni–Al_2O_3 catalyst in which the dimensions of the Ni crystals varied 40–102 Å. was investigated. C_6H_6 was hydrogenated in an excess of H_2 at 155° and 175°, the velocity of the C_6H_6 stream was 3 cc. per hr., yielding 70.2–75.0% and 83.3–85.5%, respectively, C_6H_{12}. The highest yield was in the more disperse catalyst. The catalysts with Ni crystals greater than 65 Å. had little or no activity. The activation energy also varied within 3,100–10,450 cal. per mol. with the dispersity of Ni 49–102 Å. The mixture CO+3 H_2 was hydrogenated at 230°–260° at various velocities of the mixture, 4.6–10.0 l. per hr., yielding CH_4; again the most disperse catalysts (49, 58 Å.) promoted best the transformation of CO into CH_4. Other catalysts had little or no activity. Presumably, all catalysts of the same chemical nature, metals, and oxides and having the same crystal system and cube as the above catalyst should have the same relation between activity and dispersity.

2916. Rubinshtein, A. M., Pribytkova, N. A., Kazanskiĭ, B. A., and Zelinskiĭ, N. D. [Catalysts for Benzine Synthesis From Carbon Monoxide and Hydrogen Which Do Not Require High-Temperature Reduction.] Bull. acad. sci. U. R. S. S., Classe sci. chim., 1941, pp. 41–48; Chem. Zentralb., 1942, II, p. 971; U. O. P. Co. Survey Foreign Petroleum Literature Transl. 334; Chem. Abs., vol. 37, 1943, p. 5217.

Catalysts produced from $KAlFe(CN)_6$, $Ni^2Fe(CN)_6$, and $Co_2Fe(CN)_6$ by decomposition in a H_2 atmosphere yielded no liquid hydrocarbons under the experimental conditions, temperatures 230°–280° and space velocity of 18–50, but only catalyze CH_4 formation. A Co–Cu–Mn catalyzer, produced by precipitation with K_2CO_3 on kieselguhr, in a single experiment yielded 204 cc. benzine per m.^{3} of gas, whereas a catalyst of similar composition prepared by igniting the nitrates was not as effective. The kieselguhr required no preliminary ignition or treatment with HCl or Na_2CO_3. A 2-stage synthesis with Co–Cu–Mn catalyst gave benzine yields of 160 cc. per m.^{3} over a long time with space velocities of 100–120. With prolonged tests, lower catalyst activity was noted with intermittent than with continuous operation.

2917. Rubio, F. B. L., and Pacheco, J. R. [Mechanism of the Catalytic Process for the Synthesis of Hydrocarbons by the Fisher-Tropsch Process.] Ion, vol. 8, 1948, pp. 86–89; Chem. Abs., vol. 42, 1948, p. 5643.

Most active catalysts for the Fischer-Tropsch synthesis are Fe, Co, and Ni. Of these, Fe is probably the least active, but it has the advantage of being effective over a wide range of temperatures and is characterized by production of liquid hydrocarbons with CO_2 as byproduct. Co gives a product rich in olefins. Ni tends to produce CH_4 along with liquid and solid paraffins. Previous theories have attributed the catalytic action of these metals either to formation of CH_2 groups, with carbides of the metals acting as intermediates and polymerization of the CH_2 groups, or of higher alcohols with subsequent dehydration to olefins. According to a new theory, carbonyls of the metals are the primary active materials. The existence of a compound $[Fe(CO)_5]_4$ including long chains of CO groups is assumed. This is reduced to 2 mol. of C_8H_{18} and a Fe carbonyl of much lower CO content. After a number of reactions, with Fe_3C, C_3O_2, FeO, and Fe_2O_3 among the intermediate products, the lower carbonyl is reconverted to Fe. Overall reactions are: $18\ CO+4\ Fe \rightarrow [Fe_2(CO)_9]_2$; $[Fe_2(CO)_9]_2+2\ CO \rightarrow [Fe(CO)_5]_4$; $[Fe(CO)_5]_4+34\ H_2 \rightarrow 2\ C_8H_{18}+15\ H_2O+CO_2+3\ CO+4\ Fe+H_2$. The volumes of CO and H_2 to produce 1 mol. of C_8H_{18} are 10 CO+17 H_2 instead of the previously given 8 CO+17 H_2, and the theoretical yield of octane is only 188.4 gm. per m.^{3} instead of 203.5. The presence of Fe carbides and oxides in the catalyst is consistent with this theory, but these compounds only represent stages in the regeneration of the metallic Fe. Hydrocarbon formation is by substitution of H for O in (CO_n) chains already formed. Polymerization of CH_2 groups is not inconsistent with this theory. The action of alkalies added to Fe catalyst may be either (1) removal of O from CO groups to give percarbonate, H then combining with C and the percarbonate being subsequently reduced, or (2) polymerization of CO to chains, which combine with Fe to give carbonyls.

Ruckes, W. L. *See* abs. 625.

2918. Ruer, R. [Iron-Carbon Alloys.] Ztschr. anorg. Chem., vol. 117, 1921, pp. 249–261; Chem. Abs., vol. 16, 1922, p. 702.

(1) *Solubility of cementite in molten iron.* A quenched melt of an Fe-C alloy containing 6.5% C showed a structure consisting entirely of cementite. Cementite is precipitated directly from the melt and is not formed by the reaction between 2 phases, 1 solid and the other liquid. The solubility curve of Fe_3C in molten Fe rises from the eutectic temperature to a maximum at 6.67% C corresponding to the compound Fe_3C. The melting point of Fe_3C in the metastable system Fe–C cannot be determined because Fe_3C dissociates at temperatures above 1,100°. The slope of the solubility curve of Fe_3C in the metastable system is less than that of graphite in the stable system because with increasing C content the suppression of the separation of graphite becomes more difficult. Small cubes of Swedish Fe containing 2.5–4% C and no Mn were heated in a vacuum for 10 min. at temperatures 1,100°–1,150°. The velocity of the dissociation of Fe_3C on the surface of the cubes was higher than the velocity at the center; no explanation is offered.

(2) *Complete equilibrium between austenite, ferrite, and graphite corresponding to the pearlite equilibrium.* A sample of Fe containing 3.5% C and no Mn or Si was solidified slowly. After the solid had cooled to 1,000° it was heated to just above the eutectic temperature and again slowly solidified. After a repetition of this latter procedure, the sample was cooled to room temperature. Repeated heating and cooling curves for the sample were then made. The maximum temperature reached in each experiment was 772°. The first curve showed an arrest at 734° on heating and at 720° on cooling. The second curve showed arrests at 736° and 746° on heating and at 720° on cooling. The third curve showed arrests at 736° and 746° on heating and at 720° and 707° on cooling. All these arrests were recognized on subsequent heating and cooling curves up to the twelfth. The twelfth curve showed an arrest at 736° on heating and 712° on cooling. The arrest at 736° corresponds to the transformation of pearlite into austenite. The rate of cooling was so slow that Fe and graphite rather than Fe_3C precipitated from the austenite. The arrest at 746° corresponds in the stable system Fe–C to the solution of ferrite and graphite in austenite. The gradual disappearance of the 746° arrest from the heating curves is caused by the coalescence of the graphite particles into large masses, which, under the experimental conditions, would not dissolve in austenite. The double arrest on the cooling curves is not easily explained. The upper arrest at 718° cannot be attributed to the transformation in the stable system and the lower to the transformation in the metastable system because white cast Fe shows the austenite-pearlite transformation at 718°. The simultaneous precipitation of pearlite and the graphite eutectic may occur. Since the arrest at 746° ascribed to the transformation of the eutectic in the stable system lies 12° higher than the arrest at 734° ascribed to the transformation of pearlite in the metastable system, then the equilibrium temperature of the former transformation should occur 12° higher than the equilibrium temperature of the latter transformation, that is, at 721+12=733. A horizontal should be drawn across the Fe–C diagram from 0–100% C at 733° to represent the eutectic transformation in the stable system. The concentration of C in the eutectic in the stable system is 0.7%.

2919. ———. [Magnetic Transformations of the Ferromagnetic Metals.] Ztschr. anorg. Chem., vol. 165, 1927, pp. 142–148; Chem. Abs., vol. 22, 1928, p. 208.

Discrepancies between the results of Ruer and Bode (abs. 2921) and Wever (abs. 3672 and 3673) are discussed at length. It is claimed that one of Wever's investigations was made with Fe of insufficient purity, whereas in the other there is evidence of faulty technique. This explains the failure of Wever to observe the polymorphic transformation at 769° originally reported by Ruer and Bode.

2920. ———. [Magnetic Transformations of the Ferromagnetic Metals.] Ztschr. anorg. Chem., vol. 205, 1932, pp. 230–234; Chem. Abs., vol. 26, 1932, p. 3707.

Temperature–temperature-difference curves for exceptionally pure electrolytic Fe were recorded photographically. Both the heating and the cooling curves show sharp breaks at the magnetic transformation point as well as more pronounced ones at the β–γ transformation. Wever has questioned the idea advanced by Ruer and Bode that the magnetic transformation in pure Fe at 769° is a homogeneous phase change (abs. 2919). The evidence, both experimental and theoretical, bearing on this point is reviewed.

2921. Ruer, R., and Bode, K. [Magnetic Transformations of Ferromagnetic Metals.] Stahl u. Eisen, vol. 45, 1925, pp. 1184–1189; Chem. Abs., vol. 20, 1926, p. 3426.

Experiments were made with a view to find a fixed point at 700°–800° for the purpose of calibrating thermocouples. 3 cooling curves and 1 heating curve for electrolytic Fe are given, that show an arrest point at 769°. Electrolytic Fe from the Langbein-Pfanhauser works showed the point at the same temperature. Kahlbaum Fe in rods gave the point on heating but not on cooling and gave results midway between those for electrolytic Fe and mild steel. The arrest is suppressed by impurities, but the impurity that is effective has not been identified. The heat set free at the β–α change is 1/6 that at the γ–β change, or about 1 cal. per gm. The change, which must be truly polymorphic, also occurs in Ni and Co. As α– and β–Fe have the same space lattice, a polymorphic change does not necessarily involve a change in the space lattice, and the inverse must also be true.

2922. Ruff, O. [Equilibrium Diagram of Iron-Carbon Alloys.] Metallurgie, vol. 8, 1911, pp. 456–464, 497–508; Chem. Abs., vol. 5, 1911, p. 3793.

It is concluded from experiments that besides cementite, Fe_3C, which has been called triferrocarbide, a diferrocarbide exists, Fe_2C. The equilibrium concentrate of the triferrocarbide is always less than the saturation concentrate. Above 700° the carbides are endothermic compounds and at 2,220° the diferrocarbide is quite strongly dissociated into Fe and C. As the temperature is lowered, the diferrocarbide breaks down into Fe_3C and C, and eventually the Fe_3C breaks down into Fe and C. In the metastable system, the solidification takes place in 4 periods: (1) The time up to that point when the melt reaches the equilibrium concentrate; (2) the time during which the melt remains between the equilibrium concentrate and the saturated concentrate; (3) the time during which the carbide eutectic is solidifying; (4) the time during which the solid system is cooling. The amount of solid carbide formed from the liquid phase is determined chiefly by the decomposition velocity of the carbide and the difference between the equilibrium concentrate and the saturation concentrate and also is affected by the velocity of solidification. In the solid phase, the decomposition velocity of the carbide is always less than in the liquid phase. Thus, when the carbide is once formed as solids, it remains more stable in proportion as the temperature at which it is first deposited is low. Moreover, the more finely divided its condition, the more likely the carbide is to remain in metastable equilibrium with the surrounding solid solution. The reaction velocity of the carbide decomposition at 1,135° is such that about 50% of the carbide will decompose in 2 sec. Approximation formulas are developed for the results to be expected in the solidification of Fe–C alloys during the second and third periods.

2923. ———. [Phase-Rule Diagrams of Carbon With Nickel, Iron, Cobalt, and Manganese.] Ber. deut. chem. Gesell., vol. 45, 1912, pp. 3139–3148; Chem. Abs., vol. 7, 1913, p. 581.

In his electric vacuum furnace, Ruff has succeeded in maintaining temperatures up to above 2,700°. Thus the melting-point diagram of the V-C system has been followed to about 2,750°. In the Fe–C system, the probable existence of Fe_2C has been revealed, and in the Ni–C system, the compound Ni_3C was found. The melting point and vapor pressure diagrams of these systems are reproduced, together with those of Mn–C and Co–C, worked out with the help of Gersten and

Keilig. In the Mn–C system the compound Mn_3C appears to be more stable than any of the above mentioned compounds. Unlike the other carbides, Mn_3C forms a continuous series of mixed crystals with Mn. In the Co–C series, the formation of fumes at high temperatures caused so much trouble that the work is to be repeated. The melting-point diagram is very similar to that of Ni–C, although no transition point could be detected in the liquid before the boiling point was reached. (*See also* abs. 2924 and 2933.)

RUFF, O., AND BORMANN, W. [Investigations at Higher Temperatures. VII. Iron and Carbon.] *See* abs. 2931.

———. [Investigations at Higher Temperatures. V. Manganese and Carbon.] *See* abs 2929.

———. [Investigations at Higher Temperatures. VI. Nickel and Carbon.] *See* abs. 2930.

2924. RUFF, O., AND GERSTEN, E. [Triferrocarbide (Cementite) Fe_3C.] Ber. deut. chem. Gesell., vol. 45, 1912, pp. 63–72; Chem. Abs., vol. 6, 1912, p. 1409.

Campbell (Jour. Iron Steel Inst. (London), vol. 59, 1901, p. 217) and others hold that Fe_3C is an exothermic compound, 8,940 cal. being given off in its formation. Ruff (abs. 2922) believes that it is endothermic and reports the following experimental work in confirmation of his theory. Pure Fe_3C, prepared by Werkmeister's method (Dissertation, Karlsruhe, 1910), is dark gray; its hardness is 3.2–33, sp. gr. 7.396 at 21°, mol. vol.$=1/7=24.34$. The molecular volume for 3 Fe and C is 27.84, giving a molecular contraction of 3.5. Burning Fe_3C with O_2 in a Berthelot bomb, under a pressure of 25 atm., gave 375.1 cal. for 1 mol. Fe_3C. In burning Fe to Fe_3O_4 and C to CO_2, 360 cal. are evolved, a difference of 15.1 cal. Therefore, the heat of formation of Fe_3C is 15.1 cal., and Fe_3C is endothermic. $3Fe+C \rightarrow Fe_3C+15.1$ cal.

2925. ———. [Carbides of Manganese and Nickel.] Ber. deut. chem. Gesell., vol. 46, 1913, pp. 400–413; Chem. Abs., vol. 7, 1913, p. 1848.

Molecular heats of formation of $Mn_3C=-12.9\pm2.14$, $Fe_3C=-15.3\pm0.2$ and $Ni_3C=-394\pm10$ cal. The Ni_3C is very unstable and is not obtained in a pure condition. Mn_3C is comparatively stable and is obtained by heating Mn in a C crucible with C at 1,600° in an electric vacuum furnace. Ni_3C is formed at 2,100°. The maximum amount of C found in the carbide is 6.42%.

2926. ———. [Iron Carbide.] Ber. deut. chem. Gesell., vol. 46, 1913, pp. 394–400; Chem. Abs., vol. 7, 1913, p. 1848.

Molecular heat of formation of Fe_3C was previously found to be −15.1 cal. Recalculation by Le Chatelier's method revealed the heat of oxidation of FeO to ⅓ Fe_3O_4 to be 28.6 ± 1.8, while Le Chatelier obtained 25.7. Revised calculations gave the following results: Molecular heat of formation of Fe_3O_4 $(Fe=55.8)=267.1\pm0.2$ cal.; of $FeO=60.4\pm1.8$ cal.; of Fe_3C from α–Fe and graphite$=-15.3\pm0.2$ cal. (*See* abs. 2924.)

2927. RUFF, O., AND GOECKE, O. [Solubility of Carbon in Iron.] Metallurgie, vol. 8, 1911, pp. 417–421; Chem. Abs., vol. 5, 1911, p. 3221.

Solubility shows a maximum at 2,220° corresponding to the composition Fe_2C and a change in direction at 1,887° corresponding to the composition Fe_3C.

RUFF, O., AND KEILIG, F. [Investigations at Higher Temperatures. VIII. Cobalt and Carbon.] *See* abs. 2932.

2928. RUFF, O., AND LAUSCHKE, G. [Investigations at Higher Temperatures. IV.] Ztschr. anorg. Chem., vol. 87, 1913, pp. 198–208; Chem. Abs., vol. 8, 1914, p. 2931.

2929. RUFF, O., AND BORMANN, W. [Investigations at Higher Temperatures. V. Manganese and Carbon.] Ztschr. anorg. Chem., vol. 88, 1914, pp. 365–385; Chem. Abs., vol. 9, 1915, p. 435.

The solubility of C in Mn is 6.82% at 1,312°, 6.93% at 1,427°, 7.05% at 1,492°, and 7.12% at 1,525°; the latter boils at 30 mm., and the vapor in equilibrium contains 1.94% C. Pure Mn boils at 1,510° at 30 mm. Since the vapor pressure of C up to 3,000° is small, the vapor in equilibrium with Mn melts probably contains its C as carbide; it is also probable that all of the C contained in the melt is combined as carbide.

2930. ———. [Investigations at Higher Temperatures. VI. Nickel and Carbon.] Ztschr. anorg. Chem., vol. 88, 1914, pp. 386–396; Chem. Abs., vol. 9, 1915, p. 435.

Addition of C to Ni lowers the melting point to a minimum at 1,311° and 2.20% C; the eutectic line could be followed to 0.3% C. With increasing temperature the solubility of C in the melt increases first slowly, then rapidly, to a flat maximum at 2,100° and 6.4% C; the melt is the almost pure Ni_3C. As the temperature is increased, the solubility of C first diminishes sharply then increases slowly to 6.3% C at 2,490°; the latter solution boils at 30 mm., and the vapor in equilibrium contains 0.28% C. Pure Ni boils at 30 mm. at about 2,400°.

2931. ———. [Investigations at Higher Temperatures. VII. Iron and Carbon.] Ztschr. anorg. Chem., vol. 88, 1914, pp. 397–409; Chem. Abs., vol 9, 1915, p. 435.

2932. RUFF, O., AND KEILIG, F. [Investigations at Higher Temperatures. VIII. Cobalt and Carbon.] Ztschr. anorg. Chem., vol. 88, 1914, pp. 410–423; Chem. Abs., vol. 9, 1915, p. 435.

Addition of C to Co lowers the melting point to 1,300° at 2.4% C; with increasing temperature the solubility of C in the melt increases, first slowly with increasing temperature, then more rapidly; at 2,100° and at 6.36% C and at about the composition of the compound Co_3C the solubility curve has an upward inflexion similar to, but not as marked as, that with Ni; the solubility of C then rises to 7.4% at 2,415°. The authors concluded that Co_3C had been formed, but on examination found only graphite, and, therefore, assumed that the Co_3C, if formed, had very quickly decomposed.

2933. RUFF, O., AND MARTIN, W. [Solubility of Carbon in Nickel.] Metallurgie, vol. 9, 1912, pp. 143–148; Chem. Abs., vol. 6, 1912, p. 1128.

At about 2,100°, Ni will dissolve 6.42% C, corresponding approximately to the formula Ni_3C. Under the microscope a new constituent, evidently the carbide, was distinguished from the ground mass of Ni. It was brown and resisted the etching solutions more than the Ni. The behavior of the Ni–C alloys when heated resembled that of the ~~Fe–C~~ alloys, indicating that Ni and Fe form similar carbides.

2934. RUFF, O., BORMANN, W., AND KEILIG, F. [Behavior of Carbon Toward Manganese, Nickel, Iron, and Cobalt.] Forschungsarbeiten Gebiete Ingenieurwesens, No. 209, 1918, pp. 5–46; Chem. Abs., vol. 16, 1922, p. 1713.

More extensive exposition of the data and phase rule diagrams reported in abs. 2923.

2935. RUFF, O., JELLINEK, E., AND FOEHR, T. [Constitution and Thermal Stability of Carbides.] Ztschr. Elektrochem., vol. 24, 1918, pp. 157–162; Chem. Abs., vol. 13, 1919, p. 213.

Experiments on the formation of carbides lead to the conclusion that metal carbides in general are stable up to temperatures above 2,500°, and even at these elevated temperatures, C does not dissolve in the metals as such, but as a carbide of the metals. To date, the known metal carbides conform with the following hydrocarbons: CH_4, C_2H_6, C_2H_2, C_2H_4, and C_4H_{10}. In the case of most metals the C concentration increases with increasing temperature. Within wide temperature limits carbides such as Mn_3C, Cr_3C_2, and W_3C are very stable; carbides such as Fe_3C, WC, and Cr_2C_2 decompose upon lowering the temperature to the melting point of the alloy into metal plus C. Fe_3C is difficult to obtain in the solid phase, and Ni_3C is altogether unstable as solid. All carbides dissociate more or less completely upon volatilization.

2936. RUHEMANN, M. Large-Scale Oxygen Production. Internat. Cong. Pure Appl. Chem, 11th Cong., 1947; British Abs., 1948, B, I, p. 300.

Economics of the production of O_2 so that it can compete with liquid air is reviewed. The development of new units, including expansion turbines, turbocompressors, packed regenerators and reversing heat exchangers with extended surfaces, have led to increased efficiency and reduction of losses.

2937. RUHL, O. [Liquid-Fuel Problems in Germany.] Jour. Fuel Soc. Japan, vol. 16, 1937, pp. 33–40.

Review of German developments in the I. G. coal-hydrogenation process and the Fischer process. By the latter process 1 m.³ $CO+2H_2$ (90%) produces in practice 100 gm. liquid products; about ½ of the H_2 in the gas mixture is converted to H_2O. The theoretical limit of production is 180 gm. of liquid products from 1 m.³ $CO+2H_2$. As 0.8 kg. of coal corresponding to 0.55 kg. coke is used in the production of 1 m.³ $CO+2H_2$, it follows that theoretically 35%, at most, of the heat value of the coal can be converted into liquid products, while in practice the figure is about 20%. Much steam also is produced, which is not included in the efficiency. The smallest economical size of Fischer plant is about 20,000 tons of gasoline per year. Plants at Ruhland, Rauxel, Holten, and Homberg have a capacity of 295,000 tons of gasoline per yr. Besides these plants, Kuhlmann in France is planning an installation of 30,000 tons capacity, and in Japan the Mitsui Co. is erecting a plant of 30,000 tons capacity. Two other plants are planned. Installation costs for the high pressure process and the Fischer process are about the same, and the cost of operation does not differ greatly. If gasoline is the main object, the high-pressure process operates most economically.

2938. RUHRCHEMIE A.-G. [Drawings of Medium-Pressure Reactors for the Fischer-Tropsch Process.] BIOS Microfilm FD 5422/47, frames 1–18; O. T. S. Bib. Tech. Rept., vol. 16, No. 3, 1951, p. 78, PB 104,126.

German report covering years 1942–44.

2939. ———. [Production of Soaps and Edible Fats From Fatty Acids.] BIOS Microfilm FD 5463/47, Frames 1–194; O. T. S. Bib. Tech. Rept., vol. 16, No. 3, 1951, p. 67; PB 104,187.

German report covering years 1939–43.

2940. ———. [Experiments for the Production of Aviation Spirit by Catalytic Cracking of Primary Products of the Fischer-Tropsch Synthesis.] BIOS Microfilm FD 5600/47, frames 1–387; O. T. S. Bib. Tech. Rept., vol. 16, No. 3, 1951, p. 78, PB 104,188.

German report covering years 1937–44.

2941. ———. [Technique of the Fischer-Tropsch Process.] BIOS Microfilm FD 5619/47, frames 1–43; O. T. S. Bib. Tech. Rept., vol. 16, No. 3, 1951, p. 79, PB 104,171.

German report covering years 1937–44.

2942. ———. [Course of the Pressure Synthesis When Using an Initial Gas Rich in Carbon Monoxide.] FIAT Reel K–20, no date, frames 11–17; PB 70,211; TOM Reel 287.

Gas used consisted of $CO:H_2=1:1$. Higher yields of liquid products were obtained than with normal synthesis gas. In order to obtain a good conversion of the CO, temperatures up to 215° were used. The total product consisted of about equal parts of gasoline, middle oil, and paraffin, the latter being about 8% less than in normal synthesis. The olefin content of the gasoline was 32–36 vol. % and that of the middle oil 24–27%. With a catalyst containing Co, 100; ThO_2, 15; kieselguhr, 600; and a gas rich in CO, considerably better results were obtained. The conversion of CO was 92% and the ratio of liquefaction 89%. The content of paraffin was 17% higher than with the normal catalyst.

2943. ———. [Kieselguhr.] FIAT Reel K–20, 1938, frames 18–23; PB 70,211; TOM Reel 287.

Microphotographs of 12 kieselguhr samples show great changes in structure after regeneration. It is believed that an examination of the microtexture of fresh and spent catalysts will provide valuable explanations on the evaluation of catalysts for the gasoline synthesis. The solubility of kieselguhr is determined by stirring at 80°–95° with various solutions occurring in the manufacture of catalysts, filtering and washing with hot water. In the filtrate, SiO_2, Fe_2O_3, Al_2O_3, and CaO are determined. Table and diagram.

2944. ———. [Thorium Regeneration.] FIAT Reel K–20, 1938, frames 24–31; PB 70,211; TOM Reel 287.

Auergesellschaft A.-G. has developed the following method: Fe–Th sludge is dissolved in HCl at a temperature of 80°. After cooling, the bulk of the solution is siphoned off, the residue is filtered, and the whole is mixed with H_2SO_4. The sulfate precipitates are centrifuged and covered with dilute H_2SO_4. The Th sulfate is then stirred with water and converted to Th hydrocarbonate. The yield of ThO_2 by this method is 94%. The method is compared with the Ruhrchemie method. The maximum content of SO_3 in the Th hydrocarbonate is given as 0.3%.

2945. ———. [Manufacture of a Catalyst With High Cobalt Content and High Activity.] FIAT Reel K–20, 1939, frames 40–43; PB 70,211; TOM Reel 299.

Following has been found to be the most favorable method for precipitating the catalyst consisting of 100 part Co, 15 ThO_2, and 12.5 purified kieselguhr. The boiling solution of 1 kg. Co and 150 gm. ThO_2, dissolved as nitrates in 20 l. of H_2O, is poured into the stirred boiling solution of 2.6 kg. soda in 40 l. H_2O. After addition of 125 gm. previously purified kieselguhr, the mixture is stirred for another 30–40 sec. The precipitate then is transferred to a suction filter, and the mother liquor is removed, after which the precipitate is covered 2 times with distilled H_2O and washed until less than 0.01 gm. soda per l. can be detected in the wash H_2O. After extensive dry suction the cake is placed in the drier and dried at 100° for 8 hr.

2946. ———. [Production of Cobalt Catalyst by Precipitation With Carbon Dioxide-Ammonia Gas Mixtures.] FIAT Reel K–20, frames 359–362; PB 70,211; TOM Reel, 287.

Communication from the Kaiser Wilhelm Institut für Kohlenforschung concerning the production of a very active catalyst. Co in the form of its nitrate, together with the corresponding amounts of Th or Mg nitrates, is dissolved in water. A NH_3–CO_2 gas mixture then is introduced cold. By test filtration the optimum precipitation is determined, and the stream of NH_3 is switched off. With the CO_2 still flowing, the solution is heated to the boiling point, kieselguhr is added, and the whole is mixed thoroughly. The catalyst then is dried and reduced with H_2.

2947. ———. [Fatty Acids and Soaps From the Hydrogenation of Carbon Monoxide.] FIAT Reel

K–20, various dates, 1936–43, frames 414–531; PB 70,211; TOM Reel 287.

Miscellaneous collection of papers, mostly by O. Roelen, on the development of the production of synthetic fats from Fischer-Tropsch paraffins and their transformation into soaps. The method of the Ruhrchemie and Brabag are compared. Analyses of products are given, and some rough drafts of patent specifications are presented.

2948. ———. [Recovery of Thorium.] FIAT Reel K–21, 1942, frames 806–892; PB 70,212; TOM Reel 288.

Paper reports all the experimental and practical work performed on the development of a method for recovering Th from the catalysts used in the hydrogenation of CO. The results of the entire work are contained in a patent application. The method consists in precipitating Th–K_2SO_4 from the Fe–Th sediments obtained by precipitation by adding K_2SO_4. After separation and washing, this is transformed into Th bicarbonate by boiling in concentrated soda solution.

2949. ———. [Paraffin Synthesis.] FIAT Reel K–21, 1939, frames 997–1008; PB 70,212; TOM Reel 288.

New catalysts of extraordinary efficiency are described, which differ from the previous Co catalysts by a very high $CoCO_3$ content, little kieselguhr, and a corresponding addition of Mn as activator. They bring about complete transformation of the CO–H_2 mixture at the lowest temperatures known, below 170°. This results in a high yield of paraffin.

2950. ———. [Properties of Kieselguhr.] FIAT Reel K–21, 1938, frames 1032–1075; PB 70,212; TOM Reel 288.

Average values of 3 types of reduction examined are found to lie very close together. It also was found by experiment that contrary to established theories the catalytic usefulness of kieselguhr in no way depends on its stability in alkali. It also was noticed in some samples from Kieselguhr Industrie, Hanover, that catalysts on kieselguhrs with high calcination loss did not react up to full activity. It is evident from studies made that there is a connection between the temperature treatment of a kieselguhr and its suitability as a carrier.

2951. ———. [Paraffin Synthesis on Iron Catalyst.] FIAT Reel K–21, March 3, 1941, frames 1123–1129. PB 70,212; TOM Reel 299.

Both in circulation and straight passage of gas, the Fe catalyst 100 Fe : 5 Cu : 10 : 150 kieselguhr consumes normal water gas at a pressure of 15–20 atm. and a temperature of 225°–250° in such a way as to permit operation in 2 or more stages. It is easily reproducible, has special grain solidity, and gives excellent yields of pure-white paraffin.

2952. ———. [Aromatizing Plant.] FIAT Reel K–24, July 3, 1940, frames 2,470–2,485; TOM Reel 291.

Report deals with the task of converting the gasoline boiling below 200° C., obtained from the Fischer synthesis, into a motor gasoline with an octane No. of 65. The costs and economy of a plant for catalytic cracking are compared with those of an aromatizing plant. Calculations and estimates in 8 enclosures.

2953. ———. [Manufacture of Higher Alcohols.] FIAT Reel K–24, April 9, 1940, frames 2,848–2,864; TOM Reel 291.

MeOH synthesis described, with references to literature and patents.

2954. ———. [Production of Ruhr-Gasoline Hard Paraffin in Connection With the Fuel Synthesis of Ruhrchemie.] FIAT Reel K–25, no date, frames 3, 572–3, 574; PB 70,216; TOM Reel 292.

Bergius process yields liquid fuels, while the Fischer-Tropsch method produces paraffins in small quantities. To obtain paraffin in larger quantities, this method was changed by Fischer and Pichler. They applied medium pressures of about 10 atm., and paraffin was produced in a liquid state. A solidly built-in catalyst containing Co is placed in a reactor with water pipes running vertically. In addition to light and heavy gasoline and gasol, a paraffin mixture is obtained, which can be processed into soft paraffin, through vacuum distillation, 3–6 mm. Hg., and about 300° C. and into Ruhr gasoline hard paraffin. This solid paraffin is oxidized with nitrous gases, produced by the combustion of NH_3. The long-chained molecules are less frequently cracked by this method than by O_2 oxidation.

2955. ———. [Calculation of a Plant for the Production of High-Molecular Fatty Acids With a Daily Output of 3 Tons Product.] FIAT Reel K–25, June 26, 1941, frames 3, 953–3, 956; PB 70,216; TOM Reel 292.

Method and calculations are described. (*See* abs. 3553.)

2956. ———. [Monthly Reports of the Plant Laboratories, Ruhrchemie A.-G.. Oberhausen-Holten.] FIAT Reel K–28, January 1938–March 1940, frames 5,734–6,080; PB 70,185; TOM Reel 295.

These monthly reports deal with the plant research on gasoline synthesis at the above laboratories. Aside from the general routine work for the supervision of the plants, special tasks have been carried out, the progress of which is reported. These special tasks consist of tests with gasolines, diesel oils, and paraffins; examination of the miscibility of several grades, emulsification and emulsifier properties, and oxidation of paraffins, acids, aldehydes, ketones, and alcohols.

2957. ———. [Recycle Benzine.] FIAT Reel K–28. Aug. 13. 1941, frames 6,081–6,098; PB 70,185; TOM Reel 295.

Examination was made of the suitability of recycle benzine (benzine obtained by recirculating residual gas mixed with fresh synthesis gas, obtained by synthesis over Co and Fe catalysts) for producing lubricating oil by polymerization. Recycling does not affect the polymerization properties or the value of the product. The lubricating oil prepared from benzine synthesized over the Fe catalyst possesses a more favorable viscosity pole height than that obtained with the Co catalyst. 15 tables, 4 diagrams.

2958. ———. [High-Temperature Refining and Storage Stability of Gasoline Produced Over Iron Catalyst.] FIAT Reel K–28, July 20, 1940, frames 6,268–6,271; PB 70,185; TOM Reel 295.

Gasoline produced over an Fe catalyst and refined by treatment with bleaching earth at 300° did not show the increase in octane number to be expected from the olefin content. Bomb-test results show that the storage stability of both refined and unrefined gasoline may be expected to be equally good.

2959. ———. [Carbon Dioxide in the Circulation Gas of Catalytic Reduction.] FIAT Reel K–28, July 7, 1938, frames 6,435–6,452B; PB 70,185; TOM Reel 295.

In a new catalytic reduction installation for the production of Fischer-Tropsch catalyst, the % of CO_2 in the reduction gas was examined during the reduction period. The CO_2, which originates mainly from the decomposition of the carbonates, attains its highest concentration after the first third of the reaction time. An apparatus for further formation of CH_4 converts only part of the liberated CO_2. A reaction on the already reduced catalyst thus results and leads to a loss of activity at reduction temperatures. 14 tables and graphs.

2960. ———. [Preparation of Iron Oxide for Iron Catalysts.] FIAT Reel K–29, 1939, frames 6,926–6,929; PB 70,218; TOM Reel 296.

Different electrical smelting processes for the preparation of nonconducting Fe oxide for catalysts are considered. Nothing different from the usual process is given. 1 drawing.

2961. ———. [Preparation of Catalysts With a High Cobalt Density.] FIAT Reel K–29, 1939, frames 6,968–6,972; PB 70,218; TOM Reel 296.

Directions are given for the preparation of new catalysts with a high Co density, which are supposed to give an especially good yield of paraffin.

2962. ———. [Cause of Cobalt Losses in Synthesis Installation.] FIAT Reel K–29, 1939, frames 6,981–6,986; PB 70,218; TOM Reel 296.

Sources of Co losses up to the present time in a synthesis installation are summarized. Their extent is determined in particular.

2963. ———. [Tests on the Precipitation of Cobalt Catalysts.] FIAT Reel K–29, no date, frames 6,991–6,994; PB 70,218; TOM Reel 296.

Description of tests on the precipitation of Co for the preparation of Co catalysts with kieselguhr as carrier material and with the use of a mixture of gaseous NH_3 and CO_2 for the precipitation instead of the usual Na_2CO_3. It is demonstrated that useful catalysts also can be prepared in this manner.

2964. ———. [Testing of Catalysts Under Pressure.] FIAT Reel K–29, 1940, frames 7,355–7,363; PB 70,218; TOM Reel 296.

In order to find the reaction of catalysts in the synthesis of gasoline under the conditions of operation on a large technical scale, a catalyst, which proved to be highly active in the laboratory test, has been examined in an assay furnace. The qualitative results of this test were confirmed. 2 diagrams.

2965. ———. [Synthesis of Light Hydrocarbons.] FIAT Reel K–30, Feb. 15, 1939, frames 7,593–7,595; PB 73,587; TOM Reel 297.

Brief report of an experiment to produce light hydrocarbons, particularly C_2H_4 and C_3H_6, from synthesis gas in a catalytic furnace having a small layer column. Up to 3.5% C_2H_4 could be detected in the end gas, which is nearly 20–25% of the amount of hydrocarbons produced.

2966. ———. [Gasoline Synthesis According to Fischer-Tropsch, Ruhrchemie, Oberhausen.] FIAT Reel L–2, no date, frames 1–559; FIAT Reel L–3, no date, frames 560–1,198; PB 70,156.

Film contains a collection of drawings of the entire Fischer-Tropsch plant.

2967. ———. [Drawings for Plant "F" of Ruhrchemie, Oberhausen-Holten.] FIAT Reel L–4, 1943–44, frames 1,199–1,397; PB 70,158.

Plant probably is used for production of synthetic gasoline. Drawings of several construction firms are presented.

2968. ———. [Synthetic Production of Wax Acids and Emulsifiers and Their Utilization.] FIAT Reel L–5, Feb. 16, 1943, frames 55–95; PB 70,159; TOM Reel, 299.

Report presents a survey on the wax acids and emulsifiers from products of the Fischer-Tropsch gasoline synthesis and on their utilization. The preparation of fully synthetic wax acids from synthetic paraffins has been achieved. Special consideration is given to the OP4, OP5, and OP32 acids produced by Ruhrchemie. From these wax acids the 3 emulsifiers FP 2035, 1025, and 1325 were developed. These serve to produce pastelike and liquid emulsions, respectively. The possibilities for the technical utilization of wax acids are commented on; they serve for instance for the production of high-melting lubricating greases and oils and as emulsifiers for shoe polish, etc. Wax acids and emulsifiers also can be utilized in the leather industries.

2969. ———. [Paraffin Synthesis on Iron Catalyst.] FIAT Reel L–5, Sept. 10, 1941, frames 96–108; PB 70,159; TOM Reel 299.

Paraffin synthesis was carried out with water gas ($CO:H_2=1.25$) in circulation on an Fe catalyst (100 Fe : 10 CaO : 5 Cu : 150 kieselguhr). This catalyst had been precipitated with KOH and had the highest kieselguhr content attained so far. The long duration test, 124 days at 247° and 20 atm., produced a yield of 134.6 gm. per $m.^3$ including gasoil and a $CO+H_2$ conversion of 75%. In contrast to previous tests a white crude paraffin, free of any catalyst particles was obtained. The long life of the catalyst is worthy of note.

2970. ———. [Wet Method for Paraffin Synthesis With Cobalt Catalyst.] FIAT Reel L–5, Sept. 6, 1941, frames 115–117; PB 70,159; TOM Reel 299.

Furnace was charged with a crushed Co catalyst mixture and oil condensate plus crude paraffin, m. p. 120°–320°. The temperature during the first few days of operation ranged 180°–190°. The yields obtained were not satisfactory. At 208°, the yield declined and was stabilized at about 60%. Compared with the normal dry synthesis, the wet synthesis does not offer any advantage.

2971. ———. [Olefin Synthesis by Water-Gas Circulation on Cobalt-Mixture Catalyst.] FIAT Reel L–5, Apr. 29, 1941, frames 118–135; PB 70,159; TOM Reel 299.

Synthesis operation was carried out in a double-tube furnace to obtain products with a high % of olefins. According to calculations, 1 $m.^3$ of water gas was needed to circulate for each 10 $m.^3$ of Co catalyst mixture; however, the quantity had to be increased to 1.2 $m.^3$ during the operation. The results of the synthesis, as obtained under normal conditions in a range of temperature 190°–225°, a gas pressure of 7 atm., and a catalyst life of 6 mo., are as follows: $CO+H_2$ conversion 63%; yield of liquid products 88–90 gm. per $m.^3$ of water gas; 52 wt. % benzine; 25, oil; 17, soft paraffin: 6, hard paraffin; olefins in benzine, 58–60 vol. % and in oil 42 vol. %.

2972. ———. [Paraffin Synthesis With Iron Catalyst.] FIAT Reel L–5, March 3, 1941, frames 136–143; PB 70,159: TOM Reel 299.

Summary of research development work performed in connection with the paraffin synthesis with Fe catalyst based on the general experience of all research laboratories. The following catalyst is recommended: 100 Fe : 5 Cu : 10CaO : 150 kieselguhr precipitated with KOH. The method for preparing the catalyst is given. The synthesis is performed at 15–20 atm. pressure and a temperature of 225°–250°, with circulation of water gas, a constant ratio of $CO:H_2$, and with operation in 2 or more steps. With this catalyst a 67% conversion is possible with yields of 129 gm. per $m.^3$ of synthesis gas and with 60–70% of the liquid product as pure-white paraffin.

2973. ———. [Recycle Method of Gasoline Synthesis.] FIAT Reel L–5, Feb. 19, 1941, frames 145–147; PB 70,159; TOM Reel 299.

End gas from the synthesis operation is mixed with fresh gas, and the mixture is charged into the converter. This recycle method insures the utilization of every particle of CO and H_2.

2974. ———. [Duration Test for the Olefin Synthesis in a Double Tube Furnace With a Cobalt Catalyst.] FIAT Reel L–5, Aug. 31, 1943, frames 157–172; PB 70,159; TOM Reel 299.

Test of 6 mo. duration with water gas recycle under 7 atm. pressure was carried out in a 4-m. double-tube furnace with Co catalyst mixture. The average charge on the furnace during the test amounted to 1,190 m.^{3} of water gas. With the aging of the catalyst, its converting capacity was greatly reduced, in spite of a decrease of charge and an increase of temperature. The results of the tests are shown in several tables.

2975. ———. [Test With a Paraffin-Forming Iron Catalyst.] FIAT Reel L–5, Aug. 20, 1943, frames 173–183; PB 70,159; TOM Reel 299.

Paraffin-forming Fe catalyst (100 Fe, 5 Cu, 10 CaO, 150 kieselguhr), the reduction of which had been started at the factory, was examined. The test was carried out in a 4.5–m. double-tube furnace with water-gas recirculation. The yield, which was considered to be satisfactory, amounted to 120 gm. of liquid product per m.^{3} of useful gas, including gasol, and with a gas conversion of 70%. An intermediate extraction to attain the original high generation of paraffin did not have the desired result.

2976. ———. [Paraffin Synthesis With an Iron Catalyst.] FIAT Reel L–5, July 1943, frames 184–190; PB 70,159; TOM Reel 299.

Paraffin synthesis was carried out in a double-tube, 4.5–m. furnace with a filament grain (Fadenkorn) Fe catalyst; no details. This catalyst is very well suited for the paraffin synthesis with circulation of the useful gas. In order to maintain the desired conversion of $CO+H_2$ at about 70%, the temperature had to be raised from an initial 225° to about 245° after 45 days. The yield of liquid products plus gasol was then about 124 gm. per N m.^{3} of useful gas, of which 50–60% was paraffin. The average H_2 : CO consumption ratio for this period was 1.26 corresponding virtually to the H_2 : CO ratio in the water gas. A pressure of 20 atm. was maintained throughout.

