

INTRODUCTION

Certain gas-making processes are in use in Europe, particularly in Germany, which differ radically from those in common use in America. A number of them are of particular interest because they are different. The questions naturally arise: Are any of them applicable to the making of gas in this country and, if so, with what particular type of solid fuel? It is a fact that some of them were developed with consideration of a particular set of conditions and for the utilization of solid fuels available in Germany. The latter fuels, in certain characteristics, are unlike the high-rank fuels commonly used for making gas in the United States; therefore, in attempting to evaluate the various foreign-developed processes with regard to usefulness here, one must give attention to the particular conditions that will prevail in any specified case and also the characteristics and requirements of the process and generator under consideration. Three of the processes that were developed and put into commercial operation in Germany, and which have some characteristics in common, are considered in particular in this publication; they are:

1. Lurgi pressure gasification process.
2. Winkler process.
3. The Leuna slagging-type producer-gas process.

Each of these processes requires steam and oxygen as gas-making fluids.

For a number of years, oxygen has been used in a relatively pure state, along with steam, in making gas in Germany, and many of the difficulties initially encountered have been overcome. Although it appears that oxygen recovered from air was first used in this manner as a method of utilizing a byproduct in a plant that used the nitrogen complement in the manufacture of ammonia; more recently, the oxygen was made particularly for the purpose.

The fuels - brown coal or lignite - used in processes 1 and 2 were not suitable for use in the older and commonly used intermittent-type water-gas generators, and it was necessary, therefore, to devise a different process for gasifying them. A gas of higher heating value than producer gas was desired, and the use of oxygen (not air) along with steam made possible the production of the desired gas without nitrogen dilution, which characterizes producer gas.

Operating data presented herein are based upon observations by members of the Technical Oil Mission at plants in Germany, on records, and on information vocally given to members of the Mission, including the author, while visiting those plants, and they are believed to be reasonably correct; however, certain basic observations, comparisons, and conclusions are made by the author.

ACKNOWLEDGMENTS

The information relating to the operation of the various processes used in Germany and described in this circular is from notes made by the author while on an inspection tour of the various plants as a member of the combined Technical Oil Mission of the British and United States Governments and by reference to the drafts of the following reports:

Report on Investigations by Fuels and Lubricants Teams at the I. G. Farbenindustrie A. G. Works at Leuna, edited by R. Holroyd, C. I. O. S. Item 30, File XXXII-107, issued also as Bureau of Mines I. C. 7370.

A. G. Sachsische Werke, Bohlen (near Leipzig), Germany, reported by H. Hollings, C. V. Hopton, L. L. Newman, W. A. Horne, and E. Spivey, C. I. O. S. Item 30, File XXX-13.

Report on Investigations by Fuels and Lubricants Teams at the Brabag Works at Troglitz-Zeitz, edited by J. F. Ellis and R. J. Morley, C. I. O. S. Item 30, File XXXIII-24.

The author expresses his thanks and appreciation of the cooperation of the other members of the teams who visited the various plants in which the Lurgi pressure gasification process, the Winkler process, and the Leuna slagging-type producer-gas process were investigated. The personnel of the teams was as follows:

Visitors to the Leuna Plant.

For the British Ministry of Fuel and Power: H. Hollings, J. F. Ellis, H. G. Simpson, G. U. Hopton, R. Holroyd, M. A. G. Banks, D. A. Howes, A. J. V. Underwood, R. A. Taylor, and R. J. Morley.

For the U. S. Petroleum Administration for War: E. B. Peck, P. K. Kuhne, H. M. Weir, V. Haensel, E. Cotton, W. F. Faragher, J. G. Allen, H. Schindler, W. A. Horne, and J. P. Jones.

For the Bureau of Mines: L. L. Hirst, W. W. Odell, and L. L. Newman.

Visitors to the Troglitz-Zeitz Plant.

For the British Ministry of Fuel and Power: J. F. Ellis, H. Hollings, G. U. Hopton, L. King, and R. J. Morley.

For the U. S. Petroleum Administration for War: G. S. Bays, Jr., W. F. Faragher, W. A. Horne, J. P. Jones, P. K. Kuhne, B. L. MacKusick, and H. M. Weir.

For the U. S. Foreign Economic Administration: E. B. Peck.

For the Bureau of Mines: L. L. Hirst and W. W. Odell.

Visitors to the A. G. Sachsische Werke at Bohlen.

For the British Ministry of Fuel and Power: H. Hollings, G. U. Hopton, H. Bardgett, J. F. Hurley, J. G. King, E. Spivey, and A. J. V. Underwood.

