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SOME GEOLOGICAL IMPLICATIONS OF EQUILIBRIUM BETWEEN GRAPHITE AND A C-H-O GAS PHASE AT HIGH TEMPERATURES AND PRESSURES

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SOME GEOLOGICAL IMPLICATIONS OF EQUILIBRIUM
BETWEEN GRAPHITE AND A C-H-O GAS PHASE
AT HIGH TEMPERATURES AND PRESSURES

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ABSTRACT

The occurrence of graphite as a common accessory mineral in meteorites and in terrestrial metamorphic and igneous rocks gives particular importance to the study of equilibrium between graphite and a coexisting gas phase. Using a simplified model in which T , P_{gas} , and f_{O_2} are independently specified for the system C-H-O, values of P_{CO_2} , P_{CO} , $P_{\text{H}_2\text{O}}$, P_{H_2} , and P_{CH_4} in a gas phase in equilibrium with graphite have been calculated for a wide range of geologically possible conditions by use of a high-speed computer. The numerical results support the following general conclusions: (1) The assumption that $P_{\text{gas}} = P_{\text{H}_2\text{O}} + P_{\text{CO}_2}$ is significantly in error for many graphite-bearing mineral assemblages. (2) Methane, CH_4 , may be a significant to dominant constituent of the gas phase in many possible geological environments involving moderate reduction; in particular, the occurrence of graphite with reduced minerals such as fayalite, wüstite, and iron is indicative of a methane-rich gas phase. (3) Under metamorphic conditions, pure water is not stable with graphite, but graphite can coexist with a gas phase rich in CO_2 . (4) Original graphite in a sediment will stabilize increasingly reduced mineral assemblages during progressive thermal metamorphism. (5) The presence or absence of even small amounts of graphite can explain P_{O_2} gradients observed over short distances or between adjacent layers in metamorphic rocks. (6) It is possible that the terrestrial atmosphere could have evolved by conversion of original methane to water and CO_2 by reaction with graphite and other accessory minerals within the primordial earth at temperatures of 600° to 1000°C . Material requirements for such conversion are not unreasonable, and the process itself is consistent with many proposed models for the origin of the earth.

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Symbols

- T Temperature in degrees Kelvin.
- P_{gas} Total pressure of a gas phase.
- P_i Partial pressure of component i in the gas phase.
- f_i Fugacity of component i in the gas phase.
- γ_i Fugacity coefficient of component i in the gas phase, defined by
- $$\gamma_i = f_i/P_i.$$
- K_i Equilibrium constant of the ith reaction, defined by $\Delta G^\circ = -RT \ln K_i$.
- A function of T only when written using fugacities of volatile components.
- log N Logarithm of N to the base 10.
- ln N Logarithm of N to the base e.

Abbreviations for solid phases

H	hematite	Fe_2O_3
M	magnetite	Fe_3O_4
W	wüstite	Fe_{1-x}O
I	iron	Fe
N	nickel	Ni
NO	nickel oxide (bunsenite)	NiO
Q	quartz	SiO_2
F	fayalite	Fe_2SiO_4
Gr	graphite	C

Abbreviations for solid-phase oxygen buffer assemblages (Eugster and Wones, 1962).

HM	hematite + magnetite	NNO	nickel + bunsenite
MW	magnetite + wüstite	QFM	quartz + fayalite + magnetite
WI	wüstite + iron	QFI	quartz + fayalite + iron
MI	magnetite + iron		

INTRODUCTION

The system C-H-O is of extreme importance in consideration of any fundamental problems concerning the origin and development of the earth and the solar system. Part of the importance is due to the fact that the three elements together comprise about 63 per cent by weight of the matter in the universe (Allen, 1963, p. 30-33), of which almost all is hydrogen. If the inert gases helium and argon are excluded, then carbon, hydrogen, and oxygen make up about 99 per cent. In addition, the system contains such biologically important compounds as water, oxygen, and carbon dioxide, which are of prime importance in speculations about the origin of the terrestrial oceans and atmosphere and the origin of life.

Calculations of equilibrium in the system C-H-O are complicated by the large number of organic and inorganic compounds which the system contains; high-speed computers have recently been employed to solve the numerous equilibria involved. In previous studies, the elemental composition of the system has been arbitrarily specified in order to supply sufficient constraints for solution of the equations applied to a single ideal fluid phase. Suess (1962) has presented calculations involving only the compounds H_2O , H_2 , CO_2 , CO , and CH_4 , calculating partial pressures as functions of the composition of the system. A more general calculation involving additional elemental components (Dayhoff et al., 1964) produced additional equilibrium concentrations for a number of organic compounds of biological importance.

Such calculations, in which total composition of the system is initially specified, yield considerable information, but the data are not directly applicable to a number of important geological problems. In geological

processes such as the metamorphism of sediments, it is not generally possible to specify the total composition of the system or to assume that the composition has remained constant. Commonly, the composition of the system will change during such processes by gain or loss of both volatile and involatile components. Thus, the chemical potentials of the components become more important than the original compositions in defining the behavior of the system at any given time (Thompson, 1955; Korzhinskii, 1959; Zen, 1963).

Further, in geological investigations, it is generally impossible to obtain a sample of the original fluid phase. One is thus compelled to study the compositions of the solid minerals in order to estimate the nature of the fluid phase with which they were equilibrated.

The present study considers equilibrium between graphite and a gas phase in the system C-H-O over a range of geologically reasonable temperatures and gas pressures. It is an extension of work carried out on the system C-O (French and Eugster, 1965), which considered the effect of graphite on P_{O_2} in geological assemblages. The present study consists of three stages. First, compositions of the gas phase in equilibrium with graphite are calculated by use of a high-speed computer. Second, independent estimation of P_{O_2} for assemblages of iron-bearing minerals is applied to the data to estimate the composition of the coexisting gas phase. Finally, the data are applied to a simplified model in order to suggest a possible method for evolution of the terrestrial atmosphere.

THEORETICAL CONSTRAINTS ON THE EQUILIBRIUM CALCULATIONS

The calculations described here have been obtained from a model which incorporates the following assumptions: (1) that continuous equilibrium is established between crystalline graphite and a gas phase whose composition lies in the system C-H-O; (2) that the significant species in the gas phase are CO_2 , CO , H_2O , H_2 , CH_4 , and O_2 ; equilibria involving more complex organic compounds are not considered; (3) that the gas phase exhibits ideal behavior under all conditions. The implications of these assumptions are discussed in turn.

Equilibrium between graphite and gas

In the ternary system C-H-O, under suitably reducing conditions, solid carbon (graphite at low pressures) can form over a wide range of temperatures and gas pressures. The presence of graphite in the assemblage reduces the number of variables which must be specified to fix the composition of the gas phase. The two-phase assemblage, graphite + gas, may be shown by the Gibbs Phase Rule to be trivariant, since $F = C - P + 2 = 3$ (French and Eugster, 1965, p. 1537).

Graphite, or amorphous carbonaceous material, is a common trace constituent of numerous sediments and metamorphic rocks and has occasionally been observed in terrestrial igneous rocks and in meteorites. The effects of such material on controlling P_{O_2} have been previously suggested (Miyashiro, 1964; Mueller, 1964; French, 1964). The assumption that graphite is present in natural assemblages is therefore reasonable. The calculations discussed are strictly applicable only to crystalline graphite and not to amorphous organic material which may originally be present in sediments and low-grade

metamorphic rocks. However, such material is observed to change to graphite with increasing metamorphism (Quinn and Glass, 1958; French, 1964).

The model also requires continuous equilibration with a gas phase of the proper composition. It does not apply to systems in which a large part of the gas phase is composed of additional elements (e.g., N, S, or Cl) or to systems which are so dry and impermeable that no gas phase can exist. Processes occurring only in the subsolidus, e.g., exsolution of graphite from an iron-carbon alloy, are likewise excluded from consideration.

Consideration of inorganic compounds only

It is assumed here that the compounds CO_2 , CO , H_2O , H_2 , CH_4 , and O_2 constitute the total pressure of the gas phase, since these are the major volatile species involved in reactions between minerals. A detailed calculation of equilibrium compositions for a phase containing additional organic compounds (Dayhoff et al., 1964) provides support for this assumption by indicating, (1) that the compounds listed do compose almost the entire gas pressure, and (2) that the partial pressure of CH_4 greatly exceeds that of the more complex organic compounds. It is therefore believed that no great discrepancy is introduced by this assumption.

Ideal Behavior of the Gas Phase

The assumption that the gas phase behaves ideally has been incorporated into earlier calculations involving the system C-H-O (Krauskopf, 1959; Suess, 1962; Holland, 1962; Dayhoff et al., 1964). This assumption probably introduces the largest uncertainty into the numerical results obtained in the present study. As discussed below, the effect of this assumption is difficult to estimate, but it is believed that the present results are

satisfactory for semiquantitative considerations and that none of the general conclusions is invalidated.

There is presently little experimental data on the behavior of mixtures of the gas species at high pressures, but available data do indicate that the behavior will be nonideal at low temperatures. An immiscibility gap exists in the system $\text{H}_2\text{O}-\text{CO}_2$ (Malinin, 1959; Todheide and Franck, 1963; Takenouchi and Kennedy, 1964); although there are slight differences between the experimental results, it appears that the two-phase region lies at temperatures below the critical point of water (373°C) for values of P_{gas} less than 2000 b. Below 400 b. total gas pressure, the two-phase region apparently lies below 350°C . The effect of other compounds on the location of the two-phase region is uncertain; large amounts of methane might move the critical surface to even low temperatures.

Preliminary experimental data (H. J. Greenwood, personal communication) indicate that the system $\text{H}_2\text{O}-\text{CO}_2$ exhibits nearly ideal behavior at higher temperatures. Nevertheless, it seems clear that numerical results based on an ideal-gas model are only speculative below 300°C ; only the results given here for temperatures above 600°K (327°C) are considered as reasonable approximations to the actual behavior of the system.

Although there are no data available for fugacity coefficients of the various species in mixtures, values of γ_i for individual species have been compiled as functions of temperature and pressure for CO_2 (Kennedy, 1954; Robie, 1962), CO (Newton, 1935), H_2O (Anderson, 1964), H_2 (Shaw and Wones, 1964), and CH_4 (Douslin et al., 1964). A closer approximation to the actual behavior of the gas phase could be made by assuming that values of γ_i in the mixture are the same as for the pure species at the same temperature and

pressure (Lewis and Randall's Rule; see Denbigh, 1957). Even this approximation may not be valid at extremely high pressures.

In view of the uncertainty in γ_i for the gas species, it seems unwarranted to attempt to compensate for nonideal behavior in the present calculations. An estimate of the uncertainty introduced by assuming ideal behavior is carried out below by performing parallel derivations for ideal and nonideal gas phases.

CALCULATIONS OF EQUILIBRIUM BETWEEN GRAPHITE AND GAS

In a system which conforms to the assumption listed, the various possible equilibria between graphite and the gas phase are specified by the equilibrium constants of the following four independent equations (French and Eugster, 1965, p. 1537):

$$(1) \quad C + O_2 = CO_2 \quad K_1 = \frac{f_{CO_2}}{f_{O_2}} = \frac{\gamma_{CO_2} P_{CO_2}}{\gamma_{O_2} P_{O_2}}$$

$$(2) \quad C + 1/2 O_2 = CO \quad K_2 = \frac{f_{CO}}{(f_{O_2})^{1/2}} = \frac{\gamma_{CO} P_{CO}}{(\gamma_{O_2} P_{O_2})^{1/2}}$$

$$(3) \quad C + 2 H_2 = CH_4 \quad K_3 = \frac{f_{CH_4}}{(f_{H_2})^2} = \frac{\gamma_{CH_4} P_{CH_4}}{(\gamma_{H_2} P_{H_2})^2}$$

$$(4) \quad H_2 + 1/2 O_2 = H_2O \quad K_4 = \frac{f_{H_2O}}{f_{H_2} (f_{O_2})^{1/2}} = \frac{\gamma_{H_2O} P_{H_2O}}{\gamma_{H_2} P_{H_2} (\gamma_{O_2} P_{O_2})^{1/2}}$$

Combining (1-4) with the condition that P_{gas} must equal the sum of all P_i , we obtain five equations involving six variables, P_{CO_2} , P_{CO} , P_{H_2O} , P_{H_2} , P_{CH_4} , and P_{O_2} .

$$(1a) \quad P_{CO_2} = \frac{K_1 \gamma_{O_2} P_{O_2}}{\gamma_{CO_2}} = \frac{K_1}{\gamma_{CO_2}} f_{O_2}$$

$$(2a) \quad P_{CO} = \frac{K_2 (\gamma_{O_2} P_{O_2})^{1/2}}{\gamma_{CO}} = \frac{K_2}{\gamma_{CO}} (f_{O_2})^{1/2}$$

$$(3a) \quad P_{\text{CH}_4} = \frac{K_3(\gamma_{\text{H}_2} P_{\text{H}_2})^2}{\gamma_{\text{CH}_4}}$$

$$(4a) \quad P_{\text{H}_2\text{O}} = \frac{K_4(\gamma_{\text{H}_2} P_{\text{H}_2})(\gamma_{\text{O}_2} P_{\text{O}_2})^{1/2}}{\gamma_{\text{H}_2\text{O}}} = \frac{K_4(\gamma_{\text{H}_2} P_{\text{H}_2})}{\gamma_{\text{H}_2\text{O}}} (f_{\text{O}_2})^{1/2}$$

$$(5) \quad P_{\text{gas}} = P_{\text{CO}_2} + P_{\text{CO}} + P_{\text{H}_2\text{O}} + P_{\text{H}_2} + P_{\text{CH}_4} + P_{\text{O}_2}$$

Thus, for any specified T and P_{gas} , the values of any five P_i are explicitly determined if the sixth is independently specified. This result agrees with that of the Gibbs Phase Rule; the system graphite-gas is trivariant and becomes univariant if any two variables (e.g., temperature and total gas pressure) are specified.

Theoretically, one can specify any P_i for calculation of the others. In practice, in systems involving both natural minerals and synthetic phases, it is convenient to specify P_{O_2} (or f_{O_2}) as the independent variable. Numerous mineral assemblages which contain iron- and manganese-bearing phases are related by oxidation-reduction reactions which are conveniently written in terms of P_{O_2} . Changes in P_{O_2} will be reflected by resultant changes in the mineral assemblage (Eugster, 1959; Eugster and Wones, 1962; Buddington and Lindsley, 1964). Conversely, it may be possible to deduce approximate values of P_{O_2} from the mineral assemblage and thereby calculate partial pressures of other species.

The subsequent calculations are therefore carried out by specifying T , P_{gas} , and f_{O_2} (specifying f_{O_2} removes the necessity of considering γ_{O_2} in the equations).

Equations (1a) and (2a) demonstrate that values of P_{CO_2} and P_{CO} depend only on temperature and f_{O_2} and are independent of P_{gas} (except for the slight effect of P_{gas} on γ_i). The values of P_{CO_2} and P_{CO} can thus be calculated directly and substituted in (5), as:

$$(5a) \quad P_{\text{CH}_4} + P_{\text{H}_2} + P_{\text{H}_2\text{O}} = P_{\text{gas}} - (P_{\text{CO}_2} + P_{\text{CO}} + P_{\text{O}_2})$$

The value of P_{O_2} will be under 10^{-10} b. in most geological assemblages, particularly if graphite is also present (Eugster, 1959; French and Eugster, 1965); the term can therefore be neglected.

