

## SUMMARY

A number of tests were made with various methanation catalysts in fixed-bed, conventional fluidized-bed, and multiple-feed, fluidized-bed equipment to develop catalysts and processes for methanation of synthesis gas. The results show:

1. Methanation reactions may be carried out in 1-inch, bench-scale equipment at high synthesis-gas throughputs with good temperature control of the reactions if a multiple-feed type of fluidized-bed design is used.
2. Nickel is superior to iron as a catalyst for the methanation of synthesis gas, unless the process is considered in terms of a combined operation that produces both gaseous and liquid products.
3. Techniques of catalyst preparation determine, to a large extent, the process life of nickel catalysts, and these techniques must be thoroughly investigated before any conclusions can be reached.
4. Enough data are available to indicate that the sulfur concentrations in synthesis gas that is used for methanation are extremely critical, and maximum process limits should be carefully evaluated.

## INTRODUCTION

Since the beginning of the century when Sabatier and Senderens first produced methane by passing a mixture of hydrogen and the oxides of carbon over finely divided metals,<sup>6,7</sup> there has been considerable speculation over whether catalytic synthesis of methane could be utilized to produce high-B.t.u. fuel gas. Heretofore little attention has been directed toward the production of major supplies of high-B.t.u. gas from coal in the United States because of the large reserves of natural gas that are now available. However, because natural gas has certain advantages over other types of fuel, the demands for natural gas have greatly increased in recent years. Owing to these increased demands and in view of the fact that natural gas, like most natural resources, is not an inexhaustible commodity, it has become increasingly apparent that the possibility of obtaining fuel gas from alternative sources should be considered.

Since July 1952, the Fuels Technology Division, Bureau of Mines, Region V, has been actively engaged in a program directed toward the synthesis of high-B.t.u. fuel gas from coal. The work has been carried out in the laboratories of the Bureau of Mines at Bruceton, Pa., and the major emphasis of the program has been placed upon developing a catalytic process that would satisfy the requirements of a commercial-scale operation for producing methane from carbon monoxide and hydrogen. The

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- 6/ Sabatier, P., and Senderens, J. B., New Synthesis of Methane: Compt. rend., vol. 134, 1902, p. 514.
- 7/ Sabatier, P., and Senderens, J. B., General Methods of Hydrogenation of Molecular Reactions Based on the Use of Finely Divided Metals: Jour. Chem. Soc., vol. 88, 1905, p. 333.

project has now reached a stage of development where large-scale pilot-plant investigations are required to determine whether or not the principles, techniques, and equipment designs that have been developed can be successfully applied to industrial operations. This report describes the catalyst and process-development work that has been carried out in this laboratory since the inception of the project in July 1952.

#### GENERAL

The natural gas that is used in the United States consists essentially of methane, has a gross heating value of approximately 1,000 B.t.u. per cu. ft., and is supplied, primarily, from gas wells in southwestern regions of the United States. The gas is distributed throughout the nation through high-pressure pipelines and is generally used as it is delivered by the pipeline, with the exception of some purification, when necessary, to remove sulfur compounds and water. Since most of the equipment for gas distribution and utilization is designed to handle natural gas, the aims of this investigation were to produce a fuel gas with characteristics similar to natural gas.

Of all the techniques for producing fuel gas from coal, the one that appears to be of most practical interest at this time is the gasification of coal with steam and oxygen to produce synthesis gas, a mixture of carbon monoxide and hydrogen having a gross heating value of 300-400 B.t.u. per cu. ft. Since the cost per energy unit of transporting such a gas in high-pressure pipelines would be high and since most utility equipment is designed to burn higher heating-value fuels, untreated synthesis gas is not suitable as a pipeline fuel. Some of these problems can be avoided, however, if all, or a large part, of the synthesis-gas mixture is converted to methane. Although the theoretical efficiency of the process is only 75 percent, it yields a product gas having most of the characteristics of natural gas.

An overall process for the conversion of coal to high-B.t.u. fuel gas by this technique would require four steps: (1) Gasification of coal to produce synthesis gas; (2) removal from the synthesis gas of carbon dioxide and sulfur compounds formed during the gasification; (3) catalytic conversion of synthesis gas to methane; and (4) removal from the methane of any carbon dioxide and high-molecular-weight hydrocarbons formed in the synthesis. Costs for a complete process have been estimated by Alberts,<sup>8/</sup> Gumz,<sup>9/</sup> and others. Most of the cost estimates, however, have been based on Lurgi gasification techniques and the catalyst studies made by the British Gas Research Board, which used nickel catalysts to produce fuel gases having heating values in the range of 400-600 B.t.u. per cu. ft.,<sup>10 11 12 13/</sup> and it is difficult to extrapolate these data to processes that yield 900-B.t.u. gas from coals that are not well suited for using in Lurgi gasifiers.

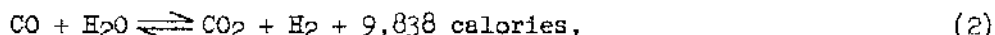
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- <sup>8/</sup> Alberts, L. W., Bardin, J. S., Beery, D. W., Jones, H. R., and Vitt, E. J., Production of Methane From Coal: Chem. Eng. Prog., vol. 48, 1952, p. 486.
- <sup>9/</sup> Gumz, W., and Foster, J. F., A Critical Survey of Methods of Making High-B.t.u. Gas From Coal: Research Bull. 6, Gas Prod. Research Committee of the Am. Gas Association, New York, N. Y., July 1953, 87 pp.
- <sup>10/</sup> Dent, F. J., Moignard, L. A., Eastwood, A. H., Blackburn, W. H., and Hebden, D., An Investigation Into the Catalytic Synthesis of Methane for Town Gas Manufacture: British Gas Research Board, Communication G.R.B. 20, 1945, 104 pp.
- <sup>11/</sup> Booth, N., Wilkins, E. T., Jolley, L. J., and Tebboth, J. A., Catalytic Synthesis of Methane: British Gas Research Board, Communication G.R.B. 21, 1945, 40 pp.
- <sup>12/</sup> Dent, F. J., and Hebden, D., The Catalytic Synthesis of Methane as a Method of Enrichment in Town Gas Manufacture: British Gas Research Board, Communication G.R.B. 51, 1950, 52 pp.
- <sup>13/</sup> Department of Scientific and Industrial Research, Catalytic Enrichment of Industrial Gases by the Synthesis of Methane: Fuel Research Tech. Paper 57, London, 1953, 51 pp.

## CHEMISTRY AND THERMODYNAMICS

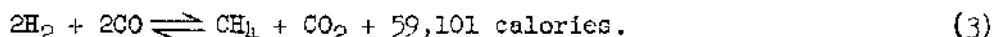
The conversion of carbon monoxide and hydrogen to methane when the hydrogen-carbon monoxide ratio in the synthesis gas is equal to or greater than 3 can be described by the reaction:



When the hydrogen-carbon monoxide ratios are reduced below 3, the secondary water-gas shift reaction,



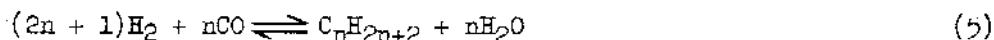
becomes prominent, and, as the ratio approaches unity, the overall reaction can be written:



Other reactions that occur during the synthesis and tend to complicate this somewhat simple picture are the deposition of carbon by decomposition of carbon monoxide,



and the formation of hydrocarbons of higher molecular weight than methane by the reactions



and



Using the techniques of the Gas Research Board 16/ and the thermodynamic data of Rossini and coworkers, 15/ equilibrium compositions for the reaction system were calculated, assuming that the equilibria for reactions (1), (2), and (4) were satisfied. The calculations were completed for the temperature range 500°-900° K., for pressures of 1, 10, and 25 atmospheres and for hydrogen-carbon monoxide ratios from 0.50 to the limiting ratio above which the deposition of carbon does not occur.