For the U. S. Petroleum Administration for War: G. S. Bays, Jr., W. A. Horne, J. P. Jones, P. K. Kuhne, B. L. MacKusick, and H. M. Weir.

For the Bureau of Mines: L. L. Hirst, L. L. Newman, and W. W. Odell.

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THE LURGI PRESSURE-GASIFICATION PROCESS

The Lurgi pressure gasification process is, in effect, a continuous water-gas process; it is carried out in a water-jacketed generator, usually under pressures ranging from 10 to 20 atmospheres. In the ordinary water-gas process employing steam and air as the gas-making fluids, the operation is necessarily intermittent or cyclic, because the heat required to promote the reaction of steam with carbon can not be supplied by simultaneously blasting the hot fuel bed with air and steam, because of the resulting dilution of the gas with nitrogen. When oxygen is substituted for air, it is not necessary to alternate the gas-making run periods and air-blasting or heating phases of the cycle, and the oxygen and steam may be introduced into the fuel bed simultaneously as a common stream. In the latter case, it is necessary to proportion the amounts of steam and oxygen in the stream so that sufficient heat is supplied by the exothermic reactions of the fuel with oxygen to support the desired gasification reactions.

Major Reactions Involved

It is of interest to note the nature of the major reactions with which one is concerned in making gas in the Lurgi generator. Briefly, it may be said that the operation comprises promoting the water-gas reactions under pressure, which so changes the equilibrium conditions that more or less methane is formed, according to the pressure and temperature maintained in the generator. The chief chemical reactions involved are represented by equations (1) to (10), as follows:

Reactions	B.t.u. on the pound-molar basis	B.t.u. per 1,000 cubic feet of dry gas made
(1) $C + H_2O = CO + H_2$	75,535	- 99,910
(2) $C + 2H_2O = CO_2 + 2H_2$	76,920	- 67,830
(3) $CO + H_2O = CO_2 + H_2$	1,385	- 1,830
(4) $C + 1/2 O_2 = CO$	47,570	+ 125,850
(5) $C + O_2 = CO_2$	169,290	+ 447,855
(6) $C + CO_2 = 2CO$	74,150	- 98,080
(7) $2CO + 2H_2 = CH_4 + CO_2$	106,250	+ 140,540
(8) $CO_2 + 4H_2 = CH_4 + 2H_2O$	109,020	+ 288,415
(9) $CO + 3H_2 = CH_4 + H_2O$	107,635	+ 284,750
(10) $C + 2H_2 = CH_4$	32,105	+ 84,925

Reactants and products at 600° F.; are carbon as a solid (graphite), water as liquid, and the others gaseous. Values used are based upon data given by D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer, and F. D. Rossini in Free Energies, and Equilibrium Constants of Some Reactions Involving O₂, H₂, H₂O, C, CO, CO₂, and CH₄: Jour. of Research, National Bureau of Standards, Research Paper RP-1634, vol. 34, 1945, pp. 143-161. Heat liberated is designated by a plus (+) sign.

A little consideration of these reactions will be helpful to a better understanding of the results obtained in the operation of the Lurgi generator; hence they are presented here but are discussed briefly in somewhat general terms.

Equations (1) and (2), the well-known steam-carbon reactions, occur at a high rate at temperatures above about 900°C. ($1,652^{\circ}\text{F.}$), the rate of reaction decreasing rapidly as the temperature falls below this level. The use of pressure in conducting these two reactions is not helpful. In other words, at a given high temperature ordinary water gas can be made as effectively at atmospheric pressure as at higher pressures. Of course, the reaction of equation (1) represents the results usually sought in preference to those of equation (2), hence the duration of the gas-generating period of the ordinary water-gas cycle is commonly selected, so that only a relatively small amount of the latter occurs; as the temperature decreases during the gas-making period, the relative amount of reaction (2) increases. A typical water gas made from coke by methods in common use in the United States is shown in column 1 of table 1. Although the heat requirements in promoting reactions (1) and (2) are of the same order of magnitude, and the amount of combustible gas made is the same in each case, it is noted that the mixed gas ($\text{CO}_2 + 2\text{H}_2$) produced according to reaction (2) is one-third inert carbon dioxide, and that twice as much steam is reacted in equation (2) as in equation (1) per unit volume of combustible gas made.

