X-613-66-456

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SEPTEMBER 21, 1966

GODDARD SPACE FLIGHT CENTER
GREENBELT, MARYLAND

GPO PRICE $

CFSTI PRICE(S) $

Hard copy (HC) 3.00

Microfiche (MF) .65

ff 653 July 65

FACILITY FORM 602

N67 18578
(ACCESSION NUMBER)

(THRU)

38
(PAGES)

1
(CODE)

TMX-55677
(NASA CR OR TMX OR AD NUMBER)

30
(CATEGORY)

X-613-66-456

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ABSTRACT

The conditions for graphite grain formation in cool stars have been examined on the basis of recently available molecular equilibrium data for stellar atmospheres. The Hoyle-Wickramasinghe mechanism for condensation in N stars has been re-examined taking into account the presence of H, O, and N. From Tsuji's (1964) tables, we find that the partial pressure of free carbon in an N star exceeds the vapor pressure of bulk graphite when the temperature falls below 2400K during a pulsation cycle. Formation of graphite grains requires nucleation followed by crystal growth. Using classical nucleation theory it is shown that the supersaturation p/p_{sat} required for graphite condensation on pre-existing

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*On leave of absence from Jesus College, Cambridge, England ions in the stellar atmosphere is only ~ 2.2. Such a supersaturation is reached when the temperature falls to $\sim$ 2300K in an N star. Crystal growth proceeds sufficiently fast at the free carbon pressures appropriate for temperatures greater than 1500K to produce grain sizes exceeding 10^{-6} cm. The actual size to which particles grow is however restricted by the amount of available carbon and the number of effective condensation nuclei. With an ion density $\sim 10^3$ cm^{-3} particle sizes $\sim 5 \times 10^{-6}$ cm would arise. Assuming a constant luminosity function it is shown that 10^5 N stars in the Galaxy (at any time) operating over a timescale of 10^9 years would suffice to produce the required grain density to explain the interstellar extinction.

The possibility that graphite particles may condense in the outer atmospheres of ordinary M giants is also discussed. Graphite condensation may take place to a limited extent in a region of the stellar atmosphere where the temperature falls to about 1600K provided the effective C/O ratio is 1.3. Such a high effective C/O ratio cannot be ruled out on account of uncertainties in the relevant equilibrium calculations.

INTRODUCTION

There now appears to be strong evidence to support the hypothesis that graphite particles are responsible for interstellar extinction or are a major contributor to it. The ultraviolet extinction law recently reported by Boggess and Borgman (1964) and by Stecher (1965) has shown features which appear identifiable with properties of graphite extinction predicted on the basis of Mie computations (Wickramasinghe and Guillaume, 1965; Stecher and Donn, 1965; Krishna Swamy and O'Dell 1966). Over the visible wavelength region detailed agreement has been shown possible between the mean regional extinction curves recently reported by Nandy (1964, 1965) and theoretical extinction curves for graphite particles (Nandy and Wickramasinghe, 1965; Wickramasinghe, 1966). It has also been shown by Wickramasinghe, Donn, Stecher and Williams (1966) that the observed wavelength dependence of interstellar polarization may be explained with either pure graphite grains or graphite core-ice mantle grains, despite the objections pointed out by Greenberg (1966). Further indirect support to the graphite grain theory comes from the recent Stratoscope experiment (Danielson et al., 1965) which failed to detect a strong 3.1μ absorption band to be expected on the basis of ice absorption. On the basis of the optical observations, particularly in the ultraviolet, the evidence clearly favors graphite particles as proposed by Hoyle and Wickramasinghe (1962) over "dirty ice" grains of the type considered by van de Hulst (1946, 1948).

If the graphite particles must exist, as the optical evidence strongly suggests, several questions relating to their formation now demand serious attention. Continual formation and growth of grains is implied by current theories of stellar and galactic evolution. Schwarszchild's calculations (1962) indicate a turnover time of $\sim 10^9$ years for the solar neighborhood. This represents the maximum average lifetime of a graphite grain, and is considerably less than the age of the Galaxy $\sim 10^{10}$ years. Growth to the required dimensions of a sufficient number of grains to account for the interstellar extinction must therefore occur in significantly less than $\sim 10^9$ years. For the more volatile ice grains, destruction in the vicinity of hot stars or in cloud collisions yields even shorter times.

If n_g is the average number density of grains with radius a and efficiency factor for extinction Q_{ext}, the extinction in magnitudes produced over a path length l is

$$\Delta m \cong 1.086\, Q_{ext}\, \pi a^2 n_g l \qquad (1)$$

To produce an extinction of 1 mag per kpc an average of $n_g \cong 3 \times 10^{-11}$ grains per cm^3 are required with a diameter (or length) of 6×10^{-6} cm. This effective size is a consequence of fitting the observed interstellar reddening law using an Oort-van de Hulst distribution. The mean radius is about half as large for a Gaussian distribution (Grevesse-Guillaume, 1966). For spherical particles the resulting mass density of grains is 6×10^{-27} gm cm^{-3}, using a graphite density of 2.2 gm cm^{-3}.

In a preliminary account of interstellar crystal growth (Donn, 1965) it was pointed out that graphite formation in the form of platelets or needles appeared probable. Such structures would result in somewhat lower densities.

The mean atomic hydrogen density near the sun obtained from radio observations is $\sim 10^{-24}$ gm cm^{-3}. The presence of molecular hydrogen with $n_{H2}/n_H \cong 2$ would raise the interstellar density to about 5×10^{-24} gm cm^{-3}. This estimate is also in agreement with the mean interstellar density obtained by Oort (1960, 1965) on the basis of measured accelerations of stars normal to the galactic plane.

Adopting a carbon to hydrogen ratio of 5×10^{-4}, the total carbon density in the interstellar medium is about $\sim 10^{-26}$ gm cm^{-3}. We would thus require about 1/2 the interstellar carbon atoms to be condensed for spherical particles, and somewhat less for platelets or needles.

A stellar source of graphite grains was proposed by Hoyle and Wickramasinghe (1962) who suggested that suitable carbon particles may condense in the carbon rich N stars. Their calculations were, however, for condensation from a pure carbon vapor, neglecting the carbon-hydrogen molecular equilibrium in a system with a C/H ratio of $\sim 10^{-3}$. Equilibrium calculations of Duff and Bauer (1962) using theoretical estimates of free energies for a large variety of hydro-carbons when extrapolated to a C/H ratio of 2×10^{-3} predicts a condensation temperature of ~2100K. Subsequent calculations by Tsuji (1964) for stellar atmospheres indicates that carbon becomes saturated at temperatures below 2200-2400K when the total carbon is greatly in excess of oxygen. These values are somewhat lower than the condensation temperature ~2700K derived by Hoyle and Wickramasinghe (1962) on the basis of condensation in a pure vapor. The lower temperature arises essentially due to the importance of hydrocarbon molecule formation which competes rather seriously for the carbon. In the present paper we re-consider the Hoyle-Wickramasinghe mechanism of carbon condensation in N stars with the conclusion that it appears to be an important source of interstellar grains. We shall also discuss the possibility that graphite particles may be able to condense in the outer atmospheres of ordinary M giants with an effective C/O ratio only slightly exceeding unity.

