

AN APPROXIMATE SOLUTION OF CARAM-AMUNDSON'S
MODEL OF CARBON PARTICLE COMBUSTION.

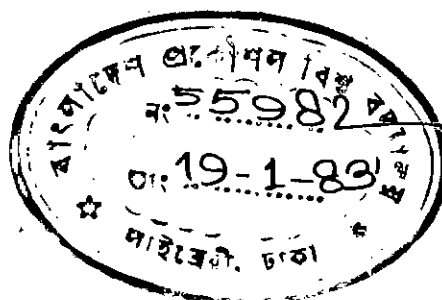
by

SHABBIR AHMED

A Thesis

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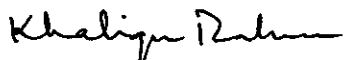
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ABSTRACT

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An approximate analytical solution has been obtained for a mathematical model of combustion of a carbon particle located in a population of similar particles. The model considers CO as the main product formed at the solid surface with subsequent oxidation of CO in the gas film surrounding a particle. The present solution is based on a polynomial expression for the homogenous reaction in the gas film. Utilizing a third degree polynomial the mass and energy balance equations together with appropriate boundary conditions have been solved and the effects of few parameters (bulk O_2 concentration, film thickness and reactivity) over a limited range have been studied. The results obtained are found to be in good agreement with the numerical solution of Earam and Amudson (1) particularly in regions of practical interest.

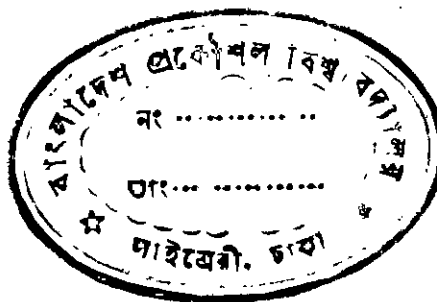
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1. INTRODUCTION:

Combustion is no new field and it has attracted researchers by merit of its practical importance. In the recent past, global energy crisis gave a further impetus to the study of combustion phenomenon and research in this field has spread in many directions. One elementary but fundamental question that has been studied over a great many years is the combustion of a single solid particle of carbon. This issue is important because understanding of the process of oxidation of a single particle gives a useful framework to analyse more complex events that occur in a realistic combustor.

In spite of the abundant literature on carbon combustion, it was not until very recently that a comprehensive model of single particle combustion was available. This was due to a work of Caram and Amundson (1) who made a detailed study of the problem of diffusion and chemical reaction in the gas film surrounding a carbon particle and the present study was motivated by their work. Conventionally, two basic models were used to study the effect of diffusion and chemical reaction on combustion: these are namely, the single film model and the double film model. These theories have the disadvantage that one needs to make a priori assumption regarding the reaction zone. Also, both single and double film models predict the same surface temperature and rate of combustion and hence one cannot check the validity of these models by measuring these quantities. Caram and Amundson made no assumption as to the number of films but showed that the necessary models may be generated by the solution of mass and energy balance equations. The approach followed by these workers is rigorous but a heavy demand on computational skill is required.

Although, with the availability of computers, numerical solution is not a limitation, it is always preferable to have an analytical solution available, even if the analytical approach requires some sacrifice in rigour. The objective of this study was thus, to provide an alternative analytical method of solution to the problems considered by Caram and Amundson.

2. LITERATURE REVIEW:

On the theoretical side the principal question that has been investigated is the reactions that occur at the carbon-particle surface. Conventional theories hold that carbon dioxide is primarily formed from the carbonaceous fuel and carbon monoxide is subsequently produced, by a reduction process. Other theories claim that carbon monoxide appears as a primary product of incomplete combustion and thereby being oxidised to CO_2 while still others disagree on the sequence of events. The following pages review briefly on different aspects of the combustion process.

2.1 FUNDAMENTAL REACTIONS:

The set of eight gas reactions listed in Table 1 is fundamental in the study of the combustion of carbonaceous solid fuels as well as of the conversion of such fuels into gaseous fuels. The principal thermodynamic constants, molar change in enthalpy (ΔH^0) and in free energy (ΔG^0) of the reactions are included in Table 1.

The first four equations represent the reactions involved in the combustion of carbon, barring dissociation of the gases. The last four equations also come into play when the combustion takes place in a moist environment or where the water content is not insignificant. This work deals with combustion with dry air and hence has no dealings with the last four reactions. At very low moisture content the last four equations may be neglected but small amount of water vapour may act as a catalytic agent for reaction 4.