To make the process continuous, it is necessary to supply the heat of reaction during the gas-making period. One procedure for doing this is to introduce oxygen along with the steam. The amount of oxygen (O_2) required is of particular interest, not only because it is expensive but because its use alters the composition of the gas made. The exothermic reactions of equations (4) and (5), typifying the oxidation of carbon, show the amounts of heat evolved by its combustion. It would be desirable, in one sense only, if the oxygen employed were consumed by reaction (5), because more heat is evolved per mol of carbon oxidized and less O_2 is required per unit of heat energy evolved. However, at high temperatures, in the presence of carbon, reaction (4) will predominate, or, to be more exact, reaction (6) occurs, whereby the carbon dioxide (CO_2) evolved by reaction (5) combines with additional carbon to form carbon monoxide (CO). At usual gas-making temperatures all of these reactions, (4), (5), and (6), will occur when O_2 is introduced into an ignited fuel bed, and the net result will be the generation of heat amounting to a minimum of 47,570 B.t.u. per mol of carbon oxidized by O_2 ; the heat actually generated will be between 47,570 and 169,290 B.t.u. Equilibrium conditions for the major reactions encountered in the generation of water gas are so well understood that for a given temperature in the fuel bed and sufficient time for the water-gas reactions to reach equilibrium, the composition of the resulting gas mixture can be computed accurately. However, equilibrium conditions are not always reached in making gas at high rates, and this fact has important bearing not only upon the variation in composition of the gas made but in some cases upon the suitability of certain processes and fuels in the manufacture of gas for particular purposes. For the purpose of economy it is usually desirable to make gas by employing high rates of flow of the gas-making fluids in the generator, and it is frequently desirable to maintain moderately low temperatures in the fuel bed because of low softening temperatures of the fuel ash;