II. CONDITIONS FOR CARBON SATURATION IN COOL STARS

We consider here the general problem of the saturation of free carbon in stellar atmospheres using the molecular equilibrium data for stellar atmospheres recently published by Tsuji (1964). A necessary, though not sufficient condition for graphite condensation is that the partial pressure of free (uncombined) carbon vapor exceeds the vapor pressure of bulk graphite. This latter quantity as given by Tsuji is tabulated in the table below.

Table 1

Vapor pressure of bulk graphite

T(deg K)	p_{sat}(dyne cm^{-2})	T	p_{sat}
1008	1.5×10^{-23}	2291	7.8×10^{-3}
1120	7.4×10^{-20}	2520	2.3×10^{-1}
1260	3.6×10^{-16}	2800	7.08
1440	1.7×10^{-12}	3150	2.1×10^{2}
1680	8.7×10^{-9}	3600	6.2×10^{3}
1800	2.7×10^{-7}	4200	1.8×10^{5}
1938	8.5×10^{-6}	5040	5.4×10^{6}
2100	8.1×10^{-4}		

These values are in general accord with recent calculations and experiments (JANAF, 1961).

Tsuji (1964) has investigated in detail the molecular equilibrium in stellar atmospheres between 1000 and 8400K for a variety of H, C, N and O abundances. From Tsuji's tables we can obtain for a given composition the partial pressure of free carbon $p = p_C + p_{C_2} + p_{C_3}$ at any temperature. By plotting the free carbon pressure against the C/O ratio at a fixed temperature, H:C:N ratio and a given total gas pressure the critical C/O ratio at which the carbon becomes saturated may be obtained. Representative curves of free carbon pressure against C/O for a total gas pressure $p_g \cong 10^4$ dyne cm^{-2} and H:C:N $\cong 1:5.10^{-4}:10^{-4}$ are shown in Figure 1. Although these curves have been constructed for the case $p_g \cong 10^4$ dyne cm^{-2}, the results are not sensitive to the precise value of p_g(see Table 2 and Fig. 3) for temperatures close to 2000K. The reason for this feature has been discussed by Tsuji (1964) in terms of the relevant chemical equilibria.

The temperature T_{sat} at which the pressure of free carbon equals the vapor pressure of graphite is obtained from the curves in Fig. 1 together with Table 1 as a function of the C/O ratio. The resulting curve of T_{sat} against C/O is plotted in Figure 2. The curves of Fig. 2, however, cannot be drawn too accurately from Tsuji's data in the interval $1 < C/O < 2$ as there are no intermediate points and the slopes change by a large amount. This introduces an uncertainty in the saturation temperature plotted in Fig. 2

From Fig. 2 it is seen that for a C/O ratio ~1.1 the saturation temperature is 1000K; for C/O ≅ 2 it rises to 2000K, reaching 2400 at C/O ≅ 5. These results are generally consistent with the saturation temperature of 2100K extrapolated from the analysis of Duff and Bauer (1962) for a pure C-H system. This agreement confirms the general validity of the calculations. Although the procedure adopted by Tsuji to obtain the saturation temperature differed from that of Duff and Bauer, Tsuji used the hydrocarbon free energies estimated by the former authors, so that a systematic error cannot be excluded.

III. SATURATION OF FREE CARBON IN N STARS

A high C/O ratio, probably exceeding 2, and photospheric temperatures below 2200K are likely to be realized for the N stars in the carbon sequence (Keenan, 1960). These conditions appear most favorable for the saturation of carbon vapor and formation of graphite particles as seen in the previous section. The R stars have temperatures upwards of 3500K and are therefore not as effective in grain formation.

For a typical N star we consider one whose effective temperature varies in the general range 1800-2500K during a pulsation cycle. We also assume an atmospheric composition similar to case VIII of Tsuji's analysis, viz, $H:C:N = 1: 5.10^{-3}:10^{-3}:10^{-3}$, corresponding to a C/O ratio of 5. Our results based on calculations for this case are however expected to hold good for $C/O \geq \sim 1.8$. We shall return to this point in Section IX. The pressure of free carbon for this composition is given in Table II and Figure 3 as a function of the temperature with (1) a total gas pressure $p_g \cong 1$ dyne cm^{-2}, (2) a total gas pressure $p_g \cong 10^4$ dyne cm^{-2}. The vapor pressure of bulk graphite is plotted as the dashed curve in Fig. 3. For the case $p_g \cong 10^4$ dyne cm^{-2} it is seen that the carbon vapor becomes aturated at $T \cong 2400K$ and for the case $p_g \cong 1$ dyne cm^{-2} the saturation temperature is 2100K.

As the temperature falls below the saturation value during a pulsation cycle two possibilities are open. Either graphite particles may condense, lowering the carbon pressure to the vapor pressure of graphite, or the carbon pressure to the vapor pressure of graphite, or the carbon vapor would become increasingly supersaturated with respect to the bulk phase. For reasons to be discussed in section IV we consider the former alternative to be more likely.

The condensation of graphite particles even in small quantities has the effect of raising the surface opacity of the star several orders of magnitude above that determined by H^-. The result is a thinning out of the stellar atmosphere as pointed out by Hoyle and Wickramasinghe (1962).

At a certain phase of the condensation process suppose a fraction x of the total carbon is condensed into platelets of radius a and thickness w. The mass absorption coefficient k for such grains is given by

$$k \cong \frac{1}{2} \frac{\pi a^2 Q_{ext}}{\pi a^2 w s} = \frac{Q_{ext}}{2 w s} \; cm^2 \, gm^{-1} \qquad (2)$$

where s is the density of graphite, Q_{ext} is the efficiency factor for extinction and the factor 1/2 allows for random orientation of the platelets. For a particle of radius $a \cong 3.10^{-6}$cm, $Q_{ext} \cong 0.2$ at $\lambda \approx 8400$A. For smaller particles the variation in $Q_{ext} \approx 0.2a/3.10^{-6} \approx 7 \times 10^{4}a$. (Guillaume and Wickramasinghe, 1966). With a platelet thickness 5×10^{-7} cm and a graphite density $s = 2.2$ gm cm^{-3} the mass absorption coefficient given by (2) is

$$k = 3 \times 10^{10}\, a \ \mathrm{cm}^2\, \mathrm{gm}^{-1} \tag{3}$$

The mean absorption coefficient per cm^3 of the stellar atmosphere is therefore

$$\left(5\times10^{-3}\frac{P_g}{kT} . 12 m_H x\right) 3\times10^{10} a \ \mathrm{cm}^2 \tag{4}$$

where x is the fraction of carbon condensed.
Multiplying by the scale height $\sim kT/2m_H g$, where g is the surface gravity, the photospheric condition (optical depth $\cong$ unity) is

$$10^9 a x g P_g \sim 1 \tag{5}$$

For a giant star with $g \approx 1$ cm sec^{-2} we have

$$P_g \cong 10^{-9} a^{-1} x^{-1} \tag{6}$$

With a percent ($x \cong 10^{-2}$) of the total carbon condensed into particles of radius $a \cong 10^{-7}$ cm the total gas pressure given by equation (6) is $p_g \cong 1$ dyne cm^{-2}. The growth process of grains from initial nuclei would therefore be expected to take place under conditions where the total gas pressure has fallen from an initial 10^2 - 10^3 dyne cm^{-2} to $\sim$ 1 dyne cm^{-2}. The gas pressure further decreases as grains grow to larger sizes depleting more of the available carbon. With $x \approx 1$, $a \cong 10^{-6}$cm, $\sim p_g = 10^{-3}$ dyne cm^{-2}. As pointed out by Hoyle and Wickramasinghe (1962), it is this low density that permits the escape of grains.