Figures 1, 2, and 3 are summaries of the theoretical equilibrium yields of methane, in moles per mole of synthesis gas, that can be obtained over the range of variables previously indicated. The most critical variables of the system appear to be temperature and hydrogen-carbon monoxide ratio, the methane yield being highest at the higher ratios and lower temperatures. Pressure, however, exerts little influence on the system, except at the higher temperatures around 800°-900° K., when increases in pressure tend to increase methane yields to those obtained at lower temperature.

14/  $\Delta H$  values taken at 298.16° K.

15/ Rossini, F. D., Pitzer, K. S., Taylor, W. J., Ebert, J. P., Kilpatrick, J. E., Beckett, C. W., Williams, M. G., and Werner, H. G., Selected Values of Properties of Hydrocarbons: Nat. Bureau of Standards Circ. C-461, November 1947, 483 pp.

16/ See work cited in footnote 10.

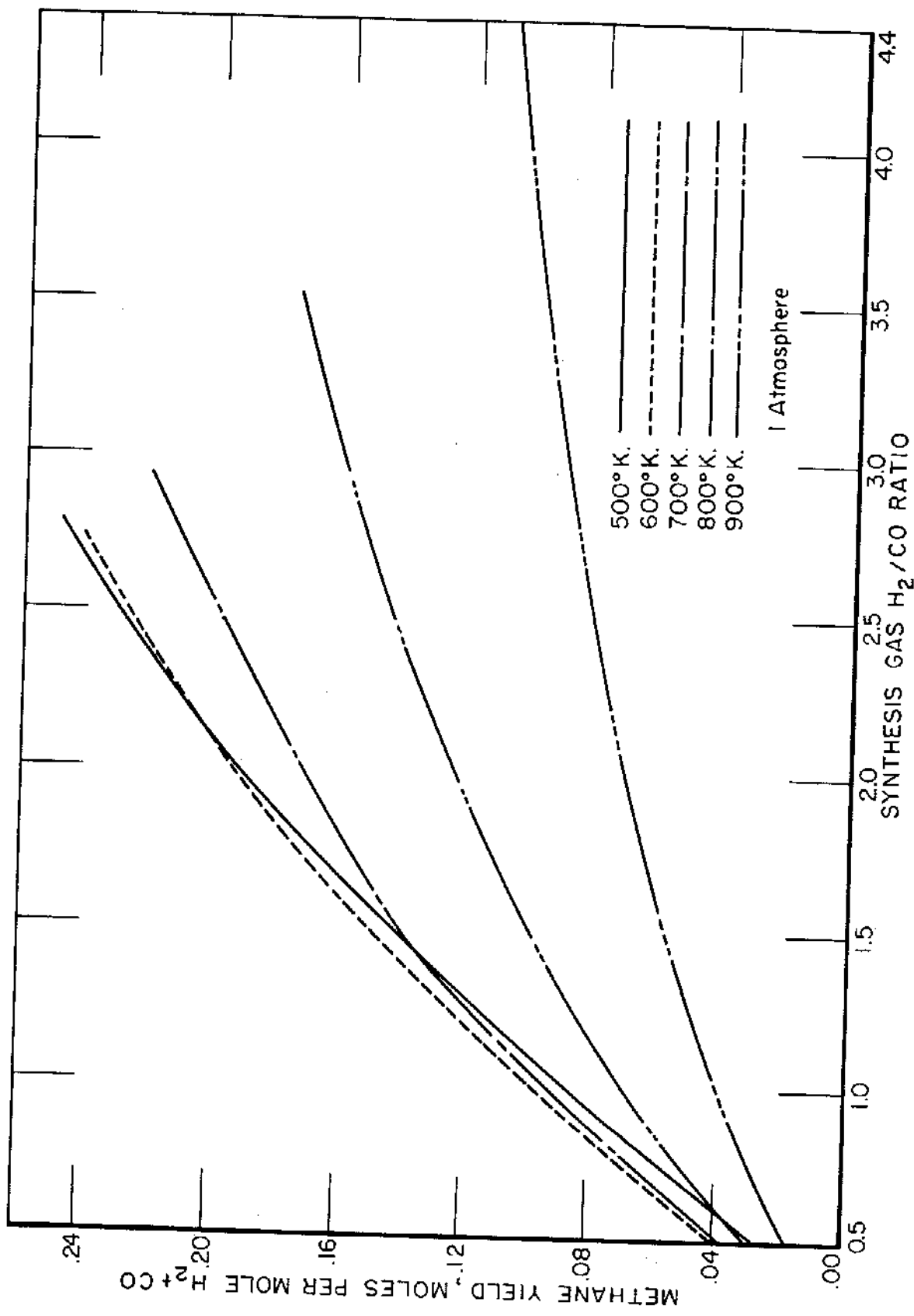


Figure 1. - Equilibrium yields of  $CH_4$  (1 atmosphere).