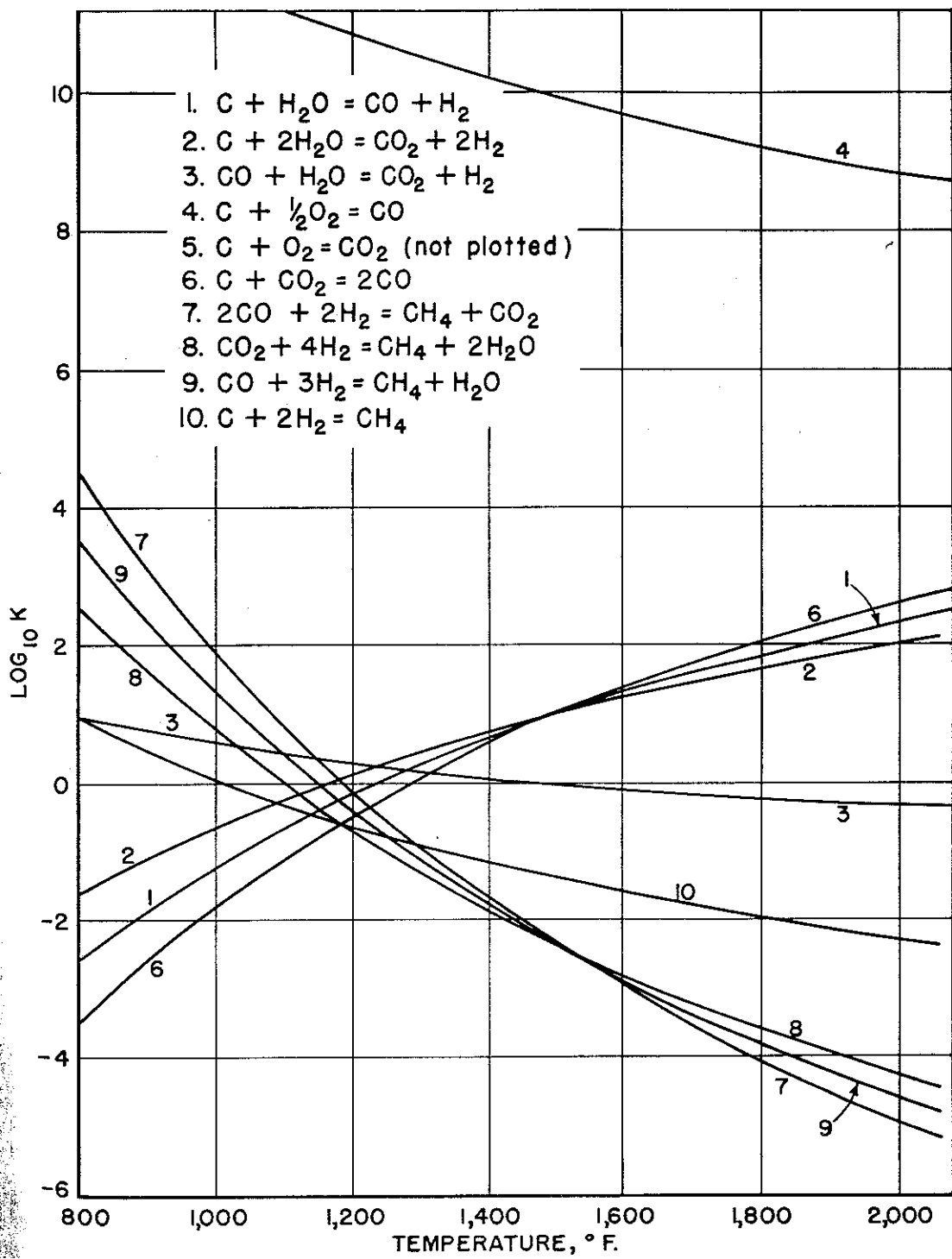


Figure 1.—Variation of the logarithm of the equilibrium constant ($\log_{10}K$) with temperature for several reactions involving O_2 , H_2 , H_2O , C (graphite), CO , CO_2 , and CH_4 .