2977. ———. [Water-Gas Circulation Test Over Iron Catalyst.] FIAT Reel L–5, July 25, 1942, frames 201–221; PB 70,159; TOM Reel 299.

Test was carried out with water-gas circulation in a Lamella furnace with a filament-grain Fe catalyst. The test was run for 140 operating days. From the values obtained it is plainly revealed that shortening the operating time of the Fe catalyst would produce the highest yields of hard paraffins. The test justifies the conclusion that the Fe catalyst can be effectively used for 3 months if a double-tube furnace is employed.

2978. ———. [Influence of a Variable H_2 : CO Ratio in the Synthesis Gas on the Medium-Pressure Synthesis.] FIAT Reel L–5, Mar. 20, 1942, frames 222–232; PB 70,159; TOM Reel 299.

Object of this test was to determine whether, in the medium pressure synthesis, reactions different from those obtained under normal operating conditions would result from a constant change at regular intervals of the H_2 : CO ratio in the synthesis gas. As a result of the tests, no disadvantages, which might have been caused by the constantly recurring change in the proportional share of H_2 : CO from 1.75 to 2.25 in the synthesis gas at regular 6-hr. intervals, were observed. The conversion was slightly increased by this change and resulted in a corresponding increase in the yield. The constant change in the H_2 : CO ratio does not allow a definite balance of reaction and thus prevents certain fatigue symptoms.

2979. ———. [Production of Aviation Gasoline.] FIAT Reel L–5, June 17, 1941, frames 242–268; PB 70,159; TOM Reel 299.

Properties required in an aviation gasoline are discussed, and the operating procedure for its production from the products of the Fischer-Tropsch synthesis is presented. There are 2 principal groups of substances to be used as base materials: The C_4 and C_5 hydrocarbons and those constituents boiling above 200°. The latter are cracked in a plant especially developed by Ruhrchemie, while the primarily produced straight chain unsaturated C_4–C_5 hydrocarbons are isomerized into the corresponding branched hydrocarbons. These have the same qualities as the C_4–C_5 hydrocarbons obtained from the catalytic cracking. From these products a pure aliphatic aviation gasoline of high quality is obtained by polymerization and distillation.

2980. ———. [Properties of the Primary Products From Thorium and Magnesium–Thorium Catalysts.] FIAT Reel L–5, July 29, 1938, frames 423–451; June 17, 1938, frames 452–456; PB 70,159; TOM Reel 299.

Comparative survey of the results obtained from the examination of primary products from the above 2 catalysts when applied in single furnaces and in furnaces under ordinary working plant conditions, respectively. The gasolines produced in the single furnace from Mg–Th catalysts differ in no way from those obtained in actual plant operation. Any variations noted in the olefin content of the gasoline hydrocarbons are irrelevant. There is a definite relation between the boiling point and the octane number of the gasolines. A large amount of tabular data is presented.

2981. ———. [Hydrogenation of Carbon Monoxide at Normal Pressure With Addition of Acetylene or of Acetylene and Ethylene.] FIAT Reel L–5, 1942, frames 536–543; PB 70,159; TOM Reel 299.

Tests revealed that with the addition of C_2H_2 and C_2H_4 at normal pressure a highly olefinic product can be obtained in a comparatively simple manner. A further advantage is that the apparatus used in the normal pressure synthesis needs no alteration for this method.

2982. ———. [Hydrogenation of Carbon Monoxide by Addition of Acetylene in the Liquid Phase Under Pressure.] FIAT Reel L–5, Oct. 7, 1941, frames 565–567; PB 70,159; TOM Reel 299.

In the tests carried out under pressure in the liquid phase, heptane was used as the base material. It was ascertained that low-uressure hydrogenation of CO by addition of C_2H_2 in the liquid phase is not favorable for the production of unsaturated O–containing compounds. Comparative tests carried out under analogous conditions but with the addition of C_2H_2 in the gas phase show a considerable decline of the olefinic constituents in the gasolines thus produced.

2983. ———. [Fischer-Tropsch Plant.] FIAT Reel AA–77. Oct. 12. 1945, frames 1–135; PB 70,267; TOM Reel 281.

Report is a comprehensive description, in both German and English, of the Ruhrchemie Fischer–Tropsch plant and equipment, with flow sheets and plant diagrams. The following operations are described: Water-gas production, including feed-water purification and recooling; the synthesis plant, including desulfurizing of synthesis gas, H_2 production (CO conversion), and low-pressure and medium-pressure synthesis; condensation plant and operation; adsorption by active C; working up and stabilization of primary products; paraffin production; the alkazid process for production of CO_2 from residual gas; lubricating-oil production; and Oxo synthesis with flow sheet. Estimates are made of plant damage and time necessary to place the separate units in operation.

Ruka, R. *See* abs. 1284.

2984. Rumford, F. Correlation of Adsorption and Catalytic Activity. I. Hydrogen Adsorption on Zinc-Chromium Catalysts. Jour. Roy. Tech. Coll. (Glasgow). vol. 4, 1939, pp. 427–440; Chem. Abs., 33, 1939, p. 5269.

Relation between catalytic activity and activated adsorption was investigated, but results are inconclusive. ZnO suspensions were mixed with chromic acid solution, dried at a temperature below 110°, and reened to 10–40 mesh. Catalysts were reduced by H_3OH vapor in the presence of airfree N_2. The ethod of operation was to introduce into the catalyst ith a known weight of catalyst, approximately 5 cc volume. The whole system then was closed, the pparatus evacuated, and the catalyst temperature ised to 500°. H_2 then was admitted to atmospheric ressure level and left for 15 min.; after this, the gas as removed again, and the catalyst was maintained the lowest possible pressure for another 15 min. was then removed and the catalyst cooled to the esired temperature. H_2 gas for test then was admitted in 3 portions; this brought the pressure to evels of 250, 500, and 760 mm. of Hg, respectively. After each addition, the adsorption was continued for 20 min. The quantities of gas adsorbed varied 0.5–2.0 cc. By use of the method previously outlined, a series of adsorptions at 300°–500°, with 50° intervals was made. Plotting the results shows the catalysts fall into 2 classes—first, those in which a definite type of activated adsorption appears 300°–350°, and second, those in which a somewhat less definite change appears some 50° higher. Use of these measurements in calculating heats of adsorption or of activation are disappointing. The effect of CO on the mechanism of adsorption is not known.

2985. ———. Correlation of Adsorption and Catalytic Activity. II. Carbon Monoxide and Hydrogen Adsorption on Zinc-Chromium Catalysts. Jour. Roy. Tech. Coll. (Glasgow), vol. 4, 1940, pp. 643–649; Chem. Abs., vol. 34, 1940, pp. 4971–4972.

In 2 series of experiments, one at 300°, 360°, and 400° and the other at 360°, adsorption of CO on Zn–Cr catalyst decreased with increasing Zn content of the catalyst until the catalyst contained approximately 80 at. % Zn, then it passed through a maximum at approximately 85–88 at. % Zn. Adsorption of H_2 passed through a maximum at 60 at. % Zn in the first series, but, in the second series of experiments, the maximum was not determined, because values were obtained only with catalysts up to 78 at. % Zn content. In the decomposition of MeOH over Zn–Cr catalyst at 360°, each of 2 series of experiments showed a maximum decomposition with catalyst containing approximately 65 at. % Zn. Since approximately an equal number of molecules of H_2 and CO are adsorbed on catalysts, both series, containing 60–67 at. % Zn, which includes the catalyst composition corresponding to greatest MeOH decomposition, reaction is possibly greatest when the H_2 and CO are adsorbed in equal molecular quantities and less when one of the gases is adsorbed in excess. However, this does not explain why MeOH decomposition did not approach zero when adsorption of CO became zero in one series of results with a catalyst containing approximately 77 at. % Zn.

Runtso, A. P. *See* abs. 849.

Ruping, H. *See* abs. 1402.

Rupp, J. *See* abs. 1782.

2986. Ruprecht, P. [Japan Plant.] Oel u. Kohle, Erdoel Teer, vol. 14, 1938, pp. 83–85.

In an attempt to create independence from imported oil, a Fischer-Tropsch plant was completed in 1932 at Fushun with an output of 100,000,000 l. per year, and another will be completed in 1938 at Kyushu by the Mitsui Mining Co. with an output of 50,000,000 l. per year.

Ruschenburg, E. *See* abs. 1955.

2987. Rushton, J. H. Liquid Fuels From Natural Gas. Am. Gas Jour., vol. 168, No. 3, 1948, p. 38.

Possibilities of producing liquid fuels from natural gas are outlined. There are enough reserves of natural gas in the southwest United States and southern California to support the operation of about 30 plants devoted to the synthetic production of fuels for approximately 140 years. Their daily production would be about 250,000 bbl.

———. *See* abs. 742.

2988. Rushton, J. H., and Stevenson, E. P. Developments in Oxygen Production. Chem. Eng. Progress, vol. 1, No. 2, 1947; Trans. Am. Inst. Chem. Eng., vol. 43, 1947, pp. 61–69; Chem. Abs., vol. 41, 1947, p. 2213.

Rushton and Stevenson review process considerations, the low-pressure processes, the 1,000 cu. ft. per hr. unit, the low-pressure plants, the high-pressure processes including the Keyes unit, the Le Rouget process, and other high-pressure plants; equipment developments in terms of lightweight, high-speed reciprocating and rotary compressors, interchange and fractionating equipment, columns and packing, and the purification of the gases from H_2O and CO_2.

Rusov, M. T. *See* abs. 2913.

2989. Russell, R. P. Costs of Fischer-Tropsch Gasoline. Oil Gas Jour., vol. 43, No. 27, 1944, p. 95; Am. Gas Assoc. Monthly, vol. 26, 1944, pp. 87–92; Chem. Abs., vol. 38, 1944, p. 1861.

Figures given before Senate subcommittee on war minerals. The cost of gasoline from coal by hydrogenation ranges from $0.155 in large (30,000 bbl. per day) plants to $0.226 in small (3,000–bbl.) units, using coal at $2.75 per ton. The Fischer process using coal gives gasoline for $0.192 per gal., with natural gas as the charging stock, $0.088. If suitable development is carried out, this synthesis will make gasoline for $0.048 per gal. or about equal that of petroleum gasoline.

2990. ———. Industrial Research and Its Importance to the South. Advisory Council, Southern Research Inst. Rept., 1946, 16 pp.

Paper presented at the annual meeting, Birmingham, Ala. In discussing the conversion of natural gas and coal into liquid fuels, it is remarked that the reason for placing so much emphasis on this field of research and development basically is not due to any fear of future oil shortage but to the cost of finding and producing oil. It has been stated that the oil industry expects to have as large proved reserves of crude oil in this country 20 yr. from now as it has today. In consequence of new developments demonstrated in large-scale pilot-plant operations, conversion of natural gas to gasoline already appears to be competitive with production of gasoline from petroleum. Largely because of the additional plant facilities required, the production cost of synthetic gasoline from coal is today slightly higher than the cost of gasoline from crude oil. For example, a plant to produce about 9,000 bbl. gasoline per day from coal, together with about 1,800 bbl. of diesel fuel or gas oil, would cost about $42,000,000. Sale of the nearly 40,000,000 cu. ft. per day of high-calorific-value gas at about $0.25 per 1,000 cu. ft. and allowance of suitable credit for the diesel oil and certain chemicals produced would give a final cost of gasoline from this plant, with coal at $2.50 per ton, of approximately $0.0725 per gal.; this figure does not include any return on the added investment cost of the plant. Even with a fair return on the greater investment, the average additional cost of synthetic gasoline to the American motorist should not exceed $0.10 per day. These new advances in the production of synthetic liquid fuels have been made possible by the development of fluid catalytic cracking. (*See* abs. 2344.)

2991. ———. Petroleum Industry in 1946. Chem. Eng. News, vol. 25, 1947, pp. 86–87.

Survey of the trend in petroleum research and development. Considerable notice is given to the economic possibilities of the new developments in this country in the Fischer-Tropsch process as exemplified by the Hydrocol process with some further intimations of the process characteristics.

2992. ———. Progress in Petroleum Research. Engineer, vol. 183, 1947, pp. 490–492, 508–509; Jour. Inst. Petrol., vol. 33, 1947, pp. 391–409; Petroleum, vol. 10, 1947, pp. 151–154, 186–189, 194; Petrol. Times, vol. 51, 1947, pp. 706–709, 749–751.

Abridgment of the second Cadman Memorial Lecture. It discusses the problem of the upward trend in the world demand for liquid fuels and the development of chemical methods for increasing the supply. Two chief processes are discussed: Fluid catalytic cracking and hydrocarbon synthesis. Comparative costs on the basis of a 420,000-ton-per-day synthesis plant utilizing natural gas as raw material at 3 d. per 100 cu. ft. are 3.9 d. per imperial gal. for synthetic gasoline and 5.7 d. for the same quality gasoline from a typical crude petroleum. Because of the added plant cost required, the production cost of synthetic gasoline from coal is slightly higher than the cost from crude oil. Taking the same size plant as above and allowing suitable credit for the gas and chemicals produced, with coal at 10 s. per ton, gasoline could be produced at 6.5 d. per imperial gal., a figure only slightly higher than that for gasoline from crude oil. The above estimates are all based on United States costs and prices.

Russell, W. W. *See* abs. 2335a.

2993. Russell, W. W., and Miller, G. H. Catalytic Hydrogenation of Carbon Dioxide to Higher Hydrocarbons. Jour. Am. Chem. Soc., vol. 72, 1950, pp. 2446–2454.

Study was made of several types of Cu–activated, Co catalysts for the synthesis of higher hydrocarbons from CO_2 and H_2 at atmospheric pressure and in temperature range 175°–300°. Catalysts containing no alkali produced no liquid hydrocarbons or only traces but yielded small amounts after suitable poisoning. Alkalizing with K carbonate or phosphate, was necessary in order to produce catalysts active for liquid hydrocarbon synthesis and it appears that the alkali can act as a selective poison for CH_4-forming catalyst centers. Small additions of Ce oxides to the alkalized catalysts were very effective in increasing synthesis life and catalyst stability. Although an alkalized, Ce-containing catalyst supported on a natural kieselguhr produced only CH_4, when a flux-calcined kieselguhr was substituted as a support, a catalyst was obtained that synthesized nearly as much liquid hydrocarbons as unsupported catalysts of about the same composition. The optimum synthesis temperature was near 225°, but it depended on catalyst composition and activity. Raising synthesis temperature some 25°–100° for several hours produced a selective poisoning of catalyst hydrogenation centers, which caused a marked increase in liquid hydrocarbon formation upon resumption of synthesis at the initial temperature. While the CO theoretically available from the water gas reaction is in all cases ample to account for all of the higher hydrocarbons formed, it is entirely inadequate to account also for the amounts of CH_4 formed. The maximum liquid hydrocarbon yield obtained was 95 ml. per m.³ of CO_2 passed and was accompanied by 360 l. of gaseous hydrocarbons. The apparent activation energy for the overall synthesis was found to be 23.1 kcal.

2994. Russell, W. W., and Taylor, H. S. Promoter Action of Thoria on Nickel Catalysts. Jour. Phys. Chem., vol. 29, 1925, pp. 1325–1341; Chem. Abs., vol. 20, 1926, p. 325.

Reaction $CO_2+4H_2=CH_4+2H_2O$ is a surface reaction strongly affected by the adsorbing power of the catalyst surface for the reactant. The activity of Ni alone as catalyst, either supported or unsupported, is greater the lower the temperature at which the Ni was reduced, presumably because the number of highly unsaturated Ni atoms per vol. of catalyst is greater the lower the temperature of reduction. Heating a catalyst above the temperature at which it was reduced markedly reduces its activity, because the increase in the mobility of the atoms with temperatures brings about the coalescence of the unsaturated atoms with loss of effective adsorptive power. The primary function of ThO_2 as promoter with supported Ni catalysts is to make possible the existence of a greater number of Ni atoms of a highly unsaturated character per unit of catalyst, through the creation of ThO_2–Ni interfaces. With unsupported Ni catalysts, ThO_2 may function as promoter (*a*) by the creation of a more active surface through the above interface mechanism, (*b*) by an increase in the extent of surface, inasmuch as the promoter acts as a support, and (*c*) by a favorable alteration in the ratio in which the reacting substances, and possibly the products, are adsorbed. The activation of Ni by Th may be so extensive that the speed of reduction of CO_2 by H_2 to CH_4 is increased 10-fold. This may be due to the increase in surface area and the adsorption ability of this type of Ni catalyst. The conclusions are based on the results of both adsorption and reaction-velocity measurements on samples of promoted and unpromoted, supported and unsupported Ni catalysts.

2995. Rutherford, R. W. Oil From Coal in Japan. Colliery Eng., vol. 21, 1944, pp. 40–42.

Brief review of industrial progress in hydrogenation of coal and Fischer synthesis for obtaining oils. Information is given on about 15 companies that are entering the coal-to-oil industry.

2996. Ruthruff, R. F. Petroleum: Basic Raw Material for Surface Coatings. Petrol. Processing, vol. 3, No. 1, 1948, pp. 21–24.

Various potentialities are presented for obtaining from both gaseous and liquid hydrocarbons the intermediates for representative polyhydric alcohol-polycarboxylic acid resins. The preparation of phthalic anhydride, intermediate for alkyd resins, from *o*–xylene secured by the aromatization of paraffinic naphthas is already relieving an acute shortage of naphthalene, formerly the principal charging stock for phthalic anhydride manufacture. Possibilities are seen and discussed for synthesizing drying or semidrying oil fatty acids from a synthetic petroleum oil produced by the Fischer-Tropsch synthesis.

2997. Ryan, P. Synthol Process. Oil Gas Jour., vol. 43, No. 47, 1945, pp. 264, 267, 268; Nat. Petrol. News, vol. 37, No. 14, 1945, pp. 36, 38; Gas Age, vol. 95, No. 10, 1945, pp. 18–19, 54, 56; Chem. Products, vol. 8, Nos. 11–12, 1945, pp. 86–88; Chem. Inds., vol. 56, 1945, p. 783; Petrol. Refiner, vol. 24, No. 4, 1945, pp. 130–136; Gas, vol. 21, No. 7, 1945, p. 30; Chem. Abs., vol. 39, 1945, p. 4218.

Process as developed by the M. W. Kellogg Co. is discussed from the point of view of its economic possibility when operated in conjunction with a petroleum refinery having available large reserves of natural gas and contiguous to low-cost transportation facilities. This process will produce motor gasoline, 75 clear octane CFR–M, for approximately $0.05 per gal., including 10% depreciation, from natural gas valued at $0.05 per 1,000 cu. ft. It is calculated that such a plant would pay out in about 8 yr., and in about 3 yr. if combined with a chemical plant for manufacture of hydrocarbons other than gasoline and of oxygenated chemical compounds. Approximately 11,000 cu. ft. of natural gas are required to produce 1 bbl. of liquid hydrocarbons.

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2998. Sabalitschka, T., and Harnisch, C. [Synthesis of Formaldehyde and Acetone From Oxides of Carbon and Hydrogen or Water Through Contact Substances.] Biochem. Ztschr., vol. 190, 1927, pp. 265–277; Chem. Abs., vol. 22, 1928, p. 1571.

Presence of demonstrable quantities of HCHO and Me_2CO in a mixture of CO and H_2, or CO_2 and H_2O at 300° in the presence of a great variety of contact substances (Ca_2C, SiO_2, kaolin, Fe, NaOH, wood charcoal, active C, etc.) is discussed. Data are presented in tabular form.

2999. Sabatier, P. Inversion of Reactions in Catalysis. Chem. and Ind., vol. 46, 1927, pp. 681–683, 702–705; Chem. Abs., vol. 22, 1928, p. 1085.

Ni catalysts generally are too active in the reduction of water gas to MeOH, the reduction going right to the CH_4 stage. Metallic oxides lead to the formation of primary and secondary alcohols. The use of high pressures stabilizes the MeOH and methyl aldehyde.

3000. Sabatier, P., and Mailhe, A. [Catalytic Decomposition of Formic Acid.] Compt. rend., vol. 152, 1911, pp. 1212–1215; Chem. Abs., vol. 6, 1912, p. 619.

HCO_2H vapors were passed over 0.5 m. of the catalyzer at the rate of about 0.27 gm. per min. The following catalyzers decompose the acid almost exclusively into CO_2 and H_2: Pd sponge, action begins at 110° and at 245° decomposition is virtually complete; Pt sponge, begins 120°, complete 215°; reduced Cu produces 278 cm.³ gas per min. at 190°; Ni, 290 cm.³ at 280°; Cd, 325 cm.³ at 280°; SnO begins above 150° and gives 172 cm.³ gas at 285°; ZnO begins about 190° and gives 192 cm.³ gas at 230°. TiO_2 and W_2O_5 (blue) decompose the acid exclusively into CO and H_2O above 170°. The same decomposition is produced by SiO_2, ZrO_2, Al_2O_3 and UO_2, but at the same time CO_2 is formed without H_2, indicating the decomposition of the acid into HCHO, CO_2, and H_2O; with Al_2O_3, the gas at 235° contains 6% CO_2; with UO_2 at 230°, 14% CO_2. Some catalyzers effect all 3 of the above decompositions. Thus, ThO_2 at 250° yields HCHO and a gas containing 75% (by vol.) of CO, 15% of CO_2, and 10% of H_2; at 320° the % of CO_2 increases to 45, and the condensed liquid contains $CH_2\,(OMe)_2$ (owing to the formation of MeOH from HCO_2H and HCHO); as the temperature is raised, the amount of MeOH formed increases; and, as the HCHO is then partly decomposed into CO and H_2, the % of the latter increases and that of CO_2 decreases. At 375°, the gas contains only 35% of CO_2. The blue Mo_2O_5, CaO, FeO, and Jena glass produce chiefly the decomposition into CO_2 and H_2; ordinary white glass brings about this decomposition and that into CO and H_2O to about the same extent; the latter is predominant, with pulverized pumice, MgO, light wood charcoal, CrO_3, V_2O_5, MnO, and BeO. These facts indicate that the action of the catalyzers cannot consist simply in lowering the temperature of reactions, which would take place without them; their chemical nature comes into play.

3001. Sabatier, P., and Senderens, J. B. [Direct Hydrogenation of Oxides of Carbon in Presence of Various Finely Divided Metals.] Compt. rend., vol. 134, 1902, pp. 689–691; Bull. soc. chim., vol. 29, III, 1903, p. 294; Jour. Chem. Soc., vol. 82, II, 1902, p. 317.

Although CO is converted completely into CH_4 by H_2 in the presence of finely divided Ni at 250°, at 280° another reaction becomes obvious, the formation of CO_2 and finely divided C. Thus, at 280°, CO and H_2 (1:3) yield a gaseous mixture, which consists of CO_2, 10.5; CH_4, 67.9; H_2, 21.6%; whereas, when equal volumes of CO and H_2 (water gas) are used, 52.5% CO_2, 39.8 CH_4, 7.1 H_2, and 0.6 CO are formed. Co resembles Ni in its action on mixtures of CO_2 and H_2 and on CO and H_2 but is less energetic; the reduction of CO_2 begins at 300° and is rapid at 360°–400°; no formation of C or CO and no oxidation of the metal occur. CO begins to be reduced at 270°, but at 300° the formation of CO_2 and C also is noticeable; the latter reaction plays a more prominent part the higher the temperature and the greater the proportion of CO in the mixture of this gas and H_2, that is led over the Co. Pt sponge and Pt black, Pd sponge and reduced Fe do not bring about reduction of the oxides of C. Reduced Cu converts a mixture of H_2 and CO_2 into CO and H_2O at 430°.

3002. ———. [New Synthesis of Methane.] Compt. rend., vol. 134, 1902, pp. 514–516; Jour. Chem. Soc., vol. 82, I, 1902, p. 333.

When a mixture of CO and H_2 (1:3 vol.) is passed over reduced Ni at 250°, the 2 gases are converted completely into CH_4 and H_2O. CO_2 and H_2 react similarly in the presence of reduced Ni at a somewhat higher temperature yielding only CH_4 and H_2O.

3003. ———. [Synthesis of Varieties of Petroleum. Contribution to the Theory of Formation of Natural Petroleum.] Compt. rend., vol. 134, 1902, pp. 1185–1188; Jour. Soc. Chem. Ind. (Japan), vol. 21, 1902, p. 853.

When H_2 and C_2H_2 are passed over reduced Ni below 180° C., the liquid obtained consists almost entirely of paraffin hydrocarbons.

3004. ———. [Decarbonization of Carbon Monoxide.] Bull. soc. chim., vol. 29, No. 3, 1903, p. 294.

Decomposition of CO in presence of Ni begins at 230° and increases rapidly to 349°, at which point decomposition is complete.

3005. ———. [General Methods of Hydrogenation and of Molecular Reactions Based on the Use of Finely Divided Metals. I. II. Molecular Decomposition and Condensations.] Jour. Chem. Soc., vol. 88, 1905, I, pp. 333, 401; Ann. chim. phys., vol. 4, No. 8, 1905, pp. 319–432, 433–488.

General discussion of the mechanism of the action of metals in a finely divided condition on various classes of organic compounds. The catalytic action of Ni, Co, Pt, Pd, Cu, and Fe upon mixtures of CO and H_2 has been investigated at different temperatures and under a variety of conditions. The results show that, in the case of the hydrogenation of CO in the presence of finely divided Ni, the reaction $CO+3\ H_2=CH_4+H_2O$ begins at 180°–200° and proceeds rapidly and without complications at 230°–250°. If care is taken that the temperature of 250° is not exceeded, the Ni is not impaired and retains its activity over long periods of time. By maintaining the volumetric relations of $CO:H_2=1:3$, the reaction is virtually complete and yields almost pure CH_4. The action of Co is similar to that of Ni but requires a higher temperature, whereas only negative results are obtained with Pt, Pd, Cu, and Fe. It is found that the passage of the vapors of primary and secondary alcohols over heated finely divided Cu is a convenient method of preparing the corresponding aldehydes and ketones.

3006. Sabel, —. [Ten Years of Oxygen Gasification at Leuna.] BIOS Final Rept. 199, 1945, 32 pp.; PB 67,541; TOM Reel 227.

Comprehensive coverage of experimental and operating data from 1929–43 on the production of water gas in Winkler generators by O_2 gasification of various type fuels. The development of the process is traced, and the reaction mechanism and the technical principles of O_2 gasification are discussed at length. Fuels for the process are analyzed and it is compared with the make-and-blow process.

3007. Sablatnög, A. [Purification of Synthesis Gases.] Österr. Chem.-Ztg., vol. 51, 1950, pp. 198–201, 220–223, 242–244; Chem. Abs., vol. 45, 1951, p. 4022.

In cleaning water gas for use in the Fischer-Tropsch synthesis, investigation was made of various purification masses to remove the so-called condensates that passed the usual purifiers and were present in the gas in a concentration of about 1 gm. per m.^{3} The mode of origin, the thermal stability, and the constituents of the condensates are discussed. The water-gas process of Koppers and Didier-Bubiag is described, and it is shown that the amount and composition of the condensates vary widely according to the process used, when the same brown coal was used for gasification. Four purification masses were investigated: (1) A mixture of Fe oxide and Na_2CO_3—this mixture does not remove all organic S compounds; thiophenes especially pass almost undecomposed, and gum-forming hydrocarbons always occur in the gas. (2) Active C—complete removal of gum formers and H_2S could be obtained and the organic S content was down to 0.01 gm. per m.^{3} synthesis gas. The method, however, was objectionable because the active C must be regenerated with a loss of absorption power after each regeneration. (3) Granular coke from brown coal—this cheap material almost equaled active C in purification power, but the service time was very short, so that replacements were often necessary. (4) Addition of finely powdered coke from brown coal to the synthesis gas—this method proved satisfactory and economical. With a gas flow of 50–100 m.^{3} per hr. the condensates with a concentration of 1 gm. per m.^{3} could be entirely removed by adding 30 gm. powdered brown coal coke per m.^{3} of gas, washed out after a contact time of 2–3 sec. The H_2S must be oxidized first by adding 1% air and then removed. The absorption temperature should not be higher than 30° if complete absorption is desired. Finally the method was tested in a large-capacity water-gas plant by using the Didier-Bubiag process. The conditions here were not so favorable as in the pilot plant. The gas had a powdered coke content of only 1–2 gm. per m.^{3}, the temp. was 50°–60°, and the contact time 1 sec. Even under these conditions the condensates concentration dropped from 1.0–1.5 gm. per m.^{3} to 0.2–0.3 gm. These residual condensates can only be removed with a higher coke-dust content, a longer contact time, and lower absorption temperature.

3008. Sachanen, A. N. Conversion of Petroleum. Reinhold Publishing Corp., New York, 2d ed., chap. 2, 1948, pp. 172–181.

Fischer-Tropsch synthesis process and a modification of it. the Hydrocol process, are briefly summarized. The effect of certain operating variables upon the synthesis process, CO : H_2 ratio, catalysts, temperature, pressure, space velocity, and method of operation, are discussed.

———. *See* abs. 3154.

3009. Sachs, A. P. Production of Synthetic Liquid Fuels. Combustion, vol. 13, 1925, pp. 358–360.

Brief discussion of the Badische MeOH process, the Fischer synthol process, and the Bergius process, with comments on the work of Fierz-David along the lines of the Bergius process.

Sachs, G. *See* abs. 2013, 2014.

3010. Sachsse, H. [Chemical Processing of Coking Gas.] Chemie-Ing. Tech., vol. 21, 1949, pp. 1–6; Chem. Abs., vol. 43, 1949, p. 3,595.

Conversion of coking gas to CO and H_2 by means of partial combustion of the main portion of CH_4 and C_2H_4 with O_2 (not air) and subsequent catalytic conversion of the remaining hydrocarbons with H_2O is discussed in detail with data and diagrams. A flow sheet for a N_2–H_2 synthesis gas is described, and a brief comparison of 4 methods for the production of synthesis gas is presented.

———. *See* abs. 149.

3011. Sachsse, H., and Kienitz, H. [Thermodynamics of Hydrocarbon Synthesis.] Ztschr. Elektrochem., vol. 53, 1949, pp. 254–257; Chem. Abs., vol. 44, 1950, p. 2358.

Summary and discussion of 15 yrs. of research on catalysts used in the synthesis of hydrocarbons from CO_2 and H_2.

Sachsze, W. *See* abs. 1649.

Sadek, H., and Taylor, H. S. Heterogeneity of Catalyst Surfaces for Chemisorption. III. Metallic Nickel. *See* abs. 3339.

3012. Sage, B. H. Status of Thermodynamics in the Petroleum Industry. Ind. Eng. Chem., vol. 42, 1950, pp. 631–639; Chem. Abs., vol. 44, 1950, p. 5083.

Status of experimental and derived thermodynamic data for the pure light paraffin hydrocarbons from CH_4 through decane, and for binary mixtures of these hydrocarbons, as well as for some binary mixtures of normal C_1 to C_5 hydrocarbons with the nonhydrocarbon components, CO_2. H_2S, N_2, and H_2O is reviewed. 274 refs.

———. *See* abs. 626.

3013. Sahasrabudhey, R. H., and Kalyanasundaram, A. Interaction of Carbon Monoxide and Hydrogen in Silent Discharge: Production of Formaldehyde. Proc. Indian Acad. Sci., vol. 27A. No. 5, 1948, pp. 366–374; Chem. Abs., vol. 43, 1949, p. 1272.

Report of work dealing with the production of formaldehyde by interaction of CO and H_2 in silent discharge at 500 cycles per sec. The absolute yield of formaldehyde was highest with an approximately equimolecular mixture of the constituent gases. An excess of either CO or H_2 appeared to affect the yield adversely. A decrease in yield was obtained at higher rates of circulation of the gases.

3014. Saitô, S. Saturation Value of Magnetization of Cementite. Sci. Repts. Tôhoku Imp. Univ., vol. 9, 1920, pp. 319–322; Proc. Phys. Math. Soc. Japan, vol. 2, No. 3, 1920, p. 91; Chem. Abs., vol. 15, 1921, p. 1650.

Cementite was electrolytically isolated from a steel containing 1.58% C and pressed into the form of a cylindrical rod. The density ρ was 4.35. The intensity of magnetization was measured in the field of a Du Bois electromagnet. The magnetization reached saturation in a field of over 10,000 gausses, the value found being $\sigma = I/\rho = 135$ C. G. S. units. Measurements also were made on white cast Fe containing 3.75% C. From the known proportion of ferrite and cementite and from the measured saturation value of the specimen, the saturation value of cementite was calculated to be $I = 955$ or $\sigma = I/\rho = 135$, which is the same value as was found directly. The same measurements were made for the double carbides of Fe and W and Fe and Cr and for a number of different steels; the results are given graphically.

———. *See* abs. 1897, 1898, 1899.

3015. Sakata, T. [Effect of Pressure on the Catalytic Reaction Between Hydrogen and Carbon Monoxide.] Rev. Phys. Chem. Japan, vol. 19, 1945, pp. 50–66; Chem. Abs., vol. 45, 1951, p. 3681.

Synthesis of MeOH with a catalyst prepared from CrO_3 and ZnO was studied at 330°–400° in the pressure range 100–300 atm. The content of MeOH in the crude liquid product increased with pressure. A catalyst prepared from $K_2Cr_2O_7$, ZnO, and KOH was used for the synthesis of isobutanol from H_2 and CO. The crude liquid product obtained at 300 atm. was richer in isobutanol than that at 100 atm., but the ratio isobutanol : MeOH was not affected by the pressure.

3016. Sakmin, P. K. [Obtaining Crude Nitrogen–Hydrogen Mixtures for the Synthesis of Methanol and Ammonia.] Jour. Chem. Ind. (U. S. S. R.), vol. 13, 1936, pp. 1459–1462; Chem. Abs., vol. 31, 1937, p. 2783.

To separate coke gas at −160°, the optimum pressure is 100 atm. The gas phase then contains 94% H_2 and N_2, 2% CH_4, and 4% CO and O_2. 90% of the H_2 can be obtained for synthesis.

3017. ———. [Recovery of a Crude Nitrogen–Hydrogen Mixture for Methanol and Ammonia Synthesis by Condensation of Charkow Coke-Oven Gas at Low Temperature and High Pressure.] Brennstoff-Chem., vol. 18, 1937, pp. 69–71; Chem. Abs., vol. 31, 1937, p. 4794.

Resulting mixture, suitable for synthesis use above 1,000 atm., contains 18.4% N_2 and 74.5% H_2.

Sakon, K. *See* abs. 2413, 2425.

3018. Salvi, G. [Synthetic Fatty Acids From Paraffin.] Riv. combustibili, vol. 2, 1948, pp. 221–230; Fuel Abs., 1949, abs. 2932.

Oxidation with air or air–O_2, generally in the presence of $KMnO_4$, was applied on a large scale in Germany for the purpose of working up the gatsch residue from the Fischer-Tropsch synthesis and low-temperature carbonization and producing useful products and artificial fatty acids. The methods are described briefly. The lower fractions, C_4–C_9, were used as plasticizers, the medium fractions, C_{10}–C_{15}, for soaps, and the higher range, C_{18}–C_{20}, for lubricants. A portion of the C_{10}–C_{18} fraction was used for manufacturing triglycerides to make up the shortage of natural fats. These artificial triglycerides with odd number of C atoms were regarded as very suitable ingredients for the diet of diabetics as they are converted to propionic acid and, finally, to CO_2 and H_2O and do not raise the acetone content of the blood above the limit of tolerance as the natural triglycerides do.

———. *See* abs. 2560.

Salzer, F. *See* abs. 938.

3019. Sanbougi, K. Reduction Equilibria of Iron Oxides. I. Measurements of the Equilibria of Reaction. Sci. Repts. Tohôku Imp. Univ., ser. A, vol. 1, 1949, pp. 213–222; Chem. Abs., vol. 45, 1951, p. 6020.

Equilibria equations were derived for the following reactions: Fe_3O_4 (in wüstite) $+ CO = 3$ FeO (in wüstite) $+ CO_2$; Fe_3O_4 (in wüstite) $+ H_2 = 3$ FeO (in wüstite) $+ H_2O$; Fe_3O_4 (in wüstite) $= 3$ FeO (in wüstite) $+ \frac{1}{2} O_2$. Calculations were given of the activities of FeO and Fe_3O_4 in wüstite at several O_2 concentrations and temperatures. Other thermodynamic calculations were made for the various equilibria in wüstite.

3020. Sander, A. [Chemical Transformation of Methane.] Glückauf, vol. 66, 1930, pp. 89–93; Chem. Abs., vol. 24, 1930, p. 2575.

Technical and economic outlook for the transformation of CH_4 into liquid fuel by several new methods developed at the Kaiser Wilhelm Institut für Kohlenforschung, is discussed. In addition to the production of CO–H_2 mixtures for catalytic syntheses, 3 other processes are of economic importance to the welfare of Germany: 1. The thermal conversion of CH_4 into benzol and its homologs 1,000°–1,100°. 2. Conversion of CH_4 into C_2H_2 by means of electric discharges at low pressure and polymerization of the C_2H_2 to benzol over active C or silica gel at 650°–700°. 3. The first step as in 2, then the hydrogenation and condensation of the C_2H_2 in gasoline and homologs over Fe, Cu, Ni, and alkali-mixed catalysts at about 250°.

Sandford, F. *See* abs. 1386.

3021. Sandonnini, C. [Action of Acetylene on Carbon Oxides.] Gazz. chim. ital., vol. 57, 1927, pp. 781–792; Brennstoff-Chem., vol. 9, 1928, pp. 162–163; Chem. Abs., vol. 22, 1928, pp. 758–759.

Following a review of the literature, experiments are described that deal with the reactions of CO and of CO_2 and C_2H_2 in the presence of catalysts, the object of which is to aid in explaining the origin of higher hydrocarbons in the reduction of CO and of CO_2 by H_2. The gaseous mixture was passed over the catalyst at constant temperature and the compositions of the entering and issuing gases were compared.

Sands, A. E. *See* abs. 144a.

3022. Sands, A. E., and Schmidt, L. D. Recovery of Sulfur From Synthesis Gas. Ind. Eng. Chem., vol. 42, No. 11, 1950, pp. 2277–2287.

Review of the more important commercial processes for removing H_2S from synthesis gas made from coal. Factors that differentiate synthesis gas-purification from other gas-purification problems are discussed. The relation between S content of the coal used for synthesis-gas production and the cost of synthesis-gas purification is explored by cost estimates for gas purification and S recovery. These estimates are not to be considered precise or final but have been prepared as a basis for discussion and future revised cost estimates of a more accurate nature.

3023. Sands, A. E., Wainwright, H. W., and Egleson, G. C. Organic Sulfur in Synthesis Gas—Occurrence, Determination, and Removal. Proc. Am. Gas Assoc., 1950, pp. 564–602; Bureau of Mines Rept. of Investigations 4699, 1950, 51 pp.

Progress report on the determination and removal of organic S from synthesis gas with some calculations as to the cost of S removal on a commercial basis. Laboratory studies were made of several known methods for the determination of organic S and details and modifications of the methods are presented. Among the methods investigated were the following: Referee method, Institute of Gas Technology burner method, Rogers and Baldaste method. Betz-Hellige turbidimetric method, Lusby's Pt spiral method, Huffs catalytic method, and the activated C method. In general, purification was found effective down to less than 0.1 grain of total S per 100 cu. ft. of purified gas. Tentative cost estimates of total S removal in a hypothetical plant indicate that costs would decrease from a figure of about $0.01 per 1,000 cu. ft., when the coal S content is 1%, to a cost of about $0.006 per 1,000 cu. ft., when the S content of the coal is 5%. These costs are predicated on the conditions that recovered S is credited at $18.00 per ton, less costs for conversion of H_2S to elemental S and at a plant capacity of 336,000,000 cu. ft. per day.

3024. Sands, A. E., Wainwright, H. W., and Schmidt, L. D. Purification of Synthesis Gas Produced From Pulverized Coal. Ind. Eng. Chem., vol. 40, 1948, pp. 607–620; Chem. Abs., vol. 42, 1948, p. 4330.

Production of synthesis gas directly from coal, instead of using coke as generator fuel, presents new and greater difficulties in connection with purification of the gas to render it suitable for synthesis purposes. With special reference to gas made directly from pulverized coal, this paper outlines the purification specifications for Fischer-Tropsch synthesis gas, some of the established purification processes that may be used to meet these specifications, and the analytical methods that may be used to deal with the extremely low concentrations of impurities that may be tolerated in the purified gas. Bibliography of 92 refs.

3025. Sands, A. E., Grafins, M. A., Wainwright, H. W., and Wilson, M. W. Determination of Low Concentrations of Hydrogen Sulfide in Gas by the

Methylene-Blue Method. Bureau of Mines Rept. of Investigations 4547, 1949, 19 pp.

Colorimetric method has been developed for determining traces of H_2S in synthesis gas used in the Fischer-Tropsch process. The maximum concentration of S that can be tolerated to avoid poisoning of the catalyst is 0.1 grain per 100 cu. ft. The method is applicable not only to synthetic mixtures of CO–H_2 but to coke-oven gas, carburetted water gas, and blue water gas. Mercaptans, CS_2, and thiophene do not interfere with H_2S determination. The preferred absorbent for H_2S is 2% zinc acetate solution. H_2S is determined by the photoelectric or spectrophotometric measurement of the quantity of light absorbed by solutions of methylene blue produced by the reaction of H_2S with p-aminodimethylaniline sulfate. Absorption measurements are made with a Klett-Summerson photoelectric colorimeter, employing a No. 66 filter, and with a Beckman spectrophotometer at a wavelength of 745 mμ. As little as 0.001 grain of S per 100 cu. ft. can be detected by means of this test, when the volume of gas sample is 1 cu. ft. When the gas contains 0.05 grain of S as H_2S, only 1 per 10 cu. ft. of gas is required, and the result is obtained in less than 30 min.

3025a. Sapper, W. Polymerization of Gaseous Olefins to Gasoline Hydrocarbons on Phosphoric Acid Catalysts. Erdöl u. Kohle, vol. 4, 1951, pp. 550–557; Jour. Inst. Petrol., vol. 38, 1952, p. 34 A; Chem. Abs., vol. 46, 1952, p. 1238.