IV. NUCLEATION OF GRAINS IN N STARS

The total carbon density in the photosphere before nuclei begins to form is $\sim 10^{12}$ cm^{-3}. The number of carbon atoms in the grain of radius $\sim 3.10^{-6}$ cm is $\sim 10^{7}$. An effective condensation of all the carbon (or an appreciable fraction of it) into grains of this size over a pulsation period would require a production of $\sim 10^{5}$ stable nuclei per cm^{3} in 10^{7} seconds, or a nucleation rate of $\sim 10^{-2}$ cm^{-3} sec^{-1}.

A stellar atmosphere is sufficiently near thermodynamic equilibrium that classical nucleation theory may be applied (Turnbull, 1956; Hirth and Pound, 1963). This theory envisages the presence in the vapor phase of multiatomic carbon particles, having a positive free energy of formation, but existing in finite concentrations because of the entropy of mixing associated with their presence in the vapor. The size distribution of these particles is given by

$$n_i = n_1 \exp(-\Delta G_1/kT) \qquad (7)$$

where n_i is the number density of clusters containing i atoms, n_1 is the number density of the monomer species around which particles may form, and ΔG_i is the Gibbs free energy of formation of the cluster. Initially, ΔG_i increases as atoms are added, but at a critical size the free energy begins to decrease, making the aggregate more stable with further addition of atoms. It is envisaged that particles build up by a series of bimolecular reactions where each reaction increases the particle size by a single atom. The rate of formation of condensation nuclei is the rate of that particular reaction which increases the cluster size from the critical size associated with the free energy maximum to the next larger size by the addition of a single atom.

Further growth proceeds spontaneously with continuing reduction of free energy. The rate of this critical reaction, that is the nucleation rate, J, is given by

$$J = \omega n_{i*} \tag{8}$$

where ω is the rate of addition of single atoms to a critical cluster and n_i* is the critical cluster concentration. With n_i* given by equation (7) wherein ΔG_i is set equal to ΔG_i*, the free energy of formation of the critical cluster, we have

$$J = \omega n_1 \exp(-\Delta G_{i*}/kT) \tag{9}$$

The critical sized clusters may form by at least three reaction paths in the stellar atmosphere: (1) by the growth of a particle of the pure condensing species through a series of bimolecular reactions; (2) by the formation of a particle of the condensing species around a pre-existing ion in the vapor; or, (3) by the formation of a particle around some pre-existing molecular aggregate of a different chemical species. Let us now consider each of these alternatives.

In the first case, for homogeneous nucleation, ΔG_i* is given by

$$\Delta G_{i*} = \frac{16\pi\sigma^3}{3\Delta G_v^2} \tag{10}$$

where σ is the surface energy of the particle and ΔG_ν is the volume free energy change accompanying condensation. (Turnbull, 1956) ΔG_ν is given by

$$\Delta G_v = -\frac{kT}{\Omega} \ln \frac{p}{p_{sat}} \tag{11}$$

where Ω is the volume per molecule, p is the ambient free carbon pressure, p_{sat} is the vapor pressure of bulk carbon at the ambient temperature T. The pre-exponential terms in (9) for this case, ωn_1 are given by

$$\omega n_1 = \alpha \left(4\pi r^{*2}\right) \frac{p}{(2\pi m k T)^{1/2}} Z n_1 \qquad (12)$$

where α is the sticking coefficient for vapor impinging on the cluster, $4\pi r^{*2}$ is the surface area of the critical sized cluster $p/(2\pi mkT)^{1/2}$ is the impingement rate of single carbon atoms on unit area of cluster, and Z is a non-equilibrium factor that takes into account the depletion of critical clusters by formation of stable nuclei. At moderate supersaturations r^* may be approximated by

$$r^* \approx \frac{-2\sigma}{\Delta G_v} \qquad (13)$$

(Turnbull, 1956). With $\omega \sim 10^2$ sec^{-1}, $n_1 \sim 10^8$ atom cm^{-3}, $\sigma \sim 1000$ erg cm^{-2} and using (11) and (13) the pre-exponential factor is $\sim 10^{10}$. Consequently to achieve the desired nucleation rate, we require that

$$\exp(-\Delta G_{i^*}/kT) = \frac{J}{\omega n_1} \geq 10^{-12} \qquad (14)$$

that is

$$\Delta G_{i^*} \leq 28\,kT \qquad (15)$$

This result may be expressed alternatively in terms of the supersaturation ratio by using equations (10) and (11) with $\sigma \sim 1000$ erg cm^{-2}, $\Omega \sim 10^{-23}$ cm^3 and T $\sim$1500K. This yields

(16)

$$\frac{\rho}{\rho_{sat}} \geq 12 \qquad (16)$$

as the supersaturation required to produce the desired nucleation rate by the pure particle mechanism.

Alternatively, we may consider the process of forming a graphite nucleus around a pre-existing ion in the vapor. For this case, the free energy of formation of the critical-sized cluster is given by

$$(\Delta G_{i*})_{ion} = \frac{4\pi\sigma}{3}\left(r^{*2} - r_1^{2}\right) - 2e^{2}\left(1-\frac{1}{\varepsilon}\right)\left(\frac{1}{r_1} - \frac{1}{r^*}\right) \qquad (17)$$

where r_1 is the radius of the equilibrium subcritical cluster which forms spontaneously around a free ion in the vapor, and ε is the dielectric constant of the particle (Hirth and Pound, 1963). At moderate supersaturations r_1 may be approximated by

$$r_1 \approx \left(\frac{e^{2}}{16\pi\sigma}\right)^{1/3} \qquad (18)$$

and r^*, as before, by (13). For this case, the pre-exponential factor in (9) is given with the same ω as in the preceding case, provided n_1 is replaced by n_c, the number density of ions in the region of interest. We take $n_c \sim 10^{6}$ ions cm^{-3}, arising from ionization of metallic elements which could yield $10^{4} - 10^{7}$ per cm^{3}. With $\omega \cong 10^{2}$ sec^{-1} as before we obtain as our condition for the nucleation rate

$$\exp\left[(-\Delta G_{i*})_{ion}/kT\right] = \frac{J}{\omega n_c} \geq 10^{-10} \qquad (19)$$

that is,

$$(\Delta G_{i*})_{ion} \leq 23\,kT \qquad (20)$$

Again we may express this result in terms of the supersaturation ratio by solving equations (11), (13), (17) and (18) with $\epsilon = 1$. This yields

$$\frac{\rho}{\rho_{sat}} \geq 2.2 \tag{21}$$

as the required condition for nucleation on ions.

For the third case, that of nucleation of graphite on a pre-existing molecular species, no detailed theory exists from which quantitive results may be obtained. A small molecule may conceivably act so as to reduce the volume free energy of a cluster, hence facilitating nucleation. If the molecule is sufficiently large, it may resemble a surface site for heteregenous nucleation of graphite. In either case the effect would be to further reduce the supersaturation required to obtain the desired nucleation rate. In the stellar atmosphere, it does not seem likely that the presence of molecules would be significant for nucleation compared to nucleation on ions or even homogeneous nucleation.