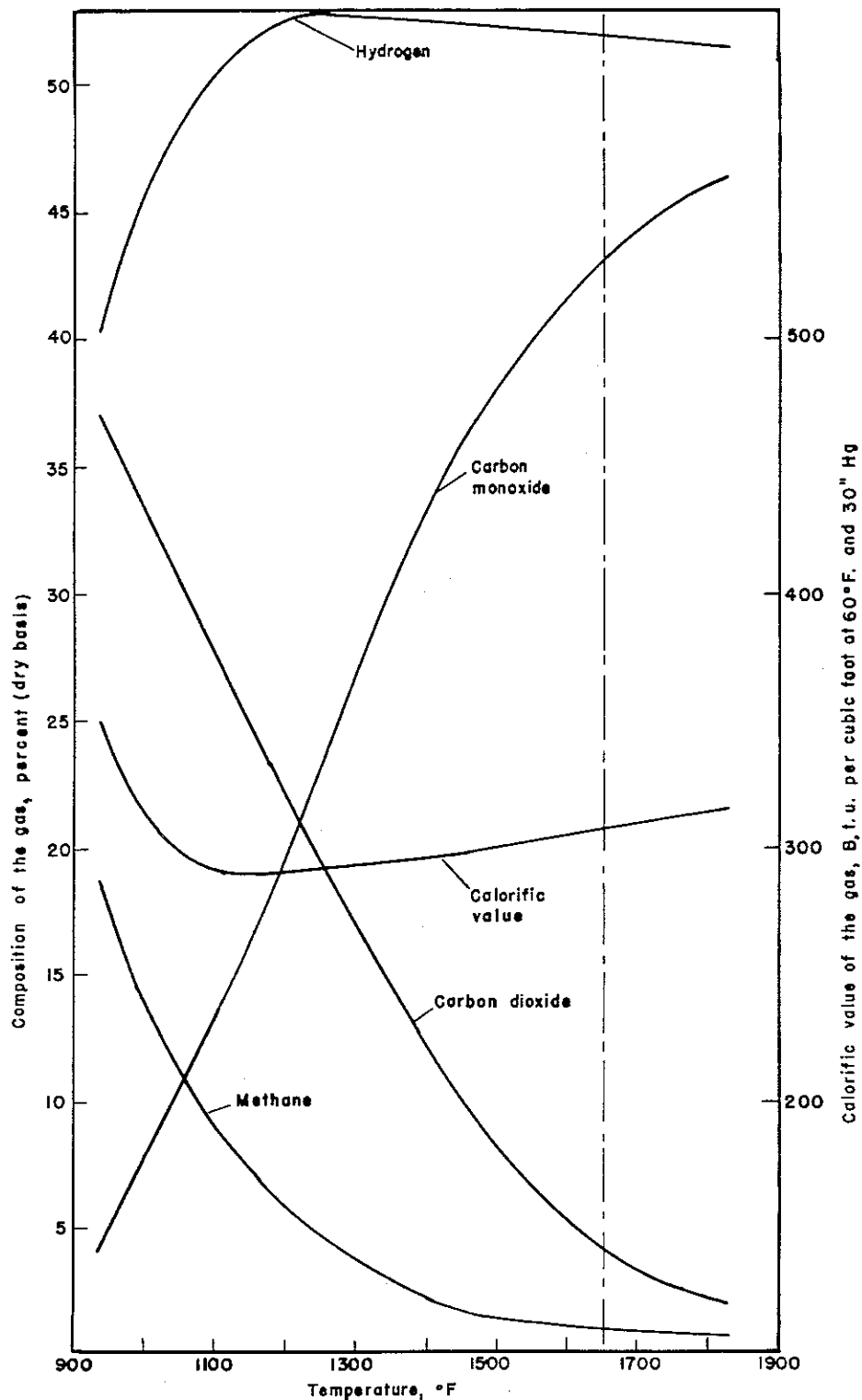


Figure 2.—Variation with temperature; composition and calorific value of water gas made from steam and carbon under equilibrium conditions (approximations from equilibrium data).

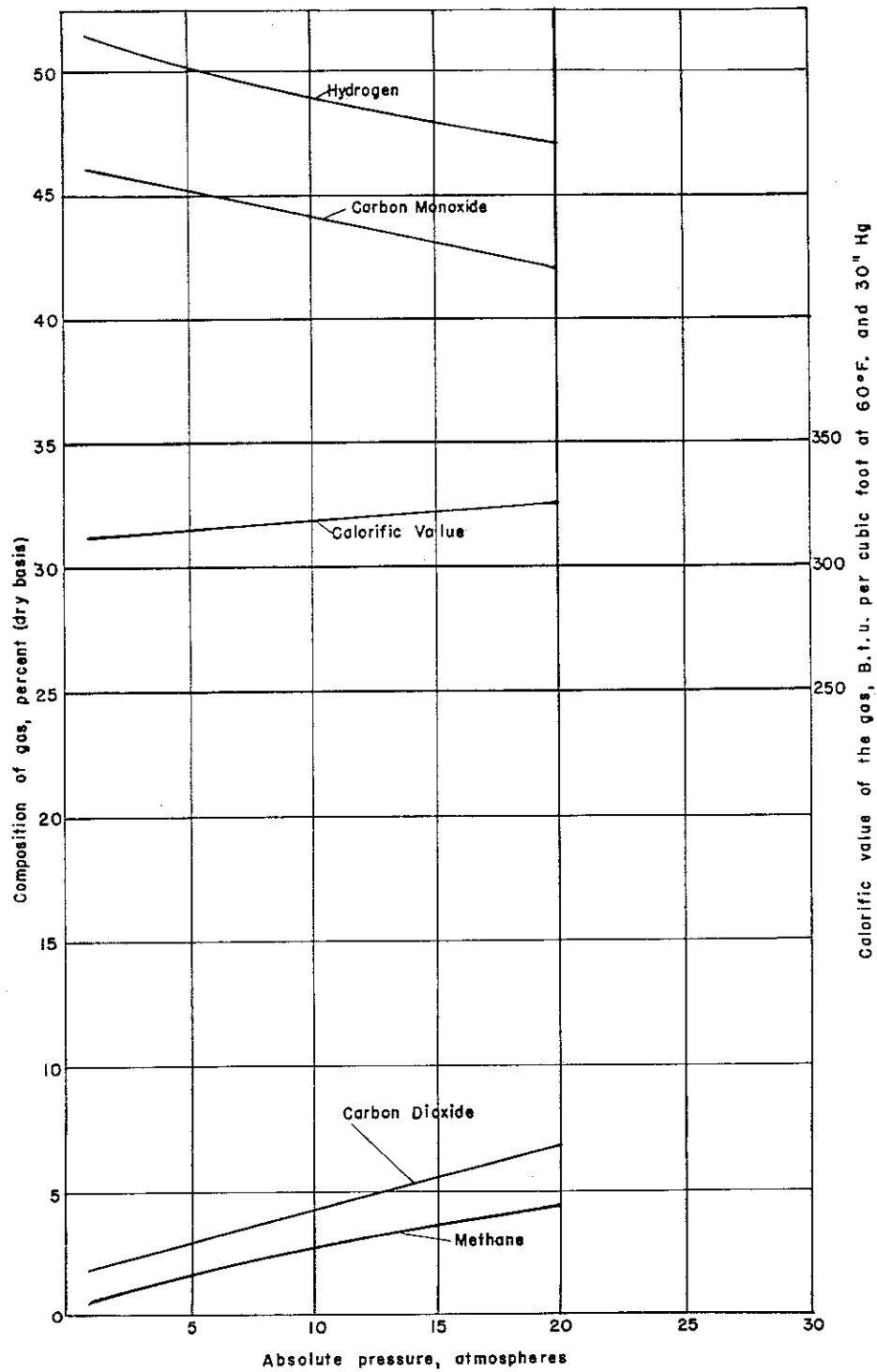


Figure 3.-Variation with pressure in composition and calorific value of water gas made when steam alone is reacted with carbon at 1,832°F. (1,000°C.), approximations from equilibrium values.