Gaseous olefins and corresponding paraffins are found in cracked gases, in primary and cracked products of the Fischer-Tropsch synthesis, and in primary products of the Hydrocol process, the C_3–C_4 fraction of which consists almost completely of olefins. Polymerization processes embodying phosphoric and sulfuric acid catalysts with low temperature and pressure are used to convert such olefins to gasoline hydrocarbons. Catalytic polymerization of olefinic gases combined with procedures such as thermal cracking, Fischer-Tropsch, and the Carburol Kogasin-cracking process, give marked improvement in gasoline yields, since about 80% of the charge is convertible to high octane number product. Mechanism of reactions, effects of pressure and temperature, influence of molecular size of feed gases, and operating techniques are discussed. The following average yields were obtained on polymerization plant at 30–300 atm. with Fischer-Tropsch olefins as feed: 29% polymer gasoline, 62% propane butane, 5% polymers b. >200° and 4% gases. Polymer gasoline was blended with Fischer-Tropsch primary gasoline; propane-butane fraction was used partly as motor fuel and partly fractionated, propane being sold for domestic use, while butane was used as running-in fuel for aircraft engines. High-boiling polymers were added to Kogasin Diesel fuel, while the gases were used for heating. Differences are noted between the polymerization of naturally occurring iso–C_4 olefins and that of straight-chain synthetic Fischer-Tropsch olefins.

Sarker, J. M. *See* abs. 466.

3026. Sartori, G. [Adsorption of Hydrogen, Carbon Monoxide, and Carbon Dioxide on Zinc Oxide at the Temperature of Synthesis of Methyl Alcohol.] Gazz. chim. ital., vol. 67, 1937, pp. 98–104; Chem. Zentralb., 1937, II, p. 944; Chem Abs., vol. 31, 1937, p. 6077.

Adsorption of H_2 and CO on ZnO is greater at 430° than at 0°–120°. This fact is attributable in part to an activated adsorption and in part to diffusion within the catalyst. CO_2 is adsorbed to a smaller extent at 430° than at room temperature, because at 430° chemical sorption is no longer possible and because diffusion is less than for the lighter gases. Mathematical assumptions made in analyzing the phenomena were verified by the fact that the experimental results could be recalculated in a satisfactory manner with the formulas derived from them. A further confirmation perhaps is to be found in the fact that the velocity constants of adsorption are related in the same way as are the dipolar moments and diffusion constants, that is, inversely to the square roots of the molecular weights of the individual gases. The conclusions that may be drawn from these facts with respect to the catalytic synthesis of MeOH and comparisons of various catalysts will be published in a forthcoming paper.

3027. Sartori, G., and Fano, U. [Adsorption of Hydrogen, Carbon Dioxide, and Methanol on Zinc Oxide.] Gazz. chim. ital., vol. 67, 1937, pp. 69–85; Chem. Zentralb., 1937, II, p. 944; Chem. Abs., vol. 31, 1937, p. 6077.

Work is an extension, with an improved apparatus, of the experiments of Natta and Casazza (abs. 2386). The adsorption isotherms of H_2, CO, CO_2, and MeOH on ZnO at 0°, 36°, 76°, 106°, and 120° were measured. The ZnO was prepared by thermal dissociation of smithsonite. Adsorption of H_2 and CO followed closely the Langmuir law, but that of CO_2 and MeOH showed deviations from this law, as a result of chemical sorption of CO_2 and capillary condensation of MeOH. The periods of permanence of the adsorbed molecules were determined. The periods for CO_2 and MeOH were much longer than for H_2 and CO, and this fact is shown to be related to the character of their adsorption isotherms. The thermal coefficients were not linear functions; this indicates that the centers of adsorption activity at different temperatures have different potentials. The calculated heats of adsorption agree with the experimental values of Taylor and Sickman (abs. 3342). The heat of adsorption of MeOH equals the heat of condensation; this confirms the concept of capillary condensation. The kinetics of adsorption of H_2 can be derived from the equation of Langmuir. CO and CO_2 show deviations proportional to the square roots of their molecular weights, and related to the rates of diffusion in the pores of the catalyst. The kinetics of adsorption of MeOH can be derived by dividing the phenomenon into 2 phases, an instantaneous phase and an exponential phase.

3028. Sartori, G., and Newitt, D. M. Influence of Pressure Upon the Water-Gas and Other Equilibria. Inst. Gas Eng., Copyright Pub. 222–92, 21 pp.; Gas World, vol. 111, 1939, pp. 414–415; Gas Jour., vol. 229, 1940, pp. 32, 81; Chem. Abs., vol. 34, 1940, p. 5337.

Effect of pressure upon the equilibrium constants of reversible gas reactions is discussed. At high pressures, the partial pressure of a reactant gas is not a true measure of its active mass, hence, even in gaseous systems in which reaction takes place with no change in density, the value of equilibrium constant K_p shows a drift with progressive changes in the total pressure. Experimental data for the water-gas reaction over a pressure range of 100 atm. are given. By replacing partial pressures by equilibrium pressures, a true constant independent of total pressure is obtained. Compressibility and other derived physical properties of reversible gaseous systems are discussed and illustrated by references to the variation of heat capacity with pressure.

3029. Sastri, M. V. C. Theory of the Fischer-Tropsch Synthesis. Current Sci., vol. 16, 1947, pp. 4–5; British Abs., 1948, B, I, p. 95.

Review of the theory of the formation of a carbide surface and its limited reduction to long CH_2 chains, stressing the importance of the chemisorbed H_2 in the disruptive reduction of these chains to molecules of appropriate length.

———. *See* abs. 1192, 1193, 1193a, 1194.

3029a. Sastri, M. V. C., and Srikant, H. Adsorption of Hydrogen at Elevated Pressures on a Promoted Iron-Synthetic Ammonia Catalyst. Current Sci., vol. 19, 1950, p. 313; Chem. Abs., vol. 45, 1951, p. 9,993.

Static volumetric method for measuring adsorption gases by solids at elevated pressures was developed, d the adsorption of H_2 on a Fe–K_2O–Al_2O_3–TiO_2 talyst at temp. 50°–350° and pressures 15–50 atm. s studied. 2 distinct types of activated adsorption H_2 were found, 1 with a maximum at about 150°, other with a maximum at about 300°. The results dicate the superposition of adsorption on the chemrption of the H_2.

30. ———. Adsorption of Nitrogen at Elevated Pressures on a Promoted Iron Synthetic-Ammonia Catalyst. Current Sci., vol. 19, 1950, p. 343; Chem. Abs., vol. 45, 1951, p. 7406.

Adsorption isotherms were determined for N_2 on an e–K_2O–Al_2O_3–TiO_2 catalyst at 7 temperatures 50°–50°, and 15–50 atm. Adsorption at lower pressures 20 and 30 atm.) exhibits only 2 maxima at 150° and 00°, respectively; however, at 50 atm., 3 maxima are observed, 100°, 200°, and 300°. For an adsorption of 0.05–0.15 cc. per gm. at 20 atm., a value of 23 kcal. s obtained for the isobaric heat of adsorption.

3030a. ———. Mixed Adsorption of Hydrogen and Nitrogen at Elevated Pressures on a Promoted-Iron Synthetic-Ammonio Catalyst. Current Sci., vol. 20, 1951, pp. 15–16; Chem. Abs., vol. 45, 1951, p. 10018.

An Fe–K_2O–Al_2O_3–TiO_2 catalyst was used. The individual adsorption of H_2 and N_2 from a 3:1 mixture were determined on the same catalyst at 50°–350° and at a total gas pressure up to 50 atm. Adsorption of H_2 from the mixture increased regularly with its partial pressure at all the temperatures studied, whereas that of N_2 exhibited this regularity only at the highest temperature. In practically every case the adsorption of H_2 at a given partial pressure from the mixture was considerably higher than that from the pure gas at an equivalent pressure. Similarly, except at 203° and 300°, N_2 adsorption was increased in the presence of H_2. At 350° when the partial pressure of N_2 exceeded 7 atm., the ratio of the respective increments of N_2 and H_2 adsorption varied successively from 1 N : 1 H, through 1 N : 2 H, to finally 1 N : 3 H. These observations suggested the successive formation of –NH–, –NH_2, and NH_3 complexes on the active surface of the catalyst.

Sastry, S. L. *See* abs. 1185.

Sato, K. *See* abs. 12.

3031. Sauerland, W. [Iron Carbide.] Neue Giesserei, Tech.-Wiss. Beihefte 1, 1949, pp. 43–44; Chem. Abs., vol. 44, 1950, p. 5242.

Relations among heat of reaction, reaction entropy, reaction work, and equilibrium constant are indicated for the reaction $3Fe + C = Fe_3C$. Up to 627°, the reaction does not proceed spontaneously. Although the driving force of the reaction increases with increasing temperature, the equilibrium in this range remains on the side $3Fe + C$. Numerical values for the reaction heat, entropy, work, and equilibrium constant are given at 100° intervals for the temperature range 300°–900° K.

3032. Sauvageot, —. [Delayed Solution and the Premature Precipitation of Cementite in Eutectoid and Hypereutectoid Carbon Steel.] Compt. rend., vol. 173, 1921, pp. 297–300; Chem. Abs., vol. 15, 1921, p. 3813.

Temperature necessary for complete solution of cementite is not always proportional to the C content but depends to a considerable extent on the initial condition of the Fe_3C.

Sawada, Y. *See* abs. 1893, 1894, 3314.

3033. Sawamura, H. [Dissociation of Carbon Monoxide in Contact With Various Kinds of Iron Ore.] Tetsu-to-Hagane, vol. 22, 1936, pp. 121–126; Japan. Jour. Eng., vol. 16, p. 122; Chem. Abs., vol. 33, 1939, p. 4500.

Sawamura made experiments on 2 important behaviors of CO in contact with various kinds of Fe ore in a more rigid manner than was done in the experiments hitherto published, namely: (1) The dissociation velocity of CO at 450°; (2) effect of C deposited in Fe ore owing to the dissociation of CO upon the disintegration of Fe ore. For this purpose, 13 kinds of original ore, besides 5 agglomerated and 1 roasted ore, were taken as samples. For measuring the dissociation velocity of CO, Honda's thermobalance was used. Disintegration of Fe ore heated in CO takes place when it expands, owing to the C deposited in it. This expansion was measured by a special dilatometer, the so-called gas-dilatometer devised by Sawamura. No definite relation could be found between the experimental results and the porosity and the content of Fe having 2 valences in Fe ore. It was found, however, that the dissociation velocity of CO is greater when in contact with hematite or limonite than when in contact with magnetite, and that hematite or limonite in CO is liable to disintegrate more easily than magnetite.

3034. Sayers, R. R. Natural-Gas Research; Its Importance and Possibilities. Am. Gas Assoc. Monthly, vol. 26, 1944, p. 247.

After the recovery of liquid hydrocarbons from condensate wells, these gas wells become a reservoir of dry gas, and research is now in progress for the utilization of this gas as a source of liquid hydrocarbons by the Fischer-Tropsch process.

3035. Scarlott, C. A. Bright New Future of Coal. Westinghouse Eng., vol. 7, 1947, pp. 143–149.

Review of information taken from many sources on the processing of coal to produce liquid fuel. The article discusses our fuel reserves, gas synthesis by Fischer-Tropsch process, coal hydrogenation, high- and low-temperature coke making, underground gasification of coal, and the factors affecting coal conversion, including costs and economic possibilities.

3036. ———. [Future for Coal.] Rev. quim. ind., vol. 18, No. 212, 1949, pp. 16–19; British Abs., 1950, B, I, p. 827.

Account of the Fischer-Tropsch process for making synthetic fuels and of the Bergius hydrogenation process, the steps of the processes being shown in diagrams. Brief note on the possibilities of the underground gasification of coal.

3037. Schaarschmidt, A., and Marder, M. [Synthetic Benzine From Water Gas.] Brennstoff-Chem., vol. 13, 1932, pp. 412–413; Chem. Abs., vol. 27, 1933, p. 2017.

Heptane fraction of the aliphatic portion of synthetic benzine by the Fischer-Tropsch process has been found, with 20 mol. % $SbCl_5$ at 0°, to consist of ⅓ R_3CH-type hydrocarbons and ⅔ *N* or quaternary hydrocarbons.

3038. Schade, H. A., Foran, E., and Aldrich, R. C. Fischer-Tropsch Process. Nat. Petrol. News, vol. 37, No. 45, 1945, p. R924; CIOS Rept. VI–22, X–18, X–22, XV–5, 1944, 25 pp., PB 373; TOM Reel 199; Chem. Abs., vol. 40, 1946, p. 7565.

Further extract from a study of the Harnes plant in France. The plant capacity was 20,000 ton of liquid products per yr. One-third of the water gas (CO, 40; H_2, 50; CO_2, 5; N_2 and CH_4, 5%) produced from high-temperature coke in water-gas generators of conventional design was passed over a catalyst of FeO at 500° with steam, giving a product rich in H_2 and CO_2.

This gas was blended with the rest of the original water gas to give a synthesis gas (CO, 27; H_2, 54; CO_2, 14; N_2 and CH_4, 5%). S was removed in 3 stages: A countercurrent tower wash with NH_3 water to remove H_2S; passage through purifying boxes containing Fe oxide and sawdust; and removal of organic S by passing over a catalyst of FeO and Na_2CO_3 at 200°–300°. The gas ready for synthesis is compressed to 3 p. s. i. before entering the 24 reactors, all cooled by a hot water-steam system so arranged that each pair of reactors shares a common header and control valve. A cooling system capable of removing approximately 7,000 B. t. u. of heat per lb.-mol. of liquid product is important for 2 reasons: The reaction must occur at a definite temperature range (in this case 200°+or−3°), enough to promote the reaction but not so high as to decompose the products into CH_4, and the catalyst itself is a very poor conductor of heat. Therefore, to prevent a hot spot in the catalyst bed, the mean path of heat travel from any catalyst particle to the cooling surface is kept below 2 mm. The reactors are square boxes consisting of 600 thin baffles pierced by 600 tubes filled with hot water. Each reactor has a total surface of 5,000 m.^{2} and weighs 50 metric tons. The catalyst fills the voids between baffles and tubes. The density of the reactor thus filled is approximately 60% of that of solid steel. Of the 24 reactors, 16 are normally used for the 1st pass. The effluent from these is cooled and condensed, and the resulting heavy product is removed. The gases are sent next to the remaining 8 reactors for the 2d pass, which produces a lighter product than the 1st pass.

3039. Schaub, —. [Removal of the Heat of Reaction in the Synthesis of Hydrocarbons.] Erdöl u. Kohle, vol. 3, No. 1, 1950, p. 9.

Paper presented at the 1949 meeting of the Deutsche Gesellschaft Mineralölwissenschaft u. Kohlechemie. Discusses derivation of equations for the conductivity of heat in catalytic reactions, such as those of the Fischer-Tropsch synthesis.

3039a. Schaub, F. [Applications and Limitations of the Fluidization Technique.] Chem. Ing.-Tech., vol. 24, 1952, pp. 98–103; Chem. Abs., vol. 46, 1952, p. 3810.

Discussion of factors which influence the fluidized state, of dust removal, solids transport, heat transfer, and pressure drop. Some of the applications mentioned are catalytic cracking of hydrocarbons, Fischer-Tropsch synthesis, coal hydrogenation, gas generation.

3040. Scheepers, L. [Catalytic Dissociation of Carbon Monoxide.] Rev. univ. mines, vol. 19, 1943, pp. 121–131; Chem. Zentralb., 1943, II, pp. 1782–1783; Chem. Abs., vol. 38, 1944, p. 5720.

Experiments on the dissociation of CO with catalysts of the Fe group, according to $2\ CO=CO_2+C+36.4$ kcal., are described in which the dissociation of CO was investigated with natural magnetite and, at the same time, the reduction of the Fe_3O_4 contained therein in a semiautomatic apparatus under a current of gas. The crushed magnetite was separated into 3 fractions of which the 1st (largest) was strongly magnetic, the 2d (smaller) weakly magnetic, and the 3d (about 3%) nonmagnetic with no dissociating action. The strongly magnetic material had, in a constant gas current, at first a small and then increasing reaction; the formation of CO_2 tended to assume a constant value, even though the reduction was not yet complete. With increasing temperature the dissociation increased up to a maximum at 550° and then decreased again. The less magnetic material had a much stronger and almost immediate action. Although the 1st fraction gave, at 515°, at the start, only 2 cc. CO_2 per hr., an addition of 0.2 gm. of the 2d fraction increased CO_2 formation suddenly to 760 cc. per hr. Natural magnetite, crushed but not separated magnetically, showed an increase of CO_2 formation with decreasing flow velocity of the gas and with decreasing grain size. The catalytic effect of a mixture of Fe_2O_3–Al_2O_3 was investigated also with regard to the effect of CO, in which it seems that the Fe produced by the reduction leads to the dissociation of the CO. Two types of such mixed catalyst are prepared (*A*) by precipitating the Fe hydroxide from a suspension of Al and calcining of the product at 750° and (*B*) by simultaneous precipitation of both substances and calcining as before. Results show at first a period of rapid CO_2 formation, which gradually slows down and becomes stationary. The catalyst mixture with 15% Al had an effect superior to all others and to Fe_2O_3. The destruction of ceramic materials (lining of blast furnaces) by CO is probably due to C precipitations in the vicinity of Fe-containing impurities, whereby even minute amounts of C are enough to disintegrate the brick.

3041. Scheer, W. [Synthesis of Aliphatic Benzines From Low-Molecular Hydrocarbons.] Oel u. Kohle, vol. 38, 1942, pp. 691–696; Chem. Abs., vol. 36, 1942, p. 5974.

Use of the low-molecular hydrocarbons produced as byproducts in the hydrogenation or synthesis of higher hydrocarbons from pit coal and lignite, the polymerization of the olefins they contain, and the condensation of the saturated and unsaturated hydrocarbons present by known processes is discussed.

3042. ———. [Franz Fischer and the Chemistry of Coal.] Glückauf, vol. 80, 1944, pp. 76–78.

Chronological survey of Fischer's work as director of the Kaiser Wilhelm Institut für Kohlenforschung. The first results of the research by Fischer and Tropsch on oil synthesis from water gas were attained in 1922 when Synthol, a mixture of hydrocarbons, acid-containing compounds, and lower alcohols, was produced by conducting the $CO+H_2$ mixture over alkalized Fe catalyst at 100–150 atm. pressure and 400°–450°. It was later discovered that by using a Zn–Cr oxide catalyst, MeOH could be produced. Further tests, largely by varying the catalyst, led in 1926 to the Kogasin synthesis, by which the same synthesis gas, under normal pressure and temperature around 200°, was converted into saturated hydrocarbons of the paraffin series ranging from CH_4 to high molecular paraffins. In conjunction with Koch, Meyer, and Roelen, this process was so far perfected that in 1934 the Ruhrchemie A.-G. established it on a commercial scale. Experiments were continued to raise the yield of solid paraffins, and, in 1936, Fischer and Pichler developed the medium-pressure synthesis with the Co catalyst at 10 atm. pressure. A year later the use of an Fe catalyst was established. The next development was the use of the Ru catalyst and the production of still higher paraffins. The high versatility of the Fischer synthesis was next revealed by the discovery that, under specific conditions, the formation of unbranched paraffins could be curtailed and the production of branched hydrocarbons promoted. These hydrocarbons as produced by the so-called isosynthesis are distinguished by their high antiknock value. Thus, the final development by Fischer before his retirement in October 1943, went far to correct a serious disadvantage positively connected with the original benzine synthesis process, that of a low-octane fuel.

———. *See* abs. 2044.

Scheffer, F. E. C. *See* abs. 2243, 2244, 2245, 2246, 2247.

3043. Scheffer, F. E. C., Dokkum, T., and Al, J. [Dissociation of Methane.] Rec. trav. chim., vol. 45, 1926, pp. 803–816; Chem. Abs., vol. 21, 1927, p. 690.

Continuous current method has been replaced by one of circulation of the gas. Both C_2H_4 and CH_4 were used as a source of activated C obtained in the presence of Ni as a catalyst. An account of the preparation of the gas and manner of carrying on experiments is outlined carefully. The reaction was studied 480°–680°, since below these temperatures, C reacts with the Ni catalyst. The substance formed is stable at 340°–420° and has an exothermic formation. Mathematical deductions of the 2 equilibrium curves are given from data obtained at atmospheric pressure and different temperatures.

3044. Scheil, E. [Stability of Iron Carbide at High Pressure.] Ztschr. anorg. Chem., vol. 158, 1926, pp. 175–180; Chem. Abs., vol. 21, 1927, p. 848.

By means of temperature-concentration diagrams and from theoretical considerations, a *p*, *t*, *x*, diagram has been built up, showing that Fe_3C is stable at high pressure.

3045. Schellenberg, A. [Decomposition of Methanol by Metals and Metallic Oxides.] Ges. Abhandl. Kenntnis Kohle, vol. 7, 1925, pp. 9–12; Chem. Zentralb., 1926, I, p. 3298; Chem. Abs., vol. 21, 1927, p. 3531.

Compilation of literature on thermal decomposition of MeOH by various contact substances.

———. *See* abs. 1045, 1046, 3460, 3461, 3464.

3046. Schenck, H. Einführung in die physikalische Chemie der Eisenhüttenprozesse. Die Grundstoffe und Grundreaktionen der Eisenhüttenprozesse. J. Springer, Berlin, 1932, vol. I, pp. 137–170; Chem. Abs., Vol. 26, 1932, p. 4293.

Literature review and critical discussion of the reactions $2\ CO \rightleftharpoons CO_2+C$; the equilibrium constants of Fe_3O_4 with CO–CO_2 mixtures, $3\ Fe+2\ CO \rightleftharpoons Fe_3C+CO_2$; Fe carbonyl; and the water gas reaction, $CO+H_2O \rightleftharpoons CO_2+H_2$, and H_2–H_2O with Fe_3O_4.

3047. Schenck, R. [Decomposition of Carbon Monoxide. Correction.] Ber. deut. chem. Gesell., vol. 36, 1903, pp. 3663–3664; Jour. Chem. Soc., 1904, II, p. 28.

There are a few corrections of the numbers in the previous paper (abs. 3068). These do not affect the main deductions already given.

3048. ———. [Chemical Equilibrium in the Reduction and Cementation of Iron.] Ztschr. Elektrochem., vol. 24, 1918, pp. 248–255; Jour. Soc. Chem. Ind., 1918, A, p. 624; Chem. Abs., vol. 14, 1920, p. 396.

In the interaction between Fe and CO, the Fe is carburized by C resulting from the decomposition of the CO. This is concluded from a comparison of the temperature and pressure equilibrium involved in this reaction and those involved in the reaction $C+CO_2 \rightleftharpoons 2\ CO$. The unpublished work of Juschkewitsch on the equilibrium between 618°–718° in the reaction $C+CO_2 \rightleftharpoons 2\ CO$ in which metallic Co was used as a catalyzer furnishes the missing data for the temperature-pressure curve and makes possible the comparison. The presence of the C resulting from the action $Fe+CO$ is not shown by the usual treatment with HCl, since, having interacted with the ferrite, it is present as carbide. The equilibrium between ferrite, carbide, and the oxides of Fe and C exist at low pressures. The CO content of the gaseous phase is somewhat larger than that in the equilibrium $C+CO_2 \rightleftharpoons 2\ CO$. The carbide obtained in this manner is different from cementite Fe_3C in that it does not decompose into $Fe+C$ on being heated to 400° and, according to theoretical consideration, contains less C. This new carbide is likened to a manganese carbide, which is different from Mn_3C and contains enough C to correspond to Mn_2C or Mn_6C. The new Fe carbide is named bunsenite after Robert Bunsen.

3049. ———. [Equilibrium Relations Between Iron, Oxygen, and Carbon.] Stahl u. Eisen, vol. 46, 1926, pp. 665–682; Chem. Abs., vol. 21, 1927, p. 1743.

It is established from data on indirect reduction of Fe oxides by CO, that, in addition to magnetic Fe oxide and FeO, solid solutions of these in one another and in Fe take part in the equilibria as O-containing phases. The probable presence of an Fe suboxide, stable only below 720°, is deduced from these equilibria. The equilibria for the system Fe, Fe carbide, CO, CO_2 cannot be determined experimentally because of simultaneous oxidation, but data for the system Fe, Fe carbide, CH_4, H_2 are given, and from these the constants for the first named system are calculated. The results are used to deduce the conditions for indirect cementation of Fe by CO and CH_4 as well as for direct cementation processes. From the equilibrium between Fe and CO below 600°, the existence of a percarbide of Fe, with a considerably higher C vapor pressure than cementite or elementary C, is rendered probable. The equilibrium isotherms for CO–CO_2 in the presence of Fe are determined and from them a space model showing the relation between temperature, pressure, and concentration in the gaseous phase is constructed; from this a curve is derived for the relation of gas composition to temperature, which is very similar to curves experimentally obtained from observations on blast furnaces. Information on the equilibria in ore-roasting processes is derived from these isotherms.

3050. ———. [Equilibrium Relations in the Reduction, Oxidation and Carburization of Iron. I.] Ztschr. anorg. Chem., vol. 164, 1927, pp. 145–185; Chem. Abs., vol. 21, 1927, p. 3334.

Thorough study of the systems represented by the following 2 reactions is undertaken: (I) $CH_4=C+2H_2$, (II) $CH_4+3Fe=Fe_3C+2H_2$. CH_4 was prepared either by treating Al_4C_3 with water or by fractionating liquefied natural gas. H_2 was prepared electrolytically and by the action of Al on alkali. To facilitate reaction the Fe used was deposited on porous pieces of pumice. The pumice was soaked in $Fe(NO_3)_3$ solution, heated to redness, and the Fe was obtained by reduction in H_2. Pure Fe_3C was prepared by the action of CH_4 on Fe at 700°. The reactions 300°–500° were carried out in a Jena glass tube heated to constant temperatures by contact with liquids at their boiling points. Reactions 500°–900° were carried out in porcelain tubes heated in an electric tube furnace, the temperature being kept constant to within 2°. The progress of reactions (I) and (II) at the various temperatures was followed by reading the pressure developed in the reaction tubes. No CH_4 is decomposed by Fe at 300°. At 350°, about 1% by vol. is decomposed, and the presence of Fe_3C can be detected. At 445°, about 4.4% is decomposed. The proportions are the same if H_2 is passed over heated Fe_3C, thus proving the existence of a true equilibrium in reaction (II). The decomposition of CH_4, according to reactions (I) and (II), is plotted against the temperature. Above 695°, the curve for (II) has 2 branches. One along which CH_4 and H_2 are in equilibrium with ferrite and dilute carbide-ferrite mixed crystals, the other along which the gases are in equilibrium with Fe_3C and concentrated carbide-ferrite mixed crystals. The points of similarity between the systems studied and the Fe–C system are pointed out. Using his experimental results, Schenck calculates that the heat of formation of Fe_3C is −15,405 cal., in close agreement with the values obtained calorimetrically. This is taken as a proof that the observations made really pertain to the equilibrium represented by reaction (II). Schenck outlines the application of the findings to problems arising in the carburization of Fe by hydrocarbons. From the data obtained for systems (I) and (II) and the previously determined equilibrium relations in the system $2\ CO=C+CO_2$, are calculated and plotted the equilibrium relations, which, theoretically, should exist in the system $3\ Fe+2\ CO=Fe_3C+CO_2$.

3051. Schenck, R., Krägeloh, F., and Eisenstecken, F. [Equilibria in the Reduction, Oxidation, and Carburization of Iron. II. Methane-Hydrogen Equilibria in the Presence of Cobalt.] Ztschr. anorg. Chem., vol. 164, 1927, pp. 313–325; Chem. Abs., vol. 21, 1927, p. 3799.

Authors wish to show whether the equilibrium conditions resulting from the action of Co upon CO are solely those due to the reaction (1) $2\ CO \rightleftharpoons C + CO_2$, or whether other equilibria involving a Co carbide also must be considered. The results of an incomplete series of experiments performed in 1914 are given. At that time, Co was considered to act solely as a catalyst in the recation mentioned above and no carbide equilibria were thought to be involved. Doubt in the matter has led the authors to determine the equilibrium conditions in the closely related system $CH_4 \rightleftharpoons C + 2\ H_2$ catalyzed by Co. The procedure is the same as that used in the system $Fe–CH_4$ (abs. 3050). The primary reaction is a catalytic decomposition of the CO according to (I). Co is a better catalyst for this reaction than Fe. Superimposed upon this equilibrium is another involving Co carbide. This equilibrium is reached more slowly than the former. Both equilibria are studied quantitatively over the range 310°–740°. Above 680°, the reaction involving the carbide is no longer encountered. Although Co carbide was not isolated, its properties are predicted. The parallelism between the effects of Fe_3C and Co carbide on the decomposition of CH_4 leads the authors to believe that, as with Fe, it is likely that Co carbide forms mixed crystals with Co. The heat of formation of Co carbide is found by calculation to be —11,300 cal. The authors draw the following conclusions with regard to the influence of Co upon equilibrium (I): Above 668° the influence is purely catalytic; below this temperature it is difficult to explain the equilibrium relations unless the existence of dilute mixed crystals of Co carbide in Co is postulated.

3052. Schenck, R., Dingmann, T., Bökmann, J., Ebert, W., Kesting, W., Lepetit, G., Müller, J., and Pratje, W. [Equilibrium Relations in the Reduction, Oxidation, and Carburization of Iron. III. (4). Systematic Investigations of the Oxidation-Reduction Relations Existing in the Systems of the Iron Oxides With Iron, Carbon Monoxide, and Carbon Dioxide.] Ztschr. anorg. Chem., vol. 166, 1927, pp. 113–154; Chem. Abs., vol. 22, 1928, p. 566.

Continuation of the work that will finally lead to knowledge of the equilibrium relations in the system $Fe–C–O_2$. A precision method is used to determine the equilibrium relations in the systems $Fe_3O_4 + CO \rightleftharpoons 3\ FeO + CO_2$ and $FeO + CO \rightleftharpoons Fe + CO_2$, the vapor phase in each case being a mixture of CO and CO_2. Simultaneously the regions of stability of solid solutions of FeO and Fe_3O_4 and of FeO and Fe were established. The method used allowed the oxides of Fe to interact at a definite temperature with a small quantity of CO until equilibrium was established. The gaseous phase consisting of CO and CO_2 then was withdrawn and analyzed. These small additions of CO were continued until the oxides were deoxidized almost completely. The material composing the boat containing the oxides had a pronounced influence upon the equilibria resulting. The presence of MgO or SiO_2 produced noticeable changes in the equilibrium curves. Similar changes in the curves would result from the addition of any foreign substances likely to form solid solutions with the Fe oxides or to combine with them. Al_2O_3 produces little effect. By plotting the % of CO or CO_2 in the gas phase against the temperature, the equilibrium diagram is obtained. It discloses an invariant point, 560°, at which Fe, FeO, Fe_3O_4, CO, and CO_2 can coexist. The existence of 2 solid solutions is shown: (1) A solution of small quantities of Fe_3O_4 in FeO for which the name "wüstite" is coined, and (2) a solution of small quantities of FeO in pure Fe for which the name "oxoferrite" is coined. Wüstite exists only above the nonvariant point, 560°, and 76% Fe, 24% O_2. Below this it separates in Fe_3O_4 and oxoferrite. FeO was not encountered as an independent solid phase, and it is, concluded, therefore, that this oxide cannot be made in a stable condition at temperatures up to 1,100°. Below 560° Fe_3O_4 can be deoxidized to oxoferrite directly. Adding MgO to the system lowers the invariant point markedly and broadens out the area of existence of wüstite. The authors intend to study in detail the influence of CaO, Al_2O_3, MnO, and SiO_2. The practical value of these researches is discussed.

3053. ———. [Equilibrium Relations in the Reduction, Oxidation, and Carburization of Iron. IV. (5). Iron Carbide, Iron Oxides, and Iron Under an Atmosphere of Carbon Monoxide and Carbon Dioxide.] Ztschr. anorg. Chem., vol. 167, 1927, pp. 254–314; Chem. Abs., vol. 22, 1928, p. 937.

FeO is prepared by heating FeC_2O_4 in vacuo. It is mixed with powdered Fe and finely divided C, and the mixture is subjected to a CO_2 atmosphere at definite temperatures. The concentrations of CO and CO_2 are determined after equilibrium has been established. Wüstite and oxoferrite are formed as has been reported. The addition of small quantities of Hg to the system reduced the solubility of FeO in Fe and, thus, produced an oxoferrite (solid solution of FeO in Fe) of relatively low O_2 content. Likewise the wüstite formed was poorer in O_2 and, hence, was nearer FeO in composition. The $CO–CO_2$ atmosphere above the mixture also was poorer in the O_2-rich CO_2 than was the case when Hg was absent from the mixture. This is another illustration of the marked influence that foreign substances have upon the equilibrium in the $Fe–C–O_2$ system. Quantitative studies of the influence of additions of other substances are in progress. Pure Fe was partly changed to Fe_3C by cementation, CH_4 being used. This carburized mixture then was allowed to come to equilibrium at various temperatures under an atmosphere of CO and CO_2. Both C and O_2 are absorbed by the solid phases. The results indicate a bivariant equilibrium with the following 3 phases: (1) Gaseous (CO and CO_2); (2) Fe_3C; (3) ternary solid solution of Fe_3C, FeO, and Fe. For the ternary solid solution the name "oxoaustenite" is suggested. This solution also is undoubtedly present in the univariant equilibrium mixtures of wüstite, oxoferrite, CO, and CO_2, since the solid phases always yield either free C or hydrocarbons upon treatment with diluted acids. The reaction between Fe_3C and Fe_2O_3 and Fe_3O_4 was studied by heating known mixtures to 600°, 650°, and 700°. When equilibrium has been attained, the pressure and composition of the evolved gases are determined. The following concurrent reactions occur: (1) $4\ Fe_3C + Fe_3O_4 \rightleftharpoons 15\ Fe + 4\ CO$, (2) $2\ Fe_3C + Fe_3O_4 \rightleftharpoons 9\ Fe + 2\ CO_2$. An isotherm at 650° shows the equilibrium existing at definite total pressures and definite concentrations of CO. The phases appearing are Fe_3O_4, wüstite, Fe_3C, oxoaustenite, and gas. The equilibrium diagram is given for the system wüstite–oxoferrite–oxoaustenite from 600°–1,000° at 1 atm. pressure and under varying concentrations of CO.

3054. Schenck, R. [Equilibrium in the Reduction, Oxidation, and Carburization of Iron. V.] Ztschr. anorg. Chem., vol. 167, 1927, pp. 315–328; Chem Abs., vol. 22, 1928, p. 2132.

Summary of the previous papers in this series. The 3-dimensional equilibrium model of the system $Fe–C–O_2$ is discussed, the system being under an atmosphere of CO and CO_2 and at various temperatures 500°–1,000°. An isobar at 1 atm. shows the concentrations of CO and CO_2 and the temperatures at which the following will be stable: Fe_3C, Fe_3O_4, wüstite, oxoferrite, and oxoaustenite. Isotherms at 50° intervals 542°–1,000° show the range of stability of the above-mentioned substances when under pressures ranging from 0–1,200 mm. The remarkable influence that impurities have upon the equilibrium is stressed again. The effect of MgO is given in detail. Problems for future solution are: (1) The systematic investigations of the influence of impurities; and (2) the determination of the composition of the solid solutions oxoferrite and oxoaustenite as they exist under various gas pressures and compositions.

3055. Schenck, R., and Dingmann, T. [Equilibrium Relations in the Reduction, Oxidation, and Carburization of iron. VI.)7). Solubility of Oxygen in Iron.] Ztschr. anorg. Chem., vol. 171, 1928, pp. 239–257; Chem. Abs., vol. 22, 1928, p. 3612.

Polemical. 16 refs. (*See* abs. 193.)

3056. Schenck, R., and Klas, H. [Equilibrium Relations in the Reduction, Oxidation, and Carburization of Iron. VII. (8). Cobalt in a Methane–Hydrogen Atmosphere.] Ztschr. anorg. Chem., vol. 178, 1929, pp. 146–156; Chem. Abs., vol. 23, 1929, p. 2116.

Two reactions are possible, 1 in which Co acts purely as a contact substance, expressed by the equation $CH_4 \rightleftharpoons C + 2\ H_2$, and 1 in which the formation of carbide occurs; $n Co + CH_4 \rightleftharpoons Co_n C + 2\ H_2$. The system is investigated in the range 680°–900°, and the composition of the gas phase is varied between 0 and 100% for both H_2 and CH_4, with small additions of CO and N_2. The presence of Co–Co carbide mixed crystals follows from the gradual increase in % CH_4. At first more diluted mixed crystals are formed, which are in equilibrium with low CH_4 concentrations. With carbide increase in the solid solution, CH_4 concentration increases, reaching its maximum when saturation with carbide is attained, and the occurrence of the pure carbide phase begins. This saturation concentration of CH_4 is about 18% at 680°, 15% at 700°, 14% at 720°, 10% at 760°, 7.5% at 800°, and 3.7% at 900°. Co carbide is found to be more stable than Fe carbide. Complete decarburization is not obtained with less than 97% H_2 in the gas phase. Phase diagrams are given that show the limits of the mixed crystal field.

3057. Schenck, R., Dingmann, T., Kirscht, P. H., and Wesselkock, H. [Equilibrium Studies of the Reduction, Oxidation, and Carburization Processes of Iron. VIII. (9). System Iron–Oxygen.] Ztschr. anorg. Chem., vol. 182, 1929, pp. 97–117; Chem. Abs., vol. 24, 1930, p. 44.

Object was to study the minima attained in the oxidation of Fe with small quantities of CO_2 and their dependence upon the O_2 content of the basic material. The O_2 saturation of the homogeneous *oxyferrite* phase at different temperatures likewise was determined. The metal used in the experiments was carefully freed of H_2 by many days heating in a high vacuum, while the gas used was pure CO_2 gas under diminished pressure or, in a few cases, mixtures of CO_2 and CO. At 700°, the reaction velocity was very slow, while at 1,000° the stable zone was reached in the course of the 1st day. The stable *wüstite-oxyferrite* equilibrium corresponds at 700° to a gas phase composition of 40.3% CO_2 and 59.7% CO, at 800° to 35.1% CO_2 and 63.9% CO, and at 1,000° to 28.5% CO_2 and 71.5% CO. At 800° and 1,000° the O_2 taken up in homogeneous solid solution is about 0.4%, the higher values previously obtained being due to the occurrence of a metastable wüstite poor in Fe_3O_4. With mixtures of $CO_2–CO$, the relation between CO and CO_2 in the gas phase was determined along the stable wüstite-oxyferrite boundary. The new values for maximum O_2 content require a diminution in the extent of the oxyferrite zone in the Fe–O equilibrium diagram. The possibility of preparing FeO in the pure state is discussed, and it is suggested that small additions of MgO or MnO would increase the stability of FeO. Addition of 0.5%, 1.0%, and 4.0% Cu as well as 4% Ni was studied and resulted in a slight displacement of the wüstite-oxyferrite border toward higher CO_2 concentration, as well as a more rapid attainment of the stable wüstite-metal boundary. The solubility of O_2 is reduced more than 50%.

3058. Schenck, R., Franz, H., and Willeke, H. [Equilibrium Relations in the Reduction, Oxidation, and Carburization of Iron. IX. (10). Influence of Foreign Oxides Upon the Equilbria.] Ztschr. anorg. Chem., vol. 184, 1929, pp. 1–38; Chem. Abs., vol. 24, 1930, p. 1788.

By means of an apparatus and a method previously described, the effect of MnO, ZnO, BeO, CaO, and Al_2O_3 on the equilibrium obtained during the reduction of Fe oxides by CO was studied. The mixed oxides usually were obtained by the ignition of a mixture of the corresponding nitrates, which had been formed by evaporation of a solution. In the case of the lime mixtures, mixed hydroxide and carbonates were ignited; the MnO mixtures were obtained by ignition of a mixture of oxalates. The molecule mixtures used were Fe_2O_3: MnO 1 : 8, 1 : 1, 2 : 1 at 800°; Fe_2O_3 : ZnO 1 : 1, 2 : 1, 1 : 10 at 700°, Fe_2O_3 : Al_2O_3 1 : 10, 1 : 3, 1.5 : 1 at 800°, 900°; Fe_2O_3 : CaO 1 : 10, 1 : 1, 1.5 : 1, 3 : 1 at 900°, 1.050° Fe_2O_3 : BeO 2 : 1, 1 : 1, 1 : 18 at 800°. Even when the foreign oxide is not reduced by CO it affects the equilibrium of the Fe_2O_3 reduction if it (1) forms mixed crystals with the oxides of Fe, for example, Al_2O_3 with Fe_2O_3 or MnO with FeO; (2) forms compounds with the oxides of Fe as spinels or ferrites. This is the case with Al_2O_3, MnO, ZnO, and particularly with CaO. The mixed crystals become more difficult to reduce than the wüstite phase, the greater the content of foreign oxide. Oxides that form neither mixed crystals nor compounds do not affect the equilibrium in any way, for example, BeO. ZnO does not affect the wüstite-metal equilibrium. The reduction of ZnO by CO is hampered by the presence of any oxide phase of Fe.

3059. Schenck, R., Dingmann, T., Kirscht, P. H., and Kortengraber, A. [Equilibrium Investigations of the Reduction, Oxidation, and Carburization Process of iron. X. (11). The System: Iron–Oxygen; Abnormal Oxidation: Activation of Iron Without Additions.] Ztschr. anorg. Chem., vol. 206, 1932, pp. 73–96; Chem. Abs., vol. 26, 1932, p. 4571.

Constancy of weight of Fe foil in a stream of $CO_2–CO$ (19.15% CO_2) at high temperatures is due to the compensation of 2 effects, oxidation and the loss of small quantities of volatile Fe carbonyl. In a CO-rich atmosphere Fe powder gives up Fe carbonyl, but its formation is suppressed if the CO_2 content of the atmosphere is above that corresponding to the stable metal-wüstite limit. The high absorption of O_2 observed with finely powdered Fe is attributed to the presence of active particles, which are oxidized in a $CO_2–CO$ mixture, the composition of which is below the normal metal-wüstite range.

3060. Schenck, R., Franz, H., and Laymann, A. [Equilibrium Investigations in the Reduction, Oxidation, and Carburization Processes of Iron. XI.] Ztschr. anorg. Chem., vol. 206, 1932, pp. 129–151; Chem. Abs., vol. 26, 1932, p. 5521.

Influence of the oxides of Si, Ti, and P upon reduction equilibrium was studied. Reduction to metal is most favorable with wüstite free from added oxides, and, in practice, the goal is to add suitable materials, which will favor the greatest possible wüstite formation.

3061. Schenk, R., and Dingmann, T. [*Equilibrium* Studies in the Reduction, Oxidation, and Carburization Processes of Iron. XII.] Ztschr. anorg. Chem., vol. 209, 1932, pp. 1–10; Chem. Abs., vol. 27, 1933, p. 1302.

Micro methods of gas analysis used in this series of investigations are described. Apparatus is shown for the accurate collection and analysis of small quantities of CO_2 and CO, depending on CO_2 absorption and measurement of the residual volume of CO. Where the gas mixture contains other constituents, a type of micro Orsat apparatus is used, containing, however, no rubber connections. CO is not determined by absorption but is burned to CO_2 and then absorbed. Unsaturated hydrocarbons are absorbed in fuming H_2SO_4, but the time of contact must be limited to 3–5 min. to prevent absorption of some CH_4 and H_2. If CH_4 content is high, it is better to keep it below 40% by adding H_2, otherwise some of it will be converted into CH_3OH or CH_2O in the combustion pipet. Details of the apparatus are shown in sketches.