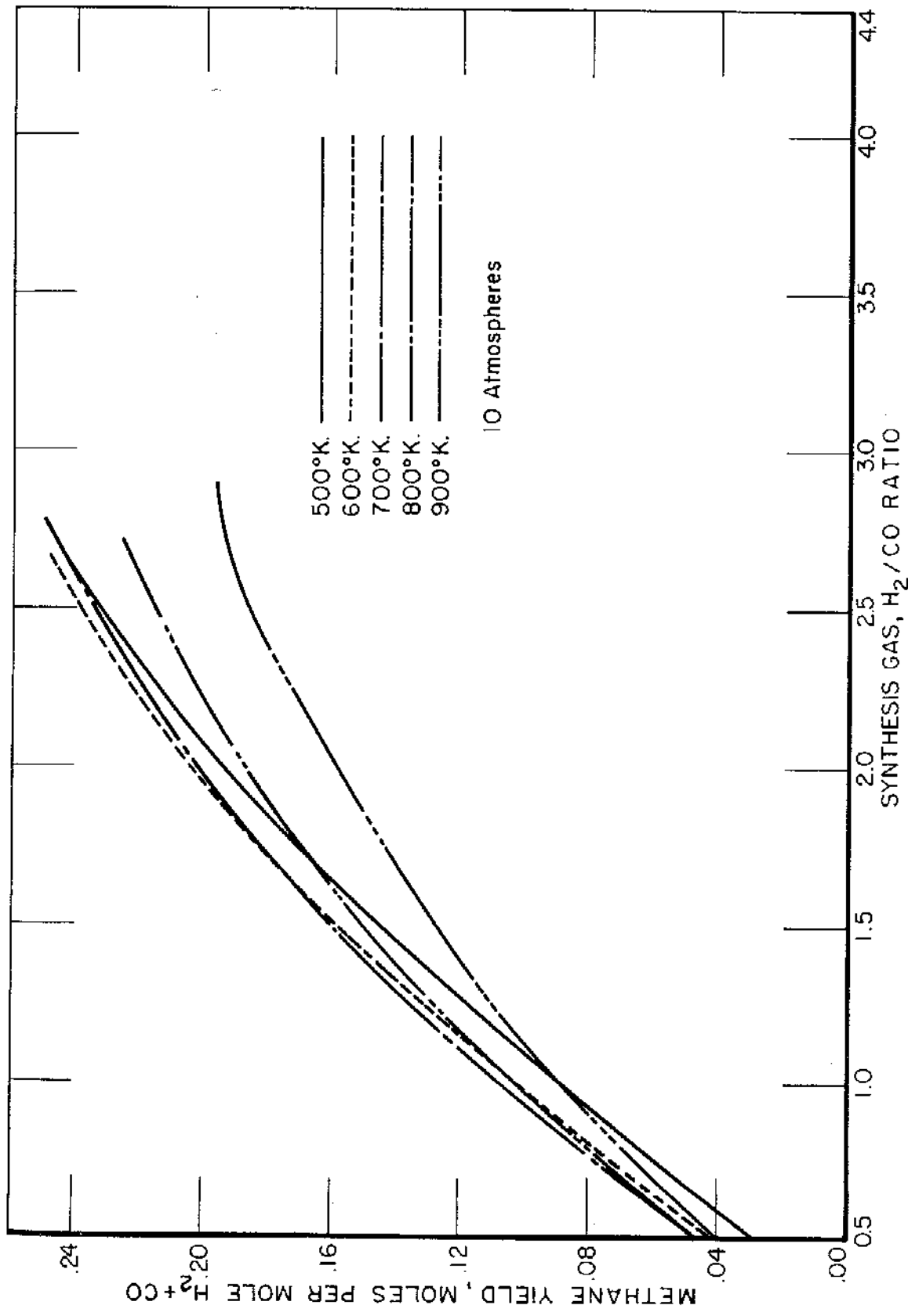
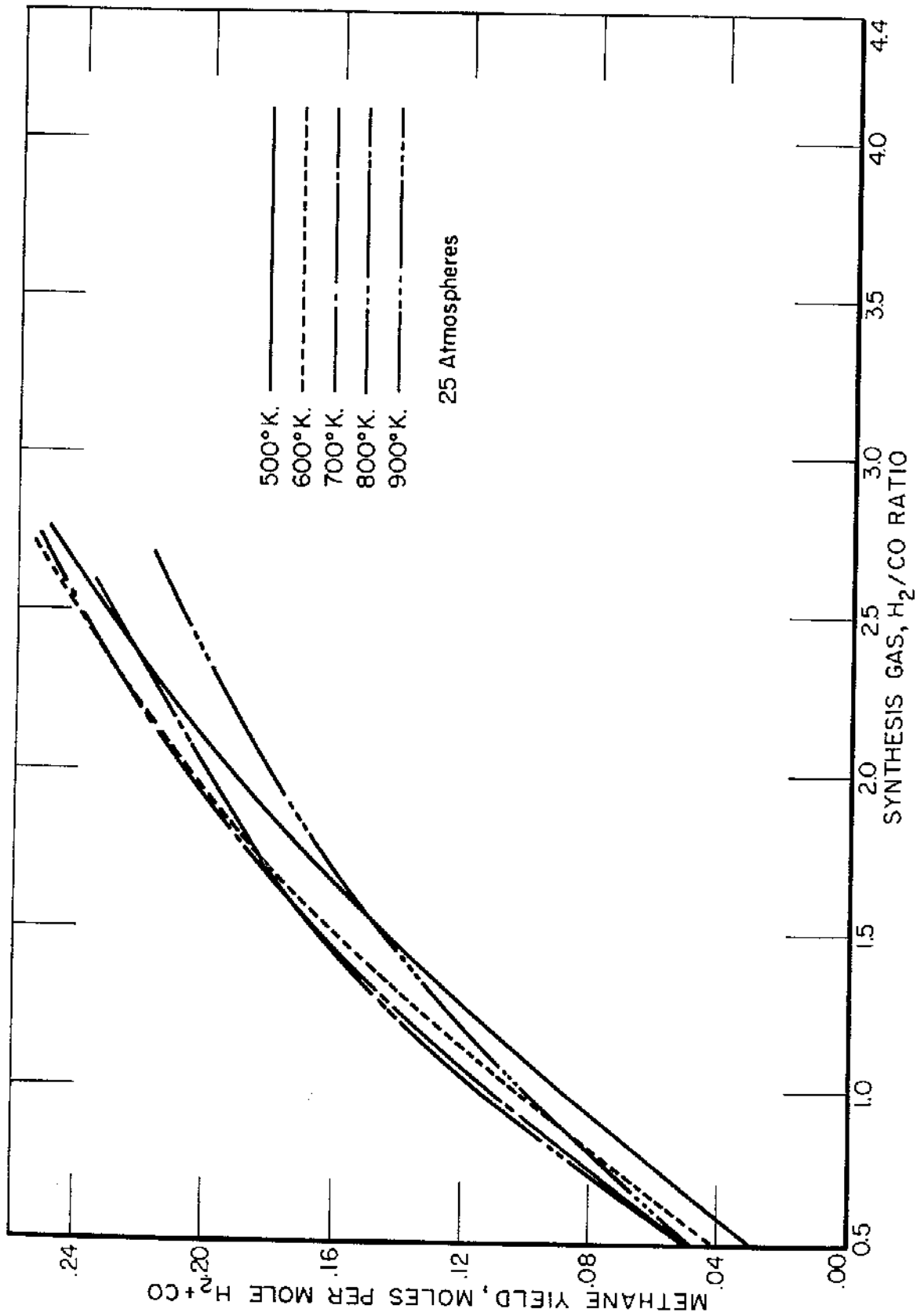


Figure 2. - Equilibrium yields of CH<sub>4</sub> (10 atmospheres).

Figure 3. - Equilibrium yields of CH<sub>4</sub> (25 atmospheres).

The minimum hydrogen-carbon monoxide ratios for the temperature range 500°-1,400° K., below which carbon deposition occurs, are shown in figure 4. As with methane yields, pressure exerts a maximum influence at temperatures at which methane yields are low, increases in pressure resulting in lower minimum hydrogen-carbon monoxide ratios. The beneficial pressure effect is also reflected in the amount of carbon that is deposited, which is shown in figures 5, 6, and 7.

The overall effects of pressure on water and carbon dioxide yields are small. The curves for the yields of these components are shown in figures 8, 9, and 10. Although slight increases in pressure result in slight increases in water yields, carbon dioxide yields are not appreciably affected, and both variables are, primarily, functions of hydrogen-carbon monoxide ratio.

The total conversion of synthesis gas is, unlike the other variables of the system, primarily a function of temperature and pressure. This is shown in figure 11, in which mole fractions of synthesis gas converted are plotted as functions of pressure, temperature, and synthesis-gas ratio. Pressure acts here in the same manner as with the other variables to increase the degree of conversion, particularly at the higher temperature.

The overall effects of the system variables on the heating value of the product gas are illustrated in figure 12, in which heating values, corrected to a carbon dioxide- and water-free basis and referred to 0° C. and 1 atmosphere of pressure, are plotted as functions of temperature, pressure, and synthesis-gas ratio.<sup>17/</sup> Here, as in the other figures, temperature and synthesis-gas ratio appear to be the most critical factors, the highest heating values being obtained at the lowest temperatures and highest synthesis-gas ratios. These values, however, give no indication of the quantity of fuel gas that can be obtained from a mole of synthesis gas at a specified set of operating conditions. To determine this measure of process efficiency, the yield of methane and total conversion of synthesis gas must be considered. These factors are considered in a later section of this report, which deals with the experimental portion of the work, and a method of computing the efficiency of a process has been devised.