The conditions for obtaining the desired nucleation rate $\sim 10^{-2}$ cm^{-3} sec^{-1} through each of the reaction paths considered here may be summarized as follows:

$$\begin{aligned} \left(\frac{\rho}{\rho_{sat}}\right)_{homogeneous} &\geq 12 \\ \left(\frac{\rho}{\rho_{sat}}\right)_{ion} &\geq 2 \end{aligned} \tag{22}$$

Thus it appears that both the pure particle and ion mechanism will operate at very low supersaturations, with the ion mechanism being the easiest. It may further be noted that the critical supersaturation ratio in the ion case is not too sensitive to the free carbon concentration assumed. Moreover, from (15) and (17) it may be shown that a change in the ratio of nucleation rate to ion density J/n_c by a factor $\sim 10^6$ causes the critical supersaturation ratio to change only by a factor less than 2. Our result (21) is therefore not sensitive to the assumed values of J and n_c.

From Figure 3 it is seen that a supersaturation $p/p_{sat} \approx 10$ may be obtained when $T_{eff} \approx 2100K$, in the stellar photosphere. An even higher supersaturation may arise in the "boundary" of the stellar atmosphere where the optical depth $\tau \approx 0$. The boundary temperature in radiative equilibrium corresponding to an effective temperature $\sim$ 2100K is $T_{eff}/2^{1/4} \approx 1700K$. The total gas pressure in this region would have decreased from its photospheric value by a few powers of 10, but the free carbon pressure would have decreased only by a factor of order unity. From Fig. 3 it is seen that a supersaturation ratio p/p_{sat} in the range $10^2 - 10^3$ may arise in such a region where the temperature is $\sim$1700K. Condensation of carbon grains is thus likely to begin in a region somewhat above the photosphere and spread inwards as the temperature falls during the pulsation cycle.

V. CRYSTAL GROWTH

Provided the nucleation requirements are satisfied solid particles will begin to grow out of the carbon vapor. If condensation occurs at high supersaturation an appreciable proportion of polycrystalline soot-like particles may be expected form. At low supersaturations, on the other hand, platelet or whisker growth will be favored (Donn and Sears, 1963). For the case of condensation in N stars, at intermediate p/p_{sat} ratios, both polycrystalline particles as well as platelets and whiskers are to be expected.

We first consider the growth of a spherical polycrystalline grains. In carbon stars where $p_c > p_{sat}$ the rate of growth of such a particle of radius r is given by

$$\frac{dr}{dt} = \alpha \frac{p_c}{s} \left(\frac{1}{2\pi m k T} \right)^{1/2} \qquad (23)$$

where α is the sticking coefficient, p_C is the vapor pressure of free carbon, m is the mass of a C atom, T is the temperature and s is the density of graphite. With $\alpha \cong 0.5$ (Thorn and Winslow, 1957), $s \cong 2.2$ gm cm^{-3}, $T \cong 2.10^3$K we have

$$\frac{dr}{dt} \cong 10^{-6} p_c \text{ cm sec}^{-1} \tag{24}$$

Thus for a particle to be able to grow to a size $r \cong 3.10^{-6}$cm, or larger, in a time-scale $\sim 10^7$ sec we have the following condition on the free carbon pressure:

$$p_c \geq 3 \times 10^{-7} \text{ dyne cm}^{-2} \tag{25}$$

It is seen from Fig. 3 (Table 2) that this condition is satisfied at temperatures exceeding 1600K. If condition (25) is satisfied as a strict inequality the resulting particle size will exceed 3.10^{-6} cm provided there is an unlimited supply of free carbon. The size to which particles may grow is, however, likely to be modulated by the number of available condensation nuclei (in this case ions) and the limited supply of carbon atoms. Before condensation begins the total photospheric carbon density is 10^{12} cm^{-3} and the ion density is 10^3 - 10^4 cm^{-3} (from ionization of Na, Ca). If all the carbon is able to condense this sets an upper limit to the number of carbon atoms per grain in the region 10^8 - 10^9, resulting in a grain radius $\sim 5.10^{-6}$ cm. Larger grains, even if they are able to form, would not be effectively pushed out by the radiation pressure. The critical radius for escape is also $\sim 10^{-5}$ cm (Hoyle and Wickramasinghe, 1962).

Next consider the mechanism of platelet or whisker growth. Such particles are composed mostly of smooth, low index crystal planes, except where this symmetry is disturbed by dislocations. These dislocations emerge to form growth steps in one or two crystallographic directions. Molecules incident on the nearly perfect faces diffuse over the surface until they either re-evaporate or become trapped at the step associated with a dislocation. Molecular trapping causes the steps associated with screw dislocations to rotate around the dislocation axis and therefore perpetuate themselves. At low supersaturations, two dimensional nucleation on the surface cannot occur and continual growth only occurs via the dislocation mechanism and only along the direction normal to the dislocated surface. Growth along a single such axis leads to the formation of whiskers. A two dimensional array of dislocations produces platelets.

The growth rate of these crystals depends on the area over which molecules are collected and diffuse to the growing tip or edge. This is in turn related to the crystallite radius and the mean diffusion path on the surface. The mean diffusion path λ, or the mean distance which an incident atom diffuses before re-evaporating, is given by

$$\lambda = 2a \exp\left(\frac{W' - U}{2kT}\right) \tag{26}$$

where a is the lattice spacing and jump distance, W' is the adsorption energy and U is the activation energy for diffusion determined by the potential barrier which must be overcome in jumping from one site to the next.

The formation of graphite whiskers by decomposition of hydrocarbons on carbon filaments at 2000K (Meyer, 1957) indicates diffusion to the whisker tip from an appreciable area. This implies an adsorption energy W' comparable to the chemisorption energy ~2 ev. Calculations of the activation energy U for inert gases resulted in nearly zero values (Young and Crowell, 1961) so that $W'-U \approx 2$ ev in our case. With $a \approx 3.10^{-8}$ cm equation (26) gives $\lambda \approx 7 \times 10^{-6}$ cm at T = 2000K increasing to 4×10^{-5} cm at T = 1500K. Thus, in our case where the final particle size is $\sim 6 \times 10^{-6}$ cm, the whole growth process proceeds under conditions where $r < \lambda$.

The growth rate of a platelet under these conditions may now be calculated using the equation (Sears, 1951).

$$r = 2r_0 \exp\left(\frac{J\Omega t}{w}\right) - r_0 \qquad (27)$$

where r_o is the initial platelet radius, J is the impinging molecular flux, Ω is the atomic volume, $\sim 10^{-23}\text{cm}^3$, w is the platelet thickness (assumed constant throughout growth) and t is the time. The molecular flux J is related to the free carbon pressure p_C by

$$J = \frac{p_c}{(2\pi mkT)^{1/2}} \qquad (28)$$

where T is the temperature. Assuming a platelet thickness $w \cong 5 \times 10^{-7}$ cm and an initial radius $r_o \cong 10^{-7}$cm in equations (27) and (28) we find that growth $\sim r \cong 3 \times 10^{-6}$ cm in a time-scale of $\sim 10^7$ sec requires a free carbon pressure $p_C \geq 7 \times 10^{-9}$ dyne cm^{-2}. From Table II it is seen that this condition is satisfied provided T $>$ 1440K in a region of the stellar atmosphere.