The lefthand side of (5a) can be written in terms of P_{H_2} and known quantities by substituting (3a) and (4a).

$$\frac{K_3(\gamma_{\text{H}_2} P_{\text{H}_2})^2}{\gamma_{\text{CH}_4}} + P_{\text{H}_2} + \frac{K_4(\gamma_{\text{H}_2} P_{\text{H}_2})}{\gamma_{\text{H}_2\text{O}}} (f_{\text{O}_2})^{1/2} = P_{\text{gas}} - (P_{\text{CO}_2} + P_{\text{CO}})$$

This expression is rearranged to obtain a quadratic equation in which P_{H_2} is the only unknown.

$$(6) \quad (P_{\text{H}_2})^2 \left[\frac{K_3 \gamma_{\text{H}_2}^2}{\gamma_{\text{CH}_4}} \right] + P_{\text{H}_2} \left[\frac{K_4 \gamma_{\text{H}_2} (f_{\text{O}_2})^{1/2}}{\gamma_{\text{H}_2\text{O}}} + 1 \right] - \left[P_{\text{gas}} - (P_{\text{CO}_2} + P_{\text{CO}}) \right] = 0$$

Solving, we obtain,

$$(7) \quad P_{\text{H}_2} = \frac{- \left[\frac{K_4 \gamma_{\text{H}_2} (f_{\text{O}_2})^{1/2}}{\gamma_{\text{H}_2\text{O}}} + 1 \right]}{2 \left[\frac{K_3 \gamma_{\text{H}_2}^2}{\gamma_{\text{CH}_4}} \right]}$$

$$+ \frac{\left\{ \left[\frac{K_4 \gamma_{H_2} (f_{O_2})^{\frac{1}{2}}}{\gamma_{H_2O}} + 1 \right]^2 + 4 \left[\frac{K_3 \gamma_{H_2}^2}{\gamma_{CH_4}} \right] \left[P_{gas} - (P_{CO_2} + P_{CO}) \right] \right\}^{\frac{1}{2}}}{2 \left[\frac{K_3 \gamma_{H_2}^2}{\gamma_{CH_4}} \right]}$$

Values of P_{H_2} obtained from the positive root of (7) can then be substituted in (3a) and (4a) to derive, respectively, P_{CH_4} and P_{H_2O} . For an ideal gas, all $P_i = f_i$ and all $\gamma_i = 1$. Under these conditions, (7) becomes:

$$(8) \quad P_{H_2} = \frac{- \left[K_4 (f_{O_2})^{\frac{1}{2}} + 1 \right]}{2K_3}$$

$$+ \frac{\left\{ \left[K_4 (f_{O_2})^{\frac{1}{2}} + 1 \right]^2 + 4 K_3 \left[P_{gas} - (P_{CO_2} + P_{CO}) \right] \right\}^{\frac{1}{2}}}{2 K_3}$$

Comparison of (7) and (8) indicates that the difference between values of P_{H_2} obtained by each method will probably be less than an order of magnitude. Available data on the fugacity coefficients of the pure species indicate that, above 500°K, values of γ_i lie within the range 0.7 - 3.0. This variability will be reduced because the fugacity coefficients appear in (7) as ratios, and values of γ_i will tend to be similar for the same temperature and pressure (Newton, 1935).

It is therefore believed that the errors introduced into the calculated P_i by postulating an ideal gas phase will be less than an order of magnitude and probably closer to a factor of two. Such a discrepancy is not believed sufficient to change the general conclusions obtained and may be minimized

by presenting results in terms of $\log P_i$. Further experimental work would be necessary to obtain more accurate values of γ_i for refinement of the results. One possible refinement would involve using values of γ_i for the pure species in accordance with Lewis and Randall's Rule, but the small anticipated correction does not seem to justify introduction of the additional complications into the present study.

Accordingly, calculations of P_i are carried out for an ideal gas, using values of T , P_{gas} , and f_{O_2} selected to cover a wide range of possible geological environments. Calculations were carried out on an IBM 7090/7094 system, using a program written in FORTRAN IV language by Mr. Arthur Smith of the Theoretical Division, NASA, Goddard Space Flight Center. The values of K_i were obtained from JANAF Tables and did not differ significantly from those of earlier compilations (Wagman et al., 1945). The calculations covered a temperature range of 300° to 1500°K , a pressure range of 1 bar to 100 kilobars, and values of f_{O_2} approximating the interval between the quartz-fayalite-iron and hematite-magnetite buffers (Eugster and Wones, 1962). The results presented in the text figures were checked by substituting the values of P_i into (1-5) to calculate K_i .¹

¹Between 298° and 1200°K , graphite becomes metastable with respect to diamond at pressures above about 16 to 40 kb, respectively (Bundy et al., 1961). The transformation introduces a slight additional uncertainty into the numerical results obtained for values of P_{gas} above these limits. No correction for this effect has been made, since the probable nonideality of the gas phase at such high pressures will introduce a greater error into

the results than that caused by the slight difference in ΔG° , 0.5 to 1.7 kcal./mole, involved in the diamond-graphite transformation. Furthermore, the following discussion is concerned almost exclusively with the region within which graphite is stable.

No correction has been made for the effect of pressure on the equilibrium constants of the heterogeneous reactions (1-3), in which the solid phase graphite participates. Because of the small molar volume of graphite, the change in $\log K_i$ for these reactions with pressure is only $-0.028(P_{\text{gas}} - 1)/T$ (French and Eugster, 1965, p. 1534). For extreme conditions ($P_{\text{gas}} = 10 \text{ kb.}$, $T = 600^\circ \text{K}$), the change in $\log K_i$ is less than -0.5 ; for pressures up to 2 kb. , the difference will be less than 0.1 , and the resultant uncertainties do not appear to exceed those introduced by the assumption of ideal behavior.

NUMERICAL RESULTS AND SOME GEOLOGICAL IMPLICATIONS

Composition of the Gas Phase as a Function of f_{O_2}

The figures and discussion which follow represent only selected samples of the large amount of numerical data obtained through use of a high-speed computer. The choice is relatively arbitrary, but a selection has been made which is intended to apply chiefly to terrestrial geological processes under conditions for which the original assumptions remain reasonably valid.

Figures (1-3) present values of $\log P_i$ as a function of $\log f_{O_2}$ for specified values of T and P_{gas} . Numerical results for $600^\circ K$ ($327^\circ C$) are shown in Figure 1 for total gas pressures of 1 bar, 1000 bars, and 10 kilobars. This temperature is reasonable for low-grade metamorphism (approximately the greenschist facies; Turner and Verhoogen, 1960, p. 534). The dotted portions of the curves correspond to values of $\log f_{O_2}$ for which the quantity $(P_{CO_2} + P_{CO})$ becomes greater than P_{gas} , and for which solutions of (8) are not possible. Values of $\log f_{O_2}$ for various solid-phase oxygen buffer assemblages (Eugster and Wones, 1962) are indicated on the abscissa.

Similar plots are presented for $900^\circ K$ ($627^\circ C$), a temperature which represents probable high-grade metamorphic conditions (Fig. 2) and for $1200^\circ K$ ($927^\circ C$), a reasonable estimate for pyrometamorphism or for some igneous phenomena (Fig. 3).

Several general conclusions appear from the figures. At constant T and f_{O_2} , higher gas pressures favor a reduced gas phase richer in CH_4 and H_2 . Conversely, for a given P_{gas} and f_{O_2} , increasing temperatures produce a gas phase which becomes more oxidized and H_2O and CO_2 appear at the expense of CH_4 .

Throughout the temperature range considered, H_2O exceeds CO_2 in the gas, even though the gas phase may consist chiefly of other species.

Finally, for a wide range of geologically reasonable conditions, corresponding to the lower part of the stability field of magnetite, methane (CH_4) is a significant to dominant constituent of the gas phase, particularly at lower temperatures (below $600^\circ C$) and higher fluid pressures. This observation has particular significance for speculations about the fluid phase in equilibrium with low- to medium-grade metamorphic rocks and with ore minerals in certain hydrothermal deposits. The data presented indicate that, at f_{O_2} values suitable for the appearance of fayalite or wüstite, the gas phase is almost entirely methane, particularly below $500^\circ C$. The amount of methane in the gas phase decreases sharply as T or f_{O_2} increases. However, it seems reasonable to state that, where graphite occurs with iron-, wüstite-, or fayalite-bearing assemblages, the contribution of methane to the coexisting gas phase will be significant. At temperatures below $400^\circ C$, the contribution of methane is also important to a gas phase coexisting with more oxidized magnetite-graphite assemblages.

To apply the data to geological environments, it is convenient to recast the results presented in Figures (1-3) in order to specify values of P_i as a function of temperature. This can be done by determining the value of f_{O_2} for a given solid-phase oxygen buffer by an equation of the type:

$$(9) \quad \log f_{O_2} = -\frac{A}{T} + B + \frac{C(P_{gas} - 1)}{T}$$

(Eugster and Wones, 1962). Thus, for a given buffer and a specified P_{gas} , $\log f_{O_2}$ is a function only of T . Values of P_i can then be calculated as unique functions of the temperature.²

²The selection of a specific solid-phase buffer to establish the divariant relationship indicated in (9) between T , P_{gas} , and f_{O_2} implies the addition of new components to the system C-H-O and the corresponding appearance of additional solid phases in equilibrium with graphite and gas. In order that the original trivariant system should become divariant, $(n + 1)$ solid phases must appear for each additional n components. Thus, the addition of Fe produces two-phase buffer assemblages (HM, MI, etc.), while addition of both Fe and Si requires three-phase buffers (QFM, QFI). In both cases, the new system now has $(n + 3)$ components, $(n + 2)$ solid phases, and a gas phase; under these conditions, it is divariant and all P_i are explicitly determined by specifying only P_{gas} and T .

Because of the rare occurrence of actual buffer assemblages in nature (Eugster and Wones, 1962, p. 115-116), it is most useful to use the buffers to establish extreme limits of f_{O_2} corresponding to the stability field of some index mineral (magnetite, fayalite, wüstite, etc.); the corresponding extreme values of P_i can then be calculated. Then, the occurrence of the mineral with graphite indicates limiting values for composition of the coexisting gas phase.

Although the present discussion has emphasized f_{O_2} , the buffer technique is perfectly general (Eugster and Wones, 1962, p. 95). Additional volatile components may be introduced into the present calculations if new f_i can be similarly limited by additional solid phases in the system. For example, inclusion of f_{S_2} could be facilitated by introduction of the corresponding iron sulfides (Toulmin and Barton, 1964); consideration of f_{N_2} might become desirable for study of certain nitride-bearing meteorite assemblages (Mason, 1958; Andersen et al., 1964; Keil and Anderson, 1965).

Most igneous and metamorphic reactions apparently occur at values of f_{O_2} within the stability field of magnetite (Eugster and Wones, 1962). Figures (4-6) present values of $\log P_i$ as a function of temperature for three buffer combinations within this region: (1) the quartz-fayalite-magnetite (QFM) buffer (Fig. 4), which fixes the highest f_{O_2} at which fayalite is stable; (2) the combined magnetite-iron (MI) and magnetite-wüstite (MW) buffers, which together specify the lowest f_{O_2} for the existence of magnetite; and (3) the combined magnetite-iron (MI) and wüstite-iron (WI) buffers, which correspond to the highest f_{O_2} for which metallic iron is stable.

Values of $\log P_i$ for the various species in a gas phase coexisting with the solid assemblage quartz + fayalite + magnetite + graphite are shown in Figure 4 as a function of temperature for P_{gas} values of 1000 b. and 10 kb. The effect of a tenfold change in total gas pressure on the relative composition of the gas phase is slight; at both pressures, equilibrium is not possible above about 550°C. The most important species in the gas phase are CH_4 , CO_2 , and H_2O ; the latter two become dominant with increasing temperature.

The behavior of the gas phase at $P_{gas} = 1000$ b., in equilibrium with the two assemblages, magnetite + iron (below 560°C) and magnetite + wüstite (above 560°C) is shown in Figure 5. Methane is dominant over much of the temperature range, but the assemblage itself becomes unstable above about 850°C. The f_{O_2} values for these buffers (Fig. 5) represent minimum values for most geological processes. By contrast, at the same values of P_{gas} , the gas phase coexisting with the more reduced assemblages, magnetite + iron (below 560°C) and wüstite + iron (above 560°C) is considerably different

(Fig. 6). In this case, equilibrium is possible up to the limit of calculation, above 1200°C. The contribution of methane is enhanced, and, at temperatures above 450°C, $P_{H_2} > P_{H_2O}$ and $P_{CO} > P_{CO_2}$. These curves represent the maximum f_{O_2} values for the occurrence of metallic iron, as in meteorites and in rare terrestrial rocks. Lower values of f_{O_2} within the iron stability field will increase the reduced character of the gas phase.

Significance of Methane in Equilibrium with Graphite

Much speculation about the nature of hydrothermal fluids has considered a fluid phase as a mixture of H_2O and CO_2 . The present results indicate that, in addition, methane may be a significant species under a range of geologically possible conditions involving low to moderate temperatures, high gas pressures, and moderately low f_{O_2} values conditioned by the presence of graphite.

The importance of methane under such conditions is indicated by the data presented in Figures (7-8), which show the percentage of methane in a gas phase in equilibrium with graphite and various buffer assemblages. Since values of P_i rather than $\log P_i$ are plotted, the assumption of ideal behavior will cause a proportionately greater uncertainty, but the relative relationships should not be affected. At $P_{gas} = 1$ b. (Fig. 7), more reducing values of f_{O_2} favor increased contribution of methane at higher temperatures. However, even at values of f_{O_2} corresponding to the upper part of the magnetite stability field (approximately the NNO buffer), methane may still contribute 30 to 50 per cent of the value of P_{gas} .

Higher gas pressures favor increased contribution of methane at higher temperatures; at $P_{\text{gas}} = 1000$ b. (Fig. 8), methane accounts for more than half of the value of P_{gas} within the stability fields of fayalite and wüstite. Increasing P_{gas} above 1000 b. will correspondingly increase the relative contribution of methane.

With increasing temperature, methane gradually disappears as H_2O and CO_2 became dominant. The relative amounts of the latter two species depend on P_{gas} , as indicated in Figure 9, where values for all P_i are plotted as a function of T for the QFM and MI-WI buffers. At $P_{\text{gas}} = 1$ b., CH_4 and H_2 are dominant at low temperatures; with increasing temperature, $P_{\text{H}_2\text{O}}$ passes through a maximum and CO_2 becomes the dominant species. By contrast, at $P_{\text{gas}} = 1000$ b., (Fig. 10), both H_2 and CO are negligible. With increasing temperature, $P_{\text{H}_2\text{O}}$ and P_{CO_2} increase continually as P_{CH_4} decreases, with $P_{\text{H}_2\text{O}}$ always greater than P_{CO_2} . Pressures above 1000 b. will increase the preferential production of water with decreasing P_{CH_4} , although somewhat higher temperatures will be required for complete conversion.

A significant feature of these data is the rapid decrease in P_{CH_4} with increasing temperature. For example, at $P_{\text{gas}} = 1$ b. (Fig. 9), P_{CH_4} drops from 0.7 b. to virtually zero between about 225° and 325°C along the QFM buffer; even at lower values of f_{O_2} along the MI-WI buffer, P_{CH_4} is reduced from 0.6 b. to zero between 450° and 650°C . Similar but less sudden decreases occur at $P_{\text{gas}} = 1000$ b. (Fig. 10); on both buffers, a temperature interval of only 150°C is sufficient to reduce P_{CH_4} from about 600 b. to zero. Such rapid changes in the composition of the gas phase with changing temperature suggest that the principal difficulty in estimating gas compositions from natural mineral assemblages will be uncertainties in temperature; the effects of uncertainties in P_{gas} will be minor in comparison. The application of these data to geological

assemblages will thus require very accurate temperature data, since a change of only 200°C is sufficient to convert a gas phase composed almost entirely of methane into one in which H₂O and CO₂ together constitute more than 80 per cent of P_{gas}. The implications of these results for a model of production of the terrestrial atmosphere by reactions within the earth is discussed later.

The detection and identification of methane in liquid inclusions and in some graphite-bearing rocks provides experimental support for the conclusion that methane may be a significant constituent of natural hydrothermal fluids. Methane has been reported as a minor constituent of liquid inclusions in quartz-bearing pegmatites (Elinson and Polykovskii, 1963a, 1963b) and in large amounts in inclusions in alkaline igneous rocks, associated with small amounts of organic matter (Petersil'ye et al., 1961). At least 5000 ppm of methane and minor amounts of other hydrocarbons were evolved from graphite from a Precambrian quartz-graphite schist (Hoering and Hart, 1964). Further studies of this type would be very desirable.

Maximum P_{gas} - Temperature Curves for Graphite-Bearing Assemblages

In the calculations presented, it was often observed that, under conditions of relatively high T and f_{O₂}, no solutions were possible to the system of Equations (1-5, 8). This incompatibility arises from the fact that values of P_{CO₂} and P_{CO} are (for the ideal-gas model) dependent only on T and f_{O₂} and completely independent of P_{gas}. It is therefore possible, as T or f_{O₂} increases, to generate a condition where the quantity, (P_{CO₂} + P_{CO}) exceeds the specified value of P_{gas}. Such a condition is impossible and the equations become insoluble.