Although a number of studies have been made on the kinetics and mechanisms of the reaction system, they have not been evaluated in a manner that is completely satisfactory.<sup>18 19 20/</sup> The reaction rates over nickel catalysts at temperatures above 300° C., however, appear to be high enough for the system to approach theoretical equilibrium, and, because high methane yields are favored by low temperatures, the problem of obtaining maximum methane yields becomes essentially one of maintaining proper temperature control in the highly exothermic system. Accordingly, the kinetics and mechanisms of the reactions are of interest only in avoiding undesirable side reactions that might occur during the synthesis with certain catalytic materials.

<sup>17/</sup> To convert heating values given here to reference conditions of 60° F., 30 in. Hg, saturated all heating values should be multiplied by 0.93.

<sup>18/</sup> Strickland-Constable, R. E., The Synthesis of Methane From Carbon Monoxide and Hydrogen on a Nickel Catalyst: British Gas Research Board, Communication G.R.B. 46, 1949, 30 pp.

<sup>19/</sup> Aikers, W. W., and White, R. R., Kinetics of Methane Synthesis: Chem. Eng. Prog., vol. 44, 1948, p. 553.

<sup>20/</sup> Gilkeson, M. M., White, R. R., and Sliepcevich, C. M., Synthesis of Methane: Ind. Eng. Chem., vol. 45, 1953, p. 460.

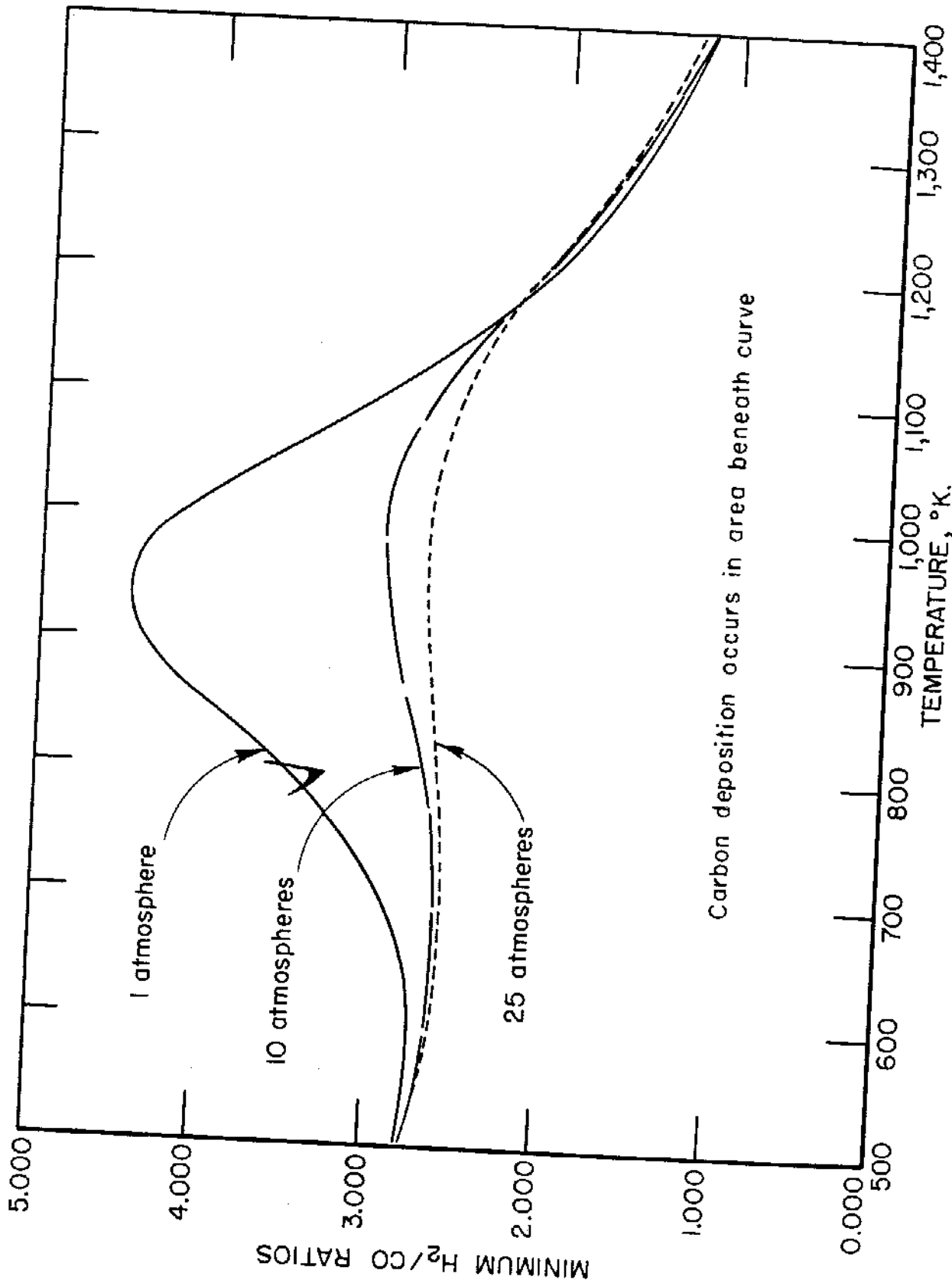


Figure 4. - Carbon-deposition boundaries.