VI. THE POSSIBILITY OF GRAPHITE FORMATION IN M STARS

Although the generally accepted value of C/O in these stars is about 0.5 there is some uncertainty in this quantity (Aller, 1961), and a value close to, but less than, unity has recently been obtained by Spinrad and Vardya, (1966). It cannot at the present moment be ruled out that the total carbon concentration in M stars exceeds the oxygen by a small margin, the excess being in the form of free carbon and hydrocarbons which are present in such trace quantities as to remain undetected. In the present section we shall investigate the overall requirements for a small fraction of the total carbon to condense as graphite particles. It has already been pointed out that the presence of graphite particles would explain several observed atmospheric phenomena. Wickramasinghe, et al. (1966) have shown that the condensation of 0.1 percent of the total carbon into grains of radius $\sim 10^{-6}$ cm could account for the observed mass loss from these stars. The recently observed intrinsic polarization in Mira variables (Serkowski, 1966) also strongly suggests a mechanism involving graphite platelets (Donn, et al. 1966).

The many parameters entering in molecular equilibrium calculations used to infer the C/O ratio are uncertain, and errors in these parameters may appreciably affect the pressures of trace quantities such as C, C_2 and C_3. The anomalous intensity of water vapor lines in red giants recently observed by a balloon borne telescope (Danielson et al., 1965) suggests that more oxygen is tied up in H_2O than has been deduced on the basis of equilibrium calculations. This could significantly increase the free carbon pressure above that indicated by Tsuji's calculations.

From Fig. 2 it is seen that the critical C/O ratio for condensation at 2000K is ~2; at 1700 it is ~1.5; at 1600K it is ~1.3, and 1000K it is 1.05. At very low temperatures ~1000K, even though the carbon vapor is saturated with a C/O ratio very close to unity, the free carbon pressure is too low to produce significant growth in 10 years.

Particle growth in M stars is likely to take place at very low supersaturations, so that equation (27) will be appropriate for the growth rate. The condition that an initial nucleus of radius $r_o \cong 10^{-7}$ cm can grow to a radius $r \cong 3.10^{-6}$cm during the time scale for escape ~10 years is therefore

$$P_c \geq 2\times 10^{-10} \text{ dyne cm}^{-2} \tag{29}$$

Condition (29) is satisfied provided T ≥1600 (Table), on the assumption that $P_C \approx P_{sat}$. The critical C/O ratio for this case is 1.2-1.3.

Effective temperatures below 2000K are found only in M giants later than spectral type M8. For a given effective temperature T_{eff}, however, the boundary temperature in the atmosphere is somewhat lower. Assuming radiative equilibrium $T_b \cong T_{eff}/2^{1/4}$. A boundary temperature ~2000, thus corresponds to an effective temperature ~ 2400, appropriate to class M6.

Tsuji's tables show that the carbon pressure (pressure of uncombined C) changes only by a factor ~1 - 10 for a change in the total pressure by $\sim 10^5$, under conditions such that the carbon pressure can reach saturation value. Hence at a distance beyond the photospheric boundary where the pressure has fallen off by several orders of magnitude and the temperature reaches the critical value, the free carbon will be saturated. Unless there is a chromospheric temperature rise we may expect either within the photosphere in very late type M giants, or somwehat beyond it in earlier type stars, to find a region where the carbon vapor becomes saturated and graphite condensation takes place. The envelope mechanism receives some support from Wyller's (1966) work on carbon stars where he finds C_2 vibrational temperatures less than the effective temperature and suggests that one may be observing C_2 in a region beyond the photospheric boundary.

We have already pointed out in Section V that graphite grains would tend to condense as platelets at low supersaturations, and as polycrystalline soot-like particles at relatively high supersaturations. On this basis platelet formation may be expected at the low supersaturations likely to be realized for the M stars. It is of interest to note here that the intrinsic polarization recently observed for M stars (Serkowski, 1966) follows a λ^{-1} dependence appropriate for graphite platelets (Donn, Stecher, Wickramasinghe and Williams, 1966). For one N star, however, for which intrinsic polarization measurements are available, the polarization is quite flat over the visible spectrum. This is in agreement with the hypothesis that in the highly supersaturated atmospheres of the carbon stars the smaller particles would be nearly spherical non-polarizing polycrystalline particles, and a small proportion of large platelets present would give rise to the flat polarization curve (Wickramasinghe, Donn, Stecher and Williams, 1966).

VII. RATE OF PRODUCTION OF GRAPHITE GRAINS

The mass density of graphite platelets required to give rise to a visual extinction of 1 mag/kpc is $\sim 10^{-27}$ gm cm ^{3}. The estimated turn over time in the solar neighborhood being $\sim 10^{9}$ years (Schwarszchild, 1962) we require this grain density to be built up in a time scale $\sim 10^{9}$ years.

For the assumed H;C:N:O composition of an N star Tsuji estimates the mass fraction of the total carbon that may be condensed at a given temperature ($<T_{sat}$) for a variety of values of the total gas pressure (Figure 5). The procedure adopted is as follows: For a given value of $T < T_{sat}$ it is assumed that bulk graphite has condensed to such an extent that the free carbon partial pressure p_c equals the vapor pressure p_{sat}. Setting $p_c = p_{sat}$ the equilibrium abundances of all the molecular species containing C are computed, so that the total density of gaseous carbon atoms in the form of monatomic and polyatomic gas and in other molecules is known. Subtracting this from the total carbon density of the initial composition the amount that has condensed is determined.

With a total gas pressure ~ 1 dyne/cm^{2} or less we may expect $\sim 60\%$ of the total carbon in the atmosphere to be condensed when the temperature falls to ~ 2000K. The estimate obtained by Hoyle and Wickramasinghe for the rate of grain production assuming essentially all the C condensing into grains was of the order of $\sim 5.10^{26}$ gm per year per star. The rate obtained here would be about half that value. Distributed throughout the volume of the interstellar medium $\sim 10^{66}$ cm^{3} the rate is $\sim 5.10^{-40}$ gm cm^{-3} per year per star and over $\sim 10^{9}$ years the production is 5.10^{-31} gm cm^{-3} per star. On the assumption of a constant luminosity function the number of N stars required to produce a grain density of 10^{-27} gm cm^{-3} is $\sim 2 \times 10^{3}$. This is considerably less than the total number of N stars according to the best estimates. The total number of N stars included in the surveys by Nassau and Blanco (1954) and by Blanco and Munch (1954) covering a 4° belt around the Lund Galactic equator (1955) add up to $\sim 10^5$. It would thus suffice if a few percent of the N stars are efficient in grain formation.

For an M star with an effective C/O $\cong$ 1.5 the mass fraction of the total carbon which condenses as graphite at a particular temperature below T_{sat} will be expected to be very small. Condensation will take place under conditions where the partial pressure of free carbon gas exceeds the vapor pressure of bulk graphite by only a small margin, say a factor of order unity. The mass fraction condensed at a given temperature may then be approximated as

$$M \approx \frac{p_c - p_{sat}}{P(C)} \qquad (30)$$

where p_C is the free carbon pressure in the absence of condensation p_{sat} is the vapor pressure of bulk graphite and P(C) is the total carbon pressure if all the carbon were uncombined. If we write

$$p_c \approx y \, p_{sat}$$

where y is a factor of order unity, we have from (30),

$$M \approx (y-1) \, p_{sat}/P(C) \approx p_{sat}/P(C) \qquad (31)$$

With C/O $\approx$ 1.5, $T_{sat} \approx 1700^{\circ}$K from Fig. 2 so that $p_{sat} \approx 5.10^{-8}$ dyne/cm^2. The total carbon pressure $P(C) \approx 5.10^{-4} p_g$. Although the photospheric value of p_g is $\sim 10^2$ dyne cm^{-3} a much lower value of p_g is appropriate in the region where the temperature falls to 1700°K. If p_g is in the range 10^{-1} to 10^{-2} dyne cm^{-3}, M is in the range 0.1 percent to 1 percent by equation (31).