Under conditions of specified T and P_{gas}, this limit is reached by increasing f_{O₂} (Figs. 1-3). In later calculations the use of a buffer to

control f_{O_2} as a function of T introduces an additional equation involving f_{O_2} . Thus, two simultaneous equations must be satisfied for equilibrium to be maintained. For graphite,



The solid-phase buffer has an equation of the form



where X, Y, and Z are solid phases.

For an ideal gas, $P_{CO_2} = K_1 f_{O_2}$. Further, the system requires that

$$P_{gas} \geq P_{CO_2} = K_1 K_{10} = K_1 f_{O_2}$$

No solutions will exist for values of T, P_{gas} and f_{O_2} for which

$$\log P_{gas} \leq \log P_{CO_2} = \log K_1 + \log P_{O_2}$$

or,

$$(11) \quad \log P_{O_2} \geq \log P_{gas} - \log K_1$$

With increasing T or f_{O_2} , such a limit occurs below $1500^{\circ}K$ for all but the more reducing buffers and corresponds to the appearance of disequilibrium between graphite and the solid-phase buffer assemblage. In general, the more oxidizing the buffer, the lower the temperature at which it becomes unstable with respect to graphite. Actual disequilibrium temperatures will be lower than suggested by (11) because of the contribution of other species to P_{gas} .

Calculation of the exact disequilibrium temperature for different values of P_{gas} establishes a maximum temperature for equilibrium between graphite and each buffer assemblage. These points form a series of univariant curves in $P_{gas}-T-f_{O_2}$ space and may be presented as projections onto the $P_{gas}-T$ plane (Fig. 11).

Each curve fixes only the maximum temperature for existence of the buffer assemblage with graphite; the phases will be in equilibrium at all temperatures below the curve. For instance, the assemblage, hematite + magnetite + graphite is stable at all temperatures and pressures to the left of Curve (1) (Fig. 11); the value of f_{O_2} in this region is specified by the HM buffer. As Curve (1) is reached with increasing temperature, the three phases become unstable and one must disappear. Three paths are possible: (1) graphite is removed by oxidation, and the assemblage hematite + magnetite continues to buffer f_{O_2} at temperatures to the right of the curve; (2) hematite is reduced to magnetite, in which case magnetite and graphite coexist to the right of the curve and do not constitute an f_{O_2} buffer; (3) magnetite is oxidized to hematite, producing the assemblage hematite + graphite, which also does not buffer f_{O_2} . If graphite remains in the assemblage at temperatures to the right of the curve, the buffering ability of the system is destroyed and two

assemblages are possible: hematite + graphite at high f_{O_2} and magnetite + graphite at low f_{O_2} .

Similar arguments apply to the other curves, particularly to Curve (3), which indicates the maximum stability temperature for the assemblage, quartz + fayalite + magnetite + graphite. The four-phase assemblage, stable to the left of Curve (3), buffers f_{O_2} rigorously. To the right of the curve, four three-phase assemblages are possible: (a) quartz + fayalite + magnetite; (b) quartz + fayalite + graphite; (c) quartz + magnetite + graphite; (d) fayalite + magnetite + graphite. Only assemblage (a) is a rigorous oxygen buffer.

In general, for each curve, the region to the left denotes equilibrium between the solid-phase oxygen buffer, graphite, and the gas phase. As the curve is crossed with increasing temperature, the buffer assemblage and graphite become unstable, and the character of the system at higher temperatures depends on whether or not graphite disappears. If graphite is oxidized, the solid-phase buffer still controls f_{O_2} , but another degree of compositional freedom is added to the gas phase by the disappearance of graphite. If graphite remains, the solid phases no longer constitute an oxygen buffer and the value of f_{O_2} can be specified only within wide limits.

The curves have considerable application to geological problems, for they provide upper temperature limits for the existence of certain mineral assemblages in equilibrium with graphite and gas. They have the added advantage of being extremely insensitive to changes in P_{gas} above a moderate pressure. The difficulty in applying the curves to natural assemblages lies in the necessity of identifying several solid phases in the same specimen and of demonstrating

that they are in fact in equilibrium (see Zen, 1963). In addition, even if it can be shown that a given curve has in fact been exceeded, careful study is necessary to distinguish between the different petrologic interpretations deriving from the presence or absence of graphite in the assemblage.

The fact that most present solid-buffer data involve iron-bearing minerals has restricted their application to metamorphosed iron formations containing some of the required assemblages (Gundersen and Schwartz, 1962; Zen, 1963; French, 1965). However, numerous possibilities exist for study of graphite and opaque accessory minerals in igneous and metamorphic rocks (see, e.g., Chinner, 1960; Buddington and Lindsley, 1964).

Progressive Metamorphism of Graphite-Bearing Sediments

There has been much consideration of the role of water and CO_2 in metamorphism, since many of the observed mineral transformations can be expressed by reactions involving these volatile components. Many speculations about the nature of hydrothermal fluids have presupposed a gas phase in which these two species are dominant. Even though other components such as methane may assume a significant role under certain conditions, it is worthwhile to consider the relationship between $P_{\text{H}_2\text{O}}$ and P_{CO_2} in a gas phase in equilibrium with graphite under conditions corresponding to progressive metamorphism.

The presence of graphite or amorphous carbon in metamorphosed sediments has been proposed to explain two observed characteristics of metamorphosed rocks: (1) apparent relative reduction of mineral assemblages with increasing metamorphic grade, corresponding to an increase in the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio (Shaw, 1956; Zen, 1963; Miyashiro, 1964), and (2) preservation of apparently steep gradients in P_{O_2} over short distances, particularly between adjacent layers of differing composition (Chinner, 1960; Kranck, 1961; Zen, 1963).

Application of the present model requires only the development of graphite during metamorphism, possibly through recrystallization of original organic matter (French, 1964; Hoering and Hart, 1964). Because of the low gram-molecular weight of graphite, a small amount will be ample for extensive equilibration; such amounts are common in metamorphosed sediments (see, e.g., Miyashiro, 1964).

Construction of P_{H_2O} - P_{CO_2} plots from the numerical results requires only the selection of P_{CO_2} as an independent variable instead of f_{O_2} . Then, for a given temperature and P_{gas} , P_{H_2O} can be plotted as a function of P_{CO_2} to form a series of isothermal curves (Figs. 12-13). Each point on a curve corresponds to a condition in which all P_i (including P_{O_2}) are explicitly specified.

At $P_{gas} = 100$ bars (Fig. 12), the P_{H_2O} - P_{CO_2} isotherms between 300° and 1500° K are a series of asymmetric curves which pass through maxima in the region of 5 to 30 b. P_{CO_2} . Additional curves corresponding to data derived from the f_{O_2} -T relations for the solid-phase oxygen buffers have been superimposed on the isotherms.

The oblique line at the top represents the locus of points for the condition, $P_{H_2O} + P_{CO_2} = 100$ b., and the vertical distance between this line and any point on an isotherm represents the total pressure of other species in the gas phase. At low values of P_{CO_2} , this difference is large for all temperatures and reflects the dominance of methane under conditions of low P_{O_2} . At higher temperatures, the difference is large for all values of P_{CO_2} because of the increasing contribution of H_2 and CO to the gas phase.

An increase in P_{gas} from 100 b. to 1000 b. (Fig. 13) produces a slight shift in the isotherms toward higher values of P_{H_2O} and P_{CO_2} ; however, the

general relations are unchanged. Increases in P_{gas} above 1000 b. will produce relatively smaller shifts.

These relations have several implications for study of the progressive metamorphism of graphite-bearing sediments. First, graphite cannot coexist with pure water under the conditions indicated; even at the lowest temperatures, the highest water content permitted is about $0.85 P_{\text{gas}}$. By contrast, graphite can coexist over a wide temperature range with a water-free atmosphere containing chiefly CO_2 .

Second, for a fixed temperature and P_{gas} , the values of $P_{\text{H}_2\text{O}}$ and P_{CO_2} cannot vary independently but must correspond to points along an isotherm. As P_{CO_2} increases, $P_{\text{H}_2\text{O}}$ increases at first, passes through a maximum in the region where $P_{\text{H}_2\text{O}} > P_{\text{CO}_2}$, then decreases to zero.

For the complete temperature range under discussion, low values of P_{CO_2} (less than $0.05 P_{\text{gas}}$) reflect a methane-rich atmosphere existing under conditions of relatively low P_{O_2} . With increasing temperature, however, the gas phase becomes progressively depleted in H_2O and CO_2 , and H_2 and CO become important. For this reason, the assumption that $P_{\text{gas}} = P_{\text{CO}_2} + P_{\text{H}_2\text{O}}$ is significantly in error over a wide range of metamorphic temperatures. At 600°K (327°C), the contribution of other components will exceed 10 per cent of P_{gas} for values of $P_{\text{CO}_2} \leq 0.4 P_{\text{gas}}$. At temperatures above 1000°K (727°C), a similar error is present for all values of P_{CO_2} .

Comparing the solid-phase buffer curves with the isothermal $P_{\text{H}_2\text{O}} - P_{\text{CO}_2}$ curves (Figs. 12-13) indicates that reaction with graphite during rising temperature will produce progressively reduced mineral assemblages. For instance, at $P_{\text{gas}} = 1000$ b. (Fig. 13), temperatures between 100° and 200°C are sufficient to convert original hematite to magnetite if graphite is

present. Such a mechanism has been suggested to explain the development of magnetite from original hematite in slightly metamorphosed sedimentary iron formations (Zen, 1963; LaBerge, 1964). More extreme reduction may be attained at higher temperatures; the development of fayalite in contact-metamorphosed iron formation may be conditioned by the presence of graphite (Gundersen and Schwartz, 1962; French, 1965). The rare occurrences of wüstite and native iron in terrestrial rocks (Walenta, 1960; Melson and Switzer, 1965) also appear associated with graphite which, at igneous temperatures, could produce extremely reducing conditions. It should be added that, when such reduced minerals are observed, the contribution to P_{gas} of species other than H_2O and CO_2 may be significant.

A specific model of particular interest is the progressive metamorphism of a sediment containing graphite and original interstitial water under conditions where the system is either completely closed or open only to water (Yoder, 1955; Thompson, 1955). It has been pointed out by earlier investigators (Eugster, 1959; Miyashiro, 1964) that, under these initial conditions, the resultant gas phase must undergo reduction in order to be in equilibrium with the observed mineral assemblages.

In applying the present calculations to such a system, we may express the additional constraint by saying that, whatever the composition of the gas phase during metamorphism, the total H/O ratio is fixed at 2/1 for both the closed and water-permeable systems. Such arbitrary selection of elemental ratios to reduce variance has been applied previously in analogous calculations (Suess, 1962; Dayhoff et al., 1964). This additional restriction makes it possible to calculate all P_i as explicit functions of T and P_{gas} only. In addition to the equilibrium relations (Eqs. 1-5), the requirements of

materials balance may be written (Suess, 1962):

$$H = 4 P_{CH_4} + 2 P_{H_2} + 2 P_{H_2O}$$

$$O = P_{H_2O} + P_{CO} + 2 P_{CO_2} + 2 P_{O_2}$$

Since $H/O = 2/1$,

$$4 P_{CH_4} + 2 P_{H_2} + 2 P_{H_2O} = 2 (P_{H_2O} + P_{CO} + 2 P_{CO_2} + 2 P_{O_2})$$

$$(12) \quad 2 P_{CO_2} + P_{CO} - 2 P_{CH_4} - 2 P_{H_2} + 2 P_{O_2} = 0$$

Equations (1-5) and (12) together constitute a system of six equations for the six unknown P_i ; explicit solutions are therefore possible once T and P_{gas} are fixed. In practice, however, the calculations became involved because of the appearance of a quartic equation in P_{H_2} . Therefore, a simpler procedure was adopted by specifying T and f_{O_2} instead. P_{gas} was calculated by summation at the end of the process and values of P_i were obtained by interpolation for any selected P_{gas} .

Under these conditions, graphite becomes a true oxygen buffer, since the value of f_{O_2} maintained in the gas phase depends only on T and P_{gas} . Values of f_{O_2} fixed by graphite in this system for values of P_{gas} of 1 b. and 2000 b. (Fig. 14) are very close to analogous values calculated earlier for a gas phase composed only of CO_2 and CO (French and Eugster, 1965). Both sets of f_{O_2} - T curves have shallower slopes than do the curves for the iron-bearing solid phase buffers. Thus, in both cases, more reduced mineral

assemblages will appear with increasing temperature, in agreement with the general conclusions discussed above (Figs. 12-13).

The interpolated values of P_i are shown in Figure 15 as a function of temperature for $P_{\text{gas}} = 1000$ b. Below about 1000°C , the gas phase consists chiefly of H_2O , CO_2 , and CH_4 ; the water content decreases sharply with rising temperature. P_{CH_4} and P_{CO_2} are approximately equal and pass through maxima where each constitutes about $0.25 P_{\text{gas}}$. Above about 1000°C , H_2 and CO become dominant, although the gas phase still contains significant amounts of all five species. The f_{O_2} - T curve for this system intersects progressively reduced buffer curves at slight angles with rising temperature. In this idealized case, fayalite would form in rocks of the proper composition at about 540°C , wüstite at 850°C , and metallic iron at 1160°C .

Mineral Assemblages in Meteorites

Numerous recent studies of the mineralogy and petrology of meteorites have attempted to apply mineralogical data to estimate conditions of formation of the various classes (see, e.g., Ringwood, 1961; Wood, 1962, 1963; Mueller, 1964). Considerable speculation has involved estimates of P_{O_2} and possible theories for evolution of the various types under differing degrees of reduction.

The general relationships between graphite and the composition of the coexisting gas phase suggest that the occurrence of graphite as an accessory mineral in meteorites is of great significance in attempting to evaluate conditions of formation. Graphite has been observed in several classes of meteorites, most prominently in the irons, but also in smaller amounts in stony meteorites, notably chondrites (Mason, 1958; Krinov, 1960; Ramdohr, 1962; Andersen, et al., 1964; Vdovykin, 1964).

In particular, the assemblage graphite + nickel-iron is common and widespread in both iron and stony meteorites. The results of the present study suggest that this assemblage formed under extremely reducing conditions in which methane may have been a dominant component of the coexisting gas phase, even at relatively high temperatures. For instance, at $P_{\text{gas}} = 1000$ b. (Figs. 5, 8), the upper limit of stability of iron + graphite is fixed by the MI and WI buffers; at all temperatures below 1000°C , P_{CH_4} exceeds 500 b. Lower values of P_{O_2} within the iron stability field will increase the contribution of methane, even at higher temperatures. The reported occurrence of quartz and tridymite in several iron-bearing meteorites (see Anders, 1964) suggests that at least some meteorites have developed at very low values of P_{O_2} below the QFI buffer where silica and iron can coexist without formation of fayalite. At these values of P_{O_2} (Fig. 8) the same P_{CH_4} could be maintained at temperatures in excess of 1200°C .

The use of buffer curves for pure iron in this discussion will not change the general conclusions. Even though the nickel-iron in meteorites will be in equilibrium with oxide at higher f_{O_2} values than pure iron, calculations suggest that the effect will not be large for small nickel contents (Olsen, 1959). Furthermore, the metal phase in at least one class of meteorites, the basaltic achondrites, is strongly depleted in nickel (Duke, 1965).

A POSSIBLE MECHANISM FOR EVOLUTION OF THE TERRESTRIAL ATMOSPHERE

The origin and evolution of the atmosphere and oceans are of profound importance in consideration of such problems as the origin of the earth and solar system, the nature of ancient geological processes, and the origin of life on earth. The purpose of the present discussion is not to review or evaluate the numerous theories and voluminous literature on the subject (for summaries, see Rutten, 1962; Brancazio and Cameron, 1964; Donn et al., 1965), but to discuss certain possible processes related to the occurrence of graphite and other minerals in the earth.

Three general methods have been used by earlier investigators to estimate the character of the primordial or Precambrian atmosphere existing at a time before deposition of most of the presently preserved sedimentary record:

(1) Calculation of the amounts of volatile compounds now present in the atmosphere and oceans which must have been produced by processes other than rock weathering (Rubey, 1951); such "excess volatiles" must either have been present in an original atmosphere or must have been added by gradual outgassing from the interior of the earth during geologic time.