3062. Schenck, R., Laymann, A., and Jenckel, E. [Equilibrium Investigations in the Reduction, Oxidation, and Carburization Processes of Iron. XIII.] Ztschr. anorg. Chem., vol. 235, 1937, pp. 65–76; Chem. Abs., vol. 32, 1938, p. 2418.

System Fe–O–Ca was studied by determining the decomposition diagrams of Fe_2O_3–CaO mixtures at 900° and with a range of 23–79% CO_2 in the atmosphere. The following phases are found to exist: Fe_3O_4, wüstite, $CaO.Fe_3O_4$, and $(CaO)_2.Fe_2O_3$. In the presence of even small concentrations of CO in the atmosphere, the phase $CaO.Fe_2O_3$ cannot exist. The results are plotted with triangular coordinates.

3063. Schenck, R. [First Stages in the Development of Our Views Concerning the Equilibrium System Iron–Carbon–Oxygen.] Ztschr. Elektrochem., vol. 34, 1928, pp. 399–403; Chem. Abs., vol. 23, 1929, p. 2086.

Reply to Falcke's criticisms (abs. 867).

———. Equilibrium in the Reduction, Oxidation, and Carburization of Iron. V. *See* abs. 3054.

Schenck, R., and Dingmann, T. Equilibrium Relations in the Reduction, Oxidation, and Carburization of Iron. VI. (7). Solubility of Oxygen in Iron. *See* abs. 3055.

———. Equilibrium Studies in the Reduction, Oxidation, and Carburization Processes of Iron. XII. *See* abs. 3061.

3064. Schenck, R., and Heller, W. [Reactions in the Reduction of Iron.] Ber. deut. chem. Gesell., vol. 38, 1905, pp. 2132–2139; Jour. Chem. Soc., 1905, II, p. 526.

When CO is heated with metallic Fe, the pressure observed after equilibrium is attained is extremely small, and it appears that virtually all the gas is removed. This is due to the oxidation of the Fe and the deposition of the C in the solid form. As pure CO cannot oxidize Fe, it is assumed that the Fe reacts in 2 ways: (1) Catalytically decomposing the CO into C and CO_2, and (2) as a reducing agent on the CO_2, producing ferrous oxide and CO. These 2 reactions proceed until equilibrium is established between Fe, ferrous oxide, C, CO, and CO_2. The partial pressures of CO and CO_2 and also the sum of these are dependent on the temperature only. For each temperature there is a definite partial pressure for each oxide and a definite total pressure. It thus follows that in the blast furnace ferrous oxide will only be reduced by CO in the presence of C if the total pressure of the CO and CO_2 is less than the pressure of the total equilibrium. If, on the other hand, the pressure of the gas mixture at the given temperature is greater, then the reoxidation of the Fe occurs and deposition of C. The pressures for the total equilibrium for temperatures 400°–800° have been determined by 2 methods: (1) Heating CO with finely divided Fe and measuring the pressure when equilibrium is attained; and (2) heating ferrous oxide and C in a vacuum and determining the pressure at fixed temperatures. The 2 methods give concordant results. Some of the numbers are: 468°, 10.3 mm.; 620°, 81.5 mm.; 728°, 438 mm.; and 780°, 780 mm. Similar experiments were performed with Mn, and, as this is much more readily oxidized than Fe, the pressures are smaller: At 1,200°, 10 mm.; 1,229°, 15.3 mm.

Schenck, R., and Klas, H. [Equilibrium Relations in the Reduction, Oxidation, and Carburization of Iron. VII. (8). Cobalt in a Methane–Hydrogen Atmosphere.] *See* abs. 3056.

Schenck, R., and Meyer. [Carbide Studies in the Methane Synthesis. IV. Chemistry of Double Carbide.] *See* abs. 3072.

———. [Studies of Carbides by the Methane Synthesis Method.] II. *See* abs. 3070.

3065. Schenck, R., and Stenkhoff, R. [Decomposition of Iron Carbide by Acids.] Ztschr. anorg. Chem., vol. 161, 1927, pp. 287–303; Chem. Abs., vol. 21, 1927, p. 2091.

Cementite (C, 6.69; Fe, 98.25; Si, 0.04; SO_4, 0.08%) prepared in the usual way and freed from ferrite and pearlite was treated separately with 600 cc. H_2SO_4 (I) (1/30, 1/3, 5 *N*) benzenesulfonic acid (II) (0.5, 1 *N*) and AcOH (III) (1, 3 *N*) in the presence of 0–220 gm. of the corresponding ferrous salts. Determinations using 0.2 gm. cementite were conducted for 3 weeks at 60°. The amount of free C precipitated increases with the increase in concentration of ferrous ion and the decrease in strength of acid. The decrease or even failure in the formation of hydrocarbon is the result of the impossibility to attain the thermodynamically possible maximum yield owing to low reaction velocity; the depression of the H-ion concentration by anions and the simultaneous ennobling of the Fe owing to ferrous ions. According to the mass law these phenomena should supplement each other. The results for the strong acid (II) are not in accord, but this probably is due to absorption of the acid by the C, thus indicating in the analysis an erroneously high value for C. The results are given in tables and graphs.

3066. Schenck, R., and Wesselkock, H. [Activation of Metals by Addition of Foreign Substances. I.] Ztschr. anorg. Chem., vol. 184, 1929, pp. 39–57; Chem. Abs., vol. 24, 1930, p. 2035.

Effect of CaO, MgO, MnO, and Al_2O_3 separately and Al_2O_3 and MgO jointly on the oxidation of Ni and Co at 900° in an atmosphere of CO_2 was studied. The mixtures M:MO (1:10): M:Al_2O_3 (1:3); M:Al_2O_3:MgO (1:10:2) were usually prepared by reduction in H_2 of mixtures of nitrates or oxalates that had been precipitated together. (*See* abs. 3055, 3057, and 3058). The equilibria appearing after the addition of CO_2 at 900° were determined as previously described. The activities of both Ni and Co were increased by the presence of the oxides in the order CaO, MgO, MnO. These oxides have the same crystal lattice as NiO and CoO. The activity does not seem to be closely related to the similarity of crystal lattice constants of these oxides with those of Ni and Co. The irregularities in the progress of the oxidation are attributed to the heterogeneous distribution of the reduced metal in the oxide. This heterogeneity, which is most evident in the Co–MnO mixtures, is due to the fact that the mixed oxalates are not homogeneous. Determination of the gaseous equilibrium by fractional oxidation (successive addition of small quantities of CO_2) offers a method for measuring the uniformity of distribution of the metal in the oxide as well as determining the areas containing metal of similar degree of dispersion. This lack of uniformity may explain the centers of activity often met in mixed catalysts. The mixtures Co–3 Al_2O_3 and Ni–3 Al_2O_3 exceed finely reduced Fe in activity. The addition of MgO to these mixtures enhanced their activity. The activation seems to be specific for O. The general problem of the activity of metals toward specific elements is indicated by the observations reported. When the O is transferred from the CO_2 to the metal, which is dispersed in the isomorphous oxide, it takes a position in the lattice occupied before reduction by O_2. If it is desired to activate a metal toward N_2 the nitride of the metal should be dispersed throughout a stable isomorphous nitride and then reduced to metal. The reasoning is carried over to activation toward S.

3067. Schenck, R., Kurzen, F., and Wesselkock, H. [Activation of Metals by Foreign Substances. II.] Ztschr. anorg. Chem., vol. 206, 1932, pp. 273–288; Chem. Abs., vol. 26, 1932, p. 4549.

Fe and W in MgO make it difficult to form carbide by action of CH_4, if in the carbides of these metals 1 C atom is attached to several metallic atoms, as in Fe_3C or W_3C_2. Carbide formation is not hindered by the addition of inert oxides if the carbide consists of an equal number of metal and C atoms, as WC. These experiments show that linkage of metal atoms with a C atom can only occur with a favorable spatial distribution of the metal atoms.

3068. Schenck, R., and Zimmermann, F. [Decomposition of Carbon Monoxide and Chemical Equilibrium in the Blast Furnace.] Ber. deut. chem. Gesell., vol. 36, 1903, pp. 1231–1251; Jour. Chem. Soc., 1903, II, pp. 423–425.

Reversible reaction $2\ CO \rightleftharpoons CO_2 + C$ has been studied as a true reaction in the presence of metals and metallic oxides. The metals employed, Fe, Co, and Ni and their oxides, were deposited on pumice, which had been reduced in a stream of pure H_2 and then extracted with diluted HCl. By this means, the whole of the original Fe compounds in the pumice were removed. The oxides were obtained by saturating the pumice with solutions of the metallic nitrates and then strongly heating. The oxides of Co and Ni completely oxidize CO to CO_2 at 445° and they are reduced to the metallic state. With Fe oxide only part of the CO is oxidized. With a gaseous mixture containing 1 CO : 4 CO_2 no reduction of the Fe oxide occurs, and the pressure remains constant. The CO_2 obtained by Boudouard must have been due to the oxidation of the CO by the Fe oxide and not to the catalytic decomposition of the CO. Finely divided metals accelerate the decomposition of CO into C and CO_2 in a remarkable manner. With Ni at 445° the reaction has been shown to be bimolecular and should be represented as $2\ CO = C + CO_2$; at 310° and 360°, however, the reaction appears to be unimolecular and probably occurs in 2 stages: $CO = C + O$ and then $CO + O = CO_2$, the 2d reaction proceeding much more rapidly than the first. The reaction does not appear to be complete but is reversible, and a state of equilibrium is established even at temperatures of 445°. When Co is used, the numbers agreed with neither a unimolecular nor a bimolecular reaction. This probably is due to Fe contained as an impurity in the Co. When Fe is used, the pressure never becomes absolutely constant so long as any gas is present, and ultimately the whole of the C present is deposited in the free state and Fe oxide is formed. It would appear that the Fe first reacts as a catalyzer, decomposing the CO into C and CO_2. When the concentration of the CO_2 has increased and that of CO decreased to a certain limit, the metal begins to reduce the CO_2, and the 2 reactions then proceed simultaneously so that the composition of the gas remains the same. Experiments made at 360° and 445° indicate that the reaction is unimolecular but that at 508° it becomes bimolecular. The compositions of the gaseous mixtures are as follows:

360° 10.5% CO and 89.5% CO_2,
445° 52.8% CO and 47.2% CO_2,
508° 47.1% CO and 52.9% CO_2.

The numbers obtained at 260° probably indicate the presence of some oxide other than ferric oxide.

Schenck, R., Franz, H., and Laymann, A. [Equilibrium Investigations in the Reduction, Oxidation, and Carburization Processes of Iron. XI.] *See* abs. 3060.

Schenck, R., Franz, H., and Willeke, H. [Equilibrium Relations in the Reduction, Oxidation, and Carburization of Iron. IX. (10). Influence of Foreign Oxides Upon the Equilibria.] *See* abs. 3058.

Schenck, R., Krägeloh, F., and Eisenstecken, F. [Equilibria in the Reduction, Oxidation, and Carburization of Iron. II. Methane-Hydrogen Equilibria in the Presence of Cobalt.] *See* Abs. 3051.

3069. Schenck, R., Kurzen, F., and Wesselkock, H. [Studies of Carbides Prepared With Methane. I.] Ztschr. anorg. Chem., vol. 203, 1931, pp. 159–187. Chem. Abs., vol. 26, 1932, p. 1536.

Formation and composition of the carbides of Fe, Cr, W, Mo, and Re are followed by analysis of the CH_4 and H_2 gases in equilibrium over the carbide. Results with Fe justify the method Cr at 600°, 700° and 800° forms a carbide, Cr_3C_2, and a mixed crystal phase containing 11.5% C (probably containing Cr_3C_2). W forms the stable WC at 800°. At 700°, the unstable W_3C_2 is observed as well as a mixed crystal phase, the composition of the higher carbide being uncertain. Mo forms the single stable Mo_2C at 800° and the metastable phase MoC at 700°. The reaction of CH_4 with Re is too slight for definite observation.

3070. Schenck, R., and Meyer, K. [Studies of Carbides by the Methane Synthesis Method. II.] Ztschr. anorg. Chem. vol. 239, 1938, pp. 161–179; Chem. Abs., vol. 32, 1938, p. 8900.

Carbonization of Mn and CH_4 is studied in the temperature range 700°–970°. CH_4:H_2 equilibrium measurements indicate a change of state at 740° and 955°. Below 740°, Mn_3C is not present as a pure compound, though solid solutions of this compound appear. Mn_4C exists in a metastable state between 700° and 750°. Above 750° and up to 950° Mn_3C exists independently. It can take up more C to form a solid solution phase whose saturation limit at 970° is about 9% C. In the range 750°–950°, the saturation limits of a solid solution phase poorer in C could be determined. Appreciable differences from the conclusions of Vogel and Döring (abs. 3570) in the number and limits of the phase fields are indicated.

3071. Schenck, R., Meyer, K., and Mayer, K. [Carbide Studies in the Methane Synthesis. III.] Ztschr. anorg. Chem., vol. 243, 1939, pp. 17–31; Chem. Abs., vol. 34, 1940, p. 4974.

Space isotherm for the Mn–Fe–C system at 800° was constructed by measuring displacements in the equilibrium, $Mn + CH_4 \rightleftharpoons MnC + 2\ H_2$, at 760 mm. The space model shows 4 zones of the compositions indicated: *A*, containing (1) a field of β–Mn and a weak MnC phase, (2) a field of mixed crystals of γ–Fe, (3) a field of mixed crystals of β–Mn and γ–Fe; *B*, containing as its fundamental phases a univariant equilibrium γ–Fe and carbides of Mn; *C*, a univariant equilibrium containing Mn carbides; *D*, in which $(Mn, Fe)_3C$ and a C-rich phase (7.4% C) prevail. An alloy, 95% Mn+5% Fe, shows a maximum solubility of C (8.4%). In the steel region, the isotherms of C show several small fields corresponding to various groups of Mn steels.

3072. Sckenck, R., and Meyer, K. [Carbide Studies in the Methane Synthesis. IV. The Chemistry of

Double Carbide.] Ztschr. anorg. Chem., vol. 243, 1940, pp. 259–268; Chem. Abs., vol. 34, 1940, p. 4974.

From the carbonization isotherms at 800° for 7 mixtures of Fe and W, a space model for the overall isotherms was prepared. By projection on the base, 6 fields were obtained, having the following compositions: *A*, consisting of the double carbide $Fe_6W_6C_6$ and γ–Fe; *B*, α–Fe, W, and $Fe_6W_6C_6$; *C*, η–W, $Fe_6W_6C_6$, and $FeW_{21}C_7$; *D*, mixed crystals of W (containing C and Fe) and $FeW_{21}C_7$; *E*, α–FE (containing W); *F*, α– and β–Fe (stable). $Fe_6W_6C_6$ is considered a compound of Fe_3C and W_2C; it decomposes above 800° into graphite and mixed crystals. Other carbides are indicated by vapor-pressure measurements on the CH_4 phase.

Schenck, R., Kurzen, F., and Wesselkock, H. [Activation of Metals by Foreign Substances. II.] *See* abs. 3067.

Schenck, R., Laymann, A., and Jenckel, E. [Equilibrium Investigations in the Reduction, Oxidation, and Carburization Processes of Iron. XIII.] *See* abs. 3062.

Schenck, R., Meyer, K., and Mayer, K. [Carbide Studies in the Methane Synthesis. III.] *See* abs. 3071.

3073. Schenck, R., Semiller, H., and Falcke, V. [Experimental Studies on the Reduction and Carbide Formation of Iron.] Ber. deut. chem. Gesell., vol. 40, 1907, pp. 1704–1725; Jour. Soc. Chem. Ind., 1907, p. 692; Chem. Abs., vol. 1, 1907, p. 2772.

Gas pressures at temperatures 550°–700° were measured in the following systems: (1) Fe, FeO, C (amorphous), CO, CO_2; (2) Fe, FeO, graphite, CO, CO_2; (3) Fe_3C, FeO, C (amorphous), CO, CO_2; (4) Fe_3O_4; FeO, C (amorphous), CO, CO_2. Moreover, in order to define the state of these systems completely, the composition of the gas phase was determined. The data enabled prediction of the proper conditions for the formation of Fe carbide, at any temperature, or for the formation of any of the other phases. The authors conclude that the equilibrium $C+CO_2 \rightleftharpoons 2\,CO$ varies with the form of C employed. Unfortunately the observations could not be carried above 700° on account of complications owing to the formation of mixed crystals between Fe and cementite. Mn lowers the pressure of the C oxides to a striking degree.

Schenck, R., Dingmann, T., Kirscht, P. H., and Kortengraber, A. [Equilibrium Investigations of the Reduction, Oxidation, and Carburization Processes of Iron. X. (11). The System: Iron-Oxygen; Abnormal Oxidation; Activation of Iron Without Additions.] *See* abs. 3059.

Schenck, R., Dingmann, T., Kirscht, P. H., and Wesselkock, H. [Equilibrium Studies of the Reduction, Oxidation, and Carburization Processes of Iron. VIII. (9). System Iron–Oxygen.] *See* abs. 3057.

Schenck, R., Dingmann, T., Bökmann, J., Ebert, W., Kesting, W., Lepetit, G., Müller, J., and Pratje, W. [Equilibrium Relations in the Reduction, Oxidation, and Carburization of Iron. IV. (5). Iron Carbide, Iron Oxides, and Iron Under an Atmosphere of Carbon Monoxide and Carbon Dioxide.] *See* abs. 3053.

———. [Equilibrium Relations in the Reduction, Oxidation, and Carburization of Iron. III. (4). Systematic Investigations of the Oxidation-Reduction Relations Existing in the Systems of the Iron Oxides With Iron, Carbon Monoxide and Carbon Dioxide.] *See* abs. 3052.

3074. Schenk, —. [Carbon Dioxide Content of Thorium and Magnesium Catalysts.] FIAT Reel K29, frame 7,184, 1938; PB 70,218; TOM Reel 296.

It is established that the CO_2 content of catalysts is subject to variations according to the degree of dryness, but that within these variations no difference exists in the CO_2 content between Th and Mg catalysts.

3075. ———. [Influence of the Reduction and the Granular Form of Cobalt Catalysts on the Cobalt Density.] FIAT Reel K–29, frames 7,164–7,165, 1938; PB 70,218; TOM Reel 296.

It is established by tests that, by reduction, an increase of the Co density of 25% (Co–kieselguhr ratio 1: 1) and 5% (Co–kiselguhr ratio 1: 2) is obtained. Besides that, the Co density depends on the method of grinding the kieselguhr. 1 table.

3076. ———. [Manufacture of a Cobalt–Magnesium Catalyst.] FIAT Reel K–20, frames 47–49, January 31, 1938, PB 70,211; TOM Reel 287.

Catalyst substance consists of 100 parts of Co, 15% of MgO, 200 kieselguhr. It is prepared as follows: 3.2 kg. soda are heated with 30 l. of distilled H_2O until boiling; then the boiling Mg solution is slowly added while stirring. The boiling Co solution now is added, and the mixture is stirred for a further 30 sec. After 2 kg. of kieselguhr has been added, the whole is thoroughly stirred again and then suction filtered, and the cake is washed with hot distilled H_2O for ½ hr. Care must be taken that the cake always is covered with a H_2O layer of 1 cm. thickness. After washing, the cake is mashed with 50 l. of distilled H_2O in a precipitating vessel, the dust from the shaping process being added. After discharge into the suction filter, the H_2O is exhausted, and the cake is pressed. The small pieces are dried in the drying oven.

3077. ———. [Manufacture of Thorium–Magnesium Thread Grain Catalyst.] FIAT Reel K–20, frames 44–46, Feb. 1, 1938, PB 70,211; TOM Reel 287.

Solution of Th and Mg nitrates is added to the Co solution before precipitation. Then all 3 parts are precipitated at once. After the thread grain has been formed, dried, and sieved, the continuous reduction takes place. The reduced grain falls directly into an impregnation container filled with oil. After drying, the grain is emptied into tight Fe barrels.

3078. ———. [Reducibility of Cobalt Catalysts.] FIAT Reel K29, frames 7, 134–7, 135, 1938; PB 70,218; TOM Reel 295.

It is established by experiments that the reducibility of a constant volume of 3 types of catalysts (Co–Th–, Co–Th–Mg–, and Co–Mg–) decreases with an increasing proportion of kieselguhr, and that, with a kieselguhr proportion of 200, about 3 times the quantity of H_2 is necessary to reduce Th–Mg and Mg catalysts, compared with pure Th catalyst under otherwise equal conditions. 1 diagram.

3079. ———. [Regeneration of Cobalt Solutions From Catalyst Production.] FIAT Reel K–29, frames 7,124–7,128, 1938; PB 70,218; TOM Reel 296.

Description of tests on the regeneration of Co solutions by evaporation by which up to 90% of the Co has been recovered in form of lime-free Co nitrate salt. 2 tables.

3080. ———. [Cobalt–Nickel Catalysts.] FIAT Reel K–21, frames 1119–1121, July 22, 1941, PB 70,212; TOM Reel 288.

When ThO_2 was used as activator and under normal precipitating conditions, 35–50% of the Co was replaced successfully by Ni. The catalysts thus obtained showed fairly normal activity and satisfactory yields but a considerably lowered durability. In medium-pressure synthesis, the same catalysts, because of low activity, showed diminished Co output and correspondingly lower yields. The abundant formation of CH_4 in case of synthesis gas can be avoided by operating with water gas. Paraffin is formed only in insignificant amounts. Increased addition of Mn has no considerable influence on this. The boiling point is virtually the same with synthesis gas and with water gas.

3081. ———. [Wet Synthesis.] FIAT Reel K–22, frames 1242–1249. FIAT Reel K–31, Jan. 20, 1942, pp. 1108–1115; Bureau of Mines Transl. T–459, July 8, 1948; TOM Reel 274, frames 1620–1631.

Wet synthesis experimental test was performed in 2 reactors: The 1st containing 55 l. of catalyst-oil mixture, the 2d, 85 l. Ten l. of catalyst (100 Fe : 5 Cu : 10 Mn : 100 kieselguhr) per reactor were found to give the highest conversion yield (73–75% in a single stage and 93–94% in 2 stages). The theoretical yield of 170 gm. has been reached in a 2-stage test with a total conversion of $CO+H_2=90–93\%$. The average operating temperature varied 230°–250°. The synthesis pressure was 15 atm. The formation of CH_4 was lower throughout than in the corresponding dry synthesis test. When catalysts are used that produce paraffin preferentially and have a low tendency for producing CH_4, and average gasification of 3–4% may be counted on with a total conversion of 70–90%. The consumption ratio $CO:H_2$ was shifted towards the H_2 side in comparison with the dry synthesis. In the 1st stage, the ratio was mostly greater than 1; 1.30. In the 2d stage, however, the reverse is true, and the consumption ratio is equal to about $CO:H_2=1.0:0.90$. The total consumption rato in the 1st and 2d stages corresponds to the proportion in the water gas and varies between 1:1.24 and 1:1.26. As in the dry synthesis, the composition of the products depends primarily on the nature of the catalysts and secondarily on experimental conditions such as temperature, pressure, circulation, etc. The products are always somewhat more saturated than in the dry synthesis. The tests have been run for 7.5 weeks without much reduction in activity. The gas throughput consisted of 1 synthesis gas to 2.5–3.0 recycle gas.

———. *See* abs. 2880.

Schenk, P. *See* abs. 408.

Schessler, D. O. *See* abs. 3501.

3082. Scheumann, W. W., and Rescorla, A. R. Aromatic Adsorption Index as Rapid Method for Approximating Catalyst Activity. Oil Gas Jour., vol. 46, No. 28, 1947, pp. 231–232, 234; Petrol. Refiner, vol. 26, No. 12, 1947, pp. 815–817; Petrol. Processing, vol. 2, No. 12, 1947, pp. 946–947; Chem. Abs., vol. 42, 1948, p. 1726.

This paper was presented at the 27th annual American Petroleum Institute meeting in Chicago. Of the various test methods for evaluating the activity of a catalyst, 2 have been used in the authors' laboratory: The Kellogg fluidized fixed-bed activity test based on a standardized laboratory cracking and the aromatic adsorption index based on surface area reactions. This paper presents data showing the degree of correlation between the 2 methods on both natural and synthetic fluid catalysts. A modified procedure, based upon the ability of a cracking catalyst selectively to adsorb aromatic hydrocarbons from a hydrocarbon mixture, is described in detail as better meeting personnel requirements and time limits for performing the tests. The test, in brief, is carried out by first heat treating the catalyst sample at a temperature of 850° F. A 3.5-gm. sample is then weighed into an adsorption vessel to which is added 5 ml. of a hydrocarbon mixture consisting of 30% toluene and 70% isooctane. The adsorption vessel is shkaen for 2 hr., after which the refractive index is determined on the supernatant liquid. The aromatic adsorption index is the difference between the refractive index of the original hydrocarbon mixture and that of the hydrocarbon mixture, after contact with the catalyst multiplied by 10^4.

Schibsted, H. *See* abs. 1454.

3083. Schick, F. [Developments in Coal Processing.] Braunkohle, vol. 24, 1926, pp. 1065–1070; Chem. Abs., vol. 20, 1926, p. 2240.

Discussion of cracking and hydrogenation processes and of the Synthol and synthetic MeOH processes.

3084. Schiller, G. [Synthetic Fats as Basis of Saturated Fatty Acids.] Ztschr. Lebensm. Untersuch. Forsch., vol. 88, 1948, pp. 174–190.

Review of the synthesis of fatty acids and fats by the Fischer-Tropsch method.

———. *See* abs. 1711, 1713, 1715, 1717.

3085. Schiller, P. Oil Synthesis in Relation to Electricity and Gas Supply. Engineering, vol. 167, 1949, pp. 17–18; Fuel Abs., vol. 5, 1949, abs. 4976.

Relative overall thermal efficiencies of coal carbonization and electricity generation are discussed and the coal-economy efficiencies of gas and electricity are compared. There is every reason to expect the gradual replacement of natural petroleum products by synthetic products in the more distant future. The manufacture of synthetic hydrocarbons from coal is considered in some detail, particularly from the economic standpoint. A decline in the use of gas for domestic and industrial purposes is anticipated, but a far wider field for the carbonizing industry is expected in the combined carbonization and synthesis plants of the future.

Schindler, H. *See* abs. 873, 874, 875, 876, 877, 878, 1477.

3086. Schlapfer, P. [Manufacture of Replacement Fuels in Switzerland.] Schweiz. Ver. Gas- u. Wasserfach., Monats-Bull., vol. 18, 1938, pp. 49–60; Chem. Abs., vol. 32, 1938, p. 7241.

Review of the nature and extent of the national fuel requirements, and a discussion of the processes available for manufacture of motor fuels in Switzerland from domestic materials. In the absence of any quantity of suitable coal, peat and wood are suggested as raw materials for the synthesis of gasoline. High-pressure hydrogenation hardly can be considered for Swiss conditions. Synthesis by the Fischer-Tropsch process is practicable in small units and can be arranged to utilize wood, lignin, or mixtures of these with coke; there is also the possibility of using electrical energy in place of coke and in the preparation of H_2 by electrolysis. Cost estimates are presented, and the energy balance of various methods for producing fuel are shown. Each of these processes is discussed, and reference is made to the possibility of supplementary industries associated with the hydrolysis of wood and to the desirability of maximum recovery of motor fuel from gas works.

3087. ———. [Gas Research and Gas Evaluation.] Schweiz. Ver. Gas- u. Wasserfach., Monats-Bull., vol. 25, 1945, pp. 3–7, 61–68, 77–82; Chem. Abs., vol. 40, 1946, p. 7565.

Lecture reviewing recent developments in gas technology, especially various types of Fischer-Tropsch reactions, with their economic significance for Switzerland.

3088. Schlattmann, O., and Koppenberg, H. Motor Fuel Produced From Coal by 3 Processes in Germany. Trans. World Power Conf., 3d Conf., II, 4–5, September 1936, 20 pp.; Nat. Petrol. News, vol. 28, No. 37, 1936, pp. 24E–24H, 26, 28, 30, 32, 34; Chem. Abs., vol. 30, 1936, p. 8569.

Motor fuel is produced by high-pressure hydrogenation of coal and the products recovered therefrom; by low-temperature carbonization and extraction by synthesis; and by low-temperature carbonization, distillation, cracking, and extraction. The properties of gasoline produced from each method are compared. It is seen that the types of gasoline obtained by hydrogenation and synthesis are fully equal to the refined gasolines obtained from crude oil. The raw material consumption per kg. of gasoline and the smallest economical operating unit for the various raw materials are as follows: By high-pressure hydrogenation of brown coal, 2.5 kg. and 40,000 tons; of bituminous coal, 1.66 kg. and 40,000 tons; of low-temperature brown coal tar, 1.25 kg. and 35,000 tons; by synthesis from brown-coal briquets, 10 kg. and 25,000 tons; from bituminous-coal coke, 5.4 kg. and 20,000 tons. Taking into account all the sources of energy, the thermodynamic efficiency (energy of finished products/energy of raw material) of the synthetic process lies 0.2–0.3, compared with 0.3–0.4 for the hydrogenation process.

3089. Schleede, A., Richter, M., and Schmidt, W. [Zinc Oxide as a Catalyst.] Ztschr. anorg. Chem., vol. 223, 1935, pp. 49–83; Chem. Abs., vol. 29, 1935, p. 6827.

ZnO prepared by the thermal decomposition of Zn $(NO_3)_2$ at 360° luminesces oranged-red when excited by ultraviolet light or X-rays; and it does not catalyze the decomposition of MeOH at 360°. The luminescence is caused by the presence of twinning planes or boundary surfaces formed by the crystallizing together from the nitrate melt of crystallites into compact particles of ZnO. The lack of catalytic action is due to the compact nature of the product. On the other hand, ZnO prepared by the thermal decomposition of hydrated $Zn(OH)_2$ or $ZnCO_3$ at 360° does not luminesce, but it is a very active catalyst for the MeOH decomposition. Inasmuch as this ZnO was not crystallized from a melt, it lacks the twinning planes that cause fluorescence, whereas its noncompact, porous character favors catalytic action. Extreme purity of the initial substances used in preparing the ZnO is not a factor involved in these differences in behavior. The properties of ZnO prepared by other methods may lie between these 2 extreme cases. The luminescence of ZnO may be used analytically as an indication of the method of its preparation. The crystalline structure, size of the crystallites, and surface development of several differently prepared samples of ZnO were studied by means of Debye and Scherrer structure diagrams, by weighing and microcounting, by the determination of the degree of packing when jolted, by precipitation velocities, and by the adsorption of CO_2 and N_2.

3090. Schlesinger, M. D., Crowell, J. H., Leva, M., and Storch, H. H. Fischer-Tropsch Synthesis in the Slurry Phase. Ind. Eng. Chem., vol. 43, No. 6, 1951, pp. 1474–1479.

Study has been made of the slurry process as a means of developing an improved method for synthesizing liquid hydrocarbons from coal. A finely divided Fe catalyst suspended in oil is circulated by natural convection through a reactor in the presence of CO and H_2. A pilot-plant operation is described. and the effect of operating conditions on the synthesis is discussed. An increase in CO conversion with increasing temperature was noted, as was the formation of light hydrocarbons. The effect of operating pressure on light hydrocarbon production was found to be small; an increase in pressure at constant space velocity is accompanied by increased synthesis gas conversion. On a basis of the CO reacted, 5% appeared as C_1+C_2 hydrocarbons, 43% as heavier hydrocarbons (58% of which boiled in the gasoline range), and 42% as CO_2. Large amounts of oxygenated compounds were obtained in the light-oil and H_2O fractions. Potentially important advantages for the slurry process are indicated by the improved temperature control, mass transfer, and flexibility of operation.

3091. Schmahl, N. G. [Hydrolysis of Carbides.] Ztschr. Elektrochem., vol. 40, 1934, pp. 68–70; Brennstoff-Chem., vol. 15, 1934, p. 154; Chem. Abs., vol. 28, 1934, p. 2288.

It is known that in the hydrolysis of various carbides, hydrocarbons are produced. Thus, in the decomposition of (Ca, Sr, Ba, Mg, Be) C_2, of (Li, Na, K, Rb, Cs)$_2$ C_2 and of $Al_2(C_2)_3$ with H_2O, C_2H_2 is formed, while with Al_4C_3 and Be_2C, CH_4 and with Mg_2C_3 propyne is obtained. The reason for the formation of specific hydrocarbons is that in the decomposition at every point of the carbide lattice through oxide formation and the splitting of the lattice, determined amounts of H_2 and energy are available, which are divided among the hydrocarbon atoms present. Thus, in the decomposition of BeC_2, only C_2H_2, and in that of Be_2C only CH_4 can be produced according to the equations: $BeC_2+H_2O=BeO+C_2H_2$ and $Be_2C+2H_2O=2BeO+CH_4$. The relations are not quite so clear when mixtures of various hydrocarbons are produced. With the carbides of the rare earths besides other hydrocarbons, C_2H_2 and CH_4 are formed, in the ratio of 3:1, according to the equation: $4XC_2+6H_2O=2X_2O_3$ (hydrate)$+3C_2H_2+CH_4+CH_2$. The CH_2 radical may form various hydrocarbons depending on the energy relations. If the heat effect of oxide formation is strictly positive, then hydrocarbons with great energy demands (for example C_2H_4) are formed, if the opposite is true, liquid hydrocarbons are formed. With acid decomposition of Fe carbides, not only gaseous and liquid hydrocarbons are produced but also solid hydrocarbons and carbon. This makes the clarification of the reaction mechanism difficult. One must assume the presence of a carbide richer in C (for example FeC_2). There is considerable known of its existence, although there is yet no sure proof of it. The operating technique of catalysts appears to agree with the points discussed.

Schmerling, L. *See* abs. 1579a.

3091a. Schmerling, L., and Ipatieff, V. N. Mechanism of the Polymerization of Alkenes. Advances in Catalysis, Academic Press, Inc., New York, 1950, vol. 2, pp. 21–80.

The discussion deals chiefly with polymerizations catalyzed by acid-acting catalysts. 80 refs. are listed.

3092. Schmidt, A. W. [Problem of Diesel Fuels.] Brennstoff-u. Wärmewirt., vol. 20, 1938, pp. 20–26; Brennstoff-Chem., vol. 19, 1938, p. 346; British Chem. Abs., 1938, p. 1007.

Developments in the production of diesel fuel from German raw material are reviewed. Cetene numbers, varying from 40 for brown-coal, low-temperature tar oils to 120 for fuels prepared by the Fischer-Tropsch process, are now available.

3093. Schmidt, A. W., and Knegle, F. [Motor Evaluation of Diesel Fuels.] Oel u. Kohle Erdoel Teer, vol. 14, 1938, pp. 1034–1041; Brennstoff-Chem., vol. 20, 1939, p. 272; British Chem. Abs., 1939, B, p. 234; Chem. Abs., vol. 33, 1939, p. 7989.

Tests for ignition characteristics are discussed and test results for several motors are tabulated. The effects of supplementary agents and various constituents, such as Kogasin, paraffins, phenol, etc., are set forth in detail with curves. Carbonization tendencies are discussed.

3094. Schmidt, J. [Catalytic Reductions of Carbon Monoxide.] Schweiz. Apoth. Ztg., vol. 64, 1926, pp. 237–240; Chem. Abs., vol. 21, 1927, p. 1699.

Review of the work of Fischer and Tropsch on Synthol produced at high pressures and on the synthesis at ordinary pressure of CH_4 and higher petroleum hydrocarbons.

3095. ———. [Nonexistence of a Higher Nickel Carbide.] Ztschr. anorg. Chem., vol. 216, 1933, pp. 85–98; Chem. Abs., vol. 28, 1934, p. 1618.

Since Fe forms a higher carbide and since H. Tutiya had reported detecting a higher Ni carbide, (abs. 505) Schmidt attempted to prepare it by X-ray analysis. CO was passed over Ni (reduced by H_2) for 40–465 hr. at 240°–250°. All samples of carbide thus obtained contained 0.4–1.3% free C and 6.8–7.8% combined C. Although the latter was higher than the theoretical (6.37%) for Ni_3C, this was the only compound detected by X-ray studies. As all the possible places for C in the space lattice of Ni_3C are not filled, Schmidt assumes that the excess C takes some of these places without distorting the crystal. The density of Ni_3C computed from crystal data is 7.880 gm. per cc.; the experimental value (d^{25}_4) was found to be 7.957 gm. per cc. The excess C in the crystal may help account for the difference. The products of decomposition with acids were CH_4, C_2H_6, C_2H_4, and H_2, all being evolved in varying proportions. The results of decomposition were not reproducible. When CH_4 was passed over Ni, C was formed but no carbide. C_2H_2 gave Ni_3C and much C. Bibliography.

3096. ———. [Decomposition of Carbides by Water or Dilute Acids.] Ztscher. Elektrochem., vol. 40, 1934, pp. 170–174; Chem. Abs., vol. 28, 1934, p. 4675.

Carbides that are decomposed by H_2O or dilute acids may be divided into 3 groups: (1) Carbides of Fe, Co, Ni, and Mn having the formula M_3C. Al_4C_3 probably is to be included in this group. These carbides have a lattice in which the C atoms are separated, so that the products formed on treatment with H_2O or dilute acid result from the action of the H_2 set free by the decomposition upon each C atom separately. The reaction proceeds in several steps; $=CH_2$ radicals are formed 1st, and these are either converted to CH_4 by hydrogenation or polymerized to C_2H_4. From C_2H_4, by hydrogenation, polymerization, and further addition of $=CH_2$, hydrocarbons are formed with a larger number of C atoms. C_2H_2 is not formed by the decomposition of these carbides. (2) Carbides that give C_2H_2 on decomposition with H_2O or dilute acid. To this group belong the carbides of the elements of groups I and II of the periodic table; also $Al_2C\vdots C)_3$ and $Ce_2(C\vdots C)_3$. The formation of C_2H_2 is due to the presence of C–C linkages in the crystal lattices of these carbides. UC_2 and the carbides of the rare earths give not only C_2H_2 but other unsaturated as well as saturated hydrocarbons, the composition of the gaseous product varying with the conditions of the decomposition. These carbides have the lattice of CaC_2 or one very similar. Their irregular behavior is due to the conversion of the metal, upon decomposition of the carbide, from the bivalent to the trivalent or quadrivalent form. (3) Carbides that give allylene upon decomposition. Only Mg_2C_3 is known here. Since the structure of its crystal lattice has not been investigated, no definite statement can be made in regard to the mechanism of the decomposition, but the production of pure allylene would indicate the presence of C–C–C linkages in the lattice.

3097. ———. Das Kohlenoxyd, seine Bedeutung und Verwendung in der technischen Chemie. Akad. Verlagsgesell., Leipzig, 1935, 235 pp.; Brennstoff-Chem., vol. 16, 1935, p. 220.

Chapter IV discusses the technical synthesis of MeOH, the higher alcohols, the CH_4 and benzine synthesis, and some others such as CH_2O, fatty acids, etc. The MeOH synthesis is treated very fully, but the benzine synthesis is covered in only 5 pages without a very comprehensive description.

3098. Schmidt, J., and Neumann, B. [Equilibrium: Methane–Carbon Dioxide and Carbon Monoxide–Hydrogen.] Ztschr. Elektrochem., vol. 38, 1932, pp. 925–934; Chem. Abs., vol. 27, 1933, p. 1260.

Equilibrium $CH_4+CO_2\rightleftharpoons 2\,CO+H_2$ was investigated experimentally, 500°–800°, and the equilibrium constants are compared with those calculated from the free energy data. Above 600° there is agreement, but below 600° the observed CH_4 transformation is larger than that calculated. This is due to 2 by reactions: $H_2+CO_2=CO+H_2O$ followed by $H_2O+CH_4=CO+3\,H_2$. The equilibrium was approached from the CH_4, CO_2 side, and the reaction proceeded without separation of C. The catalyst used was reduced Ni supported on SiO_2 gel. As an intermediate step in the primary reaction, NiO apparently is formed.

3099. Schmidt, L. D. Synthesis Gas From Pulverized Coal, Oxygen, and Highly Superheated Steam Is Produced in Pilot Plant. Am. Gas Jour., vol. 175, July 1951, pp. 10–14, 42.

Work described in this paper is given in full detail in Bureau of Mines Rept. of Investigations 4733 (abs. 3306).

———. *See* abs. 144, 768, 2455, 3022, 3024, 3150, 3151, 3152 3305a, 3306.

3100. Schmidt, L. D., McGee, J. P., and Slone, M. O. Pilot Plant for Gasifying Powdered Coal Entrained in Oxygen and Steam. Chem. Eng. Progress, vol. 44, No. 10, 1948, pp. 737–744; Chem. Abs., vol. 43, 1949, p. 378.

Pilot plant for producing low-cast synthesis gas from powdered coal, superheated steam. and O_2 is described, and some of the factors involved in its design are considered. Only a preliminary-progress report is made as the plant is not completed and no experimental operating data are yet available. Some potential thermodynamic approximations are presented for the purpose of discussion. O_2 production is to be studied in 2 plants—1 producing 1,000 cu. ft. per hr. and the other, a German Linde-Fränkl installation, 23,000 cu. ft. per hr. The latter has operated for the production of 98% O_2 at a consumption of only 13.1 kw.-hr. per 1,000 cu. ft. O_2.

3101. Schmidt, R., and Groh, E. [New Process for the Continuous Production of Water Gas and Synthesis Gas. I.] Braunkohlenarch., No. 44, 1936, pp. 50–53; Chem. Abs., vol. 30, 1936, p. 5757.

Experimental apparatus and process are described using brown-coal coke and depending upon supplying endothermic heat for the water-gas reaction by means of heated, highly conductive steel tubes.

3102. ———. [New Process for the Continuous Production of Water Gas and Synthesis Gas. II.] Oel u. Kohle Erdöl Teer, vol. 12, 1936, pp. 41–51; Chem. Abs., vol. 30, 1936, p. 5757.

Theoretical aspects and previous laboratory findings are discussed. Technical scale apparatus of 2,000 m.^{3} per day capacity and its operation are described. Tests of 90 and 69 hr. using low-temperature coke to produce synthesis gas ($CO:H_2$ ratio 1:2) were made; slight changes in design reduced CH_4 content of gas from 3.6% to 2.2%. Technical and domestic possibilities are discussed.

Schmidt, W. *See* abs. 3089.

Schmitt, K. *See* abs. 3168.

Schmitt, P. *See* abs. 1604.

3102a. Schmitz, D. [Synthetic Gasoline, Its Past and Its Prospects for the Future.] Ind. chim. belge, vol. 16, 1951, pp. 335–347.

Summary, 44 refs.