The observed mass loss rate from an M star is $\sim 10^{-6} M_{\odot}$ per year. The rate of supply of graphite grains assuming 0.1 percent of the carbon condensed is therefore $\sim 5 \times 10^{-13} M_{\odot}$ year^{-1} per star $\approx 10^{21}$ gm yr^{-1} per star. Distributed throughout the galaxy this gives a rate of increase in mass density of grains $\sim 10^{-45}$ gm cm^{-3} per year per star. To produce a density $\sim 10^{-27}$ gm cm^{-3} in 10^9 years one therefore requires $\sim 10^9$ M giant stars at any given time. This is considerably greater than the available number which is probably $\sim 10^6$. The M giant stars therefore do not contribute to more than about 0.1 percent of the required interstellar grain density.

VIII. COMPLEX MOLECULES

The theoretical calculations of Duff and Bauer and of Tsuji show that a considerable number of complex molecules form in atmospheres of carbon stars. Ejection of graphite grains by radiation pressure would carry along a substantial fraction of the atmosphere including these molecules (Wickramasinghe et al. 1966). Tsuji has already pointed out that carbon stars are a potential source of complex molecules in interstellar space. Their subsequent history, including their role as a possible source of graphite nuclei in space (Donn, 1965) and their relation to F. Johnson's (1965) mechanism for producing the diffuse interstellar bands, require further study.

Graphite grains formed near the photosphere would have to traverse a considerable thickness of an atmosphere containing these complex molecules before escaping to interstellar space. At distances from the star where the temperature of the expanding envelope has become low enough hydrocarbon molecules may be absorbed on grain surfaces. This would affect the chemical properties of both grains and molecules. Two important processes involved in this are molecular formation on the grain surface and the building of a molecular mantle. These molecular phenomena will be considered in a later paper.

IX. CONCLUDING REMARKS

We have seen in the preceding sections that graphite particles could nucleate and grow under the conditions assumed for N stars. Although the discussion for N stars was based on equilibrium calculations for the case C/O = 5, our conclusions are not expected to be significantly different if a lower value of C/O was appropriate. It is seen from Fig. 1 that the free carbon pressure varies by an order of magnitude in the C/O range 1.8-5. The atmosphere throughout this range is highly supersaturated with respect to carbon in the temperature interval between 1600 and 2000K. Therefore the results quoted in the preceding sections are not very sensitive to the precise value of C/O.

Other parameters important for determining condensation criteria are T and n_H. For the N stars we adopted the photospheric T_{eff}, and n_H initially determined by the H^- opacity. We saw that when particle growth is completed the photospheric n_H falls by a factor 10^4 due to the opacity of solid graphite. For a discussion of the graphite condensation process higher up in the atmosphere at optical depth $\tau < 1$ we would require a model of the stellar atmosphere. Reliable model atmosphere calculations for late type stars are not at present available; such models taking into account the opacity due to complex molecules and solid particles are now urgently needed. The structure of the atmosphere before condensation begins will determine rate and amount of precipitation. The opacity arising from the precipitated grains would then in turn modify the atmospheric parameters.

For M stars with T_{eff} ~3000K Tsuji (1966), taking into account the opacity due to H_2O and CO, has calculated a boundary temperature ~ 1300K. Such a low boundary temperature would certainly favor the graphite condensation process in M stars with an effective C/O ratio only slightly in excess of unity. A similar effect, of low boundary temperature, is also likely to apply for the carbon stars, again, permitting graphite condensation further out in the stellar atmosphere.

Another question that requires further discussion is the amount of impurity atoms that may be incorporated in graphite grains. If grains are grown at high supersaturations in carbon stars, an appreciably amount of silicon may be included in the polycrystalline grain structure. Tsuji's (1964) free silicon values indicate that the silicon partial pressure exceeds that of carbon, although the atmosphere is not saturated with respect to bulk silicon. At low supersaturations, however, relatively pure graphite should tend to form -- a case which may be relevant for the M stars. Reflection measurements on coals of various compositions (McCartney and Ergun, 1957) indicate that considerable quantities of impurity may be present without changing the optical properties too drastically from that of graphite.

TABLE II

Partial pressure of free carbon in an N star atmosphere with H:C:N:O = 1: 5.10^{-3}: 10^{-3}:10^{-3}

T (deg. K)	Free carbon pressure ($C + C_2 + C_3$), dyne cm^{-2} (p_g = 1 dyne cm^{-2})	(p_g = 10^4 dyne cm^{-2})
1008	4.6×10^{-16}	1.7×10^{-21}
1120	1.3×10^{-13}	4.2×10^{-16}
1260	3.6×10^{-11}	2.7×10^{-11}
1440	9.4×10^{-9}	2.6×10^{-8}
1680	1.5×10^{-6}	8.8×10^{-6}
1800	8.6×10^{-6}	8.5×10^{-5}
1938	5.0×10^{-5}	8.5×10^{-4}
2100	3.8×10^{-4}	7.0×10^{-3}
2291	2.2×10^{-3}	5.1×10^{-2}
2520	3.6×10^{-3}	3.3×10^{-1}
2800	3.9×10^{-3}	2.5
3150	4.0×10^{-3}	18
3600	4.5×10^{-3}	37

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FIGURE CAPTIONS

Fig. 1 Free carbon pressure as a function of the C/O ratio for various values of T, when H:C:N is kept constant at the value $1:5.10^{-4}:10^{-4}$ and $p_g \cong 10^4$ dyne cm^{-2}.

Fig. 2 Temperature at which free carbon becomes saturated in a stellar atmosphere with H:C:N = $1:5.10^{-4}:10^{-4}$, $p_g \cong 10^4$ dyne cm^{-2}, as a function of the C/O ratio.

Fig. 3 Solid curves 1 and 2 represent the free carbon partial pressure in an N star atmosphere with H:C:N:O = $1:5.10^{-3}:10^{-3}:10^{-3}$ for total as pressures 1 and 10^4 dyne cm^{-2} respectively. Dashed curve represents the vapor pressure of bulk graphite as a function of the temperature.

Fig. 4 The mass fraction of the total carbon that may be condensed at a given temperature on the basis of Tsuji's (1964) equilibrium calculations.