(2) Use of thermodynamic equilibria to determine relative amounts of different volatile species in the atmosphere (Rubey, 1951; Holland, 1962, 1964). Such results are of limited value because they may not consider all possible equilibria, and because the equilibrium constants involved are strongly temperature-dependent. Temperatures existing in ancient atmospheres and within the primordial earth are speculative and the arbitrary selection of high temperatures is not justified. Furthermore, if low surface temperatures

are postulated, one cannot assume that equilibrium is established, either within the atmosphere or between the atmosphere and surface rocks, any more than it is at present.

(3) Study of ancient sedimentary rocks to estimate the character of the atmosphere in which they formed. Many studies have cited the occurrence of reduced minerals in sediments as evidence that the Precambrian atmosphere was reduced with respect to the present one (Rankama, 1958; Holland, 1962; Lepp and Goldich, 1964). These studies, while valuable, are hampered by two conditions. First, there is no evidence that detrital minerals are necessarily equilibrated with the atmosphere during erosion, transport, and deposition. Such equilibration is generally not attained at present; magnetite, iron-titanium oxides, and ferrous silicates are common detrital accessory minerals, although they should oxidize to hematite or iron hydroxides in the present atmosphere. Second, the effects of burial, diagenesis, and low-grade metamorphism on the mineralogy are difficult to recognize. The sediment may be effectively insulated from the atmosphere in a local reducing environment soon after deposition. Further, the presence of organic matter or graphite may produce reduced mineral assemblages with very slight increases in temperature, destroying traces of original equilibrium with the atmosphere.

It has been generally assumed that a reducing atmosphere lacking free oxygen existed at some point in the history of the primordial earth. Such an atmosphere would be required for the development and preservation of organic compounds and their eventual combination into primitive forms of life (see Rubey, 1951; Urey, 1952; Oparin, 1957; Miller and Urey, 1959; Holland, 1962; Rutten, 1962). The exact character of this atmosphere is not agreed upon; it has variously been proposed that CH_4 , CO_2 , N_2 and H_2O were dominant species.

Holland (1962) proposed a three-stage model for development of the atmosphere through outgassing of the original crust: (1) an atmosphere formed in equilibrium with metallic iron at 1200°C , composed of CH_4 , H_2 and minor H_2O and N_2 ; liquid H_2O would also exist on the surface. (2) A later stage containing dominant N_2 and minor H_2O and CO_2 , produced by equilibrium with magnetite in a more oxidized crust; (3) A final stage developed from photosynthetic production of oxygen and corresponding to the present atmosphere.

This model has two serious objections. First, the temperature of 1200°C , while not unreasonable, is arbitrary; because of the strong dependence of equilibria on temperature, arbitrary selection of temperature strongly conditions the gas compositions obtained. Second, the equilibria in the atmosphere (at an assumed temperature of 298°K) may not be established, and the calculated compositions may not be attained.

The present discussion is somewhat similar to Holland's model, and considers the problem of converting an original methane-rich atmosphere into water and CO_2 through equilibria between a gas phase and accessory minerals existing to moderate depths within the primordial earth. In the proposed mechanism, original methane reacts with graphite and ferric-iron-bearing phases at temperatures in excess of 600°C to depths of a few hundred kilometers, producing water and CO_2 which are removed to a cool surface to form oceans and atmosphere. Such a mechanism does not require low-temperature equilibrium between atmosphere and the surface rocks or between the different species within the atmosphere itself; the surface temperature can be low enough to prevent re-equilibration of water and CO_2 to produce methane again.

Such a mechanism is independent of any detailed assumptions about the composition, thermal history, and structure of the primordial earth. Its

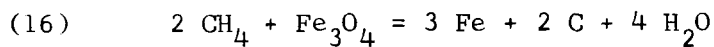
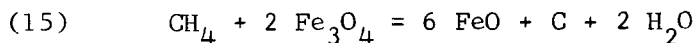
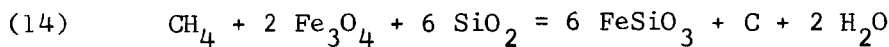
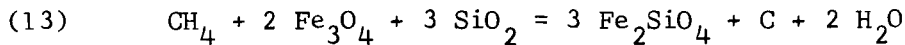
operation requires only a source of sufficient original methane and accessory minerals, sufficient heating to attain temperatures of 600° to 1000°C at moderate depths, and some mechanism for removing the product gases to the surface through fissure systems or by volcanism. In the present discussion, it is assumed that all of the "excess volatile" water and CO_2 (Rubey, 1951) originated by this mechanism; it will be found that the material requirements for even this extreme case are not excessive. Despite the obvious oversimplifications, this mechanism is consistent with a variety of earth models, even though it neglects such significant problems as the source of the original methane, the time required for the transformation, and the presence or absence of a differentiated core in the primordial earth during the process.

Data from the present study indicate that methane originally in equilibrium with graphite will be converted to water and CO_2 with increasing temperatures; at higher values of P_{gas} , water will form in excess of CO_2 (Figs. 9-10). At $P_{\text{gas}} = 1000 \text{ b.}$, temperatures above 600°C are sufficient for complete conversion at values of P_{O_2} within the stability field of magnetite (QFM buffer) (Fig. 10). At minimum values of P_{O_2} within the magnetite field, the maximum temperature is about 950°C . Increasing P_{gas} to 100 kb. increases the maximum temperature to about 1250°C . In any case, significantly lower temperatures will suffice if water and CO_2 are continually removed, allowing the reaction to proceed to completion.

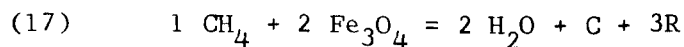
MacDonald (1959) has calculated temperature distributions resulting from radioactive heating in a number of primordial earth models as a function of time after formation. The numerical results may be subject to later modification (Wasserburg et al., 1964) but it appears that, for numerous possible models, temperatures of 800° to 1500°C could be attained at 100 to 300 km. depth within

10^9 years after formation. In fact, MacDonald has suggested (1959, p. 1987-1989) that initial temperatures well above these values could have been reasonably attained during formation of the earth by accretion. If this were the case, methane would have been converted to water and CO_2 almost simultaneously with formation of the earth and would not have existed within the body for any significant length of time. In any case, it appears that the temperatures required could have been generated, even though an exact specification of the temperature distribution in the body is not possible.

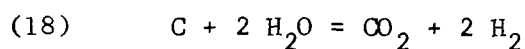
A wide variety of heterogeneous reactions may occur within the earth to convert methane into water and CO_2 through reaction with solid phases; the following are some simple examples:



Actual reactions will probably involve more complex ferrous-ferric silicates such as garnets, amphiboles, and micas, but the stoichiometry will be similar to these examples. The subsequent calculations are made using magnetite as a reactant and assuming a conversion equation of the form,

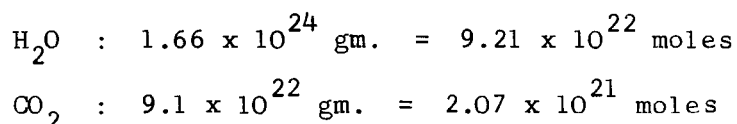


where R designates a reduced phase such as fayalite, ferrosilite, wüstite, or iron. The necessary CO_2 may be formed by reaction of a small amount of product water with graphite, i.e.,



The volatile products are transported to the surface, where water condenses and CO_2 and H_2 are incorporated into the original atmosphere, together with an undetermined amount of N_2 . If the rate of introduction of H_2 is slow, it may escape from the atmosphere without building up a high partial pressure (Holland, 1962).

The amounts of "excess volatile" water and CO_2 which should be produced are (Rubey, 1951):



From (17) and (18), the materials balance becomes (in moles):

<u>Reactants</u>		<u>Products</u>	
CH_4	4.81×10^{22}	H_2O	9.21×10^{22}
Fe_3O_4	9.63×10^{22}	CO_2	2.07×10^{21}
		H_2	4.14×10^{21}
		C	4.61×10^{22}
		R	1.44×10^{23}

The amount of methane required, 4.81×10^{22} moles, would occupy an STP volume of 1.08×10^{12} km.³, approximately that of the present earth. If this amount had originally existed as an atmosphere, it would have exerted a surface pressure of about 140 b. and would have been about 300 km. deep (scale height 15 km.). These values are probably excessive and suggest that any original methane was probably produced gradually or existed originally in the primordial earth.

Some simple calculations will show that this required methane could have been easily contained within a primordial earth as either free gas or organic compounds which could yield methane on heating. For discussion, we can postulate a primordial earth accreted out of material similar to the carbonaceous chondrites, although the chemical composition is not critical to the discussion. A body of the same mass as the present earth, with a density of 2.5 gm./cm.³, would have a radius, $R_0 = 8300$ km. and a volume, $V_0 = 2.39 \times 10^{12}$ km.³. The required methane, 7.72×10^{23} gm., would be less than 0.00015 of the mass of this body. For a primordial earth with a mean porosity of 1 per cent in its upper part, a surface pressure of 1 b., a uniform pressure gradient, and a constant original temperature of 298°K, the volume necessary to contain the required methane can be derived.

At a depth of h km. from the surface, the lithostatic pressure in bars is equal to $\rho gh = 250 h$, and the average pressure from the surface to a depth h , is $\bar{P} = 125 h$. If Boyle's Law applies to the gas, then V_h , the volume of rock required to contain the gas, can be calculated from the relationship:

$$V_{STP} = 0.01 \bar{P} V_h = 1.08 \times 10^{12} \text{ km.}^3$$

$$V_h = 0.8 \frac{V_{STP}}{h} = 8.64 \times 10^{11} h^{-1}$$

For a shell from the surface to a depth h ,

$$V_h = V_o - 4/3\pi (R_o - h)^3$$

Solution of the equations indicates that a shell about 35 km. thick would contain all required methane. The gas could be contained at a larger depth in a correspondingly smaller volume. The exact results are uncertain because of the numerous assumptions, but it appears that a primordial earth of any reasonable composition might be expected to contain sufficient methane for production of the "excess volatiles" by the mechanism suggested.

It is not unreasonable to assume that the material in the upper region of the primordial earth contained at least 1 per cent by weight of magnetite; such a condition is met by many terrestrial rocks of widely varying chemical composition and also by the carbonaceous chondrites (Mason, 1958). For such material, each km.³ of rock contains 5.18×10^{13} moles of magnetite and 4.30×10^{11} km.³ of rock will supply the magnetite needed for complete reaction. This volume of rock corresponds to a sphere of radius 4680 km., or to a shell from the surface of the present earth to a depth of 990 km. (the corresponding thickness for the primordial earth postulated above would be about 550 km.).

It is not necessary to suggest that reaction actually occurred at such great depths if some method of convection operated to bring fresh material to shallower levels. For example, if reaction can occur to a depth of only 1 km., a total of 850 overturn cycles would be needed to supply the required magnetite. The number of cycles required decreases approximately linearly as

the thickness of the reacting layer is increased; thus, a 20-km. layer requires about 40 renewals, and a 100-km. shell only 9. If such convection takes place at rates estimated for the present earth (about 1 cm./yr.; Orowan, 1964), material could move to the surface from a depth of 1000 km. in about 10^8 years. The operation of such a mechanism would not change the total amount of magnetite required, but would allow reaction to be restricted to a narrow zone closer to the surface.

The amount of hydrogen produced by complete reaction, 4.14×10^{21} moles or 8.34×10^{21} grams, would exert a maximum surface pressure of about 1.5 b. However, loss of hydrogen into space would tend to keep P_{H_2} at a lower value (Holland, 1962).

The total CO_2 produced, 2.07×10^{21} moles, would have exerted a surface pressure of about 17 b. Precipitation of carbonate sediments would probably have occurred long before such a high value was reached (Rubey, 1951) and it is questionable whether life could have originated and survived under such a high CO_2 pressure. These results suggest a gradual evolution of CO_2 into the atmosphere (Rubey, 1951).

Disposal of the hypothetical solid products is not difficult. The graphite produced, 4.61×10^{22} moles, would form a sphere about 390 km. in radius, or a layer on the surface of the earth about 0.5 km. thick. However, if it constituted 1 per cent of the upper part of the earth, it could be dispersed in a layer 50 km. thick. If the reduced phase, R, is considered as iron, a volume of 1.03×10^9 km.³ is produced, corresponding to a sphere about 625 km. in radius or to 1 per cent of the earth to a depth of about 200 km. If temperatures above the melting point of iron are reached, the metal could segregate toward the center. Other reduced phases which could

develop would have slightly larger volumes, but could still be distributed as small percentages of the material in the upper part of the earth.

Despite the oversimplified assumptions of this model and the uncertainties in the calculations, it does appear that all the "excess volatile" water and CO_2 now present could have originated from reaction of original methane with accessory minerals at moderate depths within the earth. Such a model has two significant advantages. First, no rigorous assumptions are needed as to the original mineralogy and composition of the earth; the reactions involve only small amounts of accessory minerals, and gross mineralogical characteristics are unaffected. Second, there is no necessity for equilibrium between the atmosphere and the surface rock at any time.

The high calculated surface pressure for original methane, about 140 b., suggests that it did not form an atmosphere prior to reaction. The required methane could have been contained within the upper levels of the earth, although, if temperatures above 1000°C existed in this region soon after accretion (MacDonald, 1959), methane would not remain in equilibrium with magnetite-graphite assemblages, and conversion to water and CO_2 would have proceeded rapidly. The product CO_2 would also have exerted an unreasonably high surface pressure, suggesting that it was evolved gradually until formation of carbonate-bearing sediments could occur (Rubey, 1951).

This mechanism is in general agreement with models of atmosphere development proposed earlier (Rubey, 1951; Holland, 1962). However, consideration of possible heterogeneous reactions at depth removes the necessity for an original methane-rich atmosphere. The model leads directly to an atmosphere enriched in water, CO_2 , and N_2 which resembles the second stage of Holland's

(1962) model or the original atmosphere proposed by Rubey (1951).³

The materials-balance method used here gives no indication of the time required to produce the water and CO_2 or of whether the rate of production has been constant throughout geologic time. Rubey (1951, p. 1138) has pointed out that the present rate of introduction of volatiles to the surface could product the required amounts during geologic time. There is thus no reason to require large production of volatiles early in the earth's history, but the mechanism described would be consistent with either model.

If temperatures in the atmosphere are too low for establishment of equilibrium, further compositional changes will depend largely on the initiation of photosynthesis to produce the present oxygenated atmosphere. The date for the origin of life and the magnitude of photosynthetic effects are uncertain; the discovery of apparently photosynthetic algae in Precambrian rocks (Rutten, 1962; Barghoorn and Tyler, 1965) indicates that photosynthesis was operative, at least locally, as much as 2×10^9 years ago, a result which must be included in any consideration of the evolution of the atmosphere. (Cloud, 1965).

³The system studied, including only C, H, and O, gives no indication of the behavior of N_2 during oxidation of the methane. Higher values of P_{O_2} promote the decomposition of NH_3 to N_2 and H_2 , and it is probable that such reaction, occurring in parallel with the oxidation of methane, could produce the observed N_2 in the atmosphere. The amount of "excess volatile" N_2 (Rubey, 1951, p. 1116) is 4.2×10^{21} gm. or 1.5×10^{20} moles, about 0.002 of the amount of water and CO_2 required.

GENERAL CONCLUSIONS

(1) The study of equilibrium between the mineral graphite and a coexisting gas phase in the system C-H-O is of extreme significance in estimating conditions of formation of graphite-bearing mineral assemblages which occur in metamorphosed sediments, in certain igneous rocks, and in several classes of iron and stony meteorites. Ideally, the system graphite + gas is trivariant; in the present study, values of T , P_{gas} , and f_{O_2} are independently specified. Values of P_{CO_2} , P_{CO} , $P_{\text{H}_2\text{O}}$, P_{H_2} , and P_{CH_4} in the coexisting gas phase are then explicitly calculated with a high-speed computer. The numerical results support some general conclusions about the composition of the gas phase in equilibrium with graphite-bearing assemblages over a range of temperatures and gas pressures attainable in geological environments.

(2) The contribution of methane, CH_4 , to the gas phase in equilibrium with graphite-bearing assemblages is significant over a wide range of geologically realizable conditions. In a moderately reduced gas phase, methane may constitute 30 to 50 per cent of the total gas pressure, with the excess composed chiefly of water and CO_2 . Under conditions of even lower P_{O_2} , the gas phase may be almost entirely methane. The existence of significant amounts of methane in the gas phase is indicated by the presence of minerals stable at low P_{O_2} , such as fayalite, wüstite, and native iron.