TABLE I
GAS REACTIONS AND THERMODYNAMIC CONSTANTS

			$\Delta H_{291.0k}^0 \times 10^{-8}$	$\Delta G_{298.1k}^0 \times 10^{-8}$
			<u>Joules/kgmol</u>	
1.	$C + O_2$	$= CO_2$	- 3.949	- 3.944
2.	$C + \frac{1}{2}O_2$	$= CO$	- 1.108	- 1.360
3.	$C + CO_2$	$= 2CO$	+ 1.733	+ 1.223
4.	$CO + \frac{1}{2}O_2$	$= CO_2$	- 2.841	- 2.584
5.	$H_2 + \frac{1}{2}O_2$	$= H_2O$	- 2.42	- 2.281
6.	$C + H_2O$	$= CO + H_2$	+ 1.311	+ 0.9205
7.	$C + 2H_2O$	$= CO_2 + 2H_2$	+ 0.8899	+ 0.6176
8.	$CO_2 + H_2$	$= CO + H_2O$	+ 0.4213	+ 0.3029

2.2. KINETIC MODELS

The following discussions refer to heterogenous reactions that take place at the surface of a carbon particle and it will be assumed that carbon particle is impervious to diffusion. This is certainly not the case, in general, but here our objective is to separate out the boundary layer i.e. gas phase effect.

Any heterogenous combustion reaction over a non porous solid surface involves the following six steps in series:

1. Diffusion of the gases to the reaction surface.
2. Adsorption of the gaseous reactant.
3. Reaction between the solid and gaseous reactants.

4. Desorption of the gaseous products from the surface.
5. Diffusion of the products away from the surface.
6. Homogenous gas phase reaction.

Since these steps occur in series, the slowest of them determines the overall rate. In the case of carbon combustion, steps (2) and (4) are known to be extremely fast. Two things figure prominently from the above, which are, at high temperatures if the rate of reaction is very high (which seems logical) compared to the rate of diffusion, then the process will be diffusion controlled. On the other hand if the rate of reaction is slow in comparison to the rate of diffusion, (likely to be at low temperatures) then the process is kinetically controlled. Let us now turn to what reactions, researchers over the years, have considered and how they have analysed the situation of carbon particle combustion.

The following two reactions are two of the most common ones in physical chemistry and have been studied almost incessantly.



Rhead and Wheeler (2) assumed that in the reaction of carbon with oxygen, neither (1) nor (2) actually took place but that an intermediary solid product C_xO_y was first formed and subsequently decomposed to a mixture of carbon monoxide and carbon dioxide. The ratio of monoxide to dioxide in the evolved mixture depended on temperature. Several other authors (3-5) have pursued the study of the mechanism of carbon combustion and of the

structure of the possible intermediary solid compounds of oxygen and graphite. An able review of the organo chemical work in the theory of combustion of carbon was given by Riley (6).

Nusselt (7) was probably the first to propose that oxidation of carbon is controlled by diffusion of oxygen through a stagnant film and this is known as the single film model. He considered only reaction (1) to be occurring at the surface and neglected the effect due to bulk flow. Figure 1 shows the expected profiles for the single film model.

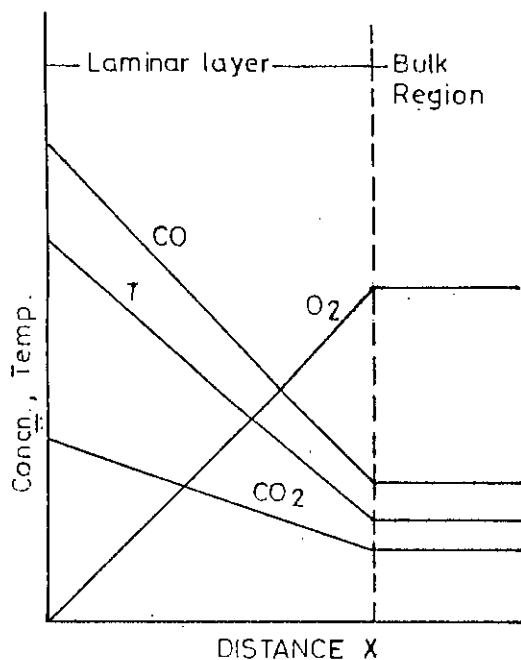


Fig. 1 : Single Film Model.