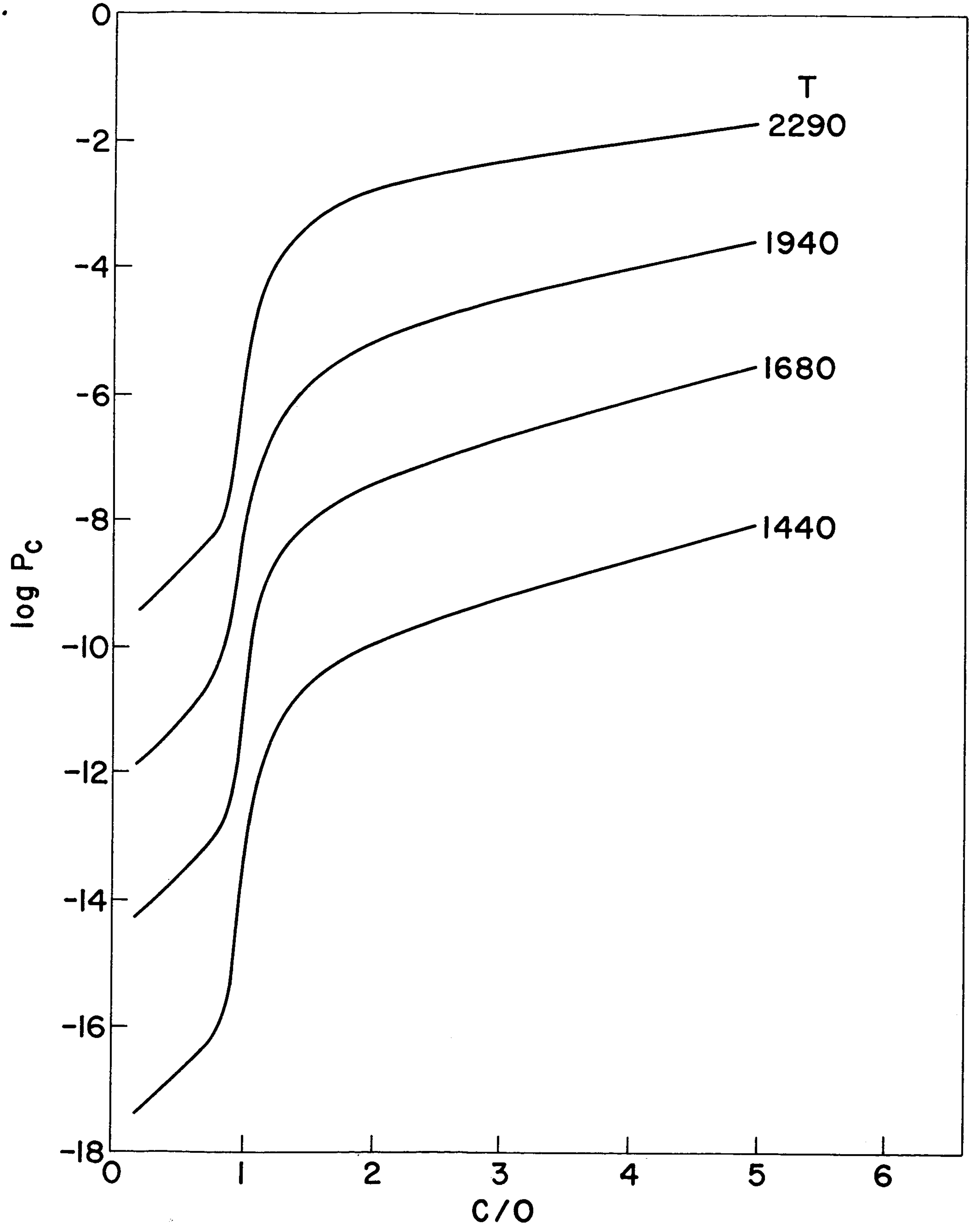

Figure 1

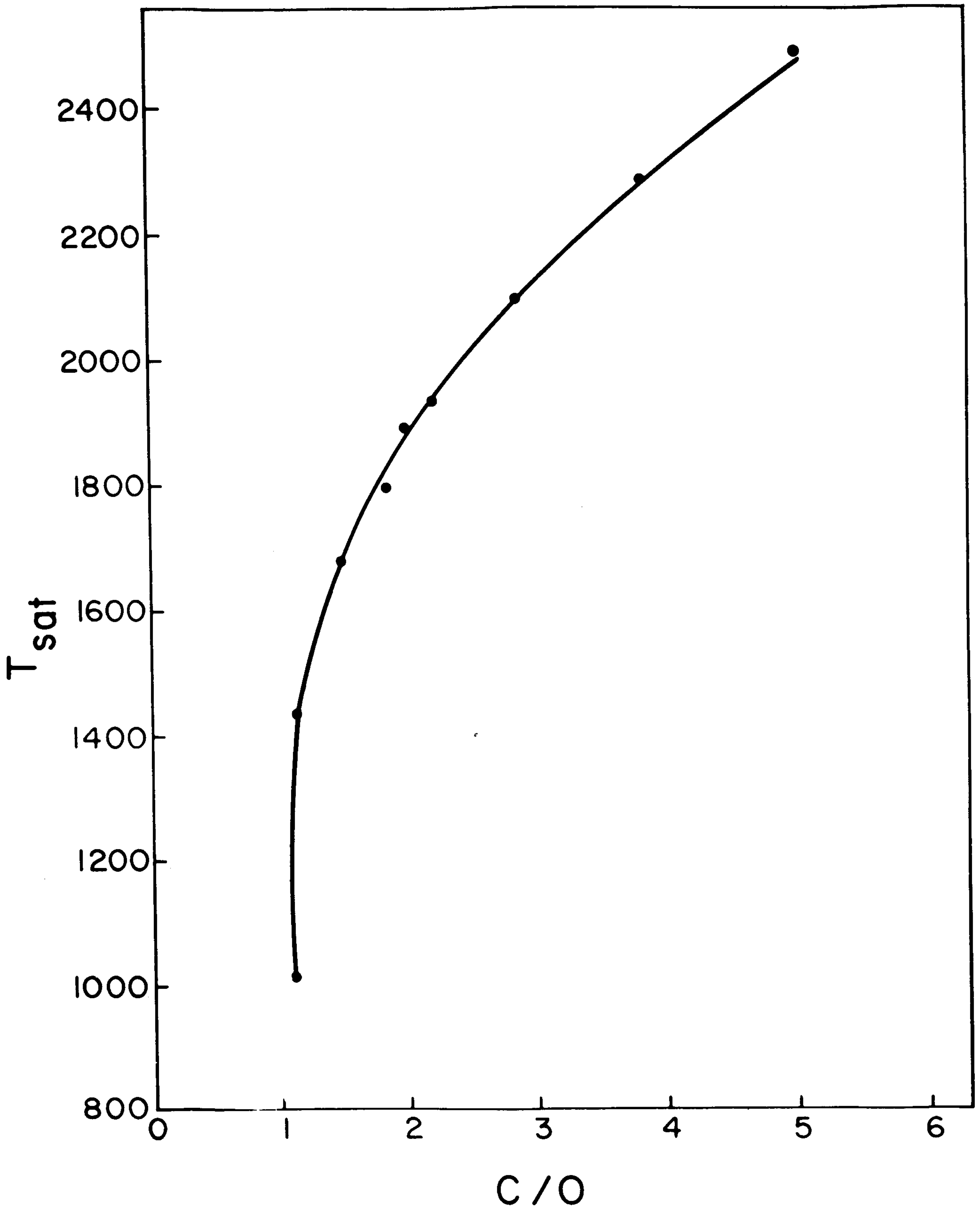

Figure 2

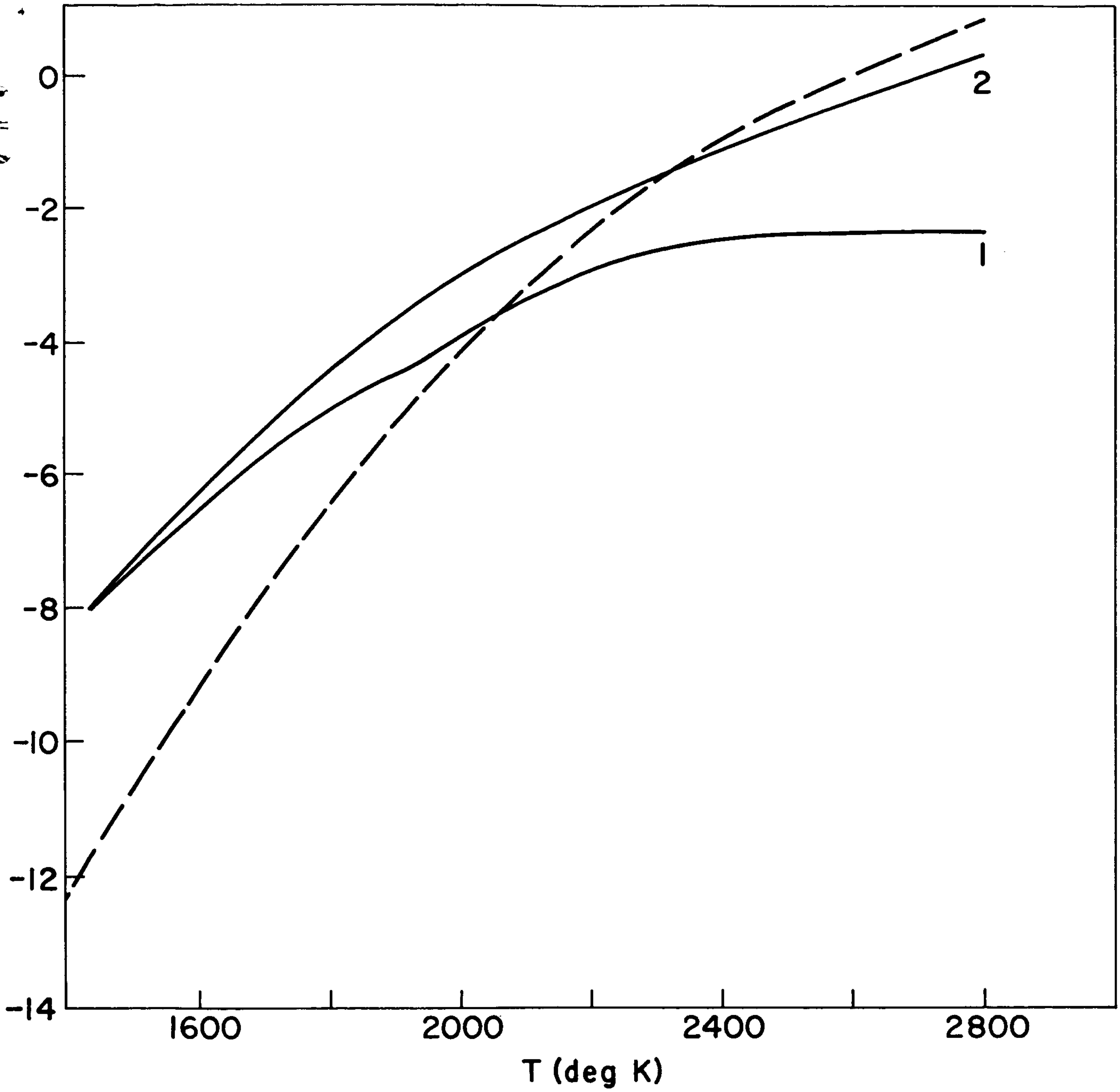

Figure 3