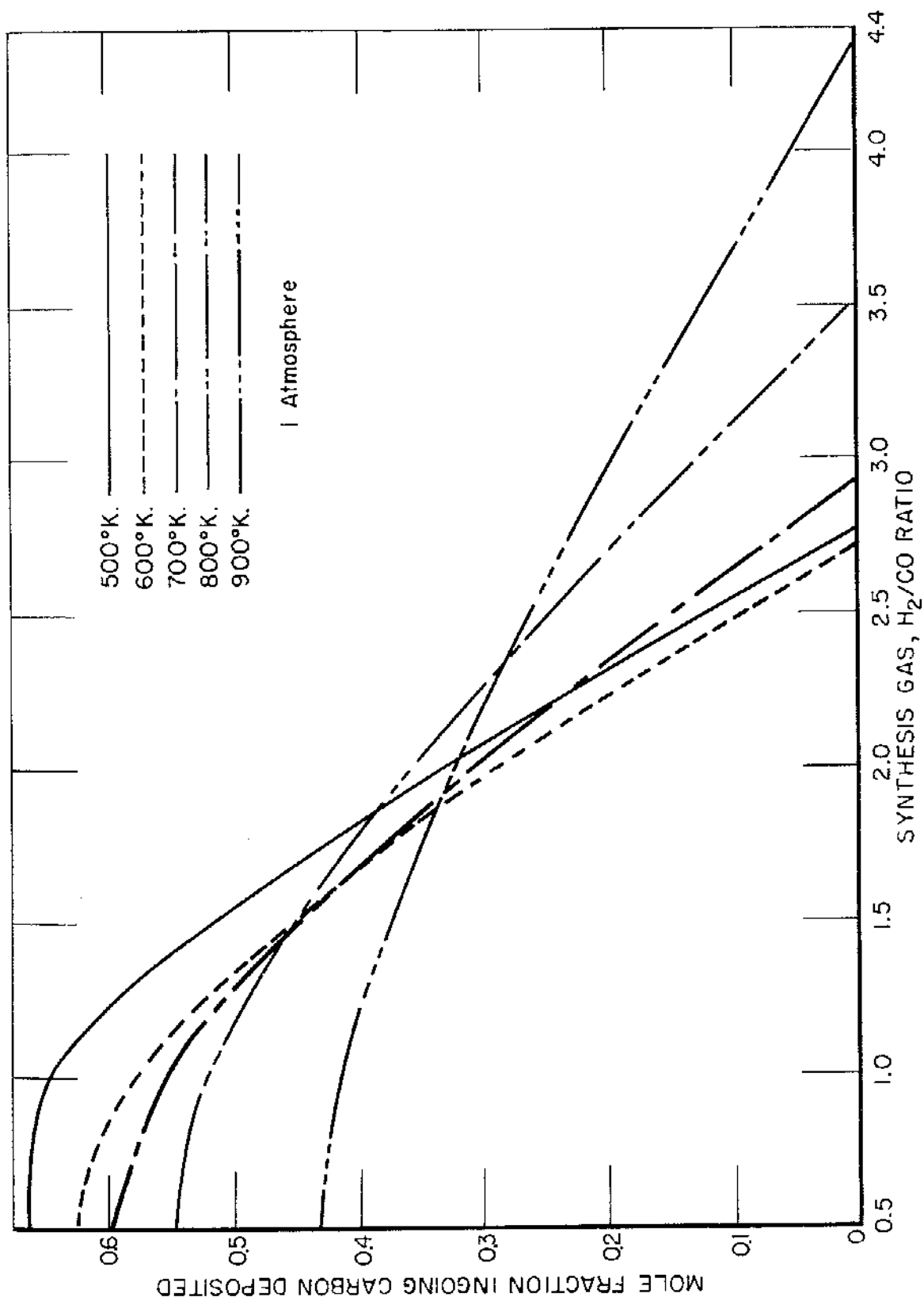


Figure 5. - Degree of carbon deposition (1 atmosphere).

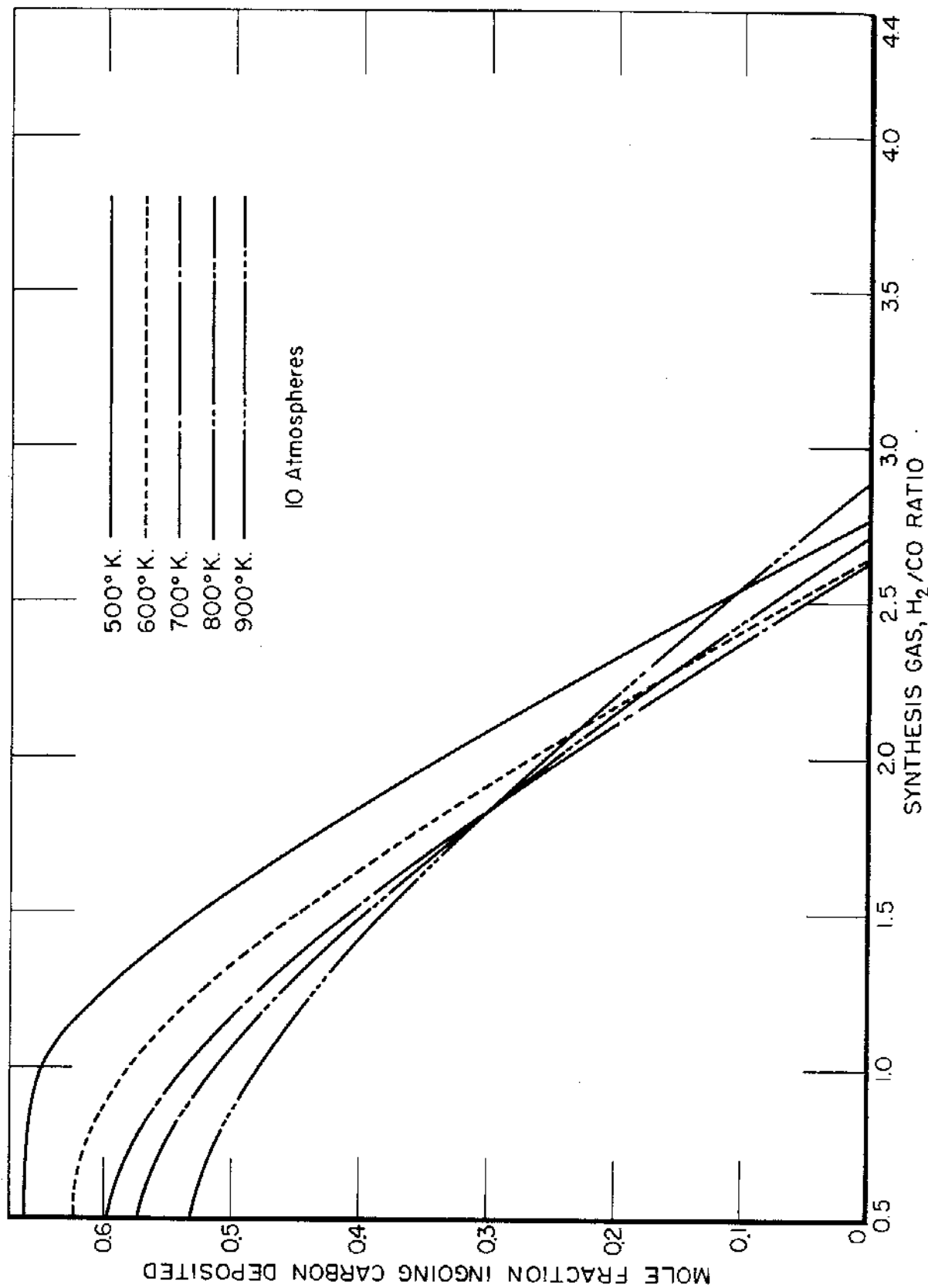


Figure 6. - Degree of carbon deposition (10 atmospheres).