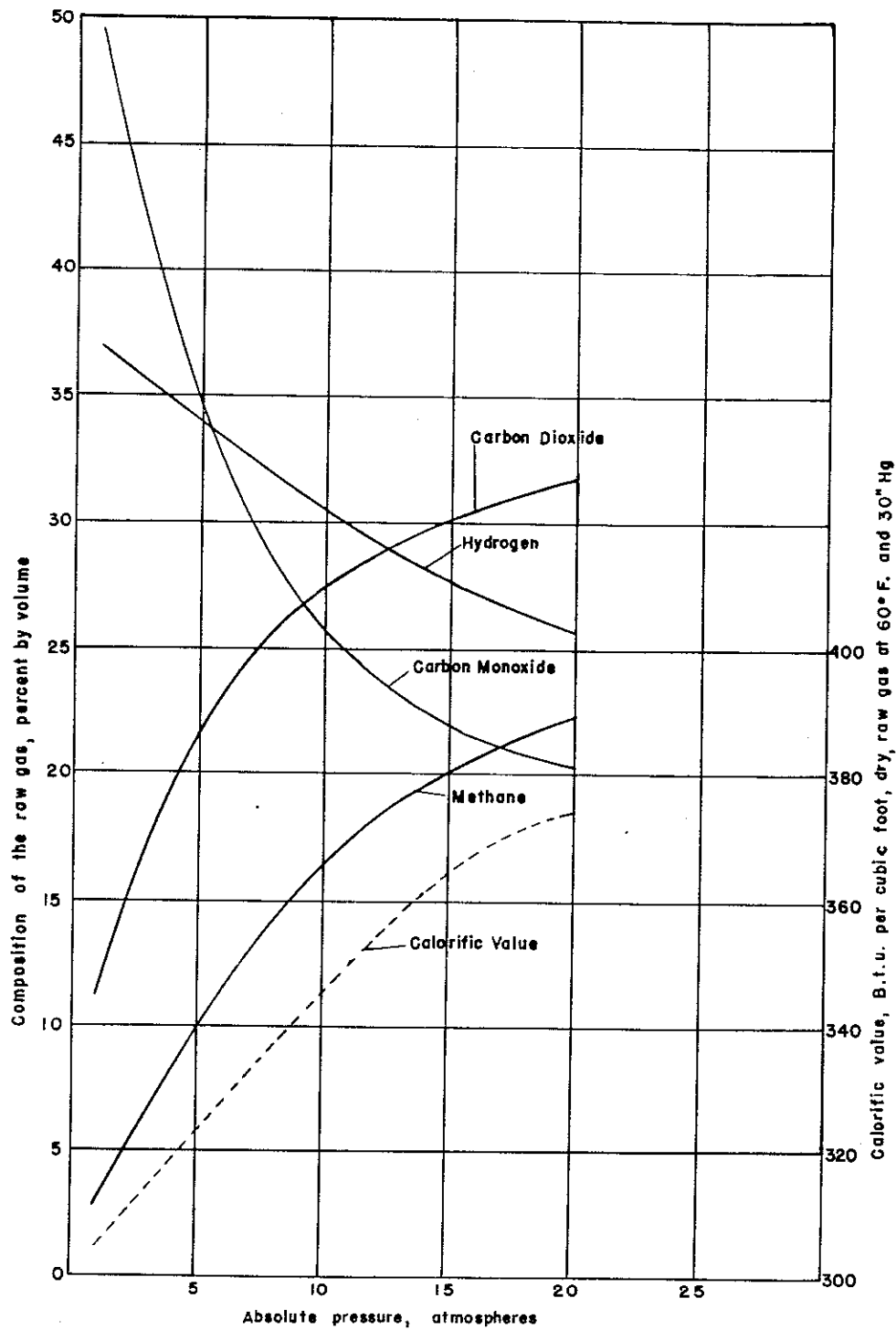


Figure 4.—Variation with pressure in composition and calorific value of raw gas made by gasifying reactive coal at 1,340° F. (1,000° K.) with oxygen and steam as gas-making fluids.