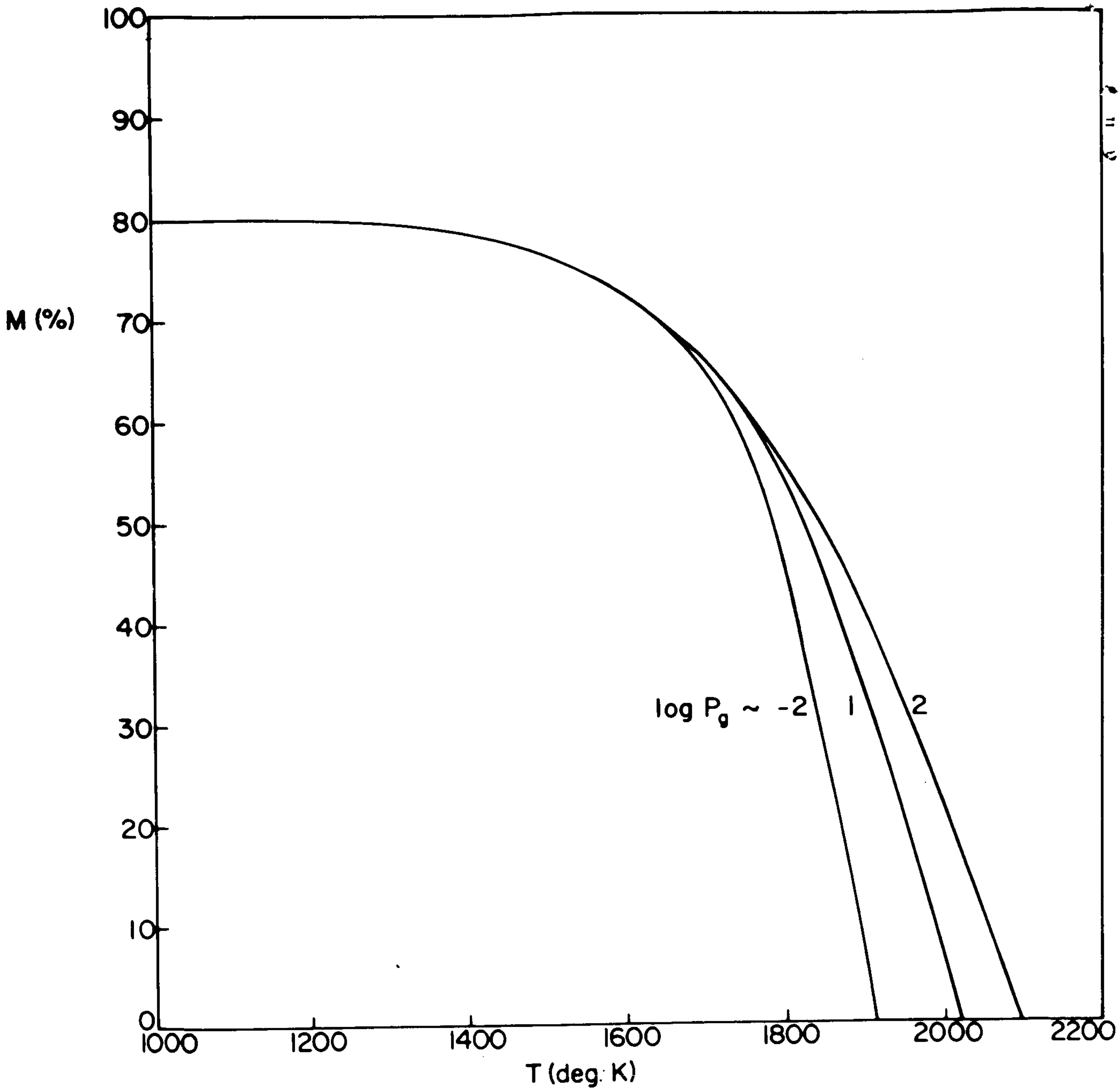
M (%)
100
90
80
70
60
50
40
30
20
10
0
1000
1200
1400
1600
1800
2000
2200
T (deg. K)
log P_g ~ -2
1
2

Figure 4