3103. Schmitz, E. [Germany and Liquid Fuels.] Chaleur et ind., vol. 16, 1935, pp. 69–70.

Brief account of the Fischer-Tropsch process with some remarks as to the nature of the products.

3104. Schneider, A. [Synthetic Mineral Oils.] Leben u. Umwelt, vol. 6, 1950, pp. 81–87; Chem. Abs., vol. 44, 1950, p. 2731.

Illustrated discussion of the Bergius and Fischer-Tropsch processes.

Schneider, H. J. *See* abs. 7.
Schönfelder, R. *See* abs. 1205.
Schoon, T. *See* abs. 1368, 1369.
Schrader, A. *See* abs. 1170, 1356.

3105. Schrader, H. [Production of Formic Acid From Carbon Monoxide and Steam, and From Carbon Dioxide and Hydrogen, at High Temperatures and Pressures.] Ges. Abhandl. Kenntnis Kohle, vol. 6, 1921, pp. 65–78; Chem. Abs., vol. 19, 1925, p. 36.

By heating 20 cc. of water with Co under 135 atm. pressure in Fe autoclaves, 14.2 and 7.2 cc. of 0.1 *N* HCO_2H were obtained at 350° and 400°, respectively, while the residual gases contained, respectively, 14.0% and 28.0% of CO_2. Considerable quantities of Fe carbonyl were in the solution. On using a Cu-lined autoclave, the quantity of HCO_2H produced increased successively from 5.55 cc. to 14.4 cc. of 0.1 *N* solution in 5 experiments, and the CO_2 content of the residual gases fell 34.1–4.2%. Apparently some impurity with a harmful catalytic action was removed gradually from the apparatus or was rendered inactive; these results, however, could not always be repeated. Only small quantities of formic acid could be obtained in autoclaves lined with Ag, and, moreover, the residual gases contained but little CO_2. The action of Fe and Cu agrees with observations by Armstrong and Hilditch (abs. 76). The hydrogenating action of CO and steam upon coal (see abs. 749 and 750, Part I, of Bibliography of Pressure Hydrogenation, Bureau of Mines Bull. 485), apparently depends upon the intermediate formation of HCO_2H. In the thermal decomposition of HCO_2H at 400° under 120 atm. pressure in Cu autoclaves, the proportion remaining undecomposed was approximately the same as that produced from CO and steam, but, at 300°, the proportion undecomposed was somewhat greater than that formed at the same temperature. The formation of HCO_2H from a mixture of CO_2 under 30 atm. and H_2 under 50 atm. pressure was much greater in Fe than in Cu autoclaves. In the presence of Na_2CO_3, the yield of 0.1 *N* HCO_2H was 78.3 cc. at 350°. H_2 and Na_2CO_3 solution, on heating in Fe autoclaves, yielded 15.7 cc. of 0.1 *N* HCO_2H, but none was obtained in Cu autoclaves.

3106. Schrauth, W. [Fatty Acids From Coal.] Chem.-Ztg., vol. 63, 1939, pp. 274–278, 303–306; Allgem. Oel- u. Fett-Ztg., vol. 36, 1939, pp. 413–419; Chem. Abs., vol. 34, 1940, p. 8315.

C_{20}–C_{22} fraction (b. above 350°) is considered most suitable for oxidation. For the mechanism of oxidation, a CH_2-group near the center is oxidized preferentially.

3107. Schreiber, —. [Dehydrogenation of Long-Chain Paraffin Hydrocarbons.] FIAT Reel K–28, frames 6426–6434, Feb. 12, 1944; PB 70,185; TOM Reel 295.

Th, Zn, and Cu chromites are suitable catalysts for the dehydrogenation of long-chain hydrocarbons. Increasing the olefin yields over 23% is not recommended, as above that a considerable aromatization begins. The olefins are well-suited for lubricating-oil synthesis, but generation of aromatics in the dehydrogenation process makes the method unfavorable from an economic point of view.

3108. Schreiner, E., and Grimnes, F. B. [Reversible Reaction Between Iron and Steam.] Ztschr. anorg. Chem., vol. 110, 1920, pp. 311–334; Chem. Abs., vol. 14, 1920, p. 3346.

Measurements of the equilibrium pressures of H_2O vapor and H_2 in the reaction $Fe+H_2O \rightleftharpoons FeO+H_2$ were made 595°–920°, using an apparatus similar to that 1st used by Denville (Compt. rend., vol. 70, 1870, pp. 1105, 1205.) It was shown that refinements in the apparatus introduced by other workers with the object of accelerating the diffusion of the gases in the reaction tube were unnecessary. The values obtained for $K = pH_2O/pH$ were in good agreement, starting from either side of the equilibrium position. There are considerable discrepancies between the results obtained by different workers, particularly at high temperatures, where, in all cases, the value of K is much lower than that calculated from thermodynamic principles. The discrepancies probably are due to reactions in the solid phase, for example, the formation of solid solutions between Fe and FeO, or to the different behavior of different modifications of Fe. Further experiments are suggested to test this hypothesis.

3109. Schroeder, W. C. Investigation of the German Synthetic Liquid Fuel Industry. PB 283–S, 13 pp.

This report supplements PB 283 (abs. 96) and deals primarily with synthetic fuels. A list of the major plants and laboratories investigated, their location, and products is shown in table I. The Winkler and Lurgi processes for gasification of solid fuels are mentioned, as well as the Fischer-Tropsch process for liquid fuels, the hydrogen process, 3 methods for producing lubricating oil, and a like number of shale extractions.

3110. ———. Fuels and Fuel Research in Great Britain During the War. Mech. Eng., vol. 65, 1943, pp. 881–884, 892.

Among other things are discussed the production of liquid fuels from coal by the Imperial Chemical Industry, Ltd., at Billingham and by the Fuel Research Station on a laboratory scale by the hydrogenation and Fischer-Tropsch processes, respectively.

3111. ———. Conversion of Coal to Oil. United States Senate, 78th Cong., 1st sess., on S. 1243, 1944, pp. 221–224.

Taken from Synthetic Liquid Fuels Hearings before a subcommittee of the Committee on Public Lands and Surveys, and touches on the status of coal hydrogenation development in Great Britain and the relation of the United States to it.

3112. ———. German Synthetic Liquid Fuels Industry. United States Senate, 79th Cong., 1st sess., on S. Res. 36, June 19–25, 1945, pp. 349–360.

Account at the hearings before a special committee investigating petroleum resources of the visit of American technologists to, and their investigations of, the German synthetic oil industry in 1945. It was found that German technology with respect to synthetic fuel was in advance of American technology, and research development had progressed so far and so rapidly that, even in the German plants, commercial application had not kept pace. However, the opinion was confirmed that, on the basis of large operating units, American engineering practice could improve materially the process development and the operating status over German standards with a considerable reduction in costs. It was thought that aviation-grade gasoline was being produced for about $0.16–0.25/gal.

3113. ———. Technical Oil Mission Studies German Petroleum-Research Activities. Oil Gas Jour., vol. 44, No. 29, 1945, pp. 112, 115, 116; Chem. and Met. Eng., vol. 53, No. 1, 1946, pp. 220, 222, 224.

Paper presented at the November meeting of the American petroleum Institute. No special progress is reported in Fischer-Tropsch technology; no plant has been built since 1938. Synthesis gas was made almost universally by the water-gas reaction, using coke; brown coal was just being tested. Both atmospheric and medium pressure (10 atm.) were being applied, the latter being preferred. All commercial operations were carried out with the Co–Th–Mg–kieselguhr catalyst; only pilot plants were using the Fe catalyst. In general, 2-stage conversion was practiced; 1 plant used a 3-stage process. Gas was not recycled except in pilot plants; this and the Fe catalyst increased the olefin content and, thus, the octane rating of the product. Synthesis of alcohols was a live problem; the Oxo process was particularly interesting (abs. 2531). At a pressure up to 200 atm. and temperatures below 300°, it was reported that C_2H_4 and C_3H_6 and probably other unsaturates could be converted to alcohols by reaction with H_2O in the presence of W oxide on silica gel. The synthesis of isoparaffins is an important laboratory development. By using catalysts of Al_2O_3, ThO_2, ZnO, or mixtures of these at pressures of 300 atm. and 400° with a synthesis gas containing 20% more CO than H_2, a product can be obtained whose C_4 and C_5 fractions contain over 90% of isocompounds. The yield is about 100 gm./per. m.^{3} of synthesis gas. Research, not considered promising in Germany, has been carried out on the synthesis of aromatics in the range 475°–500° at elevated pressures using catalysts of Cr, Mo, and Th oxides. The yield of product was low but did contain about 50% aromatics and the same amount of naphthenes. Research on lubricating oil was very successful: 4 methods were in commercial use: Cracking of Fischer-Tropsch wax or oil and subsequent polymerization; chlorination of Fischer-Tropsch middle oil and subsequent reaction with naphthalene in the presence of $AlCl_3$ catalyst; synthesis from C_2H_4 in the presence of a specially prepared $AlCl_3$ catalyst; and a modification of the first-named process (no details).

3114. ———. Production of Synthetic Liquid Fuels From Coal, Lignite, and Oil Shale. Report to Federal Power Commission, June 1946, 7 pp.

Brief review of Bureau of Mines synthetic liquid fuels program, including investigation of German plants and processes.

3115. ———. Synthetic Liquid Fuels in the United States. Mech. Eng., vol. 69, 1947, pp. 989–995; vol. 70, 1948, pp. 555–556; Oil Gas Jour., vol. 46, No. 31, 1947, p. 128; Chem. Abs., vol. 42, 1948, p. 733.

Synthetic fuels industry capable of producing 1–2,000,000 bbl./day should be established as soon as possible so as not to cause too great a drain of national resources during a possible future emergency. Depending upon the raw materials available, the H_2O supply, the predominant type of products wanted, the location of the market, and the transportation expense, such a fuel will range in cost from $0.03–$0.05 per gal. above present petroleum fuel prices. Raw materials will be natural gas, coal, and oil shale. From an available 50 trillion cu. ft. of natural gas, 4–5 billion bbl. of liquid products should be obtained. Coal hydrogenation is well adapted to the production of aviation fuel and is the only synthetic process at present that will give a base stock for 100-octane gasoline with good rich-mixture performance. It does not produce good Diesel fuel and will not produce motor gasoline as cheaply as the Fischer-Tropsch process. Oil shale is simple to process, takes less initial investment, and can be refined to yield fuel oil and Diesel fuel with a cetane rating 34–45. Gasoline from oil shale is, at present, unsuitable for motor fuel as it has an octane number of only 50–60. Two new catalytic oil-processing methods have been developed and give promise of satisfactory commercial application: The fluidized technique of the oil industry and the oil-cooled catalyst method of the Bureau of Mines.

3116. ———. Comparison of Major Processes for Synthetic Liquid Fuels. Chem. Inds., vol. 62, No. 4, 1948, pp. 575–577, 682.

Three processes for the production of synthetic liquid fuels—oil shale retorting, Fischer-Tropsch gas synthesis process using coal, and coal hydrogenation—are compared with respect to the types of fuels produced, the state of development of the process technology, the amounts and location of raw materials required, and the indicated investment and operating costs. Oil shale is now best adapted to the production of fuel and heavy Diesel oil. The Fischer-Tropsch process yields good motor gasoline and excellent Diesel fuel. Coal hydrogenation gives aviation gasoline or a range of fuel oils. Considerable variation in estimates of the cost of the finished products is to be expected. For crude shale oil under large-scale operations, the capital cost is placed at $2,000 per bbl. per day, whereas production costs are estimated at from $1.75–$2.75 per bbl. Like estimates for the gas synthesis process using coal are $9,000–$10,000 per bbl. per day for plant and $3.50–$4.50 per bbl. for the gasoline product. Any reduction in the latter figure will have to result from lower synthesis gas costs. For coal hydrogenation, the respective figures are $10,700 per bbl. per day and $0.14–$0.19 per gal. of aviation gasoline. Approximately 50% of the cost of fuel production is in the H_2. The use of natural gas at $0.05 per 1,000 cu. ft. instead of coal at $3.00 per ton would reduce this cost about ⅔. How technical improvements in the equipment and the operations are leading to lower costs also is pointed out.

3117. ———. Fischer-Tropsch Alcohol. Chem. Eng. Progress, vol. 44, No. 1, 1948, pp. 15–17.

Raw materials and the processes for making synthetic alcohols are discussed. Two processes have been developed: The Synol and the Oxo processes. The chemistry of each of these processes is explained, the former gives straight-chain, the latter branched-chain alcohols.

3118. ———. Synthetic Fuel Production. Petrol. Eng., Refining Gas Processing Sec., vol. 21, October 1949, p. A–53.

Paper presented at United Nations Resources conference. Estimates are shown on the cost of producing petroleum substitutes from coal, either by hydrogenation or by synthesis, and from oil shale by retorting: From oil shale, $0.055 per gal.; from natural gas, $0.072 per gal.; from gas derived from coal, $0.121 per gal.; from coal hydrogenation, $0.126 per gal. These figures are based on a hypothetical industry with a productive capacity of 2,000,000 bbl. per day. Such an industry would require a capital investment of about 12 billion dollars. Capital investment per bbl. per day is estimated at $3,100 for shale oil, $5,300 for synthetic oil from natural gas, $8,600 for synthetic oil from coal by gas synthesis, and $9,000 for oil from coal by hydrogenation. A comparative estimate of the capital investment necessary to find, develop, produce, transport, and refine crude petroleum is $5,000–$6,000 per bbl. per day.

3119. ———. Synthetic Fuel Production. Petrol. Eng., Refining Gas Processing Sec., vol. 22, No. 5, 1950, pp. A53, A56, A60, A64, A66, A68.

Recent progress in the production of synthetic liquid fuel by pressure coal hydrogenation, Fischer-Tropsch process and retorting of oil shale is reported. Active study of the Fischer-Tropsch synthesis process centers around the production of synthesis gas and development of reaction chambers with high production capacity. 3 types are under investigation: The 1st uses a fluidized catalyst with removal of heat by circulation of cooling water; the 2d uses a fixed-bed catalyst, either pelleted or granulated, immersed in oil to control the temperature; the 3d uses a finely powdered catalyst suspended in an oil bath and cooled by heat exchange. Intensive studies are being made of the coal-hydrogenation process to raise the thermal efficiency above the possible present practical range of 45–50%. The dry hydrogenation of coal also is receiving considerable developmental study. In the oil shale demonstration plant, mining methods and equipment have been developed to assure low-cost production. 3 retorting methods are being studied: The gas-flow retort of the

Bureau of Mines, the fluid-flow unit of the Standard Oil Development Co. and the internally fired underfeed retort of the Union Oil Co. of California. It is expected that 1 or more of these methods will be found suitable for economical retorting of American oil shales.

3120. ———. Synthesis of Chemicals From Coal and Oil Shale. Chem. and Eng. News, vol. 29, 1951, p. 1830.

Paper presented at the National Capital Section meeting of the American Institute of Chemical Engineers. Motor fuels from oil shale are now capable of competing successfully with fuels from petroleum. It is predicted that an oil-shale plant designed to produce gasoline, motor oil, and Diesel fuel will pay for itself in 8–10 yr. If operated to manufacture chemicals it could pay for itself in 2–3 yr. There should be no delay in establishing a synthetic fuels industry; a satisfactory supply of petroleum is to be expected until about 1954, and then increasing shortages will develop. Nor can the country depend upon imports, particularly during wartime, to make up severe shortages of petroleum. Furthermore, the cost of producing petroleum will inevitably rise because of the added costs for exploration and for drilling deeper wells. At the same time, the cost of obtaining synthetic fuels from coal and oil shale is bound to decline.

———. *See* abs. 96, 97, 926, 2437, 2530b.

3121. Schroeder, W. C., and Fieldner, A. C. American Advances in the Manufacture of Synthetic Liquid Fuels. Internat. Chem. Eng., vol. 31, 1950, pp. 503–506.

Paper read at the 4th World Power Conference, London, 1950. A review of developments in coal hydrogenation, the Fischer-Tropsch process, and oil-shale processing in the United States is presented. The improved relative cost position between the products of synthesis and of petroleum is discussed; the trend is growing in favor of the synthetic product, and it is probable that a large synthetic fuel industry based on coal and oil shale will develop. An estimate has been made of the initial and the operating costs of a 30,000-bbl.-per-day coal-hydrogenation plant using Wyoming bituminous coal. From a consumption of 11,830 short tons of coal per day, 21,660 bbl. gasoline, 7,100 bbl. L. P. G. and 1,240 bbl. phenols would be produced. The cost of the gasoline, with L. P. G. and phenols credited at $0.08 per gal. and $0.10 per lb., respectively, would be $0.101 per gal. The total plant cost would be 243 million dollars or $8,100 per bbl. per day. At present, cost estimates for commercial Fischer-Tropsch plants operating on coal are in a preliminary stage; estimates are awaited from the demonstration plant being erected at Louisiana, Mo. It appears at present that the initial cost of a 10,000-bbl.-per-day plant will be about $7,500 per bbl. per day. The cost of producing gasoline and other products appears to be about the same as for coal hydrogenation. Estimates have been made for an oil-shale plant to produce about 100,000 bbl. of oil per day. The initial investment for the entire plant from mining to refining would approximate 409 million dollars or $4,090 per bbl. of oil per day. Operating costs for shale-oil production are about $1.43 per metric ton of shale or $2.00 per bbl. of crude shale oil. Assuming a 75% recovery in the refinery, the final products will cost about $3.50 per bbl., or $0.084 per United States gal. A breakdown of mining costs totaling $0.65 per metric ton is given.

3122. Schroeder, W. C., and Orchin, M. Oxo Reaction. Chem. Eng., vol. 58, No. 3, 1951, pp. 135–136.

Oxo process for production of aldehydes and alcohols from olefins by reaction with CO and H_2 has stimulated considerable interest and process development. The status of the reaction is at present highly competitive and process developments have not been revealed. It has been quite firmly established that either dicobalt octacarbonyl or cobalt hydrocarbonyl is the active catalyst and that these compounds are readily formed from any salt of Co or from the activated metal. There are some advantages (such as lower reaction temperature) to using preformed dicobalt octacarbonyl as the catalyst. Basic research on the chemistry of the Oxo process being conducted at the Bureau of Mines has led to some valuable developments: (1) 1-stage production of alcohols by using fairly large Co concentrations and higher-than-usual temperatures; (2) hydrogenation of aliphatic aldehydes and ketones to alcohols and of aromatic ketones and alcohols by hydrocarbons under Oxo conditions; (3) evidence that the hydrogenation is homogeneous and, therefore, applicable to S-containing compounds; (4) the homologation reaction by which MeOH can be converted to EtOH, benzyl alcohol to 2–phenyl ethanol, and tertiary butyl alcohol to isoamyl alcohol. The process has not been in operation long enough to permit evaluation of its impact on the chemical industry. It is likely that the reaction will receive consideration wherever large quantities of any kind of olefins are available. Those of interest not only include those in cracked gases, alkylation byproducts, and Fischer-Tropsch oils but other materials, such as the terpenes and unsaturated fats and oils.

Schroeter, K. *See* abs. 3251.

3123. Schroeter, R. [New Methods in Organic Synthesis. XIII. Hydrogenation With Raney Catalysts.] Angew. Chem., vol. 54, 1941, pp. 229–234, 252–260; Chem. Abs., vol. 35, 1941, p. 6241.

Comprehensive review of the preparation and properties of Raney metals, hydrogenation with catalysts of Fe, Cu, Co, and Ni, hydrogenation of C_2H_4 and C_2H_2 bonds and of the CO group, introduction of the NH_2 group by catalytic reduction, reduction of the COOH group and of halogen-containing compounds, and hydrogenation of aromatic and heterocyclic compounds.

3124. Schuessl, F. [Conversion of Carbon Monoxide Under Increased Pressure With Steam.] Gas- u. Wasserfach, vol. 82, 1939, pp. 359–362; British Chem. Abs., 1939, B, p. 685; Chem. Abs., vol. 33, 1939, p. 6562.

Catalyst composed of active C and MgO promotes the conversion of $CO+H_2O=CO_2+H_2$ at 350°–420° and 12–14 atm. with little tendency to CH_4 formation or other side reactions. It is insensitive to S, converting organic S compounds into H_2S and destroying NO. The process is well adapted for producing gases for synthesis of NH_3, MeOH, etc. and for detoxifying town gas. Working results of 2 installations are summarized.

3125. Schuff, —. [Thorium–Magnesium Catalysts for Gasoline Synthesis.] FIAT Reel K–30, frames 7448–7453, no date, PB 73,587; TOM Reel 297.

Report of the experiences gained with the Th–Mg catalysts in the gasoline synthesis. The catalysts were supplied by the Kator-Fabrik at Holten. These catalysts were definitely superior to the Th catalysts.

3126. ———. [Experiences With Thorium and Magnesium Catalysts in the Plants of the Ruhrchemie A.-G.] FIAT Reel K29, frames 7,109–7,115, 1938; PB 70,218; TOM Reel 296.

Survey of experiences with catalysts prepared by licensees of the Ruhrchemie. No results of general importance were obtained.

3127. ———. [Influence of the Reduction Conditions on the Activity of Thorium and Thorium–Magnesium Catalysts.] FIAT Reel K–29, frames 7,136–7,138, 1938; PB 70,128; TOM Reel 296.

Description of some tests on the experimental confirmation of old conceptions concerning the nature of the catalytic process, especially of the action of catalyst additions. Some practical conclusions are drawn from the results.

———. *See* abs. 1171.

3128. Schuftan, P. M. Modern Gaseous Oxygen Production Methods. Gas Times, vol. 54, 1948, pp. 274–281; British Abs., 1948, B, I, p. 299.

Paper read to the Institute of Chemical Engineers, February 1948. Methods for the production of medium-purity O_2 are discussed in detail. The development of regenerators and reversing exchangers as efficient heat exchangers and purifiers and of highly efficient machines for cold production by isentropic expansion, assisted by the possibility of using more efficient rectification processes, led to an increase of the thermodynamic efficiency of medium-purity O_2 plants to 19%, compared with 13% achieved in the best classical plants. Prospects of further improvements are discussed. A further approach to more reversible rectification methods appears to offer most promise. In this connection the Rescol process, a development of the British Oxygen Co. is described; detailed estimates of power consumption of this and 3 other medium-purity O_2 processes, the Linde-Fränkl expansion-engine type, the Linde-Fränkl turbine type, and the Kellogg plant, are given. The problem of producing enriched air is discussed; large-scale developments are imminent.

Schulte, F. *See* abs. 167.

3129. Schultes, W. [Manufacture of Water Gas and Gas for Synthesis From Bituminous Coal.] Glückauf, vol. 72, 1936, pp. 273–285; Chem. Abs., vol. 30, 1936, p. 6168.

Development of the water-gas generator is traced, and its application in producing synthesis gas ($CO+2H_2$) for making synthol of Fischer–Tropsch is discussed. Both coke and bituminous coal are considered as fuels. The Didier chamber-oven process involving production of low-temperature gas, which is cracked in the process to supplement the water gas H_2, is one of the most economical. Low-grade noncoking coal is used. Graphs are given showing costs per kg. oil, using various water-gas methods, with varying costs per ton of fuel.

Schultz, P. R. *See* abs. 2836, 2837.

3130. Schultze, G. R. [Thermodynamic Equilibria of Hydrocarbon Reactions Applied to Destructive Hydrogenation. III.] Angew. Chem., vol. 49, 1936, pp. 284–288; Chem. Abs., vol. 30, 1936, p. 6176.

Fischer process is workable at ordinary pressures because the hydrogenated products are stable at the low temperatures used. However, the Bergius process requires high pressures owing to the unfavorable position of the equilibria of certain cyclic reaction types at the high temperatures necessary for the destructive hydrogenation. Lowering the required high pressures should be possible if highly active catalysts can be developed. This does not hold if aromatic gasolines of high knock rating are to be produced.

3131. Schulz, B. [Progress in the Production and Utilization of Liquid Fuels.] Brennstoff-u. Wärmewirt., vol. 9, 1927, pp. 9–16; Chem. Abs., vol. 21, 1927, p. 1532.

Discussion, with bibliography.

3131a. Schulz, G. [Drilling Oil.] Erdöl u. Kohle, vol. 4, 1951, pp. 288–290; Chem. Zentralb., 1951, II, p. 3,537.

Bohrmittel Hö is obtained through the action of SO_2 and Cl_2 on Mepasin (hydrogenated Kogasin), subsequent conversion of the sulfochlorinated mixture by NH_3 and chloroacetic acid. The active ingredient of the final mixture is the Na salt of Mepasinsulfamidoacetic acid. H_2O emulsions containing from 0.5–5% are effective coolants and lubricants for many types of metal working and will prevent corrosion. It is an effective emulsifier for mineral oils.

3132. Schuman, S. C. Role of the Carbides of Iron in the Fischer–Tropsch Synthesis. Jour. Chem. Phys., vol. 16, 1948, p. 1175; Chem. Abs., vol. 43, 1949, p. 1636.

Equilibrium constants have been calculated for the formation of hydrocarbons from Fe_2C, CO, and H_2 in accordance with the reactions:

$$(1)\ Fe_2C+(2n-1)H_2+(n-1)CO=C_nH_{2n}+2Fe+(n-1)H_2O$$

$$(2)\ Fe_2C+2nH_2+(n-1)CO=C_nH_{2n+2}+2Fe+(n-1)H_2O$$

by which hydrocarbons are produced with each hydrocarbon molecule containing 1 C atom derived from an Fe_2C intermediate, using the free energy data for Fe_2C given by Kummer, Browning, and Emmett, and the data for CO, H_2O, and hydrocarbons of Rossini. The equilibrium constants for both reactions are shown at 227° and 327° for $n=2$ and $n=8$. These data indicate that the formation of hydrocarbons from Fe_2C is thermodynamically possible under the conditions employed in the Fischer-Tropsch synthesis. While no claim is made that reactions (1) and (2) represent the chemical process responsible for the formation of Fischer-Tropsch hydrocarbons, they are at least as compatible with the experimental synthesis data as the reactions considered by Kummer, Browning, and Emmett.

3133. Schuster, —. [Adsorption of Gases on Catalyst Carriers and Hydrogenation Catalysts.] I. G. Farbenindustrie-Zetko Rept., FIAT Reel C–29, frames 1415–1425, April 1939, 11 pp.; PB 76,463; Bib. Sci. Ind. Repts., vol. 7, 1947, p. 570.

Measurements on catalyst carriers have been made in order to determine the conditions upon which the adsorption depends. The selective effect of adsorption for a number of gases, such as C_2H_2, C_2H_4, C_2H_6, H_2, or A, has been studied on several catalysts, such as pumice, bauxite, silica gel, charcoal, activated aluminum gel, Zn oxide, and catalyst 5058 consisting of heavy metal sulfides. Tables and graphs comparing adsorption isotherms and tables of reaction and of adsorption on the catalyst.

3133a. Schuster, C. [Oxo Synthesis.] Fortschr. chem. Forsch., vol. 2, 1951, pp. 311–374; Chem. Abs., vol. 46, 1952, p. 886.

Comprehensive summary of the literature concerning the Oxo synthesis, discussing the reaction conditions (pressure, temperature, catalysts), reaction mechanisms, and the application of the synthesis to aliphatic olefins and dienes, C_2H_2, aromatics, cyclic olefins, arylolefins, halogens, N, and O compounds. 86 references.

3134. Schuster, F. [Technical Practicability of the Production of Liquid Fuels in Gasworks and Coke-Oven Plants.] Chem.-Ztg., vol. 57, 1933, pp. 661–662; Chem. Abs., vol. 28, 1934, p. 2878.

Various methods for converting coal into liquid products by way of gasification and hydrogenation are brought together into a single flow sheet. The table shows the temperature, pressure, and catalysts necessary, and the suitability of the different methods for use in gasworks and coke ovens is discussed.

3135. ———. [Water-Gas Equilibrium and Nonpoisonous Gas.] Gas- u. Wasserfach, vol. 80, 1937, pp. 304–307; Chem. Abs., vol. 31, 1937, p. 5133.

New values for the water-gas equilibrium constant were calculated with the latest values and new equations for the specific heat of CO_2, CO, H_2, and H_2O. These values for the water gas equilibrium (given from 300°–600°) are about 12% lower than those used earlier and are in agreement with the experimental results at 400°. Experiments were made as to the effect of use on the catalyst employed. This catalyst consisted of colloidal Fe oxide activated with KOH and formed into balls with cement. Initially, absorption of CO_2 by the catalyst increased its temperature, although this was lowered somewhat by desorption. The conversion of the higher Fe oxides into lower ones by the reducing gases required less heat than was supplied by the combination of CO and H_2. When equilibrium is reached with the catalyst, heat is continually evolved owing to the exothermic nature of the reaction of CO and H_2, and this heat is enough to cover process requirements. These laboratory observations were confirmed by observations at the Hameln plant.

3136. ———. [Production of Standard Public-Utility Gases From Combustible Industrial Gases.] Gas- u. Wasserfach, vol. 85, 1942, pp. 174–177; Chem. Abs., vol. 37, 1943, p. 3907.

Discussion of the possibility of changing the composition of typical combustible gases, for example, gas from the low-temperature carbonization of coal, residual gas from the Fischer-Tropsch process, and sewage gas, to that of town gas or coke-oven gas by addition of water gas having a suitable CO : H_2 ratio. Theoretical examples are worked out.

3137. Schuster, F., Panning, G., and Buelow, H. [Methane Formation in Carbon Monoxide- and Dioxide-Containing Gas Mixtures With Various Nickel Catalysts.] Brennstoff-Chem., vol. 16, 1935, pp. 368–369; Coal Carbonisation, vol. 1, 1935, p. 127; Chem. Abs., vol. 30, 1936, p. 3967.

After referring to Fischer and Pichler's observations on the effects of Ni–Al catalyst in the formation of CH_4 from mixtures of CO_2, CO, H_2, the authors present the results of their own investigations with town gas subjected to water-gas catalysis (activated Fe oxide contact at 450° C. with steam) and then passed over electrically heated Ni contacts. The results confirm Fischer and Pichler's observations. The effects of different catalysts vary, and the following cases have been found: (1) Selective hydrogenation of CO, the CO_2 being attacked after complete conversion of CO; (2) simultaneous hydrogenation of both oxides without preferential complete conversion of either: (3) simultaneous hydrogenation of both oxides with preferential complete conversion of CO to CH_4. In (2) and (3), the formation of CH_4 depends upon the ratio of CO to CO_2 and excess H_2. With Ni catalysts the reaction continues to water-gas equilibrium after CH_4 catalysis has been poisoned.

3138. Schuster, L. [Status of Coal Liquefaction.] Dingl. poly. Jour., vol. 345, No. 10, 1929, pp. 184–187.

MeOH synthesis of I. G. Farbenindustrie A.-G. and lignite high-pressure hydrogenation are discussed, and a brief general description of Bergius, Fischer-Tropsch methods.

3139. Schütza, H. [Behavior of Active Cobalt Toward Water in the Fischer-Tropsch Catalyst.] Chemie-Ing. Tech., vol. 21, 1949, pp. 177–179; Ind. Chemist, vol. 25, 1949, pp. 450–451; Chem. Abs., vol. 43, 1949, p. 6497.

Metallic Co in active form is contained in the catalyst of very small particle size. The equilibrium $CoO+H_2 \rightleftharpoons Co+H_2O$ is calculated on the basis of increased active surface and resulting higher surface energy. The calculations and some of the experimental data indicate that in commercial practice oxidation of the catalyst may occur with corresponding inactivation of the metallic Co.

3140. Schwab, G. M., and Drikas, G. [Inhibiting Action of Methane on the Reaction of Oxygen and Hydrogen on a Copper-Oxide Catalyst.] Ztschr. Elektrochem., vol. 50, 1944, pp. 97–103; Chem. Abs., vol. 39, 1945, p. 858.

At pressures of 1–9 mm., CH_4 in a mixture with O_2 is not oxidized below 600° but is oxidized when present in H_2–O_2 mixtures at 400°. This inhibiting action is not due to displacement of the reactants from the catalyst by the CH_4, since this hypothesis is invalidated by the conditions of concentration and temperature. Nor can it be understood that, as a result of thermal diffusion, the CH_4, whose molecular weight lies between that of H_2 and O_2, drives the O_2 away from the H_2 and the wire; on the one hand, the reaction is much slower than the expected velocity of diffusion to the wire, and, on the other hand, the calculated speed of thermal diffusion is so low that the stationary thermal stratification of the gases appears to be virtually nonexistent because of the diffusion in concentration. It can be explained best by picturing the oxy-hydrogen reaction as a branched-chain reaction set up by a chain carrier formed on the catalyst; CH_4 inhibition takes place then through a further chain rupture with consumption of CH_4. The suggested chain of reactions is: (1) $Cu+O_2 \rightarrow CuO+O$, (2) $O+H_2 \rightarrow OH+H$, (3) $OH+H_2 \rightarrow H+H_2O$, (4) $H+O_2 \rightarrow OH+O_2$.

3141. Schwab, G. M., and Naicker, K. [Water-Gas Reaction on a Platinum Surface at Low Pressures.] Ztschr. Elektrochem., vol. 42, 1936, pp. 670–673; Chem. Abs., vol. 30, 1936, p. 7979.

Kinetics of the reaction $H_2+CO_2=CO+H_2O$ have been studied on a Pt filament 700°–1,200° and at pressures up to 0.3 mm. By use of H_2SO_4 for removing the H_2O formed, the authors found the rate was independent of the partial pressure of CO_2 and was a complicated function of the partial pressure of H_2 and CO. The reaction was autocatalytic in the absence, but not in the presence, of an initial partial pressure of CO. If P_2O_5 was used to remove the H_2O formed, the time of half conversion was proportional to the pressure; the rate was independent of the H_2 pressure. No autocatalysis but marked inhibition by CO was observed. If a cold bath (−90°) was placed around the reaction vessel to remove the H_2O formed, the character of the reaction changed completely. No reaction occurred below 730°; above 800° the rate was very high and independent of temperature. The observed rate was 10^{-4}, which would be calculated by assuming the surface to be covered with adsorbed H and that a reaction occurred every time a CO_2 molecule struck the surface. The results are interpreted as indicating the existence of enough active points to cover 10^{-4} of the surface and points active enough to permit the reaction to occur with no energy of activation.

3142. Schwab, G. M., and Schwab-Agallidis, E. [Alloys as Catalysts.] Naturwissenschaften, vol. 31, 1943, pp. 322–323; Chem. Abs., vol. 38, 1944, p. 1679.

Effect of separation of phases in alloys on their catalytic effect was studied. An alloy of Al with 9.7 at. % Ag has the homogenous δ phase above 490°; below this temperature it has the hexagonal γ phase. This change of phases, however, does not affect the catalytic effect of the alloy on decomposition of EtOH above and below 490°. The heat of activation of the reaction with the alloy was 25–26 kcal.; that on the separately prepared pure γ phase, 28 kcal. The same holds for MeOH decomposition. Any effect of C on the surface is considered improbable. With the decomposition of HCO_2H over Cu–Ag catalysts, it appeared that the heat of activation changed from 18 kcal. for pure Ag to 24 for Cu; it was 24 for 5 at. % Ag, and 20.2 for 7.5 at. % Cu. The method used was direct determination of gas flow (H_2 and CO_2) resulting from the vapor-phase reaction. Results by a static method agreed with the above. A simple mixing rule seems to hold.

3143. Schwab, G. M., and Zorn, H. [Kinetics of the Hydrogenation of Ethylene on Skeleton Contacts.] Ztschr. physik. Chem., vol. 32, B, 1936, pp. 169–201; Chem. Abs., vol. 30, 1936, p. 4745.

Activated centers are in the interior of the catalysts. According to the activity and the temperature, the rate-determining process depends on these activated centers or diffusion through the pores of the material. For highly dispersed substances, the configuration of the inner surfaces is extremely significant, since their active centers are accessible to gases only by diffusion.

Schwab-Agallidis, E. *See* abs. 3142.

Schwartz, F. G. *See* abs. 3595.

3144. Schwartz, H. A. Metastability of Cementite. Trans. Am. Soc. Metals, vol. 23, 1935, pp. 126–150; Chem. Abs., vol. 29, 1935, p. 3959.

In an Fe–C alloy containing also 0.03% Si and not over 0.04% of other elements, the reaction $Fe_3C \rightleftharpoons 3Fe+C$ proceeds to the right at all temperatures from 630° to above the eutectic melting point. The A_1 stable critical point is found 15° above A_1 metastable in this alloy.

3145. ———. Conversion of Solid Cementite Into Iron and Graphite. Jour. Iron Steel Inst., vol. 138, 1938, pp. 205P–240P; Chem. Abs., vol. 32, 1938, p. 9012.

Our knowledge of the heat, entropy, and free energy changes accompanying the reaction $Fe_3C=3Fe+C$ are still unsatisfactory owing to the imperfections in the best existing work on the underlying data. Evidence is offered regarding the possibility of the existence of 2 types of solid solutions and the relationship of this possibility to the constitutional diagram, especially the A_3, or $G'S'$, line of the double diagram. The graphitizing reaction involves the formation of graphite nuclei, the solution of cementite in Fe, the dissociation of cementite into Fe and C, the migration of C either before or after dissociation, and the crystallization of graphite. The reaction rate is shown to be controlled by the migratory rate, this being the slowest step except at the very beginning and end of the process. The graphitizing rate is thus, in fact, mainly a function of the nodule (nucleus) number and migratory rate. The nodule number is determined largely by the prevalence of interfaces in the metal at the graphitizing temperature. The number of interfaces depends on the fineness of the original white-Fe structure, which in turn is a function of the cooling rate. Supercooled white cast Fe, the matrix of which is hypereutectoid in composition, may carry additional interfaces into the graphitizing temperature range. For a given set of interfaces the nucleus number is a function of the graphitizing temperature, the O content of the metal, and other variables of the melting operation. The migratory rate of C is influenced mainly by the presence of other alloying elements. Certain elements present in atomic solution or as chemical compounds appear to retard the migratory rate, whereas a few accelerate graphitization, probably by increasing the migratory rate. The effectiveness of the elements of group VI of the periodic table on the migratory rate and the fact that the effectiveness of elements in a given group often decreases with increase of the atomic weight may be of interest from the electronic viewpoint. 64 refs.

3146. Schwartz, H. A., Johnson, H. H., and Junge, C. H. Graphitization of Prequenched White Cast Iron. Trans. Am. Soc. Steel Treating, vol. 17, 1930, pp. 383–399; Chem. Abs., vol. 24, 1930, p. 5272.

Study of the acceleration of graphitization produced by prequenching hard Fe before annealing. The reactions involved are interfacial in character and represent the rate of solution of Fe_3C in the metallic matrix. Prequenching accelerates migration of C rather than diffusion, because of a greatly increased number of graphite nuclei with the accompanying decrease in migratory distance.

3147. Schwarz, C., and Ulich, H. [Specific Heat, Entropy, and Energy of Formation of the Iron Carbide Fe_3C.] Arch. Eisenhüttenw., vol. 10, 1936, pp. 11–12; Chem. Abs., vol. 30, 1936, p. 7021.

Specific heat of Fe_3C can be expressed by 2 equations, 1 below and 1 above the magnetic transformation point; for the range 273.2°–407.1° K. $C=16.8-0.028\,T$ cal. per mol., and from 407.1° K. upward $C=28.2$. The energy of formation is represented by $3\ Fe_\alpha+C_\beta$—graphite$\rightarrow Fe_3C$; energy=2,600 cal. per mol. Heat content I and entropy S for temperatures above 407.1° K. (134°) and for 298.2° K. (25°) as base are expressed by 298.2 $I^T=28.2\,T-8575.4$; 298.2 $I^{407.1}=2906$ cal. per mol., ${}_0S^T=28.2\ ln\ T-137.8$; ${}_0S^{407.1}=32.176$ cal. per degree per mol. 5 refs.

Schwarz von Bergkampf, E. *See* abs. 340.

3148. Science Museum—London. Science Library Bibliographical Series No. 304; Chem. Abs., vol. 31, 1937, p. 5137.

Production of benzine from water gas, 1932–36 is reviewed. 58 refs.

Scott, H. *See* abs. 2330.

3149. Sebastian, J. J. S. Catalytic Reduction of Carbon Monoxide to Methane at Atmospheric Pressure. Carnegie Inst. Technol., Coal Research Lab. Contrib., vol. 35, 1936, 8 pp.; Cong. chim. ind., 15th Cong., Brussels, 1936, pp. 875–885; Brennstoff-Chem., vol. 17, p. 393; British Chem. Abs., 1936, B, p. 531; Chem. Abs., vol. 30, 1936, p. 3968.

Rate of reduction of CO at normal pressures over various catalysts maintained at temperatures in the range 200°–350° was studied. Mixtures (1:3) of CO and H_2, both pure and with the addition of 0.003% H_2S, were tried. Ni gave good conversion but was rapidly poisoned. Mo was active and not so sensitive to poison, but 2 Mo oxide preparations proved inactive. MoS_2, alone or mixed with silica gel, showed activity and was resistant to poisoning. The nature as well as the amount of hydrocarbons was affected by the catalyst and by the temperatures and rate of flow. Over Ni and over MoS_2, CH_4 predominated in the product, but up to 8% C_2H_6 and C_3H_8 might be present.

3149a. ———. Powdered-Coal Gasification. Effect of Variables. Ind. Eng. Chem., vol. 44, 1952, pp. 1,175–1,184.

Very large quantities of low-cost synthesis gas required for the production of synthetic gasoline and other liquid fuels necessitate the large-scale gasification of powdered coals with O_2 and superheated steam. Investigation was undertaken to determine how the considerable differences among various types of coals influence their relative value for synthesis gas production. It seemed also that investigation of the effects of other process variables should determine the conditions under which a given coal can be gasified with maximum process efficiency, lowest O_2 requirement, and lowest cost. Sufficient evidence has been obtained to conclude that young high-volatile coals of high O_2 content yield better results than high-rank, low-volatile coals of low O_2 content. Yet, high-ash or high-S coals can be gasified as easily as high-grade coals, nor does it make any difference whether the coal is strongly coking or noncoking. For a given coal of predetermined particle size, gasified in a given generator, at its maximum capacity, a proper combination of the O_2: coal ratio, steam: coal ratio, and steam temperature will result in the maximum completion of gasification and lowest O_2 requirement per unit volume of synthesis gas made. The beneficial effect of the addition of lime to the powdered coal under certain conditions (slagging generators) has been established in special experiments made.

———. *See* abs. 144.

3150. Sebastian, J. J. S., Edeburn, P. W., Bonar, F., and Schmidt, L. D. Development of Synthesis Gas Process in Experimental Unit Operating on Entrained Powdered Coal. Am. Chem. Soc., 114th Meeting Abs., September 1948.