(3) Graphite in a sediment will act to produce increasingly reduced mineral assemblages during rising temperatures associated with progressive metamorphism. Such a mechanism may explain the commonly observed reduction of original sediments with increasing metamorphic grade in both regional and contact-metamorphic environments. In particular, the existence of graphite

or equivalent organic matter will reduce original hematite to magnetite at very low temperatures.

(4) Because of the low gram-molecular weight of graphite, trace amounts will be sufficient to act as an effective internal oxygen buffer in systems as small as individual rock layers. Observed differences in P_{O_2} in metamorphic rocks over short distances may be conditioned by the presence or absence of graphite in the assemblage; a definite distinction between the two cases is necessary for a detailed study of such rocks.

(5) The equilibrium relations suggest a model for the development and evolution of the earth's atmosphere in which original methane is oxidized to water and CO_2 by reaction with trace amounts of graphite and ferrous-ferric minerals such as magnetite in the upper part of the primordial earth. Even for maximum required water and CO_2 , the materials needed are not excessive and could reasonably have been contained within a variety of possible primordial earths. Such a mechanism is independent of the gross composition and mineralogy of the earth and does not require high surface temperatures or establishment of equilibrium between atmosphere and surface. The reactions can therefore be applied to a wide range of proposed origins for the earth, its atmosphere, and its oceans. Possible reaction products are graphite, hydrogen, and iron, all of which could be incorporated into the primordial earth without difficulty. The time required for completion of the process is indeterminate, although the calculated high surface pressures of both reactant methane and product CO_2 favor the interpretation that a relatively long period of time was involved (Rubey, 1951; Holland, 1962). However, the process could have been completed early in the Precambrian before most of the available sedimentary record originated.

In summary, graphite is a common and widespread accessory mineral in both terrestrial and extraterrestrial rocks. It is of particular importance because of its relationship to the composition of a coexisting gas phase in the system C-H-O. The presence of graphite in a mineral assemblage thus provides an additional constraint on the conditions of temperature, pressure, and composition in which the assemblage formed. Furthermore, changes in composition of the coexisting gas phase in response to changes in temperature have considerable significance for studies of progressive metamorphism and for speculations about the origin and development of the terrestrial atmosphere. For these reasons, the detection and identification of even trace amounts of graphite in a mineral assemblage are of particular importance to petrologic studies.

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FIGURE CAPTIONS

1. Calculated composition of a gas phase in equilibrium with graphite as a function of f_{O_2} for a temperature of $327^{\circ}C$ ($600^{\circ}K$) and total gas pressures of 1 bar, 1000 bars, and 10 kilobars. Values of $\text{Log}_{10} P_i$ for CO_2 , CO , H_2O , H_2 , and CH_4 are plotted against $\text{Log}_{10} f_{O_2}$; dashed extensions of the curves indicate impossible values for which $P_{CO_2} + P_{CO} > P_{gas}$. Vertical lines above the curves indicate f_{O_2} values for solid-phase oxygen buffers.

2. Calculated composition of a gas phase in equilibrium with graphite as a function of f_{O_2} for a temperature of $627^{\circ}C$ ($900^{\circ}K$) and total gas pressures of 1 bar, 1000 bars, and 10 kilobars. Values of $\text{Log}_{10} P_i$ for CO_2 , CO , H_2O , H_2 , and CH_4 are plotted against $\text{Log}_{10} f_{O_2}$; dashed extensions of the curves indicate impossible values for which $P_{CO_2} + P_{CO} > P_{gas}$. Vertical lines above the curves indicate f_{O_2} values for solid-phase oxygen buffers.

3. Calculated composition of a gas phase in equilibrium with graphite as a function of f_{O_2} for a temperature of $927^{\circ}C$ ($1200^{\circ}K$) and total gas pressures of 1 bar, 1000 bars, and 10 kilobars. Values of $\text{Log}_{10} P_i$ for CO_2 , CO , H_2O , H_2 and CH_4 are plotted against $\text{Log}_{10} f_{O_2}$; dashed extensions of the curves indicate impossible values for which $P_{CO_2} + P_{CO} > P_{gas}$. Vertical lines above the curves indicate f_{O_2} values for solid-phase oxygen buffers.

4. Calculated composition of a gas phase in equilibrium with graphite as a function of temperature for f_{O_2} values specified by the quartz-fayalite-magnetite buffer. Total gas pressure equals 1000 bars (left) and 10 kilobars (right). Values of $\text{Log}_{10} P_i$ for CO_2 , CO , H_2O , H_2 , and CH_4 are plotted against temperature in the upper part of the diagrams; corresponding values of $\text{Log}_{10} f_{O_2}$ are plotted in the lower part.

5. Calculated composition of a gas phase in equilibrium with graphite as a function of temperature for f_{O_2} values specified by the combined magnetite-iron and magnetite-wüstite buffers. Total gas pressure equals 1000 bars. Values of $\text{Log}_{10} P_i$ for CO_2 , CO , H_2O , H_2 , and CH_4 are plotted against temperature in the upper part of the diagram; corresponding values of $\text{Log}_{10} f_{O_2}$ are plotted in the lower part.

6. Calculated composition of a gas phase in equilibrium with graphite as a function of temperature for f_{O_2} values controlled by the combined magnetite-iron and wüstite-iron buffers. Total gas pressure equals 1000 bars. Values of $\text{Log}_{10} P_i$ for CO_2 , CO , H_2O , H_2 , and CH_4 are plotted against temperature in the upper part of the diagram; corresponding f_{O_2} values are plotted in the lower part.

7. Calculated mole percentages of methane, CH_4 , as a function of temperature in a gas phase coexisting with graphite at f_{O_2} values established by various solid-phase oxygen buffers. Total gas pressure equals 1 bar.

8. Calculated mole percentages of methane, CH_4 , as a function of temperature in a gas phase coexisting with graphite at f_{O_2} values established by various solid-phase oxygen buffers. Total gas pressure equals 1000 bars.
9. Calculated partial pressures of CO_2 , CO , H_2O , H_2 and CH_4 as a function of temperature for gas phases coexisting with graphite. Total gas pressure equals 1 bar. The curves correspond to values of f_{O_2} specified by the quartz-fayalite-magnetite buffer (solid lines) and by the combined magnetite-iron and magnetite-wüstite buffers (dashed lines).
10. Calculated partial pressures of CO_2 , CO , H_2O , H_2 , and CH_4 as a function of temperature for gas phases coexisting with graphite. Total gas pressure equals 1000 bars. The curves correspond to values of f_{O_2} specified by the quartz-fayalite-magnetite buffer (solid lines) and by the combined magnetite-iron and magnetite-wüstite buffers (dashed lines).
11. Calculated temperature - total gas pressure curves which represent the upper limits of stability of various solid-phase buffer assemblages with graphite and a gas phase. The curves are actually projections of univariant curves along the f_{O_2} axis onto the $P_{\text{gas}}-T$ plane.
12. Calculated values of $P_{\text{H}_2\text{O}}$ and P_{CO_2} in a gas phase in equilibrium with graphite at a total gas pressure of 100 bars. At each temperature, permissible compositions lie on curved isotherms (solid lines). Dashed lines indicate estimated compositions for a gas phase in equilibrium with graphite and various solid-phase buffer assemblages.

13. Calculated values of $P_{\text{H}_2\text{O}}$ and P_{CO_2} in a gas phase in equilibrium with graphite at a total gas pressure of 1000 bars. At each temperature, permissible compositions lie on curved isotherms (solid lines). Dashed lines indicate estimated compositions for a gas phase in equilibrium with graphite and various solid-phase buffer assemblages.
14. Values of f_{O_2} established in a gas phase in equilibrium with graphite as a function of temperature for total gas pressures of 1 bar and 2000 bars. Values for a system in which the H/O ratio of the gas phase is fixed at 2/1 (heavy solid lines), corresponding to progressive metamorphism of a graphite-bearing sediment containing interstitial water, fall close to those calculated for the system C-O (heavy dashed lines) (French and Eugster, 1965). Both sets of curves intersect progressively reduced solid-phase buffers (light solid lines) with increasing temperature.
15. Calculated composition of a gas phase in equilibrium with graphite as a function of temperature for a system in which the H/O ratio of the gas phase is maintained at 2/1. For temperatures below 1000°C, H_2O dominates, and CO_2 and CH_4 are present in approximately equal amounts. The f_{O_2} -T curve for this system (heavy solid line in lower part of figure) intersects more reduced buffers; with increasing temperature, an original magnetite-quartz-graphite rock should progressively develop fayalite, wüstite, and iron.