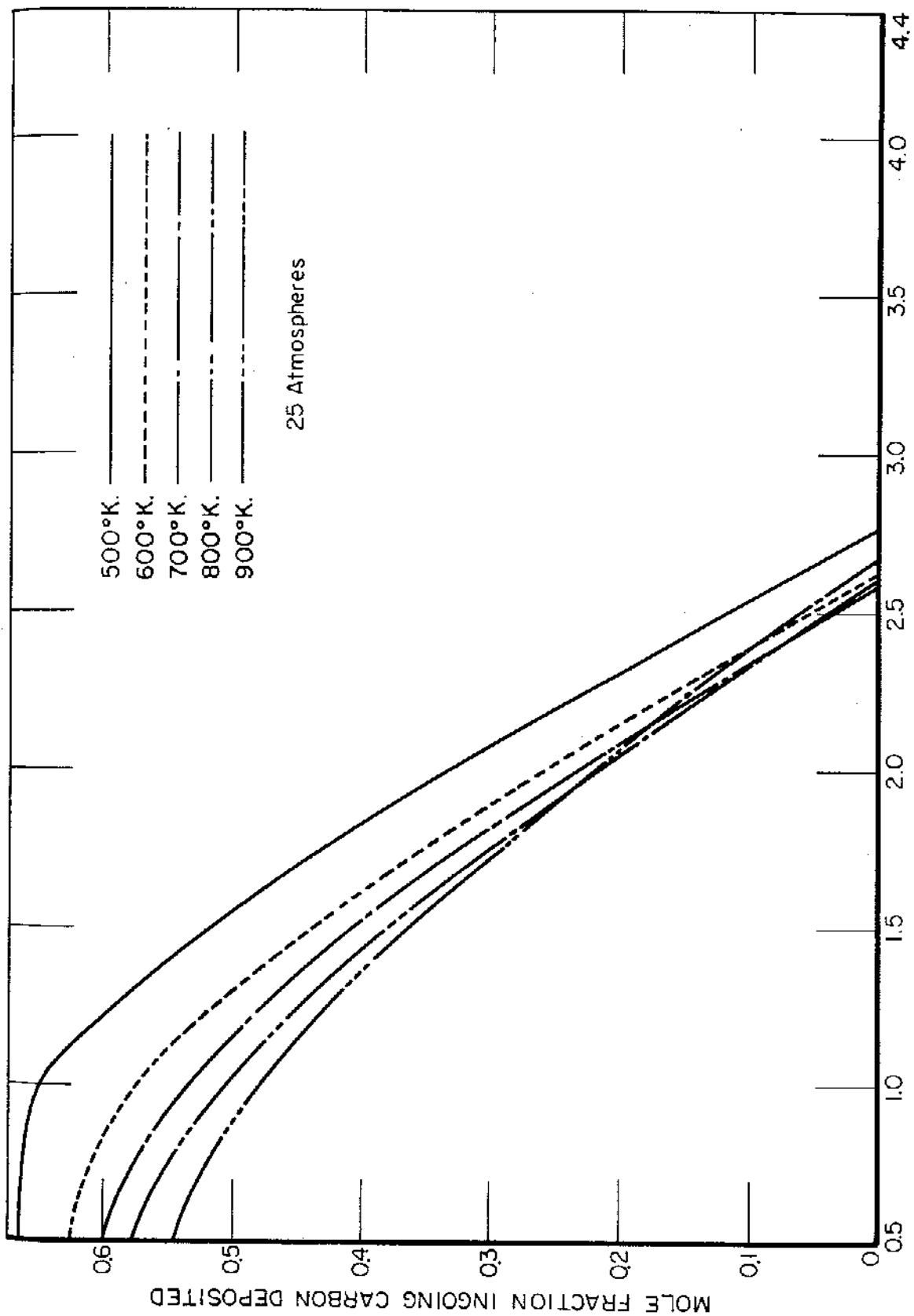


Figure 7. - Degree of carbon deposition (25 atmospheres).

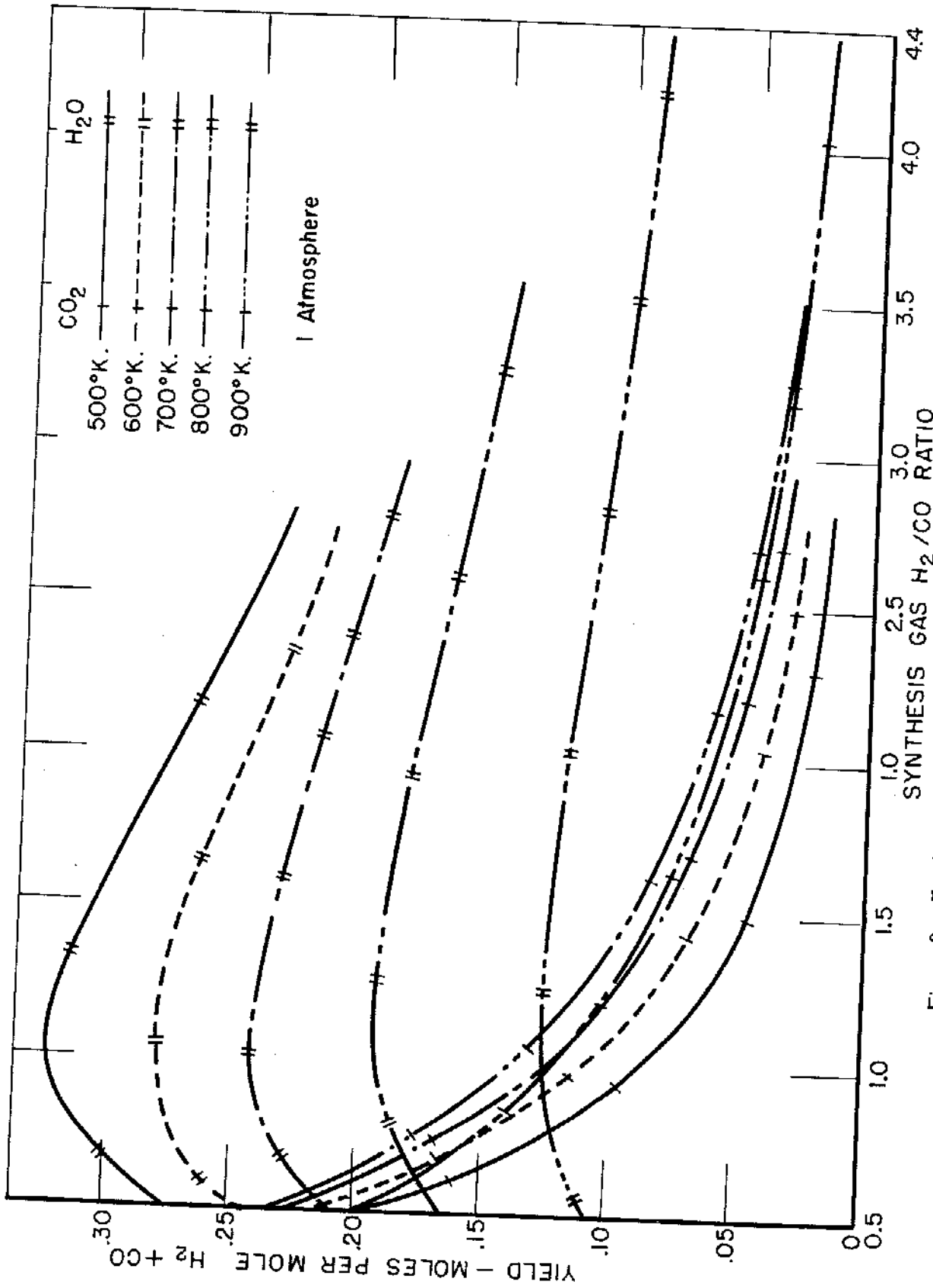


Figure 8. - Equilibrium yields of carbon dioxide and water (1 atmosphere).