Laboratory-size pilot unit has been designed, and a method has been developed for the gasification of 10–30 lb. of pulverized coal per hr. by entrainment in O_2 and steam at generator temperatures ranging 1,800°–2,400°. The purpose was to obtain the necessary engineering design data for the construction of large-scale units producing synthesis gas from powdered coal and to test various types of fuels for their relative value in synthesis gas production. A brief discussion is given of the principles of aerodynamics applied in the process utilizing a turbulent downward flow of O_2, steam, and product gases, which carry the powdered coal and residual dust along in a thorough entrainment inside an 82-in. long, vertical, refractory tube, 6-in. inside diameter. Typical data obtained in 37 runs under widely different operating conditions are given. Graphical analysis and study of the operating results led to several conclusions, which appear to be useful in controlling the quality of the synthesis gas produced and in predicting yields and efficiency under various combinations of operating conditions.

3151. Sebastian, J. J. S., Edeburn, P. W., Bonar, F., Bonifield, L. W., and Schmidt, L. D. Laboratory-Scale Work on Synthesis-Gas Production. I. Development of Process in Laboratory Unit Operating on Entrained Powdered Coal. Bureau of Mines Rept. of Investigations 4742, 1951, 33 pp.

Investigations have shown that a synthesis gas of high quality can be continuously produced from powdered coals by entrainment in O_2 and steam. The quality of the gas depends upon controllable operating variables, such as type and size of coal charged, coal feed rate, oxygen: coal and steam: coal ratios, and steam temperature. 2 different types of bituminous coal were used: A noncoking, low-ash, low–S coal from Wyoming No. 9 seam and a strongly coking, high-ash, high-S from the Sewickley seam in West Virginia. A synthesis gas of low CO_2 content (7%) can be made from both types of coal, pulverized either 70 or 90% minus-200-mesh, if the ratios of O_2: steam and $C: O_2+$ steam are high enough. The dry, ash-free coal gasified in a single pass ranged 60–70%, with yields of $CO+H_2$ ranging 15–22 standard cu. ft. per lb. of dry, ash-free coal charged, depending on the choice of values for the operating variables. The combined $CO+H_2$ in the synthesis gas produced ranged 76–91%. With coal feed rates up to 45 lb. per hr., corresponding to hourly fuel throughput rates up to 33 lb. per cu. ft. of generator volume, gas output rates as high as 600 standard cu. ft. $CO+H_2$ per cu. ft. generator space per hour have been obtained. Indications are that even this unusually high gasification rate would be considerably exceeded when younger coals are gasified. Synthesis-gas production rates as high as these per unit volume of generator space are important factors in reducing capital and production costs for the manufacture of gas on a commercial scale. (*See also* abs. 3150.)

3152. ———. Laboratory-Scale Work on Synthesis-Gas Production. II. Experimental Pilot Unit for Underground Gasification Studies With Highly Superheated Steam and Oxygen. Bureau of Mines Rept. of Investigations 4742, 1951, pp. 33–41.

As underground gasification is essentially gasification of coke walls resulting from the carbonization of coal seams by intense heat, it was decided to study the gasification of run-of-oven, high-temperature coke cemented together into a strong, circular wall about 2 ft. thick. A preliminary run of 31 hr. duration in a pilot unit was performed with O_2 and highly superheated steam. Although operating results were incomplete, it was proved that the production of synthesis gas is possible even from such unreactive substances as high-temperature coke containing 23% inert material. Although the run was discontinued because of the failure of the cemented circular coke wall, the feasibility of gasification was demonstrated.

Seelig, H. S. *See* abs. 2754a, 3618, 3642b.

3153. Seelig, H. S., and Marschner, R. F. Production of Synthesis Gas by Catalytic Decomposition of Methanol. Ind. Eng. Chem., vol. 40, No. 4, 1948, pp. 583–586; Chem. Abs., vol. 42, 1948, p. 4328.

Moderate amounts of a synthesis gas ($CO: H_2=1:2$) has been obtained by decomposing MeOH over a Filtros-supported catalyst of Cu and Ni oxides, U. S. Patent 2,010,427. The decomposition temperature is 350°–400° and 100–200 vol. of MeOH vapor pass over 1 vol. of catalyst per hr. The life of the catalyst is about 200 hr. and can be regenerated several times by periodically burning off the deposited C. The only byproducts of the operation are traces of CO_2, gaseous hydrocarbons, and C. A service unit to produce 250–300 cu. ft. per hr. of synthesis gas and its operation is described. Diagrams included.

3153a. Seelig, H. S., Weck, H. I., Voss, D. J., and Zisson, J. Hydrocarbon Synthesis Studies. Effects of Addition of Alkali to an Iron Catalyst. Am. Chem. Soc., 122d Meeting abs., September 1952, p. 4–0.

Experiments in both fixed-bed and fluidized-bed hydrocarbon synthesis reactors have shown that addition of K_2CO_3 promoter as a dry solid to Fe will produce a catalyst giving CO conversions and product yields comparable to those obtained with a catalyst prepared by a conventional aqueous impregnation method. Addition of alkali increases CO conversion, the yields of high molecular weight products and oxygenated compounds, the % of olefins in the low-molecular weight hydrocarbons, and frequently the carbide content of the catalyst. Fe_2C is a likely choice as the catalytically active Fe component. The effects produced by addition of K_2CO_3 can be explained by assuming that the catalyst has a defect or *p*-type character which is modified by the promoter.

3154. Seger, F. M., Doherty, H. G., and Sachanen, A. N. Noncatalytic Polymerization of Olefins to Lubricating Oils. Ind. Eng. Chem., vol. 42, 1951, pp. 2446–2452; Chem. Abs., vol. 45, 1951, p. 1757.

Thermal, noncatalytic polymerization of 1–olefins produces excellent lubricating oils. Reaction conditions are 600°–650° F., reaction time about 10 hr., and pressures of 250–500 p. s. i. The preferred range of 1–olefins is from hexene to dodecene. Such olefins from any source, as cracked paraffin wax or Fischer-Tropsch products, can be used for the synthesis.

3154a. Seitz, F. Fundamental Principles of Catalytic Activity. Advances in Catalysis, Academic Press, Inc., New York, 1950, vol. 2, pp. 1–19.

Activity of heterogeneous solid catalysts is discussed. Energy surface, isomeric and more complex reactions and characteristics of solid catalysts are described. Solids are classified into 4 types: Valence crystals, metals, ionic crystals, and molecular crystals.

3155. Sekito, S. [X-Ray Analysis of the Cementite Obtained by Tempering Quenched Steels.] Sci. Repts. Tôhoku Imp. Univ., vol. 20, 1931, pp. 313–322; Chem. Abs., vol. 25, 1931, p. 4833.

Method and technique are described for obtaining the quantitative measurement of cementite by X-ray analysis.

3156. Selasinsky. A. V. [Soap From Coal.] Rundschau deut. Tech., vol. 18, No. 1, 1938, p. 9; Chem. Abs., vol. 32, 1938, p. 3179.

Historical review, especially describing the Imhausen-Troschke process and its importance for Germany's economical situation.

Seligman, B. *See* abs. 44, 45, 46, 48, 50, 52, 53, 53a, 53b, 2228.

3157. Seligman, H. Application of Isotopes in Chemical Industry. Chem. and Ind., 1951, pp. 724–727.

Uses of isotopes in chemical research and in the inspection and chemical-process control.

3158. Seltz, H., McDonald, H. J., and Wells, C. Heat Capacity of Iron Carbide 68°–298° K. and the Thermodynamic Properties of Iron Carbide. Am. Inst. Min. and Met. Eng., Tech. Pub. 1137, 1939, 11 pp.; Chem. Abs., vol. 34, 1940, p. 1904.

Heat capacities of Fe_3C were determined experimentally 68°–298.1° K. The entropy was calculated $S_{298.1}=25.7$ (±1) e. u. From the solubility curves of Wells for C and Fe_3C (β) in austenite, the free energy and heat of formation of carbide are evaluated. At 298.1° K., $\Delta H=5{,}800$ cal., $\Delta F°=4{,}700$ cal. for the formation of Fe_3C (α) and $S_{298.1}=24.7$ e. u. The temperature at which $\Delta F°=0$ for 3 Fe (γ)+C (graph.)$=Fe_3C$ (β) is 1,082° K.

3159. Selvig, W. A., Ode, W. H., and Davis, J. D. Low-Temperature Carbonization of Alaskan Coals. Bureau of Mines Tech. Paper 668, 1944, 16 pp.

Assays of 14 Alaskan coals are reported as part of a general plan to test the coals of this region for their suitability as a source of liquid fuel by way of hydrogenating the tar and using the low-temperature coke for the Fischer-Tropsch synthesis.

3160. Selwood, P. W. Magnetism and Catalysis. Chem. Rev., vol. 38, 1946, pp. 41–82.

Possibility of relationships between catalytic activity on the one hand and magnetic fields and magnetic properties on the other, has interested many workers. It cannot be denied that those chemical elements that show the most pronounced catalytic activity, namely, the transition group elements, are also the elements that show the most interesting magnetic properties. In at least 1 case, the ortho-para-H_2 conversion, there is a clean-cut relationship between magnetic moment and catalytic activity. This is not to say that all catalytic activity is due to magnetism. It may yet appear that catalysis and magnetism are different manifestations of some more fundamental atomic property. But for the present, the chief applications of magnetism to catalysis are in structural studies of catalytic solids. A review of such applications and of certain related effects is the purpose of this article. Susceptibility data are included for some substances of major catalytic interest. 222 literature refs.

3160a. ———. Magnetism and the Structure of Catalytically Active Solids. Advances in Catalysis, Academic Press, Inc., New York, vol. 3, 1951, pp. 27–106.

Status of magnetic studies on catalyst structure is given. The following conclusions are drawn: The magnetic methods often give evidence for the oxidation state of catalytically active solids which contain elements of the transition series. This is especially true for V, Cr, Mn, Fe, Co, Ni, and Cu. Sometimes the magnetic method reveals the existence of valence bonds between adjacent positive ions, such as between Fe and Fe in hydrous or supported Fe sesquioxide. Almost always the magnetic method gives some information concerning the atomic environment of positive ions in hydrous or supported oxides. This information is related to the number of positive ions surrounding a given positive ion, for example, to the number of nearest Fe neighbors to a given Fe ion in Fe sesquioxide. The magnetic method, together with other methods, has revealed that the oxidation state of a supported oxide may, under certain circumstances, be influenced by the crystal structure of the support. In some cases there has been established a definite relation between the information obtainable from magnetic measurements and the actual catalytic activity. The methods described are not yet applicable to diamagnetic substances such as alumina or silica, but have definite applications to some systems in which these substances are used as supports. The thermomagnetic method of analysis is a tool of major use in detecting and estimating certain components in catalysts. These components are the ferromagnetic substances Fe, Co, Ni, Fe_3O_4, γ–Fe_2O_3, Fe_2C, and Fe_3C. In certain cases of a ferromagnetic metal supported or alloyed with a nonferromagnetic metal the thermomagnetic method can reveal alloy structure in a manner inaccessible by other tools. 62 refs. given.

———. *See* abs. 2327, 3500.

Semiller, H. *See* abs. 3073.

Sen, R. *See* abs. 467.

Sen, S. *See* abs. 1186.

Senderens, J. B. *See abs.* 3001. 3002, 3003, 3004, 3005.

Senglet, R. *See* abs. 356.

Senoo, H. *See* abs. 2502, 2503.

Seon, M. *See* abs. 2194.

3161. Sepulchre, —. [Gasification in Relation to the Synthesis of Fuels.] Petroleum et remplacement, April 1944, pp. 21–22; Chaleur et ind., vol. 26, 1945, p. 45D.

Theoretical study of gasification leading to the production of a mixture of $CO+H_2$ in the desired proportions and the necessity of eliminating the inerts CO_2 and CH_4. The idea is set forth of a total gasification by cracking, making use of the reaction $CH_4+CO_2=2\ CO+2\ H_2-61$ cal. and then removing the inerts.

3162. Sergienko, S. R. [Mechanism and Relative Rapidity of the Aromatization of Paraffinic Hydrocarbons. I.] Bull. acad. sci. U. R. S. S., classe sci. chim., 1941, pp. 177–190; Chem. Zentralb., 1942, I, p. 2219; Chem. Abs., vol. 37, 1943, p. 3064.

Octane and 1:1 mixtures of octane and heptane have been aromatized in the presence of Cr_2O_3–CoO and Al_2O_3–Cr_2O_3–CoO catalysts at 475°–500° and a throughput of 0.15–0.3 vol. % of the starting material per vol. of catalyst. By periodic regeneration (after every 2–12 hr.) of the catalyst, it will retain its original activity after 700 working hr. Under these conditions, octane is aromatized 1.5 times more rapidly than heptane. Depending on the reaction temperature, the throughput and the nature of the starting material, about 25–60% is converted to aromatics. The proposed reaction scheme agrees with the multiple theory of Balandin. By the use of oxide catalysts, the course of aromatization is through olefin intermediate products. With Pt catalysts, no olefin intermediates are formed. Along with aromatization, a partial cracking takes place, and the latter increases with increasing molecular weight of the aliphatic hydrocarbons.

3163. ———. [Catalytic Cyclization of Paraffinic Hydrocarbons. II. Investigation of the Reaction Products.] Bull. acad. sci. U. R. S. S., classe sci. chim., 1941, pp. 191–200; U. O. P. Co. Survey Foreign Petroleum Literature, Transl. 373, 1943; Chem. Zentralb., 1942, I, p. 2219; Chem. Abs., vol. 37, 1943, p. 3065.

Cyclization experiments were conducted at 475° with the catalysts Al_2O_3–Cr_2O_3–CoO and Cr_2O_3–CoO, the charge was the C_7, C_8, and C_9 fractions of synthin. The products were at least 50% aromatic. Cracked materials did not exceed 5–10% and unsaturates varied from 4–12%, depending on the catalyst used.

———. *See* abs. 1704.

Serpek, H. O. *See* abs. 2785.

3164. Serruys, M. [Use of Motor-Fuel Substitutes.] Jour. soc. ing. automobile, vol. 14, 1941, pp. 153–180; Chem. Abs., vol. 41, 1947, p. 3598.

Yield of motor fuels obtainable by different industrial processes in terms of horsepower per kg. of coal is estimated to be 0.73 in the Fischer or Bergius processes, 1.91 in the carbonization of coal, 1.98 in gas producers, 0.97 in making MeOH from coke, 1.39 in making C_2H_2 via calcium carbide, 0.240–0.577 in making alcohol from agricultural products, and 0.545 in making gas from wood.

3165. Sevastyanov, Y. [Synthesis of Ammonia and Methanol.] Khimstroi, vol. 6, 1934, pp. 112–120; Chem. Abs., vol. 28, 1934, p. 4843.

Discussion and mathematical analysis of the process.

Sever'yanova, M. G. *See* abs. 1673.

Seyfried, W. D. *See* abs. 38, 3391.

Seymour, W. *See* abs. 625.

Shapiro, M. I. *See* abs. 1107, 1584, 3769.

Sharkey, A. G. *See* abs. 1091, 1091a.

Sharkov, V. I. *See* abs. 2470.

3166. Shatwell, H. G. Production of Synthetic Motor Spirit With Special Reference to the Fischer-Tropsch Process. Colliery Guard., vol. 155, 1937, pp. 1125–1126; Iron and Coal Trades Rev., vol. 135, 1937, pp. 965–966; Jour. Inst. Fuel, vol. 11, 1938, pp. 209–213; Fuel, vol. 17, 1938, pp. 1–2; Brennstoff-Chem., vol. 19, 1938, p. 345; Chem. Abs., vol. 32, 1938, p. 8105.

Most of the subsequent work on the process since the advent of Synthol has been directed toward deciding the effect of various factors, such as composition of the initial gas mixture, nature of the catalyst, temperature and pressure in the reaction vessel, and the nature and amount of the product obtained. It now is proposed to produce the synthesis gas of proper $CO:H_2$ ratio by mixing blue water gas with the essential quantity of reformed coke-oven gas. As to catalysts, it appears that Fe, Co, and Ni, promoted by other metals and oxides, give the best results. It generally is agreed that Fe is the most sluggish but can be used over a longer temperature range, that Co yields a product containing a substantial proportion of olefins, and that Ni is extremely active but tends to produce CH_4 and liquid and solid hydrocarbons, which are almost entirely paraffinoid in nature. It has been found necessary to reduce the S content of the reaction gas to a maximum of 1 gm. per 1,000 cu. ft.; search should be made for a S-tolerant catalyst. Pressure must not be much in excess of atmospheric or alcohols and other oxygenated compounds will appear in the products. The temperature must be controlled carefully, from 190°–200° C for Ni, 200°–210° for Co, and not above 250° for Fe-base catalysts; CH_4 is produced if these temperatures are exceeded. As the reaction is strongly exothermic, this need for careful temperature control is difficult, and special types of reaction chambers with restricted depths of catalyst are required in order to effect easy cooling and prevent local overheating. The products are essentially paraffinoid in nature and straight-chain for the most part. The yield of motor fuel is relatively high but of low fuel value, whereas the diesel-oil fraction has a cetene number of 100 and is useful for blending with inferior diesel fuels, such as tar oils. In the author's opinion, the main disadvantage of the process, apart from the disappointing nature of the motor fuel, is the fact that it is conducted at atmospheric pressure, thus necessitating large reaction chambers and large quantities of catalyst with increased tendency to poisoning and probably a heavy capital expenditure on catalysts.

———. *See* abs. 757.

Shaw, L. See abs. 53a.

3167. Sheely, M. L. Production of Synthetic Fatty Acids. BIOS Misc. Rept. 26, 1945, 31 pp.; PB 93,709. Chem. Abs., vol. 38, 1944, p. 5200.

An investigation of the 2 major synthetic fatty acid producing units in Germany: I. G. Farbenindustrie A.-G. at Oppau and the Deutsche Fettsäurewerke at Witten. Describes processes of oxidation of paraffins to fatty acids and the uses made of the resulting products. The report contains a translation of abs. 2170.

3168. Sherwood, P. W. Oxidation of Methane to Formaldehyde; Interrogation of Dr. Karl Schmitt of Bergwerks Gesellschaft, Hibernia A.-G., at Herne. FIAT Final Rept. 608, June 1946, 6 pp.; PB 44,656.

Process is described for the partial oxidation of CH_4 by ozonized O_2. The reaction is said to take place at atmospheric pressure, with an $O_2:CH_4$ ratio of 40:60 and at a temperature of 110°–120° C. The catalyst is not very active $<110°$ C, and $>120°$ C. oxidation tends to go beyond the formaldehyde stage. The raw materials for the process consisted of CH_4, approximately 70% from the separation of coke-oven gas, and Linde-Frankl O_2, about 98%, which was ozonized to an ozone content of 0.5–2.0 vol. %. The preparation of the barium peroxide catalyst is also briefly described. A drawing of Dr. Schmitt's 2-pass ozonizer is shown.

3169. Sherwood, P. W. Aldehydes From Hydrocarbons. Petrol. Processing, vol. 4, No. 7, 1949, pp. 794–800.

Describes 2 processes for the manufacture of aldehydes directly from hydrocarbons. Partial oxidation of hydrocarbons can be made on the basis of formaldehyde and acetaldehyde production. The more recent Oxo process for the synthesis of aldehydes by the catalytic reaction of olefins with water gas, shows interesting potentialities for the manufacture of propionaldehyde, butyraldehyde, and valeraldehyde. At present, however, it is used only as a 1st step in the production of isooctyl and nonyl alcohols and other derivatives. By indirection, it can be used for the synthesis of an unlimited variety of aldehydes. Technical details of the oxidation and Oxo processes are described, and their possibilities and limitations are discussed briefly. German experience on the oxoation of olefins is summarized in describing the Italian Bambrini plant, which was designed by the I. G. Farbenindustrie but not constructed as planned. The economic prospects of the manufacture of aldehydes by the Oxo process are, at the present time, wholly a matter of speculation.

3170. ———. From Synthetic Fuels, What Chemicals! Chem. Eng., vol. 56, No. 9, 1949, pp. 99–101.

The chemicals obtainable from the Fischer-Tropsch reaction, from high-pressure hydrogenation, and from shale oil are enumerated. Estimates are given of the probable amounts recoverable. Their occurrence and yields vary widely. Reviews of the literature.

3171. ———. Primary Long-Chain Alcohols. New Petrochemical. Oil Gas Jour., vol. 48, No. 5, 1949, pp. 71–72, 74–76, 82.

Two processes, the Synol and the Oxo processes, are available for the synthesis of primary long-chain alcohols. The latter has achieved commercial realization, and further development is in progress. The former has not reached industrial utilization because the alcohol production is nonselective; the product ranges from EtCH to its homologs of high molecular weight as well as a large output of hydrocarbons. The reaction mechanism involving the Synol synthesis is not clearly understood but is thought to be similar to the Fischer-Tropsch mechanism. The most striking characteristic of the product is the almost complete absence of secondary or branched-chain alcohols. Separation of the alcohols from the hydrocarbons is accomplished most efficiently by forming the boric acid esters. The Oxo reaction, on the other hand, is remarkably versatile and takes place readily with a number of olefinic and acetylenic compounds. Olefins ranging from ethylene to diisobutylene from cyclohexene to pinene have been successfully processed, usually with yields in excess of 90%. Thus, it is ideally suited for the manufacture of a wide range of primary monoalcohols and a more limited range of aldehydes. Where the alcohol is the desired final product, the reaction is carried in 2 successive stages: Oxoation followed by hydrogenation of the aldehydic product. Where the desired product is 1 particular product rather than a mixture, it is necessary to employ a highly purified olefin as starting material. A limitation of the process is that it is not possible to effect the reaction with aromatic compounds.

3172. ———. Byproduct Hydrocarbon Gases. Gas, vol. 26, No. 5, 1950, pp. 54, 59–61.

Quantity and composition of byproduct gases from petroleum processing are given as a source of comparison with byproduct gases from Fischer-Tropsch, coal-hydrogenation gases, and shale-oil gases. Byproduct gases formed during the Fischer-Tropsch synthesis depend to a great extent on the catalyst employed, as well as on the interrelation of operating temperature and $CO:H_2$ ratio in the synthesis gas, operating pressure, and converter design. A striking characteristic is the high olefin content (25–60% for the Co catalyst and 20–80% for the Fe catalyst) and the comparatively small amount of C_2 hydrocarbons. Wide variations in the amount of permanent byproduct gases may be expected. An average expectancy would be about 1,000 cu. ft. per bbl. of total oil yield. In addition there may be 150 cu. ft. per bbl. of liquid petroleum gases and another 150 cu. ft. per bbl. of propylene and butene for chemical processing. Gases from coal hydrogenation differ markedly from the Fischer-Tropsch gases in the complete absence of olefins. The 2 phases of the hydrogenation process yield unequal amounts of byproduct gases; the larger portion being derived from the primary liquefaction. The composition of the gas is surprisingly independent of the feedstock employed and of operating conditions. Typical byproduct gas from coal liquefaction is about 90% C–C_3 and from the vapor phase about 90% C_3 and C_4. Unlike the dilute Fischer-Tropsch tail gases with an average heating value of only 650 B. t. u. per cu. ft., the permanent gases from coal hydrogenation are rich enough (1,065 B. t. u. per cu. ft.) to justify cross-country transmission. Byproduct gases from oil-shale retorting depend on the type of process used, but are normally of low heat value. Those gases from the hydrogenation of shale oil are quite similar to those from coal hydrogenation.

3172a. ———. Water Gas From Methane. Petrol. Processing, vol. 5, 1950, pp. 1,308–1,311; Chem. Abs., vol. 45, 1951, p. 2,650.

Survey of various methods for producing water gas from CH_4 and steam is given.

Shevyakova, L. *See* abs. 2774.

3173. Shibata, Z., and Mori, I. [Reduction Equilibrium Between Metallic Oxide and Hydrogen. I. Measurement of $CoO+H_2 \rightleftharpoons Co+H_2O$ by New Methods.] Ztschr. anorg. Chem., vol. 212, 1933, pp. 305–316; Chem. Abs., vol. 27, 1933, p. 4468.

Equilibrium $CoO+H_2 \rightleftharpoons Co+H_2O$ was studied at 921°, 821°, 721°, 622°, 522°, and 422°. The relation between the equilibrium constant K and temperature is: log $K=(494.191/T)+1.08690$. The dissociation pressure of CoO and the equilibrium of H_2O gas at 400°–1,000° are calculated.

3174. Shibata, Z., and Terasaki, Y. [Promoting Carburization of Iron by Barium Carbonate.] Nippon Kinzoku Gakukai-Shi, vol. 2, 1938, pp. 187–192; Chem. Abs., vol. 32, 1938, p. 7382.

Electrolytic Fe specimen was carburized by CO at 900° for 2 hr. When $BaCO_3$ was placed in the carburizing chamber, it accelerated the carburization. Conclusion: CO gas is adsorbed on the surface of $BaCO_3$ and then decomposed by the reaction: $4\ CO=C_3O_2+CO_2$. C_3O_2 is desorbed and partly polymerized and decomposed by the reaction: $C_3O_2=C_2+CO$. This C_2 gas will diffuse into the Fe, and solid solution is formed.

Shiffler, W. H. *See* abs. 2771.

Shilling, W. G. *See* abs. 2578, 2579.

Shimamura, K. *See* abs. 1344, 1345, 1346, 1349, 1350.

3175. Shimura, S. [Study of the Structure of Cementite.] Proc. Imper. Acad. (Tokyo), vol. 6, 1930, pp. 269–271; Proc. World Eng. Cong., Tokyo, 1929, vol. 34, 1931, pp. 223–225; Chem. Abs., vol. 24, 1930, p. 5271.

Preliminary report on the X-ray structure of cementite and spiegeleisen, both of which have the same dimensions for the unit cell. Both belong to the simple orthorhombic lattice Γ_0 and the space group V^{16}_h. It is concluded that C is contained as neutral atoms in austenite but comes to take the configuration of the cementite molecule with neighboring Fe atoms as austenite changes to martensite, and it always segregates out as cementite at the A_1 transformation point. C metastably contained in α–Fe (this is less than 0.03%) also takes the cementitic arrangement.

Shirai, S. *See* abs. 1754a, 3178.

3176. Shirai, S., Kimumaki, J., and Ogawa, T. [Iron Catalyst for Synthesis of Gasoline.] Jour. Soc. Chem. Ind. (Japan), vol. 46, 1943, pp. 329–331; Chem. Abs., vol. 42, 1948, p. 6082.

Catalyst for the hydrogenation of CO should not be heated to a temperature above that at which it is used in the synthesis. The alkali promoter should be evenly distributed; this is effected by using KNO_3 instead of K_2CO_3 to activate the catalyst.

3177. Ogawa, T., Kimumaki, J., and Fujisaki, T. [Iron Catalyst for Synthetic Petroleum. II. Some Characteristic Properties of Iron Catalyst for Synthetic Petroleum.] Jour. Soc. Chem. Ind. (Japan), vol. 47, 1944, pp. 242–243; Chem. Abs., vol. 42, 1948, p. 7011.

Activity of the ordinary Fe catalyst, which does not contain excess alkali, increases with time, passes through a maximum, and then decreases. The maximum is affected strongly by the reaction temperature. The higher the reaction temperature or activation temperature, the earlier the appearance of the maximum. Thus, it is possible to decrease the time of activation and increase the yield.

3178. Kimumaki, J., Shirai, S., and Fujisaki, T. [Iron Catalyst for Synthetic Petroleum. III. Influence of Barium Nitrate on Iron Catalyst.] Jour. Soc. Chem. Ind. (Japan), vol. 47, 1944, pp. 244–247; Chem. Abs., vol. 42, 1948, p. 7011.

$Ba(NO_3)_2$ was found to be an excellent accelerator for Fe catalyst, especially for low-alkali catalyst. The optimum amount of K_2CO_3 for the catalyst was 2%. The order of immersion in K_2CO_3 and $Ba(NO_3)_2$ did not affect the activity.

Shokal, E. C. *See* abs. 2441, 2442.

Shokol, A. A. *See* abs. 2730.

Shpulenko, K. B. *See* abs. 3366.

Shuĭkin, N. I. *See* abs. 3761.

3179. Shuĭkin, N. I., Minachev, K. M., and Rozhdestvenskaya, I. D. [Hydrogenation and Dehydrogenation of Hydrocarbons With Low-Percent Nickel Catalysts.] Doklady Akad. Nauk S. S. S. R., vol. 72, 1950, pp. 911–913; Chem. Abs., vol. 44, 1950, p. 8332.

Catalysts with Ni contents of 0.125–4% were prepared by 40–45 min. impregnation at 30°–35° of 1 gm. activated charcoal with 2 ml. solution of $Ni(NO_3)_2$, drying at 125°, and reduction in H_2 at 330°. Hydrogenation (I) of C_6H_6 was carried out in a stream of excess H_2 at 115°–176°, space velocity 0.025–0.2 l. per l. catalyst per hr.; dehydrogenation (II) of cyclohexane at 300°–302°, space velocity 0.2. (I) proceeds to a significant extent with catalysts containing 1% Ni or more; the reaction is just barely noticeable with 0.5% Ni. In (II), the initial activity of the catalyst varies very little with the Ni content, varying from 0.5–4%; with the progress of the reaction, the activity of the catalysts falls rapidly, by a factor of 3–4 after 2,000 min. In reaction (I), the degree of hydrogenation is virtually independent of the temperature at 120°–176° and is not affected by a variation of the space velocity by a factor of 4; under these conditions, it attains 100%. Further increase of the space velocity, by a factor of 8, lowers the degree of hydrogenation 68–70%. At constant space velocity of 0.06, the activity of the 4% Ni catalyst maintains itself at a near 100% level for more than 25 hr., and that of the 2% catalyst falls off only slowly.

3180. Shuler, K. E., and Laidler, K. J. Kinetics of Heterogeneous Atom and Radical Reactions. I. Recombination of Hydrogen Atoms on Surfaces. Jour. Chem. Phys., vol. 17, 1949, pp. 1212–1217; Chem. Abs., vol. 44, 1950, p. 4760.

Data on the kinetics of the recombination of H atoms on various types of surfaces are analyzed in the light of the theory of absolute reaction rates. Expressions are derived for the recombination coefficient and the 1st-order-rate constant, enabling these quantities to be calculated on the basis of postulated mechanisms. The experimental activation energies are consistent with estimates using either Hirschfelder's rule or an expression utilizing the experimental desorption temperature. For the reaction on dry oxides and dry glass, good agreement is found, assuming that reaction occurs between a gas-phase H atom and an adsorbed H atom, the adsorption being of the van der Waals type at low temperatures and chemisorption at higher ones. The mechanism of surface poisoning by water vapor is not due to the necessity for desorbing the water molecule: In the high-temperature region it is due to an increase in activation energy, the mechanism being $S-OH+H \rightarrow S-O+H_2$; in the low-temperature region it is due to a decrease in the number of active centers, the reaction being between a gaseous atom and a van der Waals adsorbed H atom above the water layer.

3181. Shull, C. G. Production of Highly Polarized Neutron Beams by Bragg Reflection From Ferromagnetic Crystals. Phys. Rev., vol. 81, 1951, p. 626; Chem. Abs., vol. 45, 1951, p. 4,517.

Monochromatic beam of neutrons (λ=1.204 A) was reflected from the (220) planes of a magnetized slice of crystalline Fe_3O_4 with the slice set in transmission orientation and with the magnetization vector perpendicular to the plane of scattering. The reflected beam was polarized 100 ±5%.

3182. Shull, C. G., Wollan, E. O., and Strauser, W. A. Magnetic Structure of Magnetite and Its Use in Studying the Neutron Magnetic Interaction. Phys. Rev., vol. 81, 1951, pp. 483–484; Chem. Abs., vol. 45, 1951, p. 4502.

Effect of the magnetization in different directions on the (111) Fe_3O_4 neutron-diffraction peak is shown. The pronounced dependence of neutron scattering intensity on magnetization direction suggests that the reflection might have interesting application as a fast-neutron shutter. In a single-crystal reflection large neutron currents are attainable and rapid field variations with the small fields required for saturation of single crystals can be achieved in this or other members of the ferrite series. 9 refs. given.

Shultz, J. F. *See* abs. 50, 53, 833, 834, 835, 3679.

Schultz, J. F., Seligman, B., Lecky, J., and Anderson, R. B. Studies of the Fischer-Tropsch Synthesis. XII. Composition Changes of Nitrided Iron Catalysts During the Synthesis. *See* abs. 53b.

Schultz, J. F., Seligman, B., Shaw, L., and Anderson, R. B. Fischer–Tropsch Synthesis. XI. Effect of Nitriding on 3 Types of Iron Catalysts. *See* abs. 53a.

Shurmovskaya, N. *See* abs. 332.

3183. Shvaĭtzer, I. [Use of the Byproducts of the Groznenskii Acetone-Butyl Alcohol Factory.] Jour. Chem. Ind. (U. S. S. R.), vol. 12, 1935, pp. 345–349; Chem. Abs., vol. 29, 1935, p. 7571.
Production of MeOH and dry ice.

Sickman, D. V. *See* abs. 3342.

3184. Sidgwick, N. V., and Bailey, R. W. Structures of the Metallic Carbonyl and Nitrosyl Compounds. Proc. Roy. Soc. (London), vol. 144, A, 1934, pp. 521–537; Chem. Abs., vol. 28, 1934, p. 4676.

For the compounds $M_x(CO)_y(NO)_z$, $G-[(xm+2y+3z)/x]=x-1$; (m=atomic number of M, G=atomic number of the next inert gas). For carbonyls (z=0) the binding must be $M^{-}-C^{+}\equiv O^{+}-M^{-}$; if x=1, the link is linear; x=3, triangular, x=4, tetrahedral; a CO is on each edge. The crystal structures of $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ are compatible with this. For ntrosyis, the binding is $M^{-}-N^{+}\equiv O^{-}$. Nearly all the carbonyls and a great many nitrosyls obey these rules.

Sidorov, N. V. *See* abs. 2757, 3364, 3365, 3366.

3185. Sieverts, A., and Hagen, H. [Ability of Cobalt to Absorb Hydrogen and Nitrogen.] Jour. Phys. Chem. (U. S. S. R.), vol. 169, A, 1934, pp. 237–240; Brennstoff-Chem., vol. 15, 1934, p. 414; Chem. Abs., vol. 28, 1934, p. 6606.

Pure Co powder was first reduced with H_2 at 800° and then at the same temperature in a quartz absorption flask stirring for 10 days. Fresh H_2 was used continuously to measure the absorption at various temperatures. The volume of the free gas was determined with argon. The solubility of the H_2 increased with rising temperature, at atmospheric pressure and 600°, 0.08 mg. H_2 and 1,200° 0.5 mg. H_2 per 100 gm. Co were absorbed. At varied pressures, the amount absorbed was proportional to the sq. root of the pressure. The absorbability of technical Co turnings containing 2.5% Fe was the same as with pure Co. N_2 is virtually insoluble in Co up to 1,200°. A comparison of H_2 absorption for Fe, Co, and Ni showed that absorbability of Co up to 900° is only a little less than that of α Fe; above 900°, the difference becomes greater because here the γ Fe with its higher solubility appears. The absorbability of Ni for H_2 is considerably greater than that of Fe. The magnetic transformations with any of the 3 metals have no noteworthy effect on the H_2 absorption. The differences in the properties of Fe, Co, and Ni, with regard to the absorbability, are correlated with the various crystal structures.

Silina, N. P. *See* abs. 729.

3186. Simcox, A. K. Future of Synthetic Detergents in Relation to the Petroleum-Chemical Industry. Chem. and Ind., 1950, pp. 178–182.

Review of development of synthetic detergents by way of fatty acids from natural fat to synthetic fatty acids from nonfat materials such as petroleum paraffins and Fischer–Tropsch paraffins. Shows growing trend in the consumption of synthetic detergents from nonfat sources and its effect on the increasing satisfaction of the demand for edible fats.

3187. Šimek, B. G., and Kassler, R. [Conversion of Carbon Monoxide by Water Vapor on Iron Catalysts.] Chim. et ind. Special No., April 1934, pp. 330–337; Chem. Abs., vol. 28, 1934, p. 5626.

In order to ascertain the part played by secondary reactions in the catalytic conversion of mixtures of water gas and water vapor over Fe catalysts, comparative tests were carried out with reduced aluminoferric and with pig Fe, both activated with K_2CO_3, with the following results: (1) at 500°, the reduction of the catalyst to oxide by CO alone stops before liberation of metallic Fe. (2) The metallic Fe formed by reduction at 500° with H_2 alone is oxidized by H_2O, so that the catalyst is in equilibrium with the gaseous phase. (3) The C liberated by known decomposition of CO on Fe catalysts, starting at 500°, can be gasified by H_2O, so that the homogeneous conversion of water gas over an Fe catalyst can be considered as the resultant of several reactions taking place successively in heterogeneous medium. (4) The importance of the conversion reaction proper, as compared to the decomposition of CO, was determined under varying conditions of flow, with reduced Fe and pig Fe as catalysts. (5) The catalyst prepared from pig Fe has a lower efficiency than the precipitated catalyst, but the secondary reactions are more intense in the former case than in the latter; their importance, however, decreases when the rate of flow is increased above a certain value. (6) H_2S exerts a poisoning action on the reduced precipitated Fe catalyst. (7) The degree of conversion over precipitated catalyst varies with the flow and exhibits a maximum for a definite flow, which itself depends on the temperature; the degree of conversion over activated pig Fe also exhibits a maximum, which does not correspond to a minimum of the secondary reactions.

3188. ———. [Conversion of Carbon Monoxide by Water Vapor on Iron Catalysts.] Zprávy Ústavu Vědecký Výzkum Uhli v Praze, vol. 2, 1935, pp. 113–128; Chem. Abs., vol. 30, 1936, p. 6168.

To determine the role of secondary reactions in the process of conversion of water gas on Fe catalysts, comparative experiments were conducted on often used precipitated ferric aluminum catalyst and on the crude Fe, both activated with K_2CO_3. The oxide catalyst, after being reduced to metallic iron by the H_2, is oxidized again by water gas. C obtained by the decomposition of CO on oxide contact can be changed into gas again by water gas, beginning around 500°. The influence of H_2S poisoning on the activity of precipitated oxide catalyst was observed also.

3189. Šimek, B. G., Coufalik, F., and Zamrzla, E. [Conversion of Methane in a Water-Gas Generator.] Mitt. Kohlenforsch.-Inst. Prag, vol. 3, 1937, pp. 236–255; Hornicky Vestnik, vol. 19, 1937, p. 414; British Chem. Abs., 1938, B, p. 1004; Chem. Abs., vol. 32, 1938, p. 7701.

Mixture of CH_4 (I) and steam (II) was passed over coke in a water-gas generator, starting at 1,200° and continuing to not lower than 1,000°. By varying conditions and proportions of (II), products having H_2: CO ratios of 1.02–11.76 were obtained. The most important factor in practicable water gas production from (I) was the temperature, which should be more than 1,100°. Increasing the rate of introducing (I) did not hinder its utilization as long as the temperature was maintained but was a hindering factor at lower temperatures. It is advantageous to use (I) and (II) in proportions required for making a product of H_2: CO=2. Use of too much (II) hinders utilization of (I); smaller amounts of (II) increased decomposition of (I), giving finely divided C and a gas of higher H_2 content. The use of (I) and (II) in a water-gas generator is more desirable than the usual process from both thermodynamic and heat-economy viewpoints. Tabulated data and methods of calculation.

Simizu, J. *See* abs. 3313.

3190. Simonet, R. [Synthesis of Methanol.] Peintures, pigments, vernis, vol. 8, 1931, pp. 1450–1452, 1475–1478; Chem. Abs., vol. 25, 1931, p. 3617.

General discussion.

3191. Simonovitch, M. Problem of Synthetic Liquid Fuels Under Present Conditions in Europe. Fuel, vol. 18, 1939, pp. 130–131; Rev. univ. mines, vol. 15, 1939, pp. 109–127.

General consideration followed by discussion of problems confronting different countries. It is concluded that Britain and the United States dominate the situation.

———. *See* abs. 2083.

Simons, H. P. *See* abs. 144.

3192. Singer, L. [Latest Literature on Motor Fuels.] Petrol. Ztschr., vol. 25, 1929, pp. 513–524; Chem. Abs., vol. 23, 1929, p. 4043.

Complete review with 227 refs.

3193. ———. [Recent Work on Motor Fuels.] Petrol. Ztschr., vol. 25, 1929, pp. 152–153; Chem. Abs., vol. 23, 1929, p. 1734.

Comprehensive review with 31 refs. to original papers.

3194. Singh, A. D. Fluidized-Coal Devolatilization. Power Plant Eng., vol. 51, No. 10, 1947, pp. 112–115.

Term "fluid devolatilization" is applied to the distillation of gas from coal fluidized by passage of gas or steam through a bed of the finely divided material. Pulverized coal is screw-fed from a hopper into pipes through which steam or recycled gas produced in the process flows fast enough to prevent settling of the largest particles. The coal is carried thus into a vertical, electrically heated retort. Tar vapor and gas are quickly evolved, and agglomeration of the char occurs only to a slight extent owing to preliminary oxidation of the coal and recirculation of about the same weight of char as that of the coal fed to the retort. The char is recovered by cyclone separators, and the tar vapor and gas pass to a cooling and condensing system for byproduct recovery. Heat transfer in the fluidized material may be nearly 6 times that of conventional coking, probably owing to the scrubbing action on the gas films surrounding the particles. Char leaving the fluidizer system at temperatures in the range 700°–800° should be an ideal fuel for cyclone burners, making possible very high rates of heat release. From 4–6% can be added to the overall heat recovery by the elimination of stack losses associated with the combustion of H_2. Char of 12,180 B. t. u. per lb. can be obtained from 11,460 B. t. u. coal, in addition to 9,300–16,600 cu. ft. of fuel gas and 14 gal. of tar per ton of coal. S is removed from the coal by the process.

3195. Singh, A. D., and Krase, N. W. Synthesis of Acetic Acid From Methanol and Carbon Monoxide. Ind. Eng. Chem., vol. 27, 1935, pp. 909–914; Chem. Abs., vol. 29, 1935, p. 6571.

Catalytic, vapor-phase synthesis of AcOH (I) from MeOH and CO under pressure was studied. The reaction goes at 300°–500° and 2,000–4,000 p. s. i. pressure.

Under the same conditions, recirculation of the exit products gave about 2 times the yield of (I) as that obtained by a once-through operation. Me_2O is 1 of the main byproducts, but since it is formed by a reversible reaction, recirculation of noncondensable gases builds its concentration to a constant value at about 2.4%. Use of 85% MeOH is best. The maximum catalyst temperature is 400°. Active C impregnated with H_3PO_4 was used as a catalyst. Its life is limited, owing, presumably, to volatilization.

3196. Sinnatt, F. S. Oils From Coal—Potentialities of a New Industry. Iron and Coal Trades Rev., vol. 128, 1934, pp. 139–140; Chem. Abs., vol. 28, 1934, p. 3873.