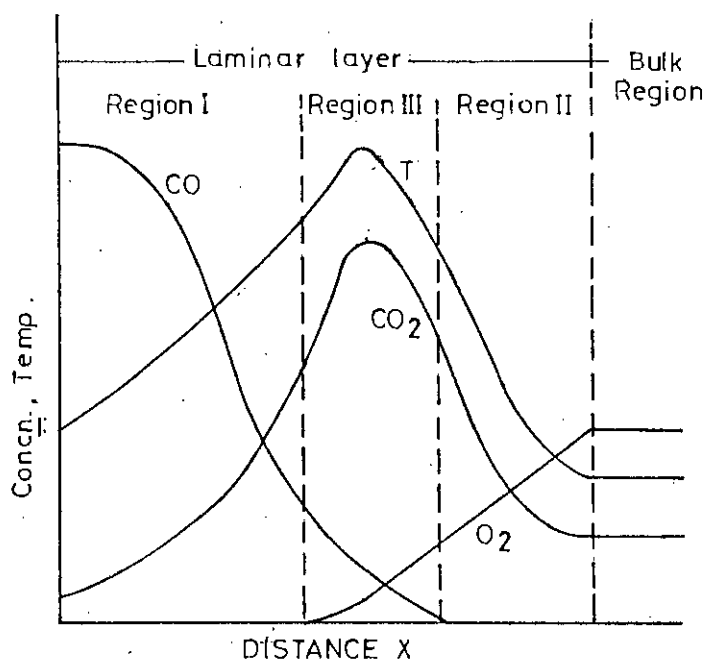


Fig. 2 : Double Film Model.

Hougen and Watson (8) also presented a model of carbon particle combustion based on the single film theory where he considered the reactions $C + O_2 \rightarrow CO$ and $C + CO_2 \rightarrow CO$ occurring at the surface, both of them

being diffusion controlled, while he assumed no further carbon monoxide oxidation in the adjacent stagnant film, but only in the region of bulk. His model was designed to study fuel beds.

Burke and Schumann (9) worked out an interesting theory, known as the double film model. In this it is assumed that, in an atmosphere containing oxygen, the carbon particles surround themselves with a film of high carbon dioxide concentration, the carbon dioxide diffusing outwardly against the incoming oxygen and also inwardly towards the carbon. This carbon dioxide on reaching the particle surface undergoes the reaction



the carbon monoxide diffusing into the film where it reacts with the incoming oxygen and consuming each other out as



Part of the carbon dioxide goes back to the surface and the remaining out of the boundary layer. It was assumed that the homogenous reaction was very fast occurring in a flame with negligible film width. According to the model, no oxygen reaches the particle surface and no carbon monoxide reaches the edge of the boundary layer. The effect of bulk flow was also neglected. Expected profiles for the double film model are given in Figure. 2 .

Fundamental research on carbon combustion has also been done by Hottel and co-workers (10). Their curves of $\log k$, the reaction constant, versus temperature had two distinct trends. At low temperatures the rise was steep, indicating that chemical resistance controlled the reaction rate while at high temperatures the diffusion to and from the carbon surface controlled the rates. The temperature at which the curve changed lay between

1000 and 1100^oK. Below 1000^oK, the increase in reaction rate followed fairly well from the values of the activation energy, indicating kinetic control. Above 1100^oK, the rate varied with 0.4-0.7 power of the mass velocity. In the diffusion controlled range, it was assumed that CO₂ was formed at the surface, diffused through the inert nitrogen layer outward from the carbon and the oxygen diffusing in the reverse direction toward the carbon surface. This is in contrast to that proposed by Burke and Schumann. Figures 3 & 4 shows the observed changes of the profile and rate of reaction in the two regimes of combustion.