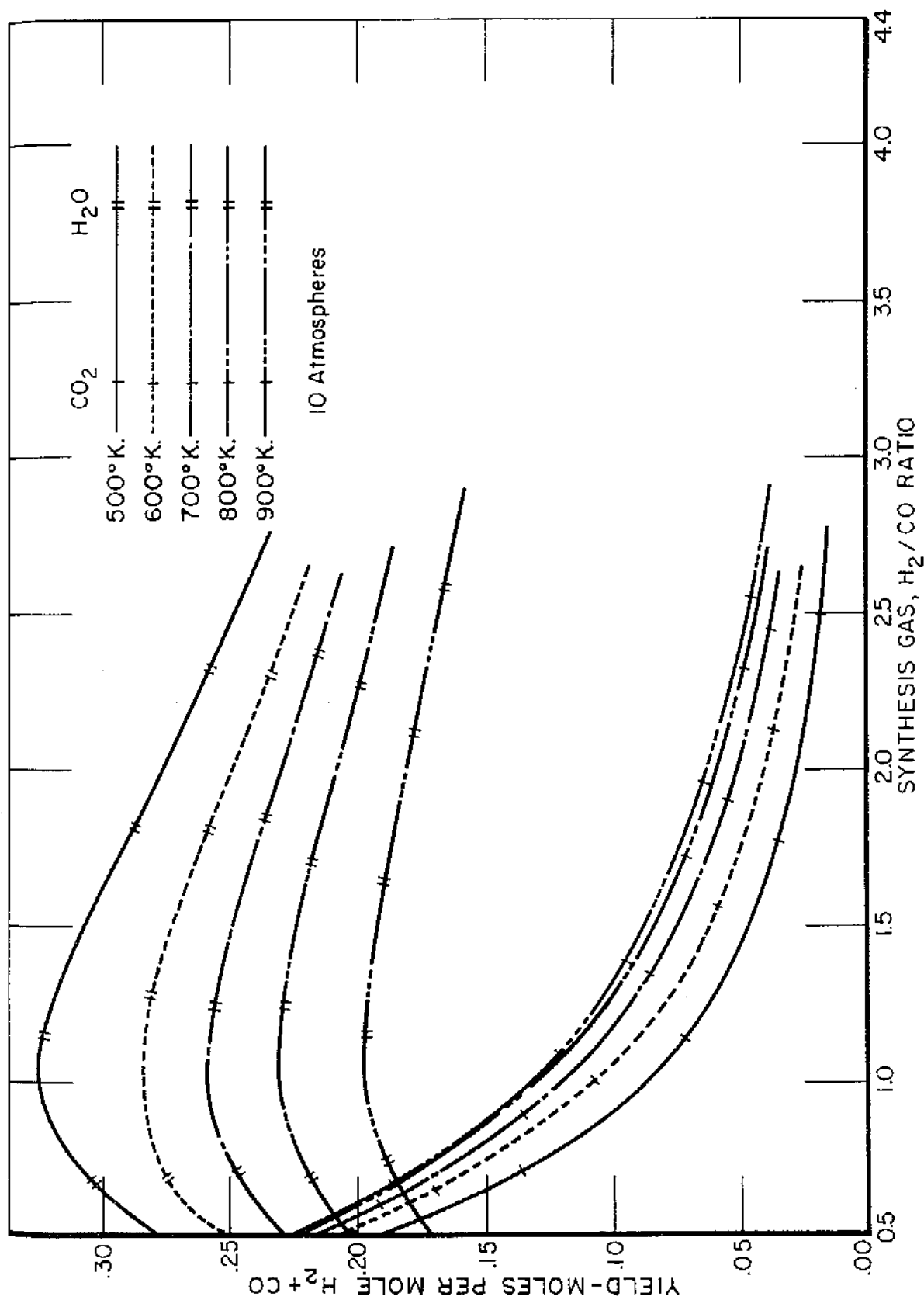


Figure 9. - Equilibrium yields of carbon dioxide and water (10 atmospheres).

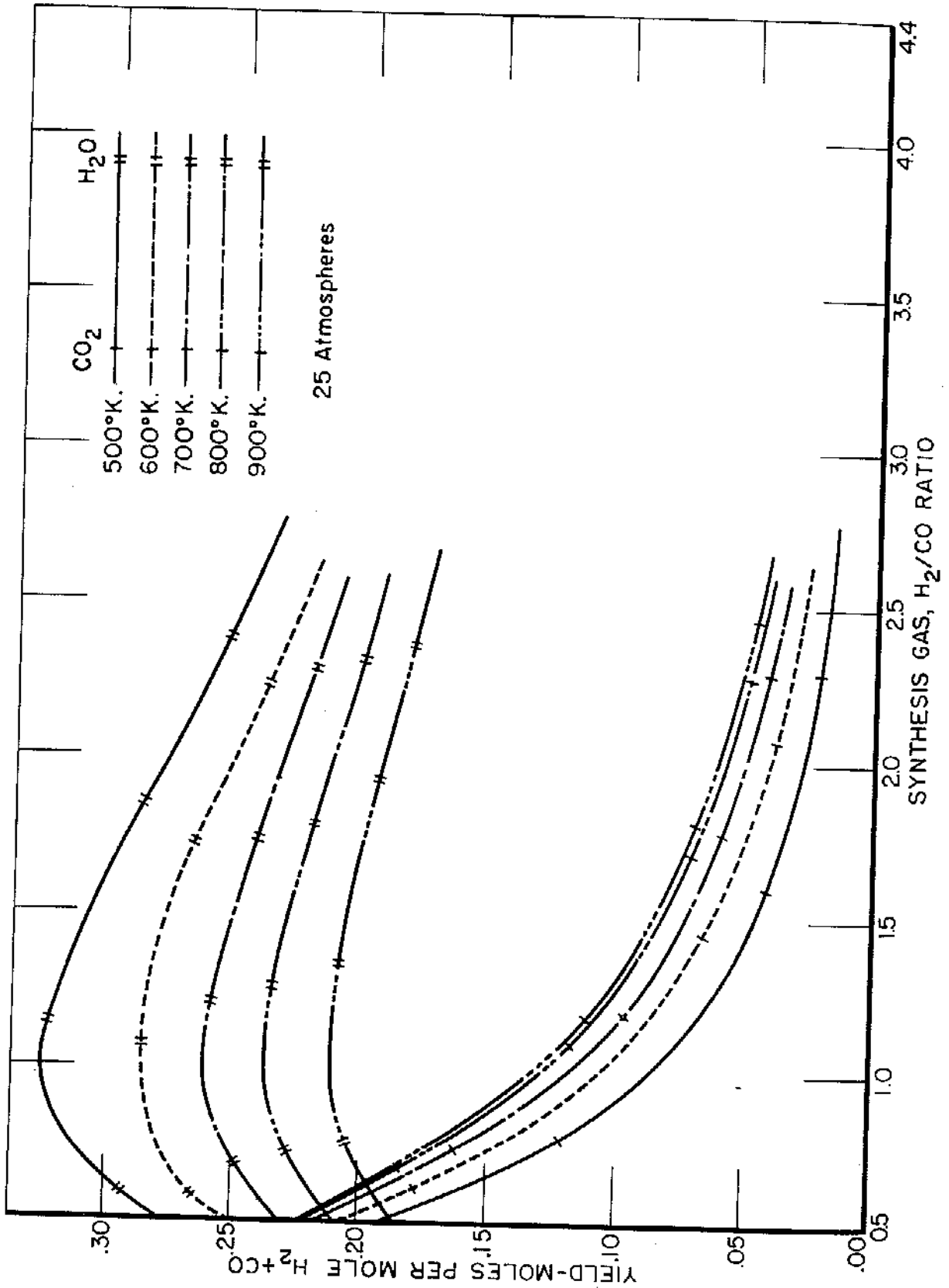


Figure 10. - Equilibrium yields of carbon dioxide and water (25 atmospheres).