Various methods (high- and low-temperature carbonization, synthesis from water gas and H_2, hydrogenation of tar and coal) are compared briefly as to yields of motor and fuel oils.

3197. ———. Coal's New Industry—the Production of Oil. Gas Jour., vol. 212, 1935, pp. 711–712; Chem. Abs., vol. 30, 1936, p. 1205.

Review. The yield of liquid products is 100–120 gm. per m.^{3} of gas containing 29% CO and 58% H_2. They consist almost exclusively of straight-chain paraffins and olefins; their antiknock value therefore is low, but, on the other hand, the synthesis can be worked to give excellent Diesel fuel. In addition, the products can be converted by further treatment into lubricating oils of good quality. A small experimental unit has been set up at the Fuel Research Station with the object of developing the process in this direction.

3198. Sinnatt, F. S., and King, J. G. [Tars and Oils From Coal.] Jour. Soc. Chem. Ind. [Japan], vol. 44, 1925, pp. 413–424T; Colliery Guard., vol. 130, 1925, p. 320; Chem. Age, vol. 13. 1925, pp. 95–96; Chem. Abs., vol. 19, 1925, p. 3156.

General discussion and compilation of relevant data; the Bergius and Synthol processes are discussed briefly.

3199. Siomi, K., and Iwamote, T. [Hydrogenation of Acetylene.] Jour. Soc. Chem. Ind. (Japan), vol. 41, 1938, p. 401B.

Best catalyst for obtaining liquid hydrocarbons and C_2H_4 from C_2H_2 and H_2 at ordinary pressure is a mixture of Ni, Co, and Cr.

3200. Sips, R. Structure of a Catalyst Surface. Jour. Chem. Phys., vol. 16, No. 5, 1948. pp. 490–495.

Mathematical method is described that makes it possible to calculate rigorously the distribution of the adsorption energies of the sites of a catalyst surface when the adsorption isotherms are known, if the adsorption is localized and there are no interactions. This method is applied to a Freundlich isotherm, and to a new theoretical isotherm, which reduces to the Freundlich type for small pressures but exhibits saturation for large pressures. It is shown that this isotherm corresponds to a distribution function that differs very little from a Gaussian one. The case of atomic adsorption of gases is considered also.

3201. Sirovich, G. [Polymorphic Transformation of Iron at 370° and the Possibility of Solution of Cementite in α_1–Iron.] Gazz. chim. ital., vol. 53, 1923, pp. 674–688; Chem. Abs., vol. 18, 1924, p. 960.

In a previous paper, Metall. italiana, vol. 14, 1922, pp. 3–17, Sirovich and Ariano demonstrated that α-Fe exists in 2 forms. One of these, called α_1, is stable and magnetically resistant and in it C is soluble in the solid state; the other, the α_2–form, is formed at 370°, is relatively soft, is magnetic, but does not dissolve C in the solid state. The above and other conclusions are confirmed in this paper by further results (1) on the existence of an A_0 point at 370° indicating polymorphic transformation of Fe and (2) on the possibility of causing solution of cementite in α_1–Fe without having recourse to tempering. Earlier work on (1) is reviewed. It has been considered generally that there is a complete continuity in the dilatometric behavior of Fe from ordinary temperatures up to 700°. The results given here were obtained with the photographically registering dilatometer of Montemartini and Bosana. A parallelpiped (4.7 cc. in vol.) of electrolytic Fe was placed in fused Sn for the determinations. Other details are given. The volume as registered showed a distinct break at 370°. The same results were obtained with a fused Fe (C 0.04, Mn 0.048, S 0.052, P 0.034%), showing that the effect is not due to any H_2 present in the other specimen of Fe used. The Sn was then replaced with melted paraffin in order to eliminate any possible effect of the Sn, but without changing the results. The same determination when carried out with a specimen of Mn-containing Fe (C 0.07 Mn 0.49, Si trace, S 0.035, P 0.04%) showed only a slight change in direction at 370°–380° but no discontinuity. Sirovich suggests that previous failures by other workers to obtain a transformation at 370° are due to the effects of impurities as in the case of Mn here reported. In the experiments on the solution of cementite in α_1–Fe steels containing cementite and ferrite in extreme dispersion, a hypoeutectoid steel with C 0.53, Mn 0.51, Si 0.11, S 0.039, P 0.06 was used. It was heated at 850° for 0.5 hr. The external decarbonized part was ground off and Brinell hardness test was made (182). The piece then was introduced into a fused Sn bath kept at 300°±5° (heated in an electric coil). The Brinell test and the micrographic structure were determined after 288, 528, and 3,501 hr., at which times the hardness was 216. 241, and 241, respectively. The micrographs showed a progressively increasing homogeneity, but completion of the process is prevented by retarded diffusion. The possibility of obtaining some solution of cementite in α_1–Fe in the field of stability of the latter with pearlitic steels was established.

3202. Sittenfield, M. Economic Outlook for Synthetic Detergents. Chem. Inds., vol. 62, No. 4, 1948, pp. 584–585, 650, 652, 658.

An appraisal of the outlook for the various types of detergents from a raw materials and cost standpoint. It is expected that within a period of 2 yr. the long-chain alcohols obtained from the Fischer-Tropsch synthesis using the Oxo process will be offering competition with sulfated alcohols from other sources. It is estimated that long-chain mixed alcohols can be produced at a cost of $0.10–0.15 per lb., at which price the sulfated alcohol type of surface active compounds will become highly competitive with soap and with other classes of synthetic detergents.

3203. Sittig, M. Exothermic Reaction Techniques. Petrol. Processing, vol. 5, 1950, pp. 1080–1082.

Exothermic reaction techniques are classified, and their application to heat removal and control in commercial chemical processes is reviewed. Use of fluidized solids reactors in the Fischer-Tropsch process has served greatly to reduce the total volume of cooling surface required. Since a rocket motor is essentially an exothermic reactor, application of the same principle in chemical process reactor design is considered a possibility.

Skaperdas, G. T. *See* abs. 2128.

Skinner, L. C. *See* abs. 155, 156, 3311.

3204. Slater, W. E. Influence of Different Surfaces on the Decomposition of Methane. Jour. Chem. Soc., vol. 109, 1916, pp. 160–164; Chem. Abs., vol. 10, 1916, p. 1589.

To determine whether the amount of decomposition of CH_4 in contact with heated surfaces depends upon the kind of substance exposed, or whether it is a function of the surface area only, the gas was heated to 910° at constant pressure and time with various refractory materials, the degree of decomposition being determined by measuring the amounts of H_2 in the residual gases. The results showed that the rate of decomposition depends upon the nature of the heated surface. It was found that Si, MgO, Al_2O_3, and BaO did not accelerate the reaction and that Cu, carborundum, graphite, charcoal, and Fe did.

Slin'ko, M. G. *See* abs. 305.

Slone, M. C. *See* abs. 3100.

3205. Slosse, —, and Solvay, —. [Electrical Discharge.] Bull. Acad. roy. Belg., vol. 35, No. 3, 1898, pp. 547–551; Chem. Zentralb., 1898, II, p. 421.

Further evidence is presented that CH_2O is produced when a mixture of CO_2 and H_2 and when one of CO and H_2 are submitted to the influence of the silent electric discharge.

Smart, J. S. *See* abs. 2216.

Smirnova, Z. M. *See* abs. 1671.

Smith, A. E. *See* abs. 181.

Smith, C. C. *See* abs. 437.

3206. Smith, D. F. Equilibrium Condition in the Formation of Hydrocarbons and Alcohols From Water Gas. Ind. Eng. Chem., vol. 19, 1927, pp. 801–803; Chem. Abs., vol. 21, 1927, p. 2783.

Study of equilibrium conditions in the reactions between CO and H_2 to produce CH_4, C_2H_6, C_3H_8, C_6H_6, MeOH, EtOH, and BuOH. Conclusions: (1) It is easier to form the higher paraffin hydrocarbons than the lower ones from water gas at all temperatures, and there is a much greater tendency for the O_2 to go to CO_2 than to H_2O; (2) the tendency to form aromatic and probably branched-chain and cyclic hydrocarbons is generally greater than to form straight-chain compounds; (3) the lower alcohols cannot be formed from water gas at atmospheric pressure and temperatures of 300° and above, while the higher alcohols can be formed in considerable amounts with water gas under these conditions; (4) the tendency to form all these compounds falls rather rapidly with increasing temperature; (5) maximum possible yields can be calculated from the values of K (given in a table); and (6) the acuracy of the free-energy values given should be satisfactory on the alcohols, and reasonably so on the hydrocarbons.

3207. ———. Note Concerning Thermodynamic Calculations. Ind. Eng. Chem., vol. 20, 1928, pp. 859–860; Chem. Abs., vol. 22, 1928, p. 4339.

Synthesis of hydrocarbons especially C_6H_6, from water gas is considered. The rate of reaction is stressed as an important factor, for free-energy values alone will not tell what species predominates. Comments are made on Francis' calculations of the free energies of various hydrocarbons and alcohols (abs. 1079), and it is pointed out that the use of thermal data often leads to erroneous results. Values from equilibrium constants, where all substances involved are at the standard fugacity of 1 atm., are more reliable.

3208. ———. [Reply to the Criticism of Hans Tropsch of My Paper on the Equilibrium Conditions for Formation of Hydrocarbons and Alcohols From Water Gas.] Brennstoff-Chem., vol. 9, 1928, pp. 248–249; Chem. Abs., vol. 22, 1928, p. 4773.

Polemical, dealing with equilibrium constants calculated by Smith and Tropsch (abs. 3206 and 3449). Smith's conclusion "at all temperatures in increasing measure it is easier to obtain the higher hydrocarbons from water gas" is attacked by Tropsch. Smith further explains his data, and Tropsch adds further comment.

3209. Smith, D. F. and Branting, B. F. Equilibrium Between Methanol, Carbon Monoxide, and Hydrogen. Jour. Am. Chem. Soc., vol. 51, 1929, pp. 129–139; Chem. Abs., vol. 23, 1929, p. 1337.

Equilibrium $CH_3OH/(CO)(H_2)^2$ at 1 atm. over ZnO and the 4 Zn : 1 Cr catalyst of Smith and Hawk (abs. 3210) was studied by a direct method giving $K=5.57\times10^{-4}$ at 303.8°, error=5%. From this equilibrium value and the heat data of Smith (abs. 3206), the free-energy change is $\Delta F=-20{,}857+41.17\ T \log T - 0.01423\ T^2 - 54.42\ T$, giving 16,070 cal. at 700° K.

3210. Smith, D. F., and Hawk, C. O. Catalytic Decomposition of Methanol. Jour. Phys. Chem., vol. 32, 1928, pp. 415–424; Chem. Abs., vol. 22, 1928, p. 1520.

Rate of decomposition of CH_3OH by 36 different metallic and oxide catalysts, at atmospheric pressure was measured, mainly at 300°, by the dynamic method. The methods of preparation and the composition of the various catalysts are given. ZnO, made by igniting $ZnCO_3$, mixtures of ZnO and Cr_2O_3 in the atomic proportions 4 Zn : 1 Cr, mixtures of ZnO and UO_2, and perhaps also mixtures of ZnO and V_2O_3 and of CdO and Cr_2O_3, would be considered very good catalysts for the decomposition of CH_3OH into CO and H_2. These substances also should be good catalysts for the formation of CH_3OH from water gas. The activity of pure ZnO and also of $ZnO–Cr_2O_3$ catalysts is to a considerable degree dependent on the heat and other treatment to which they are subjected. The specific catalytic effect of pure Cr_2O_3 is absent in the $ZnO–Cr_2O_3$ catalysts. X-ray powder photographs indicated that in these catalysts the Cr_2O_3 does not exist in the ordinary form but is either amorphous or has combined with ZnO. Small amounts of CO_2 were present as a byproduct of the decomposition in virtually all cases.

3211. Smith, D. F., and Hirst, L. L. Reactions That Occur on a Methanol Catalyst. Ind. Eng. Chem., vol. 22, 1930, pp. 1037–1040; Chem. Abs., vol. 24, 1930, p. 5586.

CO_2 and H_2 react on a $ZnO–Cr_2O_3$ catalyst at 304° to form MeOH, CO, and H_2O. CO and H_2O also react to give CO_2 and H_2, and equilibrium may be closely approached in the water gas reaction. It was found impossible to determine which of the reactions comes nearest equilibrium when this catalyst acts on $H_2CO_2–H_2O$ mixtures. It is suggested that the formation of MeOH from CO and H_2 may not be direct, especially as a steady state is approached.

3212. ———. Reliability of the Heat Data as a Factor in Calculating Equilibria Involving Methanol. Ind. Eng. Chem., vol. 22, 1930, pp. 634–635; Chem. Abs., vol. 24, 1930, p. 3408.

Reply to B. F. Dodge (abs. 704).

3213. Smith, D. F., Davis, J. D., and Reynolds, D. A. Synthesis of Higher Hydrocarbons From Water Gas. I. Ind. Eng. Chem., vol. 20, 1928, pp. 462–464; Chem. Abs., vol. 22, 1928, p. 1948.

Study was made of the efficiency of different catalysts in producing liquid hydrocarbons from water gas at atmospheric pressure. Under the best conditions, with Co–Cu–Mn catalyst, 66 gm. of oil were produced per m.^{3} water gas.

3214. Smith, D. F., Hawk, C. O., and Reynolds, D. A. Synthesis of Higher Hydrocarbons From Water Gas. II. Ind. Eng. Chem., vol. 20, 1928, pp. 1341–1348; British Chem. Abs., 1929, B, p. 82; Chem. Abs., vol. 23, 1929, p. 814.

Catalyst made from coprecipitated hydroxides of Co, Mn, and Cu was used to synthesize hydrocarbons from purified water gas at atmospheric pressure and at temperatures about 250°. Space velocities 120–360 were used. Extensive tabulation is made of the nature and quantities of hydrocarbons formed, the quantities of water gas converted, and their relation to the temperature and space velocity. The quantities of oxygenated products formed were comparatively small. The percent of CH_4 in the hydrocarbon product was higher the higher the temperature and the more active the catalyst. The proportion of very heavy hydrocarbons was greater at the lower space velocities and the higher temperatures. At the higher space velocities and higher temperatures, relatively more unsaturated hydrocarbons were formed. At 260° and 260 space velocity, the hydrocarbon product was 21% by weight CH_4, 45% enriching hydrocarbons (German Gasol), 34% motor fuel. The yields of hydrocarbons, exclusive of CH_4, vary 92–156 gm. per m.^{3} of H_2+CO converted. At 203° and 230 space velocity, about 18% of the water gas was converted in a single pass.

3215. Smith, D. F., Hawk, C. O., and Golden, P. L. Mechanism of the Formation of Higher Hydrocarbons From Water Gas. Jour. Am. Chem. Soc., vol. 52, 1930, pp. 3221–3232; Chem. Abs., vol. 24, 1930, p. 4755.

Experiments are reported that show that cracking of the heavier hydrocarbons does not play any considerable part in the formation of the mixture of hydrocarbons higher than CH_4 when the synthesis is carried out on a Co–Cu–Mn oxide catalyst under the conditions described. The experiments in which Me_2CO was passed over the catalyst with H_2, N_2, or CO indicate that Me_2CO likewise is not a predominating intermediate. Me_2CO is almost never present in the products from water gas alone. Polymerization of C_2H_4 or of higher olefins does not occur. C_2H_4, at least in concentrations over 10%, enters into reaction upon the Co–Cu–Mn oxide catalyst in the presence of water gas, forming higher hydrocarbons and large quantities of O-containing compounds. The O-containing compounds dehydrate to a greater or less extent, producing hydrocarbons. The dehydration is accompanied by some polymerization. The extent to which C_2H_4 enters into these reactions does not change largely with the C_2H_4 concentration when this is above about 10%, but formation of these intermediate products depends quite markedly upon the concentration of water gas. The mechanism forming hydrocarbons may be regarded as follows: There is some association of H_2 and CO on the catalyst surface. This complex may either decompose, giving an olefin and H_2O, or C_2H_4 or other olefin may combine with it to form an O-containing compound, which may either pass into the products or eliminate H_2O to form a higher olefin hydrocarbon. The olefins are to be regarded as the primary hydrocarbon products. They may later be hydrogenated to form paraffin hydrocarbons or pass on into the products, depending upon the experimental conditions of H_2 concentration, space velocity, catalyst, and temperature. The mechanism of H_2 formation on an Fe–Cu catalyst is essentially different from that on a Co–Cu–Mn oxide catalyst, aside from the relative amounts of CO_2 and H_2O formed, since in this case C_2H_4 does not enter into reaction.

Smith, D. F., Hawk, C. O., and Reynolds, D. A. Synthesis of Higher Hydrocarbons From Water Gas. II. *See* abs. 3214.

3216. Smith, E. W. Economic Utilization of Coke-Oven Gas. Gas World, vol. 121, 1944, pp. 130–133; Gas Jour., vol. 244, 1944, pp. 208–209; Jour. Inst. Fuel, vol. 17, 1944, pp. 188–189, 191; Chem. Abs., vol. 38, 1944, p. 5661.

Address in which the coordination of a coke plant with an undertaking distributing gas to consumers is discussed as a means for disposing of the plant's surplus gas. The use of coke-oven gas as a raw material in the synthesis of oil by the Fischer–Tropsch process also is considered.

3217. Smith, F. Chemicals From Petroleum. Jour. Inst. Petrol., vol. 32, A, p. 262; Jour Roy. Soc. Arts, vol. 45, 1945, pp. 566–598.

Three lectures are recorded. Among the many products mentioned in (I) are those from H_2 and CO by the Fischer–Tropsch synthesis. (III) gives an outline from the use of synthetic hydrocarbons as fuels. The relation between their structures and efficiency in internal combustion engines is discussed. A graph shows the approximate relation between octane numbers and the number of methyl groups in the paraffin chains.

3218. Smith, G. E. P., and Palmer, H. F. The Coming Petrochemical Industry. Nat. Petrol. News, vol. 36, 1944, pp. 571–575R; Chem. Abs., vol. 38, 1944, p. 6080.

Review showing the importance of petroleum and natural gas as raw materials in the synthesis of commercial organic chemicals.

Smith, G. H. *See* abs. 422.

3219. Smith, H. M. Possible Utilization of Natural Gas for the Production of Chemical Products. Bureau of Mines Inf. Circ. 6388, 1930, 5 pp.; Chem. Abs., vol. 25, 1931, p. 397.

Chart shows the products obtainable from natural gas by oxidation, pyrolysis and chlorination, and the uses of each. These products and the compounds derived from them are: Oxidation—water gas, H_2, MeOH acetone, formaldehyde (bakelite); pyrolysis—$H_2(NH_3)$, $C_2H_4(C_2H_5OH$, $C_2H_4Cl_2$, $C_2H_4(OH)_2)$, C_3H_6 (isopropyl alcohol), C_4H_8 (secondary Bu alcohol), anthracene (alizarin), naphthalene (indigo), C_2H_2 (CH_3CHO), butadiene (rubber), C_6H_6 (resorcinol), C_7H_8 (saccharin), xylene and C black; chlorination—CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4.

3220. Smith, H. M., and Holliman, W. C. Utilization of Natural Gas for Chemical Products. Bureau of Mines Inf. Circ. 7347, 1947, 24 pp.; Petrol, vol. 26, No. 4, 1947, p. 365; Rept. to Federal Power Commission, June 1946, 11 pp.

Revision of Bureau of Mines Inf. Circ. 7108, 1940. It shows in graphic form the general reactions used and the chemical products that can be obtained from natural gas as the raw material.

Smith, L. B. *See* abs. 1743, 1744, 2484.

Smith, L. G. *See* abs. 2824.

3220a. Smith, P. I. Soap From Synthetic Fatty Acids. Am. Perfumer Essent. Oil Rev., vol. 58, July 1951, pp. 53–55; Chem. Abs., vol. 45, 1951, p. 10,621.

Use for soap manufacture of the wax fraction obtained during the Fischer-Tropsch hydrocarbon synthesis is discussed. The unpleasant odor associated with the synthetic fatty acids must be removed by suitable treatment before and not after saponification.

Smith, P. V. *See* abs. 2325a.

Smith, R. N. *See* abs. 2700.

Smith, S. L. *See* abs. 1331, 1332, 1335a, 1336.

Smith, W. R. *See* abs. 1771.

3221. Smithells, C. J. Permeability of Metals to Hydrogen. Nature, vol. 139, 1937, p. 1113; Chem. Abs., vol. 31, 1937, p. 6088.

Rate of diffusion of H_2 was determined in cc. per cm.^{2} per sec. at 760 mm. pressure for metal 1 mm. thick at 1,000°, 500°, and 0°. Calculations were made for the following: Fe, Ni, Mo, Pt, Cu, Al. Apparatus for work at high pressures is made of steel to provide the necessary strength. The diffusion of H_2 cannot be reduced greatly by increasing the thickness. At room temperature, 1 mm. Cu would be as effective as 5 miles of steel, and 1 mm. Al would be better than 10^{13} miles of Pd in retarding this diffusion.

3222. Smits, A., and Wolff, L. K. [Velocity of Transformation of Carbon Monoxide. I.] Proc. "Koninkl. Akad. Wetenschappen Amsterdam", vol. 5, 1903, pp. 417–424; Jour. Chem. Soc., vol. 83, II, 1903, p. 276; Jour. physik. Chem., vol. 35, 1903, pp. 199–215.

From a study of the catalytic action of Fe, Ni, and Co on the system $2CO \rightleftharpoons CO_2+C$, Boudouard found that at 1,000°, CO_2 in contact with C is almost wholly converted into CO, while, at 445°, the reverse is true. The authors examine the conditions of the action below 445° when CO is in a metastable condition. The catalyst was finely divided Ni reduced at 445°. Observations made at 256°, 310°, and 340° indicated that the action was unimolecular. The reaction constants, calculated from $K=1/t \log P_0/2\,P_t-P_0$, were determined at the above temperatures, the values being 0.000279, 0.00186, and 0.00527, respectively. During these measurements the activity of the catalyst had not decreased. The 2 following hypotheses are adduced for the mechanism of the reaction: First (1) $CO_2=CO+O$ (with measurable velocity), (2) $CO+O=CO_2$ (with immeasurable velocity); secondly, (1) $CO+Ni=C+NiO$, (2) $CO+NiO=CO_2+Ni$. In the latter case, the 2d stage takes place more quickly than the 1st, but it need not be assumed that the velocity of one of the stages is immeasurable. The catalyst was actually Ni and not the C with which it was mixed.

3223. ———. [Velocity of Transformation of Carbon Monoxide. II.] Proc. "Koninkl. Akad. Wetenschappen Amsterdam." vol. 6, 1903, pp. 66–72; Jour. Chem. Soc., vol. 83, II, 1903, p. 628.

By the method previously used, it was proved, with pumice Ni–C as catalyst, that at 445° the conversion of CO into CO_2 and C is an unimolecular reaction, contrary to Schenck and Zimmerman's statement. No satisfactory reaction constant could be obtained at 445° owing to the fact that at this temperature the reaction is reversible, although Boudouard has stated that at 445° CO can be completely decomposed into C and CO_2. Starting with CO_2 in the reaction vessel at 445° it was found that after prolonged heating CO was formed, but the same equilibrium could not be obtained as when the experiment was carried out with CO. Even on using a catalyst obtained by reducing Ni oxide with H_2, it has not been found possible to verify Schenck and Zimmerman's results, and no explanation can be offered of why they obtained results leading to the conclusion that the reaction is bimolecular.

3224. Smittenberg, J. [Influence of Temperature and of Pressure on the Adsorption of Hydrogen by Nickel.] Rec. trav. chim., vol. 52, 1933, pp. 112–122; Chem. Abs., vol. 27, 1933, p. 2362.

Isotherms for the adsorption of H_2 gas on Ni at 300°, 210°, 123°, and 15° and the isobar at 760 mm. for this temperature range were obtained. Adsorption is of 2 types: Between 10 and 760 mm. it is rapid and and reversible; below 10 mm. it is slow, and equilibrium is reached only after some days.

3225. ———. [Absorption and Adsorption of Hydrogen by Nickel.] Rec. trav. chim., vol. 53, 1934, pp. 1065–1083; Chem. Abs., vol. 29, 1935, p. 977.

Adsorption of H_2 by Ni in the form of wire 0.022 mm. diameter gives data in good agreement with those found by Sieverts. Adsorption is very small even at 90° abs. The heat of absorption is calculated to be −2.62 ky-cal. Certain hysteresis effects are ascribed to impurities in the Ni. A test on adsorption also was made with A as the gas. Sorption of H_2 and He with temperature was also found from 90° to 800° abs.

3226. Smolenski, K. [Synthetic Raw Materials.] Gaz. Cukrownicza, vol. 83, 1938, pp. 115–123, 149–161; Chem. Abs., vol. 33, 1939, p. 1409.

Review of developments and methods used to produce several synthetic raw materials as gasoline, rubber, fats, etc.

3227. Smoley, E. R., Torrey, R. M., and Kniel, L. Chemicals From Petroleum. Petrol. Refiner, vol. 26, No. 11, 1947, pp. 768–772; World Petrol., vol. 18, No. 12, 1947, pp. 78–81; Chem. Abs., vol. 42, 1948, p. 1043.

Production of synthetic chemicals from petroleum has expanded from an output of 150,000 lb. in 1925 to almost 4 billion lb. in 1946. The trend still is upwards with addition of several new chemicals. The Fischer-Tropsch process also is adding many chemicals to the list, as is evidenced by the expected production from the 2 plants under construction for processing natural gas. The estimated production of chemicals from one Hydrocol plant alone amounts to 152,450,000 lb. per yr. The manufacture of C_2H_4 from petroleum and natural gas constituents is discussed at length, and a list of plants with approximate production is given.

3228. Smoluchowski, R. Diffusion Rate of Carbon in Iron–Cobalt Alloys. Phys. Rev., vol. 62, 1942, pp. 539–544; Chem. Abs., vol. 37, 1943, p. 819.

Studies of rates of various transformations and reactions in Fe alloys seem to indicate that certain elements have a definite effect on the rate of diffusion of C in γ–Fe. In particular, Co shows a pronounced accelerating effect. By direct measurement of the rate of diffusion of C in Fe–Co alloys, this conclusion is confirmed, and an increase in the diffusion coefficient is established. An addition of 4% Co decreases the activation energy from 32,500–30,000 cal., corresponding to an almost twofold increase of the diffusion rate at 1 at. % C concentration. At higher C contents, the accelerating effect of Co is smaller. This property of Co is unusual, especially in view of the fact that both Mn and Ni are known to have virtually no effect on the diffusion of C.

Snigurovska, Y. O. *See* abs. 3758.

3229. Snodgrass, C. S., and Perrin, M. Production of Fischer-Tropsch Coal Alcohol and Its Improvement by Cracking. Jour. Inst. Petrol. Technol., vol. 24, No. 175, 1938, pp. 289–301; Petrol. Times, vol. 39, No. 1002, 1938, pp. 395–397; Engineering, vol. 145, 1938, pp. 236–238; Gas Jour., vol. 221, 1938, p. 665; Colliery Guard., vol. 156, 1938, pp. 483–484; British Chem. Abs., 1938, B, p. 876; Chem. Abs., vol. 32, 1938, pp. 6447, 9441.

Description of the Fischer-Tropsch process pointing out the paraffin-wax formation and the desirability of cracking this to improve the yield of motor fuel. Fischer-Tropsch fuels are generally of poor octane number and difficult to crack. Operation of a successful vapor phase process using a cycle gas system is described; flow sheets are presented and properties of the products are tabulated. Motor fuels of octane Nos. 62–75 are produced. It is impracticable to crack the Fischer-Tropsch gaseous product directly; separation from lean gas and steam must first be made by condensation.

Snowden, F. F. *See* abs. 1214.

3230. Soap and Sanitary Chemicals. German Soap Substitutes. Vol. 22, October 1946, pp. 75, 77.

Brief account of the development and operation of the Oxo process for the manufacture, from Fischer-Tropsch olefins, of fatty alcohols, which are sulfonated to give detergents.

3230a. Sobcov, H. Analysis of Liquid Hydrocarbon Mixture by Mass Spectrometry. Anal. Chem., vol. 24, 1952, pp. 1386–1388; Chem. Abs., vol. 47, 1953, p. 298.

Application of matrices and IBM techniques is discussed in the analysis of hydrocarbon mixtures b. 82°–231° F. (isopentane to toluene). Problems of mass spectrometer reproducibility and close spectral similarities require fractionation of the sample by distillation. The smallest number of fractions required seems to be 4 and the largest useful matrix is of the 15th order. Many of the observations from this study are general enough to be applicable to other problems in mass spectrometry.

3231. SOETERS, C. J. [Synthesis of Fatty Acids.] Olien, Vetten Oliezaden, vol. 26, 1942, pp. 245–247, 275–279; Chem. Zentralb., 1943, I, p. 1431; Chem. Abs., vol. 38, 1944, p. 1731.

Technical report on the manufacture and properties of fatty acids obtained by oxidation of paraffins in Germany.

SOFER, M. A. *See* abs. 1590.

3232. SOLLIDAY, A. L. Significance of Hydrocarbon Synthesis in Western Kansas. Oil Gas Jour., vol. 46, No. 48, 1948, pp. 110–111.

In the belief that the process of synthesizing liquid hydrocarbon fuels from gas and coal will be the future cornerstone of our oil supply, the Stanolind Oil & Gas Co. has undertaken over a period of several years a vast program of research and development to improve and perfect the process. A plant to process 100 million cu. ft. of natural gas per day is being built in the Hugoton gas field. Some general details of the plant and its operation are presented, and criticism is made of the Government's entry into the production field in competition with private industry.

3233. ———. Synthetic Fuels. Oil Gas Jour., vol. 48, No. 24, 1949, pp. 86–88, 125; Petrol. Refiner, vol. 28, No. 11, 1949, pp. 81, 83, 85, 238; Jour. Inst. Petrol. Technol., vol. 1, sec. 1, October 1949, pp. 4–8.

Paper presented to the Petroleum Branch of the American Institute of Mining and Metallurgical Engineers. It is estimated that the United States has enough reserves of petroleum to supply the domestic demand until 1961 before it will need to turn to coal and oil shale. By 1965 the Nation's petroleum deficit may amount to about 420,000 bbl. per day and increase to around 1,260,000 bbl. by 1975. There is nothing to indicate that construction of synthetic fuel plants should begin immediately. By the time they are needed, technical developments in the design of plants and methods of operation should lower the construction expenditures and bring lower investment costs, enabling synthetic fuels to compete with natural petroleum. Using present designs, the motorist would have to pay $0.15–0.20 more per gal. for synthetic gasoline. An economic study is presented.

3234. ———. Public Being Misled by Bureau of Mines Synthetic Fuels Figures. Nat. Petrol. News, vol. 42, No. 12, 1950, pp. 16. 23; Oil Gas Jour., vol. 48, No. 46, 1950, p. 160.

Criticism of the 1949 annual report of the Secretary of the Interior. In arriving at cost estimates of synthetic fuels, the Bureau's figures are inadequate, it is stated, to show a basis for arriving at its published estimates. The Bureau figures of $0.09 and $0.145 per gal. for liquid fuel from oil shale and coal hydrogenation, respectively, are greatly out of line with the comparative industrial estimates of $0.225 for the same fuels. It is charged that the Bureau is confusing the public by basing its costs on calculations that are "no more than wishful thinking." This report illustrates the need for the Bureau of Mines to publish detailed breakdowns of all economic calculations including investment costs so as to allow the public to compare Government and private industry estimates and to show clearly whether synthetic fuels represent a sound or an unsound investment.

SOLVAY, —. *See* abs. 3205.

SOUTHWICK, C. A. *See* abs. 1099.

3235. SPAGHT, M. E. German Wartime Aviation Fuels by Hydrogenation of Coal. Ruhrchemie Catalytic Cracking Process. U. S. Naval Tech. Mission in Europe, Rept. 145–45, 1945, 45 pp., PB 1,657; Oil Gas Jour., vol. 44, No. 41, 1946, p. 124; BIOS Misc. Rept. 72, 1948, 45 pp., PB 1,657.

Describes process for cracking the highly paraffinic Fischer-Tropsch products to form a maximum of olefins for chemical synthesis intermediates. A synthetic silica-alumina catalyst was used, 0.7 apparent specific density, with a space velocity of 0.1. yielding a 40% conversion per pass on a 340°–660° F. Fischer-Tropsch fraction, of which nearly 70% was olefins up to C_8 and only 15% gasoline. The process was intermittent and catalyst was regenerated after 20–25 min. cycles, showing about 1.5% coke deposition. Product distribution was as follows in % wt. of feed: Gasoline C_6 to about 320° F. 6–8; C_5 7.6–9.6; C_4 10–12; C_3 8–10; C_2 2–2.8; CH_4 and H_2 0.4–0.8; coke 1.2–1.6.

3236. ———. Manufacture of Synthetic Butter. CIOS Rept. XXXI–79, 1945, 5 pp., PB 23,753. TOM Reel 199; U. S. Naval Technical Mission in Europe Rept. 144–145.

During the war, a synthetic butter was manufactured by the Deutsche Fettsäure Werke in Witten, Germany. The output of finished product was 11,000 lb. per day. The process involved the oxidation of Fischer-Tropsch wax paraffins at 230° F., with a $KMnO_4$ catalyst to produce straight-chain fatty acids of C_{11} and C_{12} and their esterification with glycerine to yield edible esters. The esterification was catalyzed with 0.2% of finely divided Sn or Zn. The resulting ester mixture was refined and purified, giving a product with all the outward appearance of natural butter; the same consistency and softening characteristics. Its taste was pleasant but slightly waxy. It was sold largely to hospitals where it was favored for certain diets, and the remainder was purchased by the Army. The product was competitive with margarine in price and could have been sold with profit at 60% of the price of natural butter. The prevailing prices in the same market for natural butter and margarine were RM 1.6 and 0.9 per lb., respectively. (*See* abs. 2176.)

3237. ———. Future Research in Hydrocarbons. Chem. and Ind., 1947, pp. 241–242.

Abridgement of a paper presented before the American Section of the Society of Chemical Industry. It is believed that the cheapest way of producing liquid hydrocarbons from coal will be via a water gas reaction and subsequent synthesis by the Fischer-Tropsch reaction. Direct hydrogenation of solids is not yet to be counted out of competition but, at this time, the Fischer-Tropsch route is the brightest hope for the conversion of coal. Recovery of oil from shale represents another possibility, but, at the moment, it is farther from commercial reality than those utilizing either CH_4 or coal.

3238. SPARKS, W. J., AND YOUNG, D. W. Plasticizers From Oxo Alcohols. Ind. Eng. Chem., vol. 41, 1949, pp. 665–670; Chem. Abs., vol. 43, 1949, p. 5627.

Information on the chemical and physical properties of new octyl and nonyl alcohols, manufactured by the Oxo reaction. Olefins are converted with H_2 and CO under high pressures in the presence of a Co catalyst to aldehydes, which are then hydrogenated to alcohols. In this study Oxo alcohols were reacted with phthalic anhydride as well as phosphorus oxychloride to form plasticizers.

3239. SPAUSTA, F. [Motor Fuels.] Österr. Chem.-Ztg., vol. 41, 1938, pp. 65–75; British Chem. Abs., 1938, B, p. 477.

Production and properties of a wide range of motor fuels (benzine from petroleum, benzol, motor fuels produced by hydrogenation or synthesis, EtOH, C_3H_8+C_4H_{10} and other compressed fuels, etc.) are summarized.

3240. SPENCER, H. M., AND JUSTICE, J. L. Reaction of Carbon Monoxide on Molybdenum Oxides. Jour. Am. Chem. Soc., vol. 56, 1934, pp. 2301–2306; Chem. Abs., vol. 29, 1935, p. 700.

MoO_2 reversibly is reduced by CO at 560°, but the reaction is masked by the catalytic decomposition of CO. At about 810°, the reaction proceeds smoothly, with no separation of C: $2\ MoO_2+6\ CO \rightleftharpoons Mo_2C+5\ CO_2$. For 810°, K_p is calculated as 1.46 for 750 mm. pressure.

SPENCER, W. B. *See* abs. 2010.

3241. SPENCER, W. D. Oil and Smokeless Fuel From Coal. Plan for the Development of the Carbonization Industry. Petroleum (London), vol. 6, No. 11, November 1943, pp. 163–167.

Process which consists of a combination of low-temperature and high-temperature carbonization together with a Fischer-Tropsch oil synthesis based on the utilization of intermediate products. From 1 ton of coal 7.5 cwt. of smokeless fuel, 50 gal. of liquid fuel, 3 gal. of refined tar acids, 20 lb. paraffin wax, and 65 lb. of pitch are produced. The overall thermal efficiency of the combined process is 70% (67% if it is found impossible to dispose of the pitch for plant fuel). A flow chart is shown. The coal is carbonized in retorts heated by producer gas; the low-temperature coke is sold as smokeless fuel, and the high-temperature coke is used for the production of producer gas to heat the retorts and to make the water gas required in the process. The gases from the retorts are cooled to separate the tar, mixed, purified, and the composition is adjusted by adding water gas and steam conversion to the requirements of the Fischer-Tropsch plant. The tar from the retorts is distilled to remove the pitch, fractionated, the fractions are refined together with the Fischer-Tropsch oil, and the final cuts are obtained. From ¼ ton of coke 16,000 cu. ft. of water gas could be obtained, this mixed with 21,500 cu. ft. (11,000 cu. ft. per ton of coal+360 lb. steam) of converted gas gives a total of 37,500 cu. ft. of synthesis gas of composition $1\ CO+2\ H_2$. A conservative estimate of oil yield per cu. ft. of synthesis gas is 4 gm., representing an efficiency of 74% of the theoretical yield, so that 42 gal. of oil (4.5 liquefied gas, 22.5 motor fuel, 15.0 diesel oil) and 19.8 lb. of paraffin wax would be obtained.

3242. ———. Science of Coal-to-Oil Conversion. IV. Fischer-Tropsch Synthesis. Petroleum (London), vol. 7, 1944, pp. 90–94; Chem. Abs., vol. 39, 1945, p. 2391.

Other articles in this series deal with: General Considerations, pp. 25–28; Low-Temperature Carbonization, pp. 34–36, 39; Hydrogenation of Coal, pp. 76–79; High-Temperature Carbonization, pp. 135–139; Summary and General Conclusions, pp. 184–186. The development of the synthesis process began in 1902 with Sabatier and Senderens, who investigated the reactions $CO+3\ H_2=CH_4+H_2O$ and $CO_2+4\ H_2=CH_4+2\ H_2O$ at 200°–250° over a reduced Ni catalyst. In 1913, the Badische Anilin und Sodafabrik, by employing catalysts consisting of the oxides of Co, Os, or Zn at 400° and 100 atm., obtained a complex mixture of hydrocarbons and their O derivatives. By increasing the pressure, the I. G. Farbenindustrie A.-G. later developed the process for synthesizing MeOH from water gas. Fischer and Tropsch in 1922, using an Fe catalyst impregnated with K_2CO_3 and passing over it a mixture of CO and H_2 at 400°–450° and 100–150 atm., obtained a product, which they called Synthol, consisting of a mixture of alcohols, aldehydes, ketones, and fatty acids. By reducing the pressure and the temperature, a less highly oxygenated product was obtained, but the rate of reaction likewise fell off, making it necessary to find a more active catalyst. It was not until 1928 that Fischer, with Koch and Meyer, succeeded in producing catalysts that were active at atmospheric pressure and temperatures below 200° and capable of retaining their activity for several months. To preserve the catalyst activity, it was found that S present in the synthesis gas, which consisted preferably of a water gas containing H_2 and CO in the ratio 2:1, must not exceed 0.1%. The product obtained by this latest process was called Kogasin; it consisted of gaseous liquid and solid hydrocarbons composed mainly of straight-chain paraffins and olefins and could be broken down into a series of fractions consisting of low-boiling hydrocarbons (up to 30° C), gasoline (30°–200°), diesel oil (200°–350°), and solid paraffin wax. The exact composition of the fractions is a function of the catalyst and of the operating conditions. By 1934, the process had reached such a stage of development that it was taken over by the Ruhrchemie A.-G., and a plant was constructed and put into operation in 1936 at Oberhausen. By 1940 German output of oil from the Fischer-Tropsch process was estimated at 1,000,000 tons per yr. The theory of the process may be represented empirically by the equation:

$$CO+2H_2=(CH_2)+H_2O+48{,}000\ \text{cal.}$$

It appears that the 1st stage in the process is adsorption of CO on the catalyst, followed by reduction to carbide, which reacts with the H_2 to form CH_2 groups, which either combine with H_2 to form CH_4 or polymerize with formation of higher hydrocarbons. The catalyst usually used industrially consists of Co:ThO_2:kieselguhr in the proportions 100:18:100. Fe or Ni can be used. The latter cannot be used at medium or high pressure, since Ni carbonyl is formed and removed from the system because of its volatility. Under low pressure, it increases the degree of saturation of the product. Fe gives good results. At low pressures, the yield of hydrocarbons is small but increases with increase in pressure. The operating temperature should be higher than with Co, and the ratio H_2:CO should be lower. The products are more unsaturated and contain less wax. A new catalyst is reported, but not named, with which a C_4 fraction is obtained containing 90% of isobutane. The temperature is above 200° and the pressure above 100 atm. With another catalyst, naphthenes and aromatics can be obtained. With Ru as a catalyst, a temperature of 200°, and pressures of 100–200 atm., a mixture of solid waxes is obtained with a m. p. up to 134° C. The Fischer-Tropsch synthesis was originally operated at atmospheric pressure to cut down the formation of alcohols and other oxygenated compounds, but it has been found that certain advantages exist in using pressures of 7–8 atm., among which is the reduction in size of the plant. The theoretical yield of hydrocarbons from 1 cu. m. of ideal synthesis gas (66.7% H_2, 33.3% CO) is 208 gm., but, in practice, the yield does not normally exceed 140 gm. per $m.^3$ for a 1-stage medium-pressure process or 160 gm. for a 2-stage process. Several steps occur in the manufacture of oils: (*a*) Manufacture of synthesis gas; (*b*) purification of gas; (*c*) hydrocarbon synthesis; (*d*) manufacture of catalyst; (*e*) distillation and refining of primary products; (*f*) further treatment of products, for example, cracking or isomerization of gasoline, conversion of wax to lubricants. Each of these steps is discussed with a variety of data and a flow sheet. The capital cost of a plant (100,000 tons per yr. of finished products) should not exceed £3,300,000 (based on 1938 prices) or £7 3s. per ton per yr. of coal consumed, calculating 4.5 tons per ton of finished products. Such a plant, allowing for certain improvements in operation and design and 10% for depreciation and overhead, should produce gasoline and diesel oil at a cost not to exceed 9 d. per gal. Whether the Fischer-Tropsch process is assessed on its own merits or regarded as an adjunct to carbonization, it has the advantage that all products are valuable materials. Although emphasis is usually placed on the production of motor fuels, it is possible that in the future the real value will be considered to be its use in the manufacture of synthetic chemicals giving hydrocarbons, alcohols, acids, esters, organic solvents, plastics, and many other aliphatic compounds containing C, H, and O. Coal tar would remain the chief source of aromatic compounds, and petroleum refinery byproducts would provide a source of aliphatic hydrocarbons and chemicals based on them. This would provide a basis for a coordinated group of processes feeding the organic chemical industries.