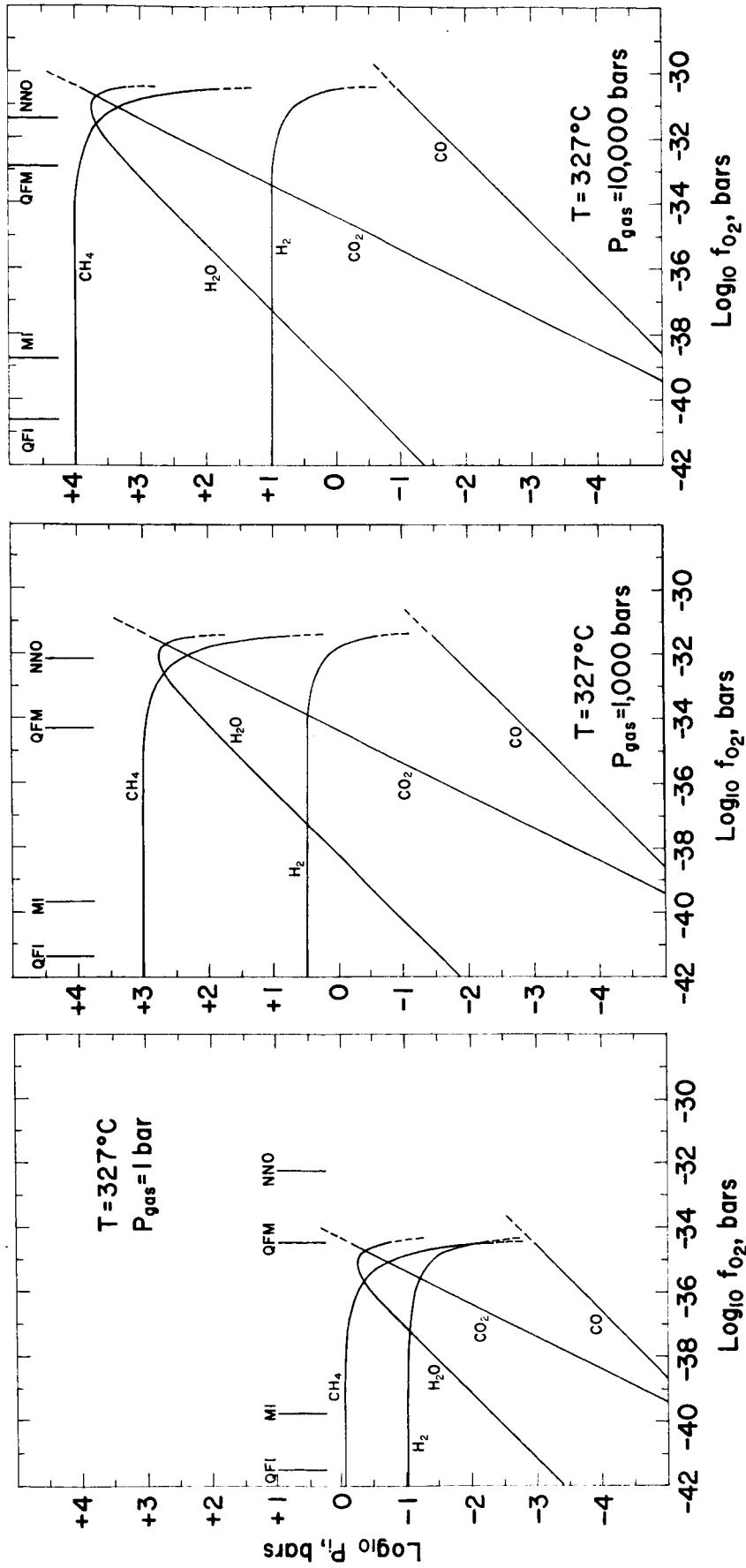


FIGURE 1

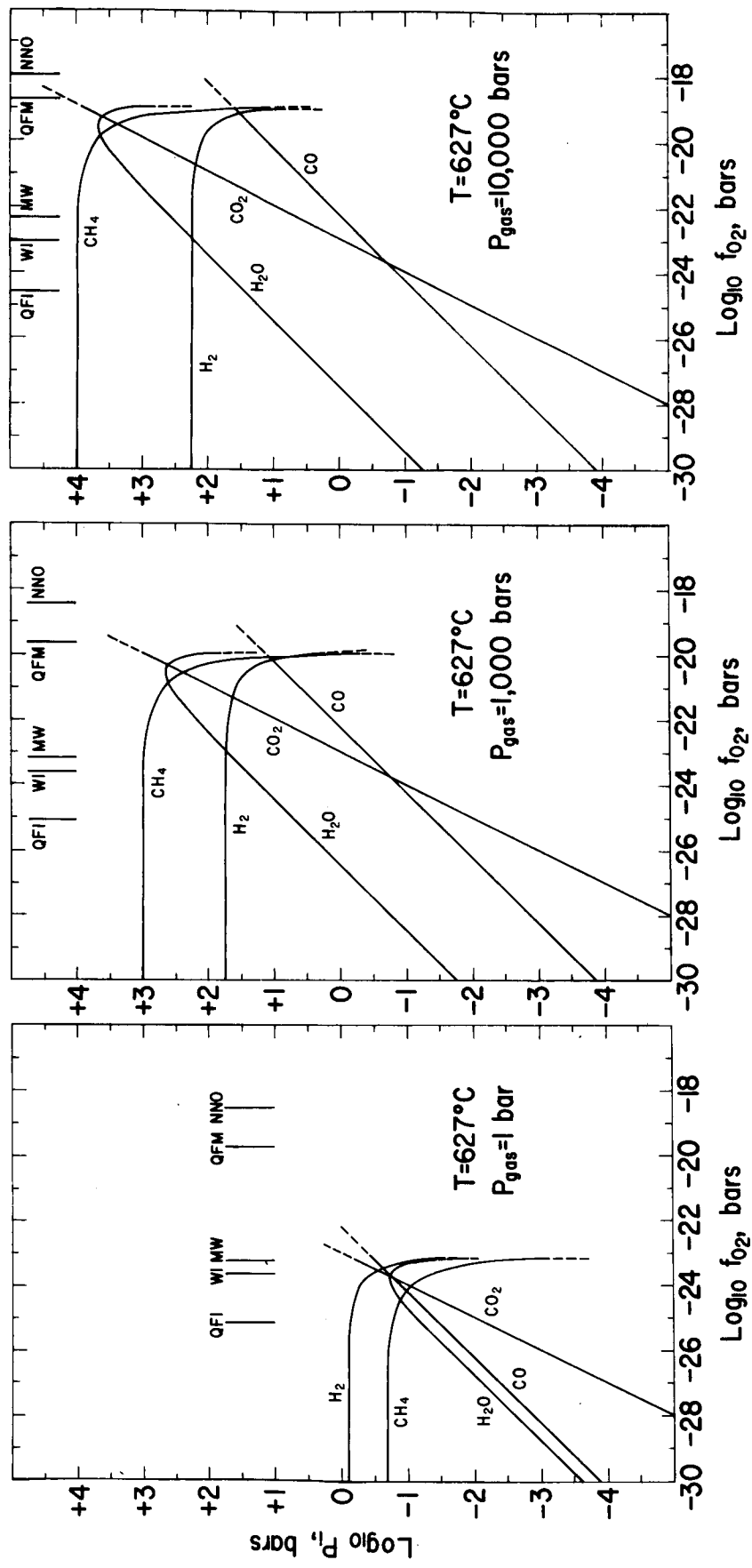


FIGURE 2

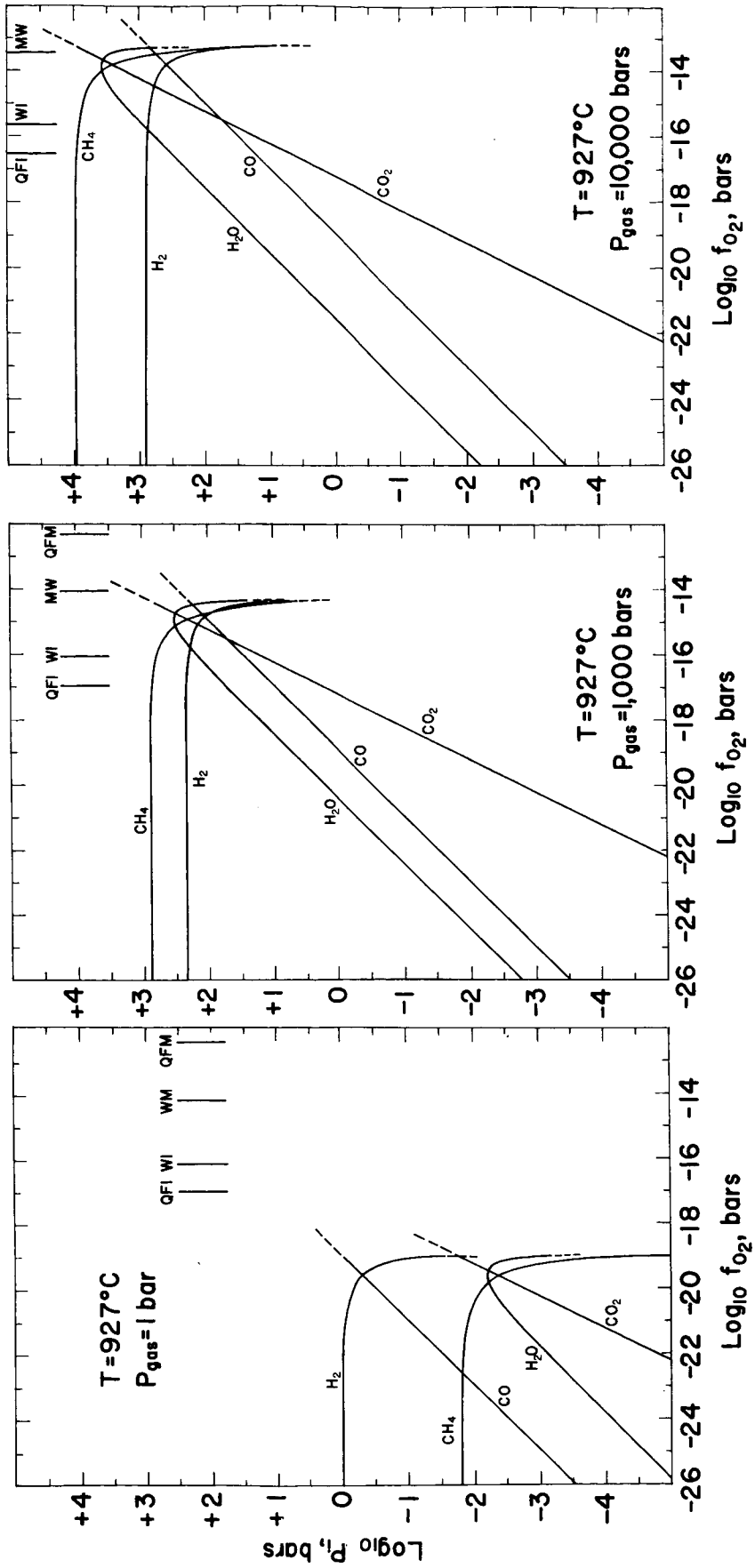


FIGURE 3

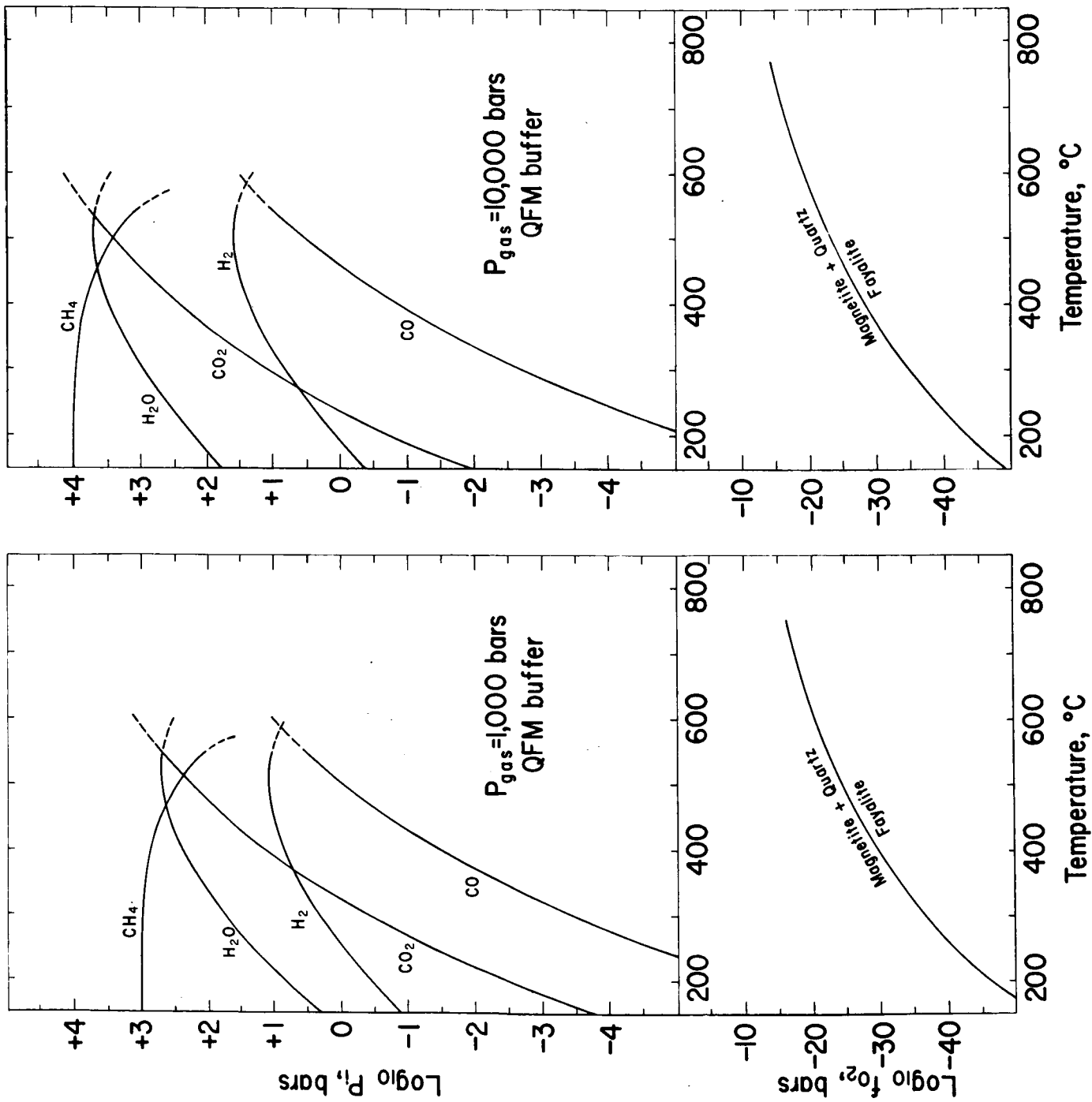


FIGURE 4

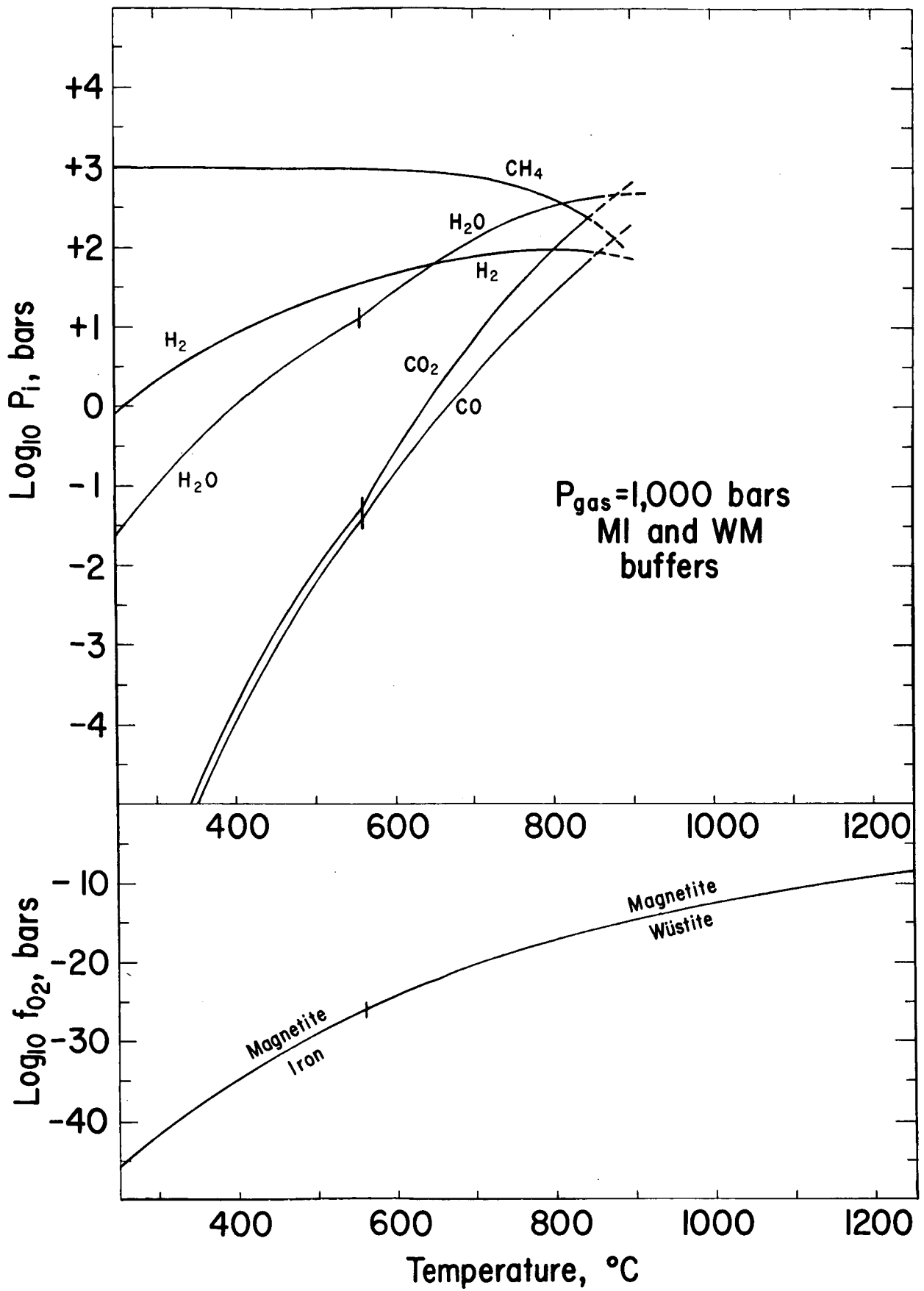