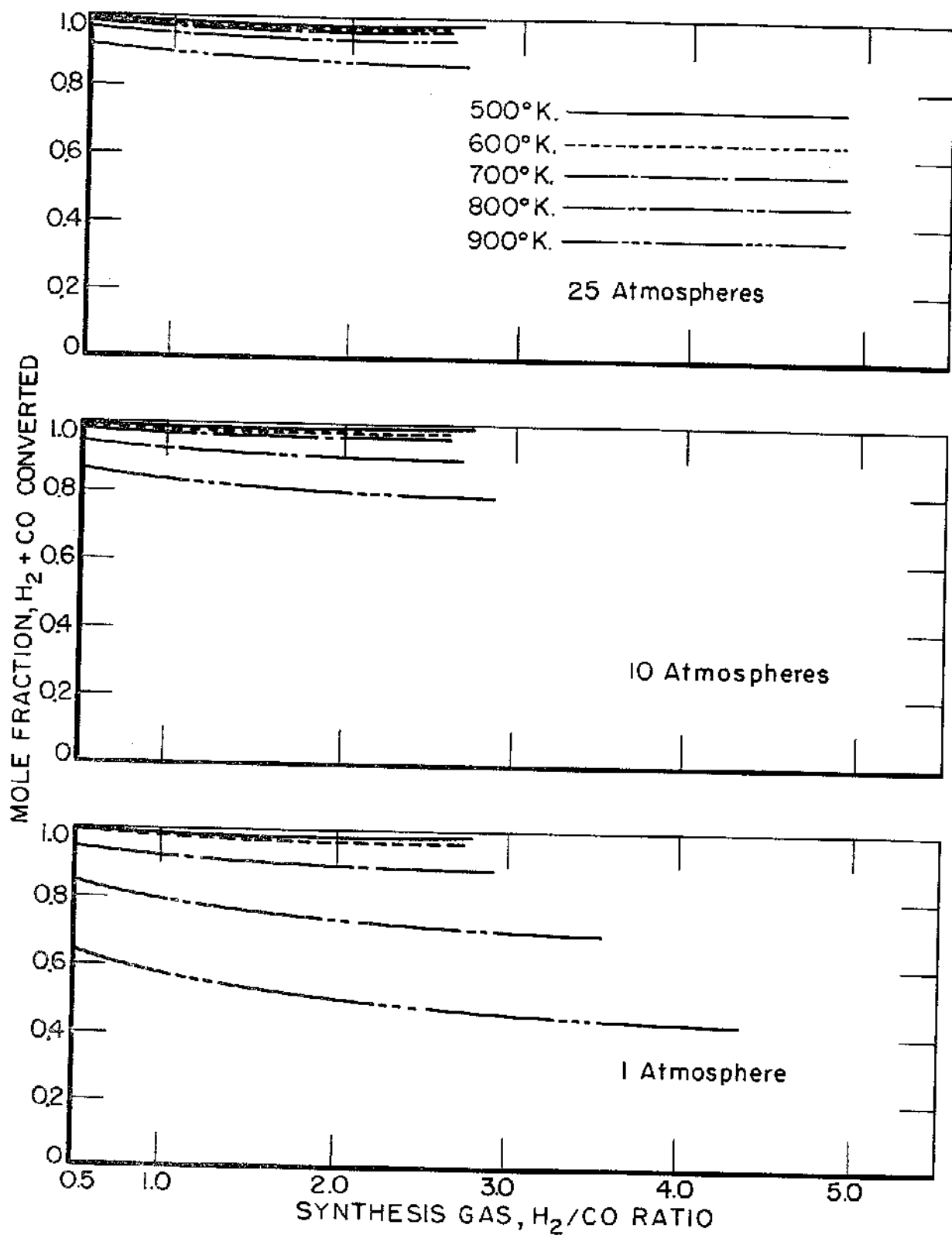


Figure 11. - Fraction synthesis gas converted.

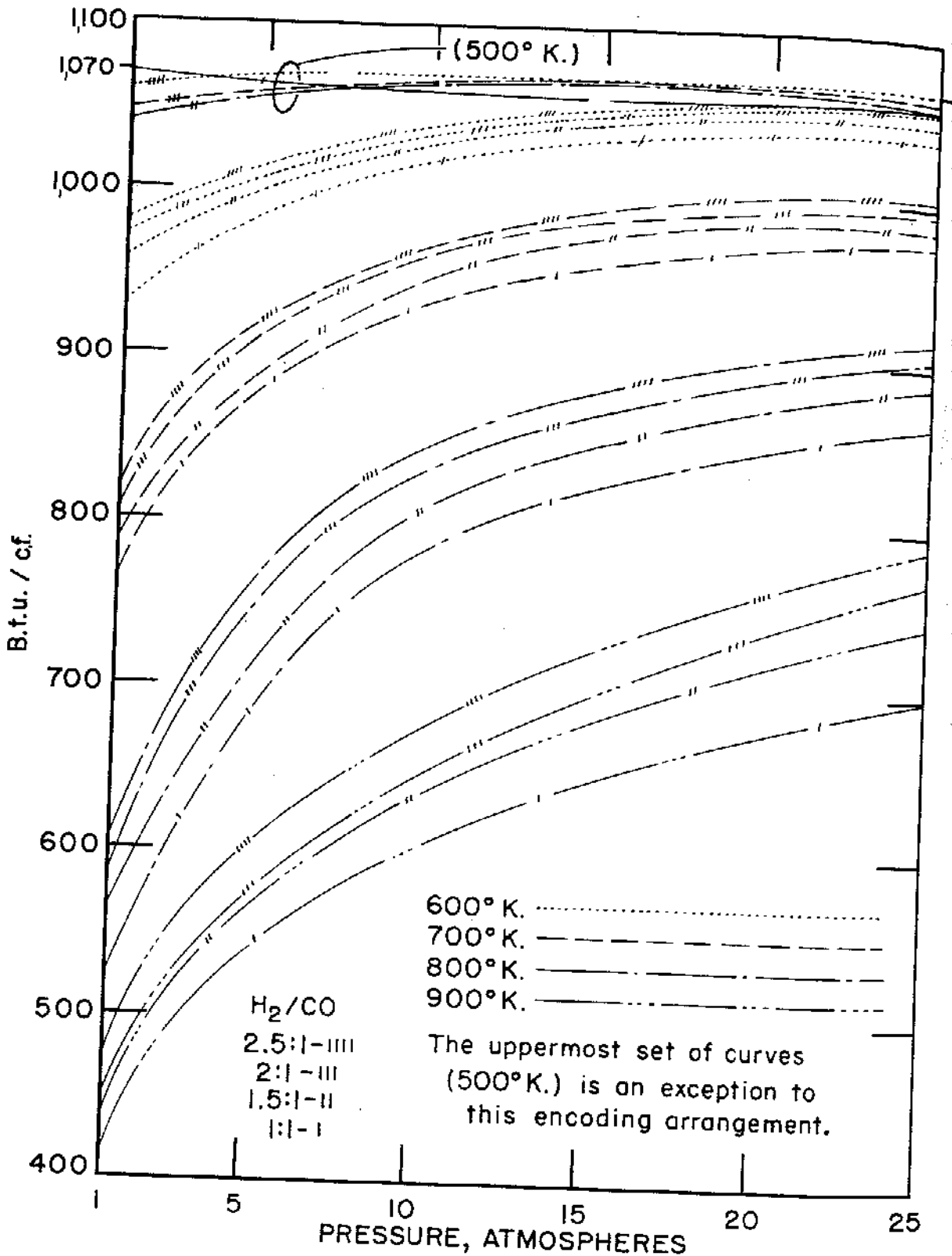


Figure 12. - Theoretical heating values of product gas.