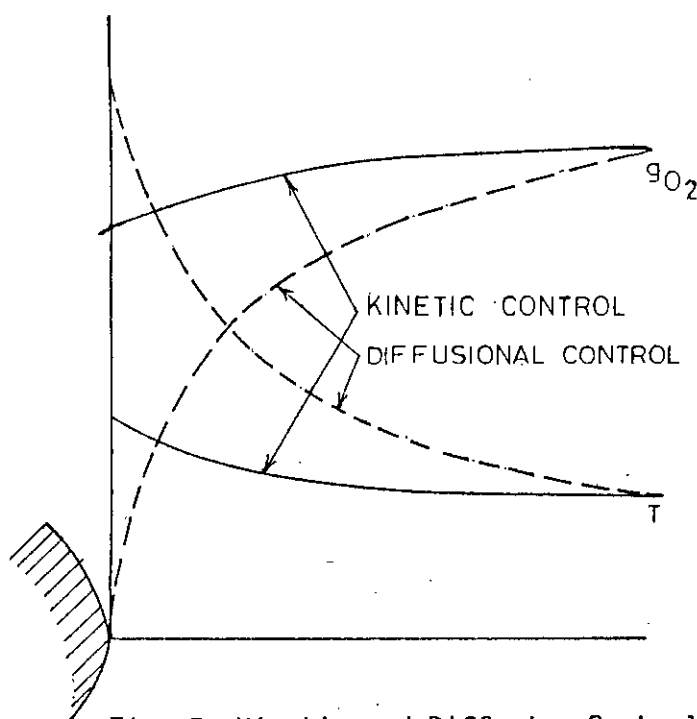


Fig. 3: Kinetic and Diffusion Controlled Combustion of a Solid Particle.

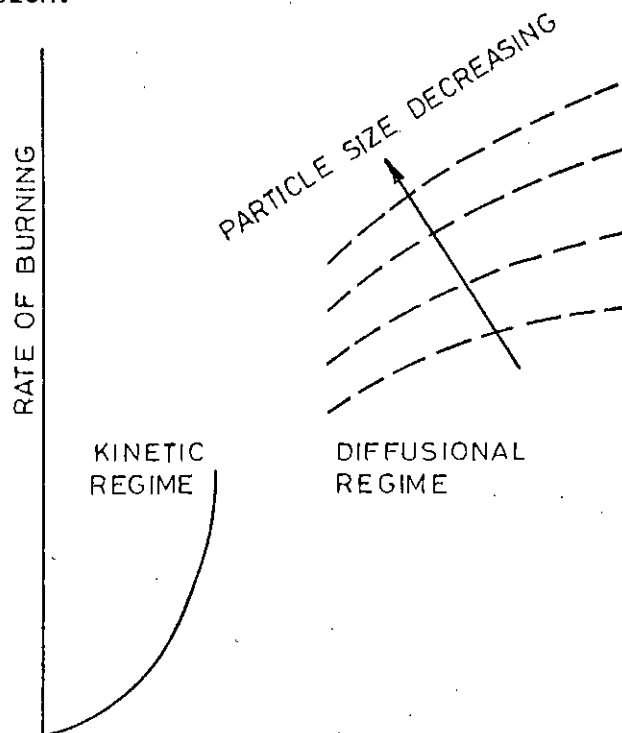


Fig. 4: Rate of Burning for Kinetic and Diffusional Regimes.

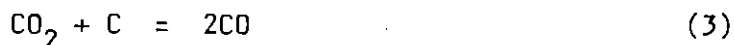
Sebastian and Mayers(11) also observed that the reaction rate, of the first order, could be fitted with an Arrhenius type of equation at lower temperatures for various samples of pulverized coke. It was also found that with increasing temperature, the reaction rate of the less reactive coke

increased more rapidly and as a result, the difference in reactivity of the various cokes diminished. Above 900°C , the aforementioned relation between the reaction rate and temperature no longer applies. In agreement with Hottel's findings, chemical resistance then no longer controls the overall rate but the latter is controlled by the rate of diffusion of oxygen to the surface. In this region, the reaction rate can be correlated with the rate of gas flow through the fuel bed and the particle size.

Interesting light has been shed on the subject of combustion of carbon by Grodzovskii and Chukhanov (12). By blowing pulverized carbon particles in a stream of air, combustion rates were determined. The reaction velocity was found to be very high, and in no instance, regardless of the rate or oxygen concentration, was any residual oxygen found. On the basis of the gas analysis, they concluded that the formation of carbon monoxide was primary and thereby explained the very rapid reaction rates which could not otherwise be explained from secondary monoxide formation by reduction of carbon dioxide. The mechanism was believed to be as follows:

At low velocities oxygen diffuses to the carbon surface, while monoxide diffuses away from the surface and encountering oxygen is converted partially or completely to the dioxide. For high gas velocities, there is no longer sufficient time for the CO combustion to take place and all the primary monoxide is carried away. It appears that the essential feature of this theory is the relatively slower rate of the reaction $\text{CO} + \text{O}_2 = \text{CO}_2$. This is contrary to the model proposed by Nusselt.