FIGURE 5

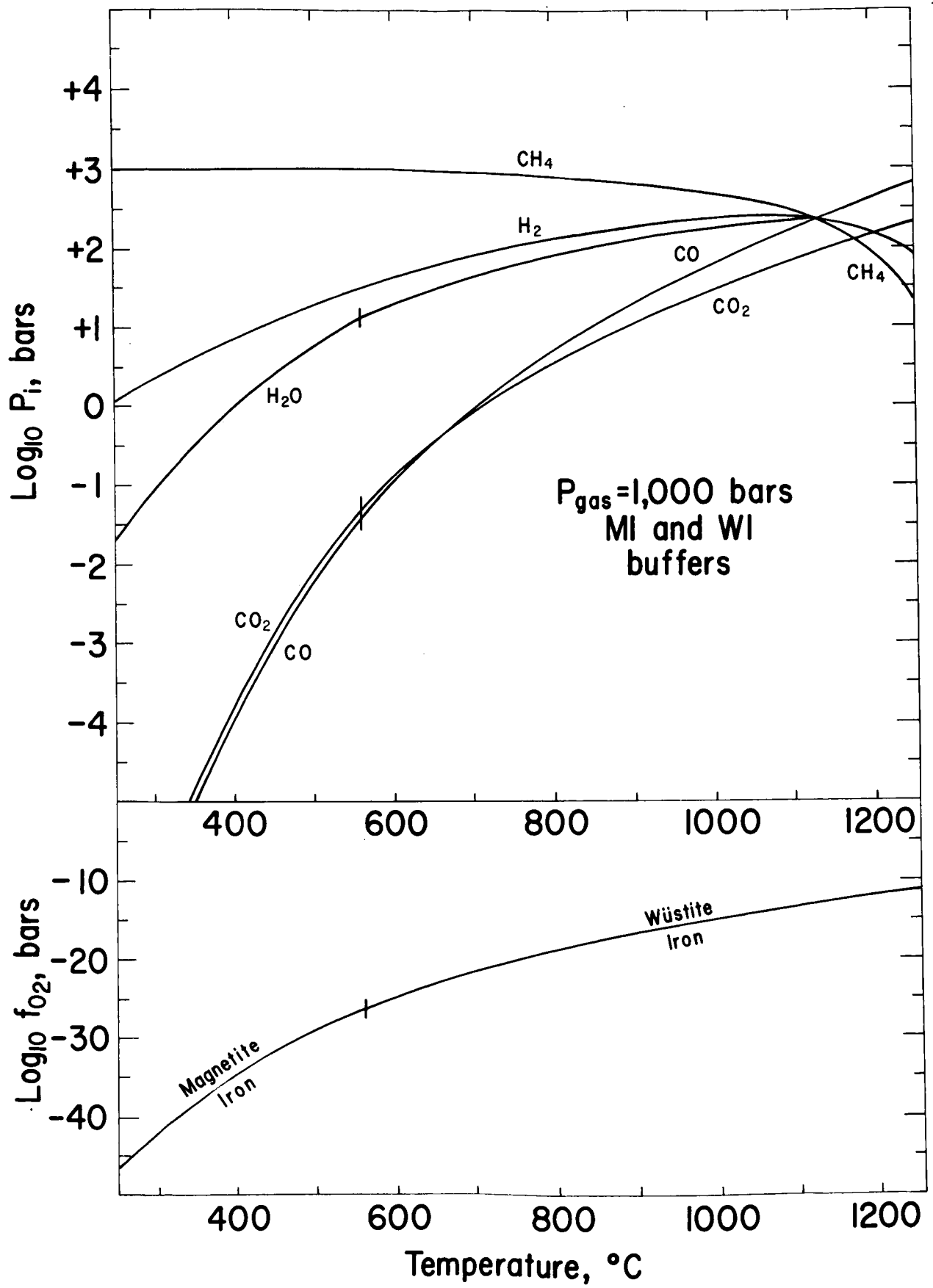


FIGURE 6

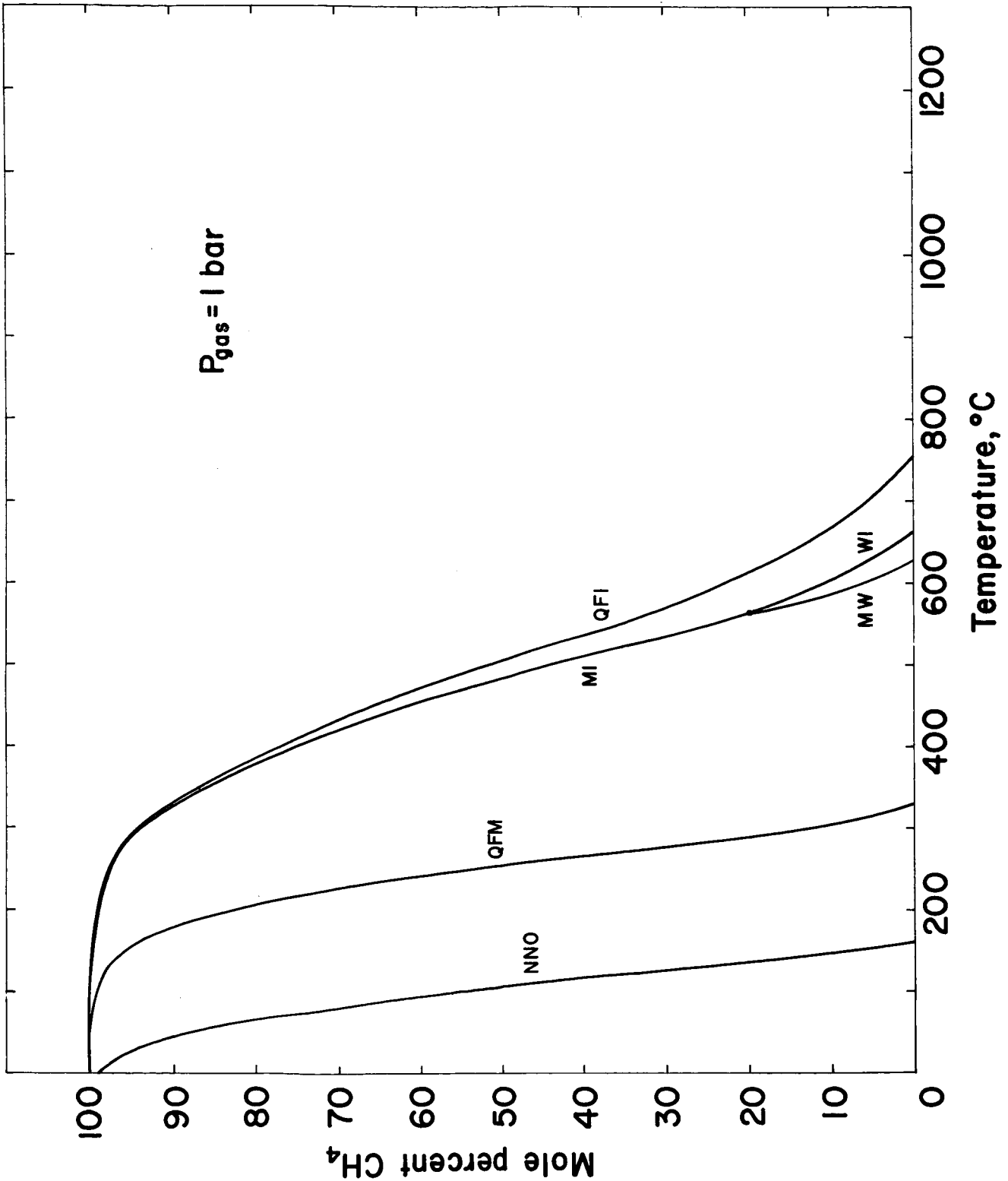


FIGURE 7

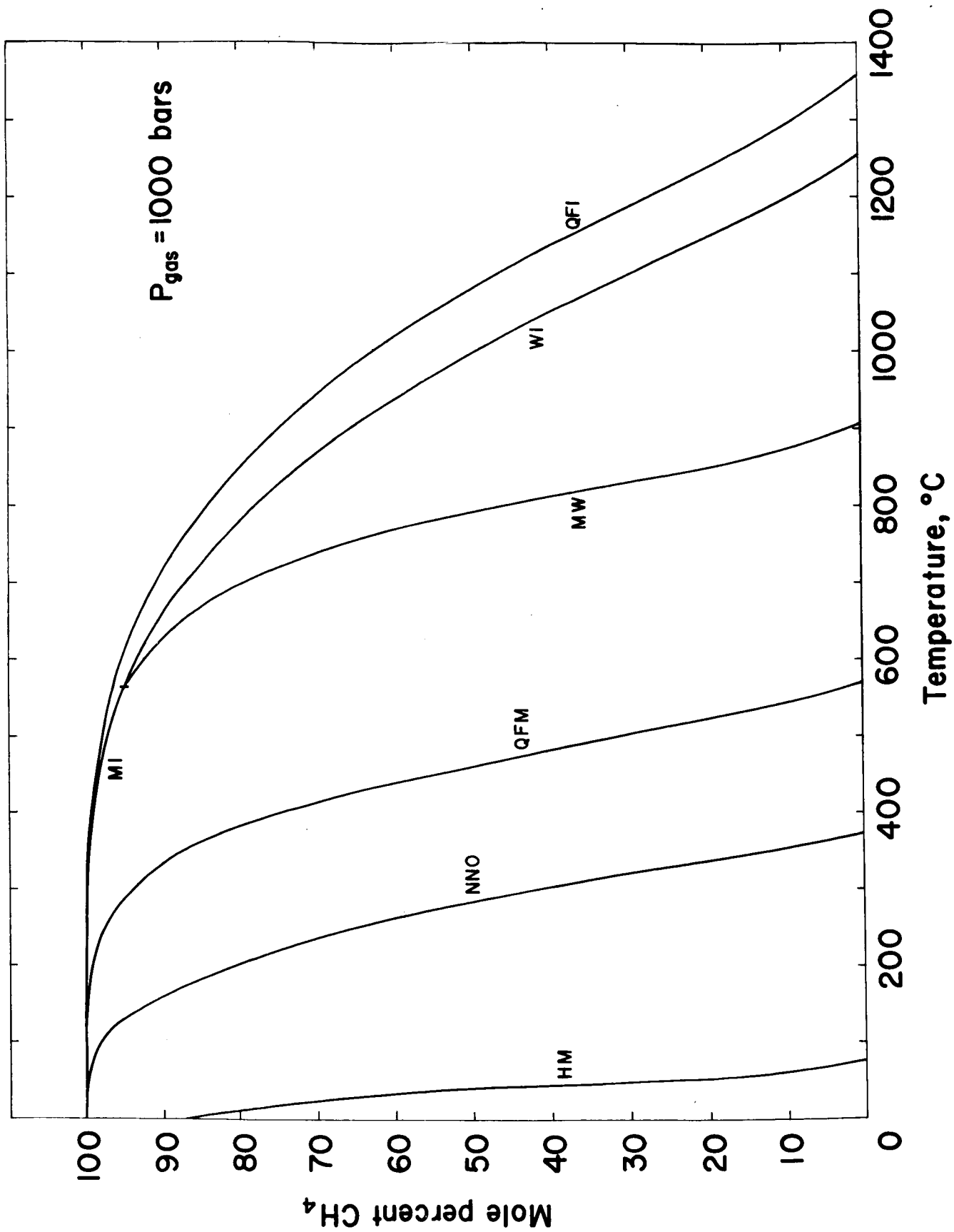


FIGURE 8

FIGURE 9

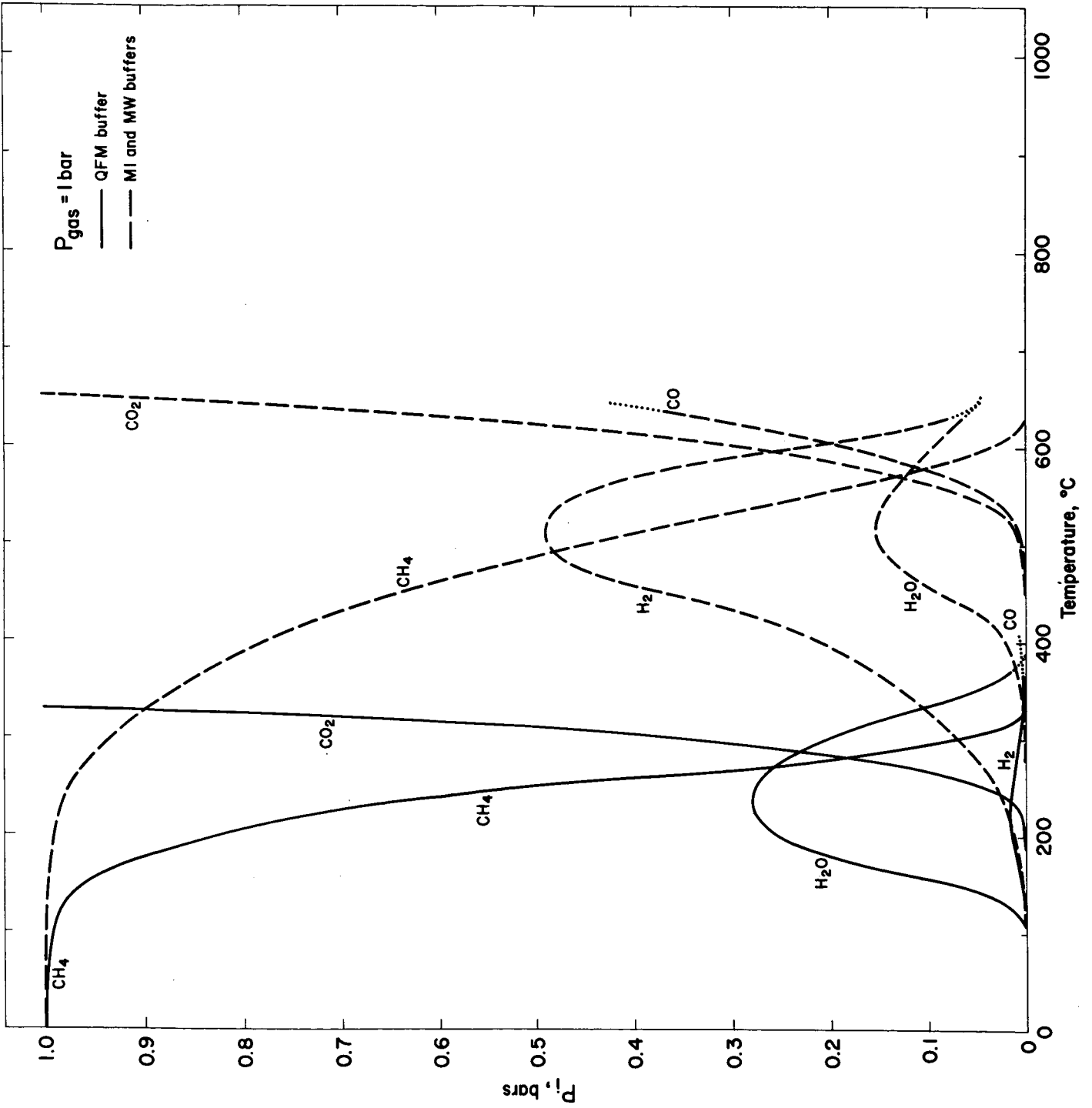
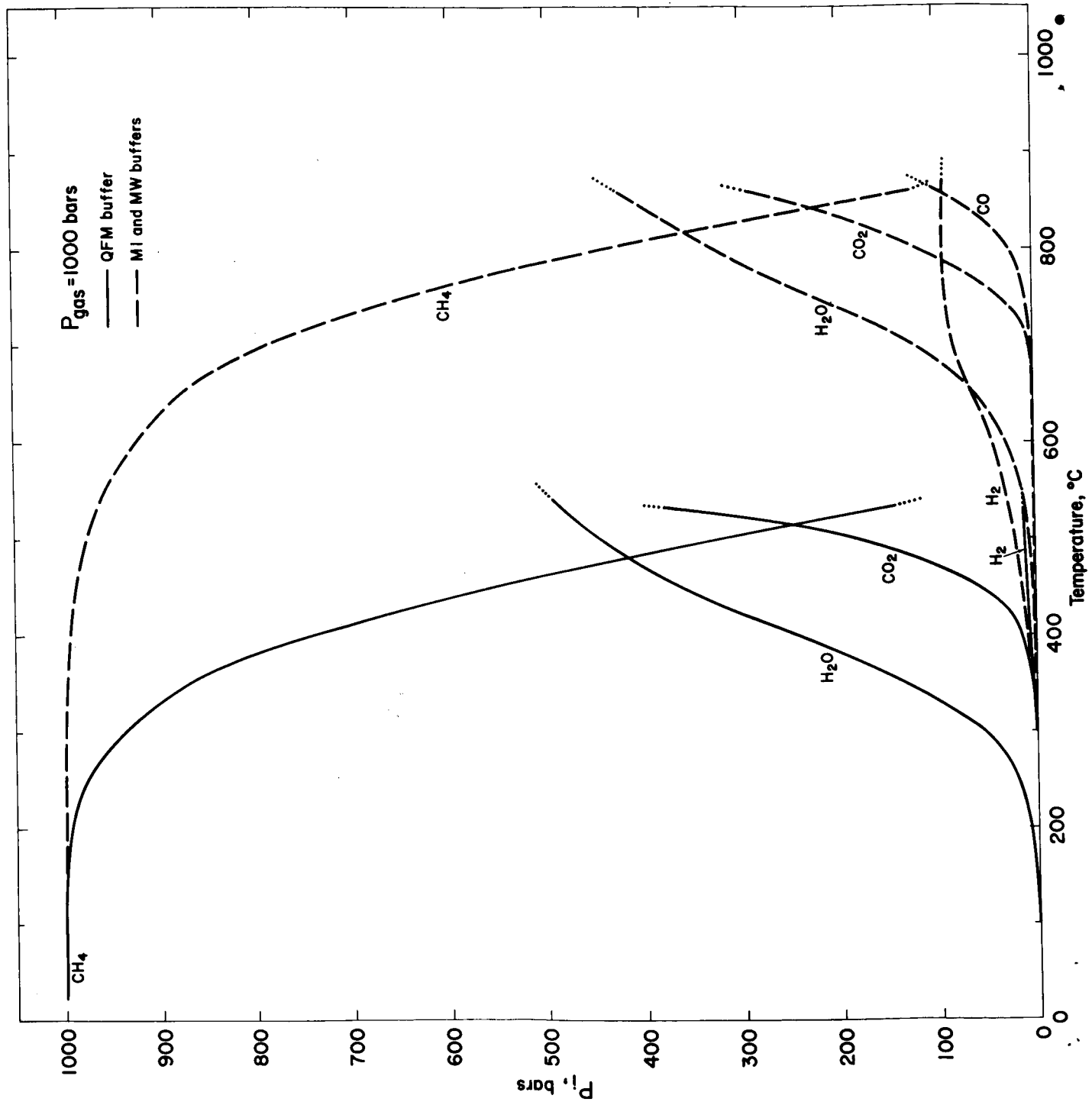