3243. Spengler, H. [Physicochemical Behavior of Fischer-Tropsch Catalysts.] Erdöl u. Kohle, vol. 3, No. 1, 1950, p. 10.

Paper presented at the 1949 meeting of the Deutsche Gesellschaft Mineralölwissenschaft u. Kohlechemie. Aside from the purely chemically limited properties, the physical or physical-chemical data for the behavior of a catalyst is important. Of special significance for the movements occurring within are the geometric structure of the catalyst grains, the inner surface area as the seat of the catalytic reactions, and the adsorption behavior in the presence of the reaction gases. Measurements of the geometric structure give numerical values for the porosity of the catalyst grains and the dimensions of the pores. Tests of the permeability of the catalyst grains with different gases show that greater amounts of H_2 and CO pass through the grain than must be the case with experimentally determined pore radii. This additional flow is called surface diffusion. It explains the otherwise difficultly explicable fact that the whole catalyst grain is utilized by the reaction, although the pores are filled with the products of the reaction. The inner surface area of a Co catalyst lies in the magnitude of 100 $m.^2$ per gm. In the range of adsorption measurements for determination of the inner surface area, the adsorption of CO and H_2 was measured also. From the measurements, it was seen that the CO molecule is more strongly bound than is the H_2 molecule, and the temperature range applied in the Fischer-Tropsch synthesis lies within the transition range of physical and chemical adsorption.

———. *See* abs. 370.

3244. Spilker, A. [Refining of Coal and Its Liquefaction.] Braunkohle, vol. 26, 1927, pp. 545–553; Chem. Abs., vol. 21, 1927, p. 4047.

General discussion of coal liquefaction, the MeOH process of the I. G. Farbenindustrie A.-G., the benzine synthesis of Fischer-Tropsch, the Synthol process, and the direct hydrogenation of coal by the Bergius process.

3245. Spingler, H., and Reinhard, O. ["Magnetocatalytic Effect" in the Hydrogenation of Carbon Dioxide or Carbon Monoxide on Nickel.] Ztschr. physik. Chem., vol. 190, A, 1942, pp. 331–340; Chem. Abs., vol. 37, 1943, p. 4958.

Mixture of CO or CO_2 and H_2 was passed over powdered Ni heated to temperatures near the Curie point (350°–360°) in an apparatus similar to that of Fischbeck and Salzer (abs. 938). The amount of reaction was determined by collecting and weighing the H_2O formed and the residual CO_2. The percent of CO_2 hydrogenated in 15 min. increased with increase in temperature, but there was no discontinuity in the curve at the Curie point. Analogous results were obtained for decreasing temperatures. In the hydrogenation of CO there is a decided increase in activity beginning at approximately 350° and ending at approximately 370° in a sudden decrease (abs. 1387). The sudden decrease at 370° apparently is independent of the proximity of the Curie point; it may result from the deposition of C on the catalyst as a result of disproportionation of CO (abs. 130). No change could be detected in the catalyst in this temperature region. Above 370°, the curve of % hydrogenation of CO versus temperature was very irregular; this is attributed to the antagonistic effects of the activating and poisoning mechanisms. The change in the catalytic activity of Ni in the region of the Curie point probably is not related to the Curie transformation but depends on the specific catalytic properties of the stable phase in that temperature region; hence, the existence of the magnetocatalytic or Hedvall effect is doubtful.

3246. Spirk, L. [Soap Production From Mixtures of Natural and Synthetic Olefinic Hydrocarbons.] Časopsis Mydlář Voňavkář, vol. 20, 1942, pp. 97–98; Chem. Zentralb., 1943, I, p. 1120; Chem. Abs., vol. 38, 1944, p. 3864.

Various raw materials are: Lignite coking oil (b. 200°–350°), definite fractions of cracked gas oil (b. 200°–325°) with 70–75% olefins of natural origin or synthesized by hydrogenation of CO. Production of these synthetic raw materials and oxidation of the products are discussed. The fatty acids produced are neutralized at 250°–300° with amines or alkaline earths. The soaps are odorless and contain no unsaponifiable matter. 4 practical methods of producing these soaps are described.

3247. Spiske, —. [Aftertreatment of a Catalytic Cracking Benzine With Borylphosphate or Bleaching Earth.] FIAT Reel L–5, frames 549–553, Dec. 22, 1941, PB 70,159; TOM Reel 299.

Tests were carried out with the object of determining whether or not an aftertreatment with borylphosphate or bleaching earth would raise the octane number of a catalytic cracking benzine. The results did not show any improvement of the aftertreated benzine over the unprocessed benzine.

Spivey, E. *See* abs. 1467a, 1468.

Srikant, H. *See* abs. 3029a, 3030, 3030a.

3248. Srikantan, B. S. Reactions at the Surface of Hot Metallic Filaments. I. The Reaction $CO_2+H_2 \rightarrow H_2O+CO$ on Platinum. Jour. Indian Chem. Soc., vol. 6, 1929, pp. 931–947; Chem. Abs., vol. 24, 1930, p. 2036.

Reaction between CO_2 and H_2 on a Pt wire at about 1,000° is unimolecular except for the initial fall in reaction velocity, which is due to poisoning of the more active centers by the CO formed. Poisoning was eliminated by prior heating *in vacuo*. The rate of reaction was not influenced by dilution of the gases with N_2. The nature and treatment of the surface of the wire are important; thus, a rough surface is more active than a smooth one. The energy of activation is 38,000 cal.

3249. ———. Reactions at the Surface of Hot Metallic Filaments. II. The Reaction $CO_2+H_2 \rightarrow CO+H_2O$ on Platinum–Iridium Alloys. Jour. Indian Chem. Soc., vol. 6, 1929, pp. 949–958; Chem. Abs., vol. 24, 1930, p. 2036.

Pt wire containing 5–30% Ir is more active than pure Pt. The 30% Ir alloy is most active. The energy of activation is less with a powerful catalyst than with a poor catalyst. Temperature coefficients are calculated.

3250. ———. Reactions at the Surface of Hot Metallic Filaments. III. The Reaction $CO_2+H_2 \rightarrow H_2O+CO$ on Platinum Coated With Barium Oxide. Jour. Indian Chem. Soc., vol. 6, 1929, pp. 959–967; Chem. Abs., vol. 24, 1930, p. 2036.

Layer of BaO, formed on a Pt wire by thermal decomposition of $Ba(NO_3)_2$, adsorbs 1 of the reactants, CO_2, and gives reproducible results in studying the formation of CO and H_2O at 612°–826°. The reaction velocity rises slowly at the beginning of the reaction until a steady state is reached. The rate increases

with increasing pressures of CO_2 up to 300 mm. and is depressed by excess H_2. The temperature coefficient and energy of activation fall with rise of temperature.

3251. Stäblein, F., and Schroeter, K. [Determination of the Magnetic Saturation of Iron Carbide.] Ztschr. anorg. Chem., vol. 174, 1928, pp. 193–215; Chem. Abs., vol. 22, 1928, p. 4349.

Ballistic method for finding the saturation value of the intensity of magnetization is described in detail, including the calibration of the apparatus and the experimental determination of the various corrections necessary. The results indicated that the method could be relied upon for powders. Fe_3C was prepared from pig Fe by solution in 0.1 N cold H_2SO_4. Tests on this gave 12,400 gausses as the saturation value for $4\pi J$, where J is the intensity of magnetization. By extrapolation from 2 specimens of C steel containing 0.46% and 0.95% of C, respectively, an average value of 12,300 gausses was obtained. The authors, therefore, conclude that the most probable value for saturation is $4\pi J=12{,}350$ gausses.

3252. Stadlinger, H. [Raw Materials for Paraffin Oxidation in Germany.] Deutsche Chem.-Ztg., vol. 1, 1949, pp. 55–60; Chem. Zentralb., 1950, I, p. 2049.

Comprehensive survey is made of the production and utilization of technical paraffin for catalytic oxidation and the recovery of fatty acids for soaps and synthetic fats. Discussion is made of lignite paraffin, high-temperature hydrogenation paraffin, and Fischer gatsch. Some instructions are included concerning the quality of the paraffin to be oxidized.

3253. Stadtherr, J. J. Basic Petroleum Chemistry for Refinery Employees. IX. Potential Sources of Liquid Fuel. Petrol. Refiner, vol. 26, No. 3, 1947, pp. 137–140.

Brief review of methods of producing substitute fuels.

3254. Stammer, K. [Phenomena Connected With Reduction, Especially of Iron by Carbon Monoxide.] Ann. Chim., vol. 82, 1851, pp. 136–141.

It is assumed that the decomposition of CO on Fe results in carbide formation.

3255. Stanburg, W. A. Making Oil From Coal. Coal Age, vol. 54, No. 7, 1949, pp. 70–77.

Comprehensive survey of plant and process development in making oil from coal in accordance with the Government program as it is being carried out at the various plants operated by the Bureau of Mines. The various steps in the coal-to-oil development are briefly described: Coal preparation, cleaning, drying and storage; complete gasification, the vortex method, underground gasification, continuous high-temperature pebble-stove gasifier, O_2–steam gasification, O_2 production; Fischer–Tropsch gas conversion and internally cooled and slurry-type converters; 2-stage hydrogenation, liquid- and vapor-phase processes, and economics.

3256. Stanley, H. M. Recent Advances in Our Knowledge of Natural Gas and Cracking Gas and Their Industrial Utilization. Jour. Inst. Petrol. Technol., vol. 15, 1929, pp. 516–552; Chem. Abs., vol. 24, 1930, p. 1496.

Comprehensive review of the subject, particularly with reference to recent work upon fractionation, analysis, utilization and synthesis. Bibliography of 74 refs.

3257. ———. Production of Water Gas From Methane and Other Hydrocarbons. Sci. Petrol., vol. 3, 1938, pp. 2164–2173.

Survey of the literature and discussion of methods for CH_4 conversion by partial oxidation, CH_4–steam reaction, CH_4–CO_2 reaction, and reaction of higher hydrocarbons with steam.

———. *See* abs. 2369.

3258. Stanley, H. M., and Nash, A. W. Higher Hydrocarbons From Methane. Nature, vol. 122, 1928, p. 725; Chem. Abs., vol. 23, 1929, p. 3212.

Fischer's work on thermal decomposition of CH_4 with formation of higher hydrocarbons (abs. 954) is confirmed.

3259. ———. Production of Gaseous, Liquid, and Solid Hydrocarbons From Methane. I. Thermal Decomposition of Methane. Jour. Soc. Chem. Ind., vol. 48, 1929, pp. 1–8T; Chem. Abs., vol. 23, 1929, p. 1866.

Under suitable conditions, CH_4 forms higher liquid and solid hydrocarbons when heated. These conditions have been found to be short times of contact on the order of less than 1 sec. and at temperatures of 1,000°–1,200°. The products may consist of C_2H_2, C_2H_4, C_2H_6, higher olefins, benzene, and higher aromatic hydrocarbons, C, and H_2. The % conversion of CH_4 into higher hydrocarbons increases rapidly with increasing gas rate and rapidly reaches a maximum at a given temperature.

3260. ———. Production of Gaseous, Liquid, and Solid Hydrocarbons From Methane. II. Action of Spark Discharge on Methane. Jour. Soc. Chem. Ind., vol. 48, 1929, pp. 238–242T; Chem. Abs., vol. 24, 1930, p. 1076.

Main primary product of the reaction is C_2H_2, the higher hydrocarbons probably being formed by the further action of the discharge on the C_2H_2–H_2 mixture produced.

3261. Stanley, J. K. Diffusion and Solubility of Carbon in α–Iron. Jour. Metals, vol. 1, No. 10, Trans., 1949, pp. 752–761; Chem. Abs., vol. 43, 1949, p. 9004.

Diffusion of C in α–Fe was determined by 2 methods. 1, the Van Orstrand-Dewey method, consisted of diffusing the C from a high-C Fe containing 0.68% C, corresponding to fine pearlite, into an essentially C-free Fe. The diffusion of C does not appear to be affected by grain size, deoxidation, or small additions of Se and Co. The present methods did not lend themselves toward determining if D varied with concentration. At 725° the diffusion of C is over 100 times as fast as it is in α–Fe.

3262. Stanley, J. K., Hoene, J. V., and Huntoon, R. T. Oxidation of Pure Iron. Trans. Am. Soc. Metals, No. 5, 1950, 21 pp.; Chem. Abs., vol. 44, 1950, p. 9886.

Oxidation of high purity electrolytic Fe (Puron) in air 500°–900° proceeds by the common parabolic rate law, $W^2=Kt+C$. The oxidation process as a function of temperature follows the usual exponential law. The rate constant, K, shows the temperature dependence $K=0.37e^{-33{,}000/RT}$. A Geiger counter X-ray spectrometer showed only 1 oxide, Fe_3O_4, at 500°, but 3 oxides, α–Fe_2O_3, Fe_3O_4, and FeO, at the higher temperatures; metallographic examination resolved the various oxide strata. FeO could be cooled to room temperature without decomposition to Fe and Fe_3O_4. Photomicrographs show typical structures.

Starkweather, H. W. *See* abs. 3331.

3263. Staveley, L. A. K., and Hinshelwood, C. N. Reaction Chains in the Decomposition of Organic Compounds. Jour. Chem. Soc., 1937, pp. 1568–1573; Chem. Abs., vol. 31, 1937, p. 8329.

Decomposition of an organic molecule involves either an internal rearrangement to stable products or the production of free radicals and chain reactions. The addition of NO inhibits the latter. With this reagent, it has been found that the decomposition of ethers, aldehydes, from $MeCH_2CHO$ up the series, and C_2H_6 involve chain reactions, whereas the decomposition of AcH, ketones, MeOH, and HCO_2Me do not. A discussion of the theoretical aspects of the chain length in the chain reactions indicates that even when these occur, it is unnecessary to change any fundamental views on the mechanism of activation in unimolecular reactions.

3264. Steacie, E. W. R., and Elkin, E. M. Comparison of the Catalytic Activities of Liquid and Solid Surfaces—Decomposition of Methanol on Solid and Liquid Zinc. Proc. Roy. Soc. (London), vol. 142, A, 1933, pp. 457–465; Chem. Abs., vol. 28, 1934, p. 960.

Temperature effect on the decomposition rate of gaseous MeOH over solid and liquid Zn was investigated 300°–440°. The catalytic activity of the Zn depends directly on the temperature. There is no discontinuity at the melting point of the catalyst. Catalytic activity is attributed to the entire uniformly active surface of the metal rather than to some limited part.

3265. ———. Further Investigations of Catalysis by Liquid Metals. Canadian Jour. Research, vol. 11, 1934, pp. 47–52; Chem. Abs., vol. 28, 1934, p. 7132.

Kinetics of MeOH decomposition on solid and liquid Zn were examined in greater detail. The order of the reaction lies between zero and ½ on both solid and liquid. The heat of activation is approximately 30,000 cal. per gm.-mol. The reaction is mainly dehydrogenation. Unsuccessful attempts to investigate certain other reactions on liquid metals are described.

3266. ———. Catalysis by Fusions: A Reply to the Paper by Adadurow and Didenko. Jour. Am. Chem. Soc., vol. 58, 1936, pp. 691–692; Chem. Abs., vol. 30, 1936, p. 3306.

Reply to the criticisms of Steacie and Elkin's work (abs. 3264) by I. E. Adadurow and P. D. Didenko (abs. 2). They are based partly on an incorrect interpretation of their own data and partly on an incorrect mechanism for the decomposition of MeOH.

3267. Stefanovskiĭ, A. M., Tatarskiĭ, E. S., and Zelyakov, N. V. Dependence of the Structure of an Ammonia Catalyzer Upon the Conditions During Its Reduction. Compt. rend. acad. sci. U. R. S. S., vol. 3, 1935, pp. 21–24 (in English); Chem. Abs., vol. 29, 1935, p. 8244.

Catalyzer prepared by oxy-acetylene fusion consisting mainly of 72% Fe_2O_3 and 27% FeO was reduced at temperatures 450°–800°. Its efficiency dropped abruptly from 61% for that prepared at 500° to 2% for that prepared at 600°. X-ray studies of changes involved show that the fall in activity cannot be accounted for by a change in size of the crystals but to a qualitative change of the surface. At higher temperatures, the defects, which are the active centers in NH_3 synthesis, disappear. This illustrates the use of X-ray photographs in the study of active centers.

Steffens, L. R. *See* abs. 1460.

Stein, K. *See* abs. 1449a.

3268. Steinberger, K. F. [Raw Materials for the Production of Acetylene and Ethylene.] Angew. Chem., vol. 19, B, No. 8, 1947, pp. 211–214.

Important prewar source for the raw materials of C_2H_2 and C_2H_4 was the hydrogenation gases from the Fischer-Tropsch and the I. G. Farbenindustrie A.–G. hydrogenation processes. The total amount was 650,000–660,000 tons per yr., of which the Fischer-Tropsch process contributed 80,000–90,000 tons. The Fischer-Tropsch gases contained 35–40% olefins, mostly C_3 and C_4, while those from the I. G. Farbenindustrie A.–G. process were mostly saturated hydrocarbons. In general, they contained about 18% CH_4, 11–12% C_2H_6, 12% C_3H_8, 5% C_4H_{10} and 1% C_5H_{12}, 32–33% H_2, with small amounts of N_2, CO, CO_2 and H_2S. These gases were processed by cracking in the electric arc, whereby mainly C_2H_2 and some C_2H_4 were obtained, and by pyrolytic cracking of the saturated hydrocarbons, whereby, mainly, C_2H_4 was produced. Cracking plants erected in Leuna, Holten, Heydebreck, and Moosburg had a capacity of 4,000 tons per yr. of C_2H_4.

3269. Steinbrecher, —. [Influence of Synthesis Gas and Its Impurities Upon the Efficiency and Life of the Catalysts in Gasoline Synthesis.] FIAT Reel K–25, frames 3,782–3,796, Jan. 5, 1938; PB 70,216; TOM Reel 292.

Research report on the influence of synthesis gas and its impurities on the efficiency and life of the catalysts in gasoline synthesis of Braunkohle-Benzin A.–G. plant, Ruhland. The life of the catalysts (Co-kieselguhr) is shorter if synthetic gas, purified by regular routine of plant operation, is applied than if ideal gas (33.3% CO+66.7% H_2) is applied. This is caused by impurities like inert gas, O_2, S–compounds, resins, and resin-forming products. By adding inert gases, the speed of reaction is decreased rapidly. Adding O_2 of more than 0.6% has a strong influence in decreasing the output. S–compounds affect the Co catalyst. The presence of over 0.2 gm. per 100 N m.^{3} causes disturbances. It appears that thiophene and other S–compounds substituted in the nucleus cause the strongest reactions, followed by mercaptan and finally CS_2 and COS. Tests to establish results on resin-forming substances were not successful. Further tests were conducted on reducing the contact period of the gas with the catalyst by increased gas flow with lower height of layer. The absolute yield was increased thereby.

3270. Steinbrecher, —., and Weingärtner, —. [Efficiency and Life of the Gasoline Synthesis Catalyst.] FIAT Reel K–30, frames 7,468–7,492, January 1938, PB 73,587; TOM Reel 297.

Laboratory and plant tests on the influence of the synthesis gas and its impurities on the efficiency and life of the catalyst. Included among the impurities of the synthesis gas are inert gases (N_2, CO_2, CH_4, C_2H_6, etc.). O_2, S compounds, resins, and resin-forming substances. All these impurities diminish the efficiency of the catalyst and shorten its life. Tests aiming at the reduction of this deterioration by increasing the gas throughout and diminishing the height of the charge still are underway.

3271. Steinbrecher, H. [Petroleum Substitutes in Germany.] Hamburger Tech. Nachrichten, Jan. 28, 1936; Coal Carbonisation, vol. 2, 1936, p. 81.

Production of oil from brown coal by low-temperature carbonization, hydrogenation, and gasification will supply about 35% of the domestic demand for motor and fuel oil; present construction of low-temperature plants will increase the national output considerably. The high-pressure hydrogenation process, mainly applied to the production of gasoline, can be adapted to the production of gas oil, fuel oil, and lubricating oil as required. The gasification of brown coal or its semicoke is very attractive, the water gas being synthesized by the Fischer-Tropsch process with a good yield of liquid hydrocarbons. It is considered that all German motor fuel requirements could be met by processing brown coal, leaving the small domestic supply of natural petroleum for use in preparing lubricants.

Steinbrink, H. *See* abs. 1834, 1835.

3272. Steinkamp, J. H. [Synthesis of Oils From the Gasification Products of Coal by the Fischer-Tropsch Process.] Het Gas, vol. 48, 1928, pp. 507–513; Chem. Zentralb., 1929, I, p. 819.

Brief review of the Bergius and Synthol processes at high pressures and a description of the newer method for producing liquid hydrocarbons from gases at atmospheric pressure and by the use of suitable catalysts.

3273. Steinkohlenbergwerk. [Fuels, Lubricants, Textile Auxiliaries, and Other Organic Products.] FIAT Reel X117, frames 2,561–3,422; PB 82,011.

In addition to brief single reports and monthly and activity reports, the film contains detailed summarizing reports on lubricating oil synthesis, Oxo synthesis,

paraffin oxidation, paraffin chlorination, etc. In particular, the reports deal with synthesis lubricating oil from kogasin and tar distillation products, condensation of cracked Fischer gatsch and naphthalene, chlorinated Fischer hydrocarbons and naphthalene, testing various oils, consistent greases from synthetic fatty acids with the use of the acids of the 1st and last runnings from the paraffin oxidation, production of solid soaps from liquid fatty acids and the application of dicarboxylic acids for fully synthetic fibers.

Steinmann, A. *See* abs. 1611.

3273a. Steitz, A., and Barnes, D. K. Products of the Hydrogenation of Carbon Monoxide Over an Iron Catalyst. Water-Soluble Oxygenated Compounds. Am. Chem. Soc., 121st Meeting abs., March–April, 1952, p. 10–M.

Seven acids and 27 nonacid chemical compounds have been identified in the H_2O stream produced by hydrogenation of CO over an Fe catalyst. These compounds are principally straight-chain alcohols, acids, aldehydes, and ketones. Esters, cyclic ketones, and branched-chain alcohols, aldehydes and acids are present in minor amounts. The nonacid chemicals were separated from the H_2O stream by fractional distillation to 96°, and the acids were separated from the aqueous residue by solvent extraction. After removal of the solvent, the acids were recovered in high purity by fractionation. Upon fractionation of the concentrated nonacid chemicals, a distinctive distillation curve exhibiting 6 plateaus was obtained. Most of these plateaus represented complex mixtures of binary and ternary azeotropes. Quantitative analysis of the nonacid chemicals was obtained by a combination of fractional distillation and analysis for functional groups.

Stenkhoff, R. *See* abs. 3065.

Sterligov, O. D. *See* abs. 1706.

3274. Stern, D. J. Production of Oil From Coal. South African Min. and Eng. Jour., vol. 61, II, 1951, pp. 851–855; Chem. Abs., vol. 45, 1951, p. 4910.

Principles of the Bergius and Fischer-Tropsch processes, the mechanical engineering problems involved, underground gasification, Russian developments, and American practices are surveyed.

3274a. ———. Production of Synthetic Gas. South African Min. and Eng. Jour., vol. 62, I, 1951, pp. 143–145, 181–193; Chem. Abs., vol. 45, 1951, p. 10545.

Exposition of basic factors and industrial processes by which coal or hydrocarbon gases can be transformed into fuels and lubricants. More detailed description devoted to the Koppers and Lurgi processes.

3275. Stern, G. [Isolation and Identification of Hydrocarbons From Mixtures by New Methods.] Reichsamt Wirtschaftsausbau, 1940, Prüf-Nr. 43, pp. 15–56, PB 52,003; Chem. Abs., vol. 41, 1947, p. 6490.

Procedures are described for the analysis of the products of the cracking of oils and the products of the CO–H_2 synthesis of hydrocarbons. Extensive tables are included, which describe the alcohols, acids, and esters isolated and identified in certain fractions of oil produced through the CO–H_2 synthesis process.

Sternberg, H. W. *See* abs. 3656a.

3275a. Sternberg, H. W., Wender, I., and Orchin, M. Analysis of Mixtures of Dicobalt Octacarbonyl and Cobalt Carbonyl Anion. Anal. Chem., vol. 24, 1952, pp. 174–176.

Study of the hydroformylation (Oxo) process in the laboratory required the analysis of mixtures containing both dicobalt octacarbonyl, $[Co)(CO_4]_2$, and Co carbonyl anion, $[Co(CO)_4]^-$, the latter being present either as Co hydrocarbonyl, $HCo(CO)_4$, or as a Co salt. Because no method was available for this purpose, the authors devised the present procedure. The 2-step method depends on the decomposition of all corbonyls, by treatment with I, to yield CO; and the selective precipitation of the anion by Ni o–phenanthroline chloride, followed by decomposition of the precipitate with liberation of CO. As the determination is based on a gasometric procedure, it is suited for the analysis of mixtures, such as those from the hydroformylation reaction, which may contain Co salts and metallic Co.

Sternberg, H. W., Wender, I., Friedel, R. A., and Orchin, M. Chemistry of the Metal Carbonyls. II. Preparation and Properties of Cobalt Hydrocarbonyls. *See* abs. 3656b.

———. Chemistry of the Metal Carbonyls. III. Reaction Between Dicobalt Octacarbonyl and Dimethylamine. *See* abs. 3656c.

Sternberg, J. C. *See* abs. 154.

Sternina, D. G. *See* abs. 2757.

Stevens, N. P. *See* abs. 175.

Stevenson, E. P. *See* abs. 2988.

Stewart, L. *See* abs. 2601.

3276. Stief, F. [Pintsch-Hillebrand Continuous Blue-Gas Generator at the Hamburg Gas Works. I.] Gas-u. Wasserfach, vol. 75, 1932, pp. 581–586; Chem. Abs. vol. 26, 1932, p. 5402.

Continuous blue-gas generator has been devised to overcome the known faults of the intermittent process, involving the distillation of brown-coal briquets by hot blue gas and the gasification of the resulting semicoke in an annular generator in a stream of blue gas at about 1,300° carrying the required amount of steam. A portion of the blue gas is burned in 1 of the 2 regenerators, while the other regenerator, previously heated, is used to heat the blue gas saturated with water at 60°–74° to the above temperature. The distillation gas is passed through an electric tar precipitator and mixed with blue gas passing to the regenerators. A portion of the gas from the generator is withdrawn for use and contains about 4.2–8.6% CO_2, 35.4–39.4% CO, 50.4–51.0% H_2, 1.0% CH_4, and 4.8–5.0% N_2. The gas yield was 27,000–29,000 cu. ft. of approximately 300 B. t. u. gas per net ton with a thermal efficiency of 52%. A plant having a capacity of about 1,500,000 cu. ft. per day was operated for some time. Difficulties were found in keeping refractory walls tight, etc., but it is believed that these difficulties have been solved.

3277. Müller, H. [Generation of Water Gas From Brown Coal in the Pintsch-Hillebrand Generator of the Hamburg Gas Works. II.] Gas- u. Wasserfach, vol. 78, 1935, pp. 431–436; Chem. Abs., vol. 29, 1935, pp. 6397–6398.

Further operation of this generator has been carried out successfully on a continuous basis with only a few minor difficulties. The generator proper is an annular ring 4.7 m. in internal diameter with a minimum thickness of 55 cm. Coal is fed to distillation chambers above this generator, where it is preheated to 700° by hot water gas. The water-gas generator is heated internally by recirculated gas from the generator, freed from dust and tar, saturated with water, and preheated in one of two regenerators to 1,300°; the other regenerator is heated to 1,350° by burning the generator gas, and then is used in turn to heat the recirculated gas. Part of the heated recirculated gas and water gas passes through the coal-distillation chambers. The gas yield is approximately 35,000 cu. ft. per net ton of brown coal briquets, with a heating value of approximately 290 B. t. u. per cu. ft. The thermal efficiency of the generator is given as 58.3%, and a complete thermal balance and a thermal diagram are given. Only a small amount of the S used to cement the brown-coal briquets appears in the gas, the larger part being fixed as CaS in the ash. Cost data are given for German conditions. Improvements suggested are use of dry producer gas for heating the regenerators, use of waste-heat boilers, and proper gas velocity to avoid combustible matter in the fly ash. This process is especially adapted for the manufacture of gas for synthetic purposes as it is readily possible to secure a H_2: CO ratio of 2 : 1.

3278. STIEF, F. [Generation of Water Gas and Synthesis Gas From Brown Coal, Peat, and Bituminous Coal in the Pintsch-Hillebrand Plant at the Hamburg Gas Works.] Gas- u. Wasserfach, vol. 83, 1940, pp. 1–6; Chem. Abs., vol. 34, 1940, p. 2569.

Present German endeavors are to increase the quantity of gas by diluting coal gas with water gas. The cheapest source of this gas is the Pintsch-Hillebrand continuous water-gas generator using brown coal. Improvements were made in this generator so that it has been possible to operate continuously and shut down the regular (coke) water-gas plant. One advantage of this process is the reduced content of organic S and H_2S in the gas, owing to the reforming of the carbonization products by passage through the generator fuel bed. The most important change has been to use producer gas for heating the regenerators, with the burners at the top of the regenerators. The length of time that the regenerators are used for heating the circulating gas also has been increased. Tar yields are about ⅔ of that indicated by the Fischer retort test. The best fuel is brown coal, preferably in briquet form. This coal should not have too high an ash content or too low an ash melting point, and the ash should not react with the refractories. Good results also were secured with peat. Bituminous coal (high volatile) also was tested, but its low reactivity did not permit complete gasification. If certain changes in construction were made, it should be possible to use this coal but it would be necessary to use the resultant high-ash coke in gas producers.

3279. ———. [Gasification of Fuels in Gas Works With Special Consideration of the Continuous Production of Water Gas.] Gas- u. Wasserfach, vol. 85, 1942, pp. 367–374; Chem. Abs., vol. 37, 1943, p. 4551.

Review of gas production from coke (generator gas with a heat of combustion of 1,200 kcal. per m.^{3} (under standard conditions) and a heating value of 1,150 kcal. per m.^{3}, water gas of a heating value of 2,700 kcal. per m.^{3}), coal (generator and water gas, heating value 3,000 kcal. per m.^{3}) and by the continuous Pintsch-Hillebrand water-gas process. A flow sheet of the latter process, together with drawings of generators of various designs for this and the older process, is given. A plant operating by the continuous process was in operation for 300 days per yr. for 6 yr. Brown coal of reasonable low ash content and fairly high melting point of the ash is a suitable raw material for the process, but the use of bituminous coal is limited to a few special grades. The temperature of the gas-steam mixture in the gas collection cupola is about 1,300°; the temperature in the regenerator chambers, which are used alternately in a 16-min. cycle, is 1,500°–1,600°. The heating value of the water gas remains virtually constant and changes only by about 40 kcal. per m.^{3} during the periodic change from one regenerator to the other. The heat of the combustion of the gas can be kept easily at 2,750–2,800 kcal. per m.^{3} The ratio CO : H_2 can be brought to 1 : 2 by increasing the amount of steam added so that the gas becomes suited for use in synthetic processes. The economy of the process is determined by the quality of the refractories used in the generator because they must be able to withstand the continuously high working temperature. 15 refs.

3280. STILES, H. A. Synthetic Liquid Fuels. Petrol. Refiner, vol. 29, No. 10, 1950, pp. 99–102; Brennstoff-Chem., vol. 31, 1950, pp. 93–95.

Summary of the development of a synthetic fuels industry by the Bureau of Mines. The status of work at each of the Government plants—coal hydrogenation, gas synthesis, and shale-oil production—is described.

3281. STINZENDÖRFER, H. [Determination of the Constitution of the Fatty Acids Produced in the Fischer-Tropsch Synthesis.] Tech. Mitt. Krupp. Forschungsber., vol. 5, 1942, pp. 34–36; Chem. Zentralb., 1942, I, p. 2955; Chem. Abs., vol. 37, 1943, p. 3623.

Fatty acids contained in the remaining gases of a large-scale plant operating according to the Fischer-Tropsch process were isolated and separated by vacuum distillation into individual fractions. The mixture of fatty acids consisted essentially of saturated monobasic fatty acids, about the series of valeric to capric acids. Only very small amounts of unsaturated fat acids occurred.

3282. STORCH, H. H. Behavior of Zinc Oxide and Zinc Oxide–Chromium Oxide Catalysts in the Decomposition and Synthesis of Methanol. Jour. Phys. Chem., vol. 32, 1928, pp. 1743–1747; Chem. Abs., vol. 23, 1929, p. 816.

Details of preparation of several precipitated and supported ZnO and ZnO–Cr_2O_3 catalysts are reported. Their activities for the synthesis of MeOH from 4 H_2 : 1 CO gas mixtures at 3,000 l. per sq. in. and about 350° are compared. The addition of Cr_2O_3 to a ZnO catalyst in proportions of 200 gm. ZnO to 22 gm. Cr_2O_3 showed more activity than pure ZnO or pure Cr_2O_3. There was, however, no appreciable difference in activity between the catalysts when used to decompose MeOH at atmospheric pressure. The mixed oxide catalyst was virtually inactive for the synthesis of MeOH below 300°, and at 350° the yield was less than at 330°.

3283. ———. Activity and Activation Energy in Heterogeneous Catalysis of Gas Reactions. Jour. Am. Chem. Soc., vol. 57, 1935, pp. 1395–1398; Chem. Abs., vol. 29, 1935, p. 6495.

Relation $A=C_0e^{cE}$ between the activity A and the energy of activation E for contact catalytic reactions cannot be due entirely to a probability distribution of active centers. 2 other factors enter: (1) the frequency of energy exchange in the adsorbed phase may be reduced by adsorption, so that it becomes a function of the spacing of the catalyst atoms; (2) in reactions of low activation, energies involving H quantum leakage through the energy barrier may be considerable. The 1st hypothesis is supported by evidence, but there is none either for or against the 2d. Further experiments are suggested.

3284. ———. Synthetic Fuel Processes. Coal Age, vol. 48, January 1944, p. 117.

Estimates of the price of gasoline per gal. are given as $0.075 for an improved indirect Fischer-Tropsch method and from $0.055–$0.13 by hydrogenation. Figures are quoted regarding the position of synthetic fuel manufacture in the United States, Germany, Japan, and Great Britain.

3285. ———. Synthetic Liquid-Fuel Processes—Their Development in Germany and Great Britain and a Suggested Program for the United States. Synthetic Liquid Fuels Hearings Before a Subcommittee of the Committee on Public Lands and Surveys, U. S. Senate, 78th Cong., 1st sess., on S 1243, 1944, pp. 268–273.

Nontechnical discussion of the development of the Bergius and Fischer-Tropsch methods of liquid-fuel production with descriptions of the processes. Recommendations for the establishment of a national synthetic liquid-fuel industry from our vast resources of coal, lignite, natural gas, and oil shale are ably set forth.

3286. ———. Catalysis in Synthetic Liquid-Fuel Processes. Ind. Eng. Chem., vol. 37, 1945, pp. 340–351.

Fischer-Tropsch catalysts that are active in the synthesis of normally liquid hydrocarbons from CO and H_2—namely, Fe, Co, Ni, and Ru—form relatively unstable carbides on exposure to CO in the temperature range of the synthesis (185°–215° for Co and 240°–320° for Fe catalysts). Since the reaction $2\ Co+2\ CO \rightarrow Co_2C+CO_2$ is much too slow to account for the rate of hydrocarbon formation, it is conceivable that H_2 acts as catalyst for metal carbide formation by way of an unstable metal hydride according to the equation $2\ Co+CO+H_2 \rightarrow Co_2C+H_2O$. The mechanism of carbide formation on the Co catalyst, where the main oxygenated product is H_2O rather than CO_2, is difficult to apply to Fe catalysts, and it is probable therefore, that, although metal carbides are formed on both Co and Fe, the mechanism of the synthesis differs for the 2 substances. The hydrocarbons produced on sintered Fe catalysts, reduced with H_2 at 650°–850°, are largely branched-chain paraffins, whereas those formed on Fe catalysts reduced at 400° or less contain very little isoparaffins. An essential condition for the production of isoparaffins, therefore, is apparently the absence of ferrous oxide in the Fe catalyst and a critical spacing of the Fe atoms in the Fe carbide lattice to permit cross linkages to form. Previous investigations are reviewed on the effect of pressure, diluents, and contact time on the Fischer-Tropsch synthesis and the poisoning of catalysts by S compounds.

3287. ———. Synthesis of Hydrocarbons From Water Gas. Chemistry of Coal Utilization (H. H. Lowry, ed.). John Wiley & Sons, Inc., New York City, 1945, vol. II, chap. 39, pp. 1797–1845.

Industrial developments, methods of production of synthesis gas and of H_2, mechanism of the reactions, factors involved that affect the composition and yield, properties of Fischer-Tropsch products, and the economics of coal and CO hydrogenation are thoroughly reviewed. Bibliography of 178 refs.

3288. ———. Fischer-Tropsch and Related Syntheses. Crucible, vol. 31, 1946, pp. 52, 54, 56, 58, 60.

Paper given before the Physical Chemistry Division of the Pittsburgh Section of the American Chemical Society, which reviews German process development, followed by an analysis of kinetic data pertaining to the mechanism of the synthesis. The prevailing operating process in Germany was that with a Co–Th–Mg–kieselguhr catalyst at 200°, 1–10 atm. pressure, and in 2–3 stages with yields of 150 gm. of product per cu. m. of 2 H_2+1 CO. This method was improved by recycling 3 vol. of endgas from the 1st stage, with condensation of product after each cycle and increase in yield of 30%. By using H_2+1 CO insead of 2 H_2+1 CO, olefins were increased 20–55%. A hot-gas recycle process was developed using a sintered Fe catalyst at 320°, 20 atm., and ¾ sec. contact time. The space-time yield was 1 kg. per l. of catalyst per day. A liquid phase operation with suspended Fe catalyst also was under development which yielded a better grade of gasoline of 90 octane number and more diesel fuel. Two outstanding developments were the Synol and Oxo processes. The former produces liquid hydrocarbons (50–65%) and alcohols (50–35%), boiling at 50°–350°, operates at 18–25 atm. and 200°–235°, with gas of 1 CO+0.8 H_2 composition, using as catalyst granules of fused Fe_3O_4 : Al_2O_3 : K_2O=97 : 2.5 : 0.4. The hydrocarbons are partly branched, the alcohols are normal. The Oxo process consists in reacting a slurry of olefins with 3–5% of Co : ThO_2 : MgO : kieselguhr=30 : 2 : 2 : 66 catalyst with 1 CO+1 H_2 gas at 200 atm. and 150°–170°. The product (80% aldehydes and 20% alcohols) is hydrogenated at the same pressure and 180°–200° to produce the alcohol corresponding to the treated olefin with the addition of a C atom. Important factors in the probable mechanism of the Fischer-Tropsch process are discussed. The order of the reaction on Co, Ni, Fe, and Ru catalyst appears to be 0–1. The life of the catalysts is increased markedly by operation at 7–20 atm. Maximum conversion is obtained with Co catalysts at 5 atm. and space velocity of 150 vol. of gas per vol. of catalyst per hr.; with Ru more than 200 atm. is necessary. The temperature coefficient on Co and Fe catalyst is about 1.6 per 10° in the range 190°–235°, corresponding to an activation energy of 20 kcal. per mol. of 2 H_2 : 1 CO. The above catalysts form relatively unstable carbides with CO, which react with H_2 at temperatures below 350° to yield, quantitatively, CH_4 plus C_2H_6. Above 350°, considerable decomposition to C occurs. For maximum activity and life, Co catalysts should be inducted and reduced with H_2, and the initial synthesis should be prolonged at atmospheric pressure for several days before increasing the pressure to 10 atm. Fe catalysts are preferably pretreated with CO at 0.1 atm. at the rate of 100 l. per 10 gm. of Fe, space velocity 4–25 l. of CO per hr., 325° before operation with synthesis gas at 10 atm. Treatment with H_2 after the carbiding does not affect the activity of Fe catalysts, although the Fe carbide is converted to elemental Fe. It is believed that the initial carbiding distorts the lattice structure enough that subsequent exposure to synthesis gas reforms the carbide. Bureau of Mines tests show that the carbiding rate on Co catalysts is of the same order of magnitude as that of the synthesis. The ratio of CH_4 : C_2 hydrocarbons in the products from a Co catalyst is about 10, while that from an Fe–Cu catalyst is 0.5. C_2H_4 plays an important role in the synthesis on Co but not on Fe-Cu catalysts. The proportion of oxygenated organic compounds (chiefly alcohols) in the liquid products from Fe catalysts is greater than that from Co catalysts. The chief oxygenated product from Co catalysts is H_2O and from Fe catalysts is CO_2, the ratio of H_2O : CO_2 in the products from the latter increasing with the pressure. The reaction in the Fischer-Tropsch synthesis is relatively slow, 30 sec. of contact for a 60–70% conversion, as compared with 0.2 sec. for the reaction CO and steam over a Co–Cu catalyst at 325°. This probably is due to the critical spacing of the metal atoms in the catalysts lattice. A possible mechanism for the synthesis on Co and Fe catalysts is outlined in a series of equations depicting the reactions involved in the formation of normal α olefins, branched paraffins and oxygenated compounds.

3289. ———. Motor-Fuel Synthesis. Oil Gas Jour., vol. 46, No. 26, 1947, p. 96.

Paper presented at the meeting of the Philadelphia section of the American Chemical Society. The fluidized catalyst technique is described, pilot-plant tests of which have shown that such a plant may operate continuously for as long as 1,600 hr. and will produce chiefly gasoline with minor amounts of diesel fuel and chemicals. The method developed by the Bureau of Mines for removing the exothermic heat of reaction from the synthesis converter by injecting oil into the converter with the gas mixture also is described. The efficiency of the method is high but still has 2 disadvantages over the fluidized catalyst method in that the latter is about 50% faster in operation and requires about 25% less steel for installation. Further experiments are under way which may improve the efficiency of the oil-cooled converter.

3290. ———. Development of Processes for Producing Synthetic Liquid Fuels From Coal. Chem. and Eng. News, vol. 26, 1948, pp. 3821–3822.

The fifteenth annual Pittsburgh award address of the Pittsburgh Section of the American Chemical Society. The work undertaken by the Bureau of Mines during the past several years on the production of syn-