FIGURE 10



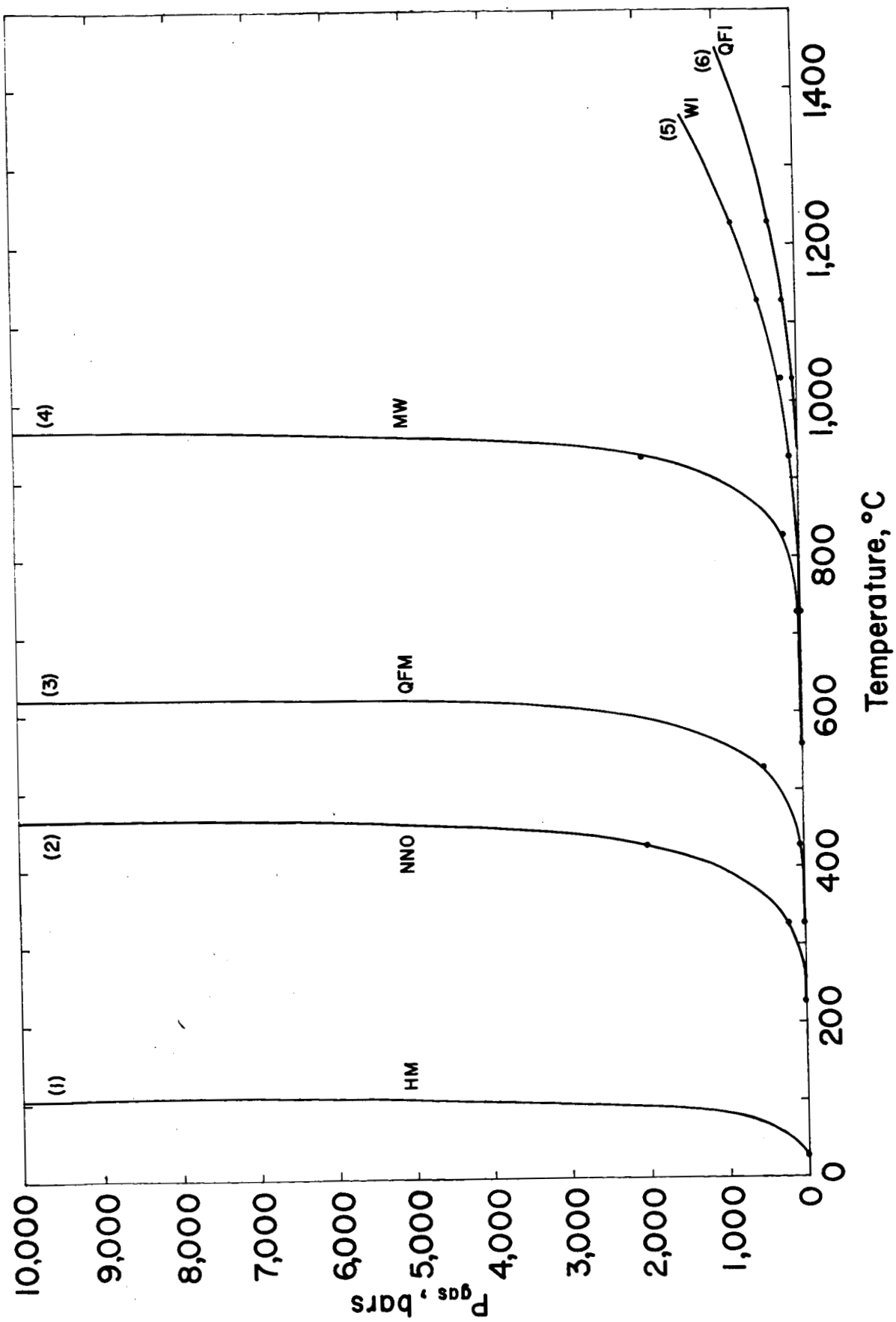


FIGURE 11

FIGURE 12

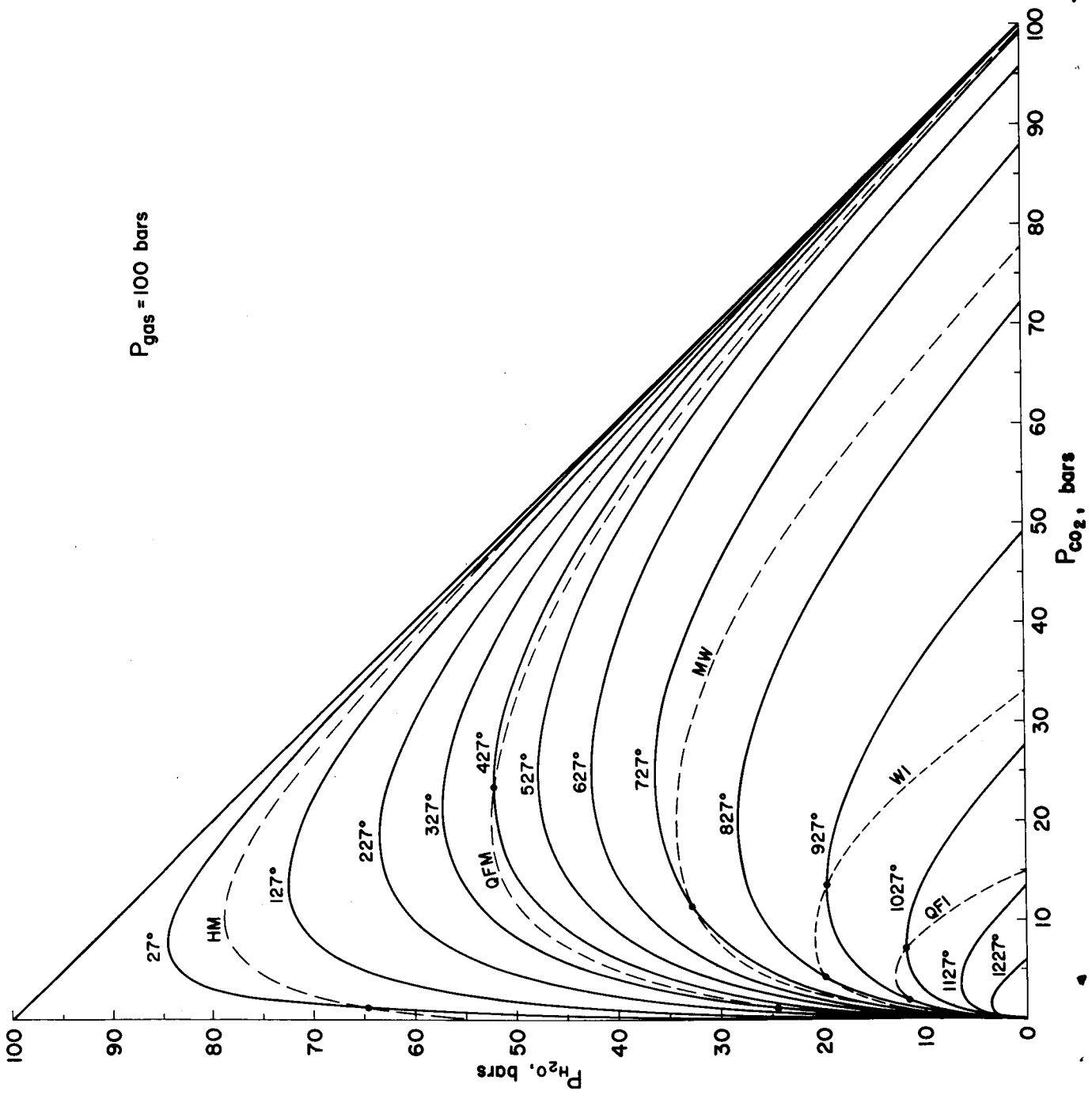
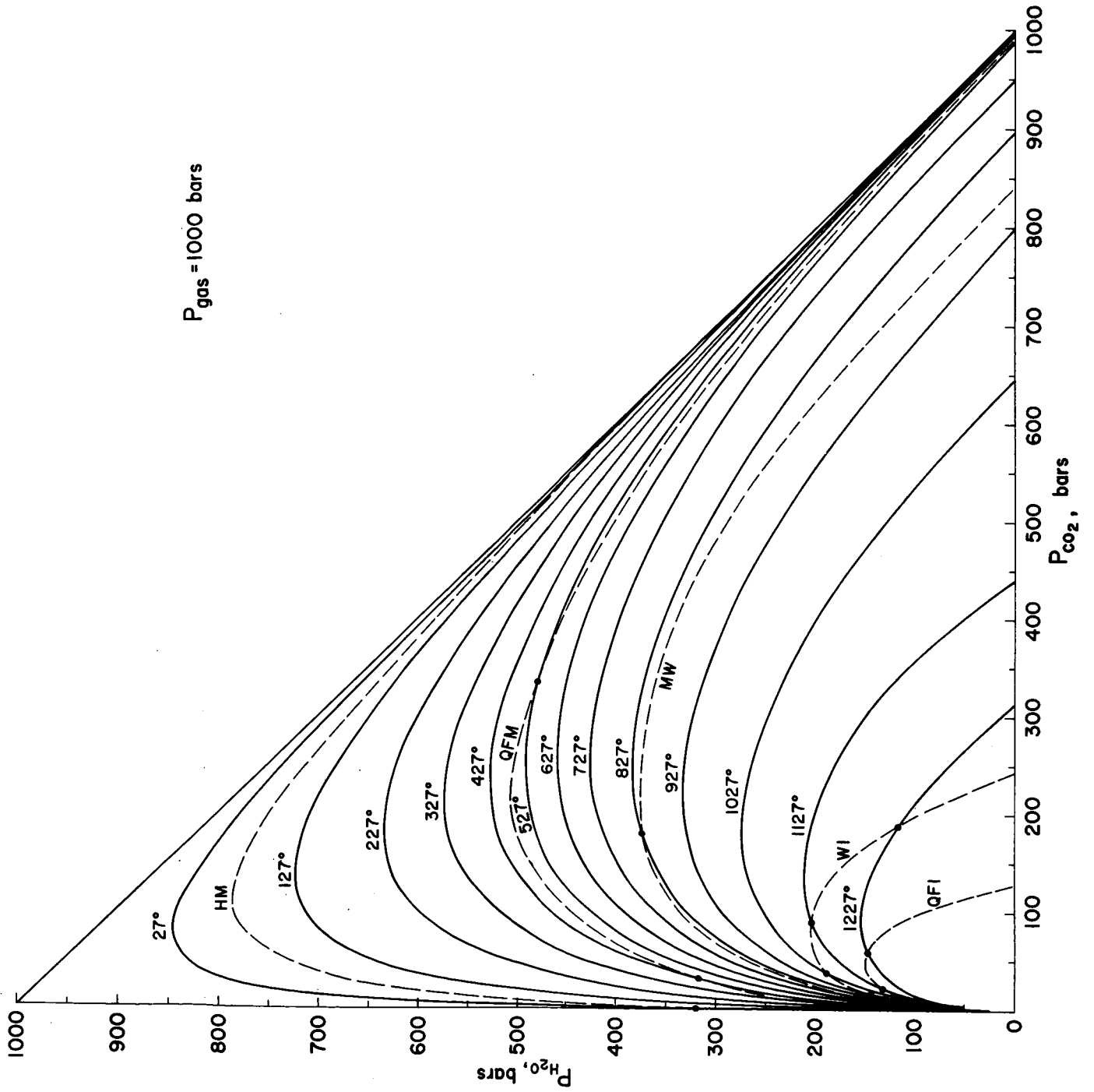


FIGURE 13



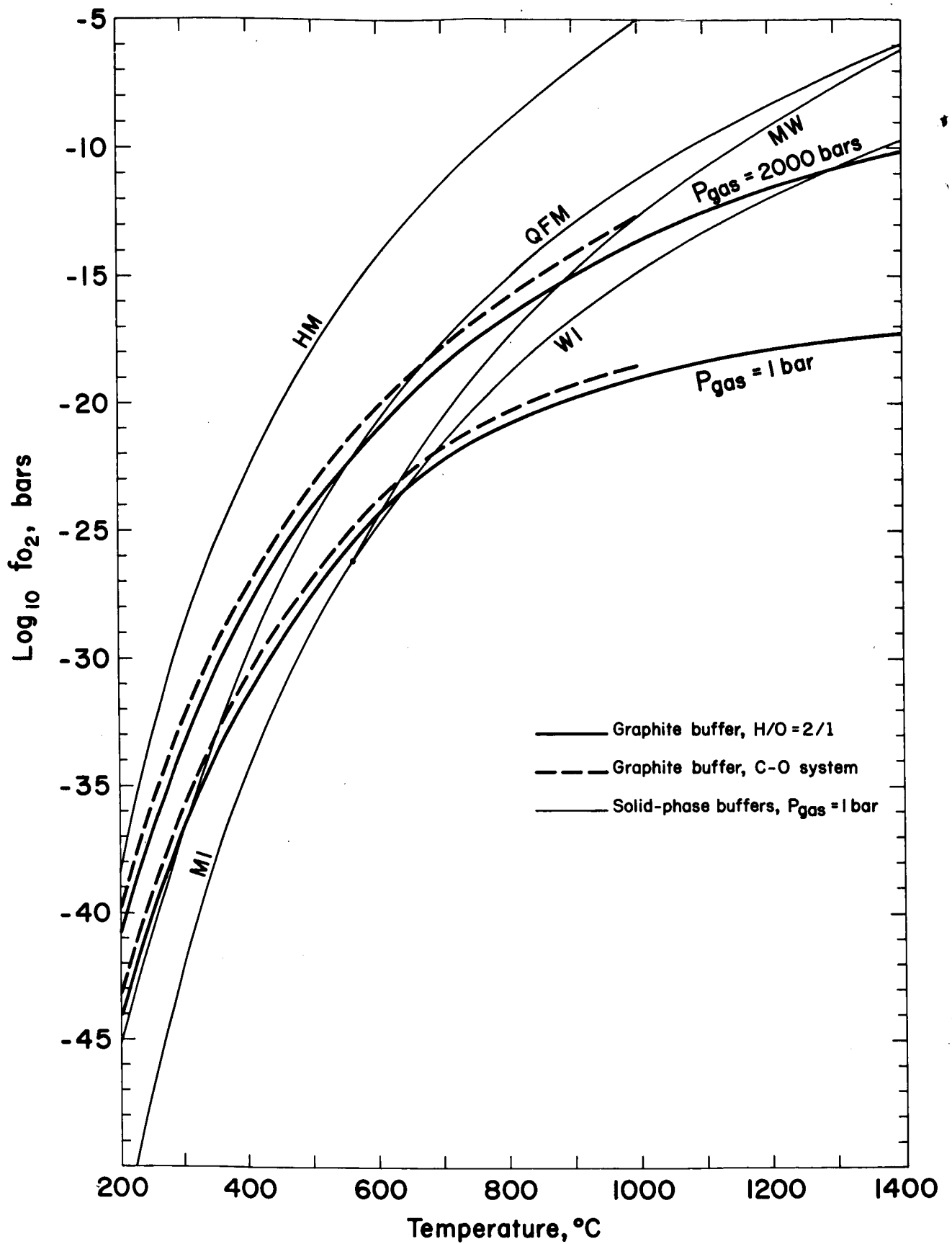


FIGURE 14

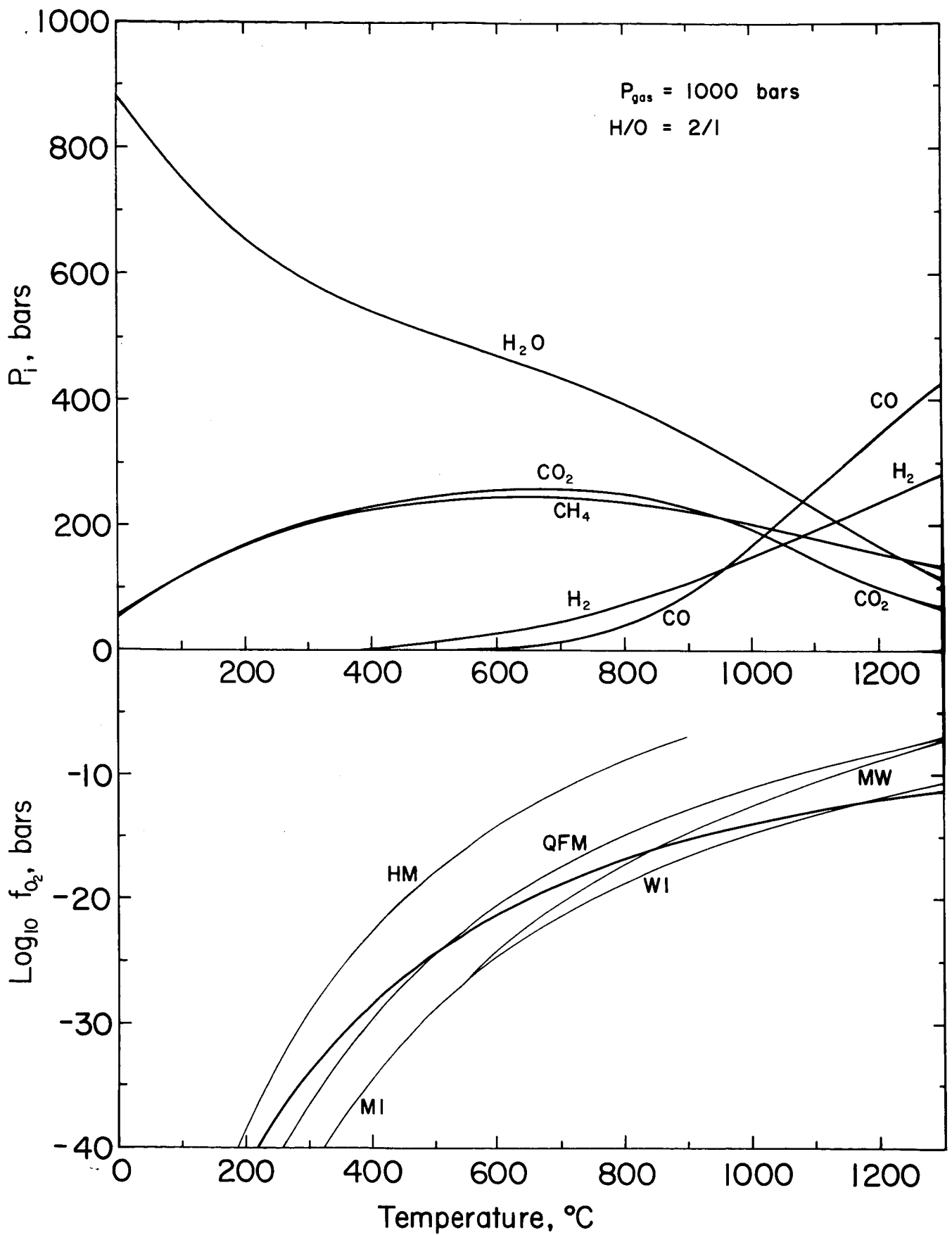


FIGURE 15