The carbon dioxide reduction reaction, mentioned earlier

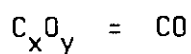
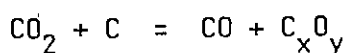


takes place in all combustion where secondary air is required to completely utilize available heat in the combustion gases (i.e. insufficient oxygen reaching the carbon surface). Boudquard, after whom the reaction is often named, was the first to study the equilibrium in a temperature range from 450 to 1000°C. Rhead and Wheeler (16) also reported reaction rate constants for this reaction. Dubinsky (13) determined the rate of reaction between brush carbon spheres and carbon dioxide. Between 1500 and 1700°K, he found a rapid increase in reaction rate. Drakely (14) studied the reaction between 950 and 1100°C and expressed the rate as,

$$R_2 = k [\text{CO}_2] - k [\text{CO}]^2 \quad (4)$$

thus indicating the influence of the reverse reaction.

Evidence of the complexity of the reaction between CO_2 and carbon has also been offered by Broom and Travers (15), who opined that the reaction occurs in two stages. - the formation and decomposition of a complex C_xO_y .



supporting to some extent the early theories of Rhead and Wheeler (16), Sihvonen (4) and others.

An elaborate study concerning the $\text{CO}_2 + \text{C}$ reaction was made by Mayers (17) where he conducted experiments at high enough flow rates to eliminate any diffusional effects. The observed rates followed two simple equations of the Arrhenius type between 850-950°C and 950-1306°C, with an apparent discontinuity at 950°C (indicated by an increase in reactivity

gradient). The discontinuity was attributed to a nature of the C_xO_y complex. The proposed theory is that the reaction $CO_2 + C = CO + C_xO_y$ complex takes place at low temperatures (below $950^\circ C$) with a rate of decomposition of complex to carbon and carbon monoxide lower than that of the reaction itself. At increasing temperatures, the decomposition of the complex takes place more rapidly and above $950^\circ C$ the two reactions add up to $CO_2 + C = 2CO$, leaving a clean surface for the reaction. It is evident that below $950^\circ C$, the reaction between CO_2 and carbon will eventually slow down to the rate of C_xO_y complex decomposition rate as soon as the entire surface is covered by the complex.

Spalding (18) offered two models. In the first one, he proposed that the reactions (2) and (3) at the surface and (4) in the stagnant layer, remained in equilibrium and that the bulk conditions were also at equilibrium. In the other model, also a two-film model, he assumed that no oxygen or carbon dioxide exists at the surface and no assumptions were made about the homogenous reaction (4). He stated that if all species are taken to have the same diffusivity then the rate of combustion and the surface temperature are independent of the reactions in the boundary layer.

Coffin and Brokaw (19) conducted experiments which showed that there was negligible amount of both carbon dioxide and oxygen present in the gas phase near the carbon surface and that the temperature and carbon dioxide profiles exhibit a maximum at some distance away from the surface in the gas phase (Fig. 5). They suggested that the reactions (2) and (3) at the surface and (4) at the gas phase were in equilibrium. They considered the effect of bulk flow but used more rigorous diffusion equations than Spalding.

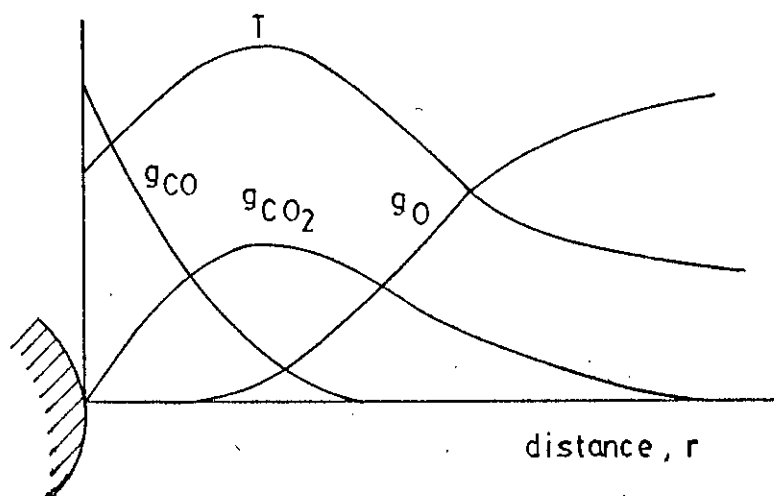


FIGURE 5 COMBUSTION OF CARBON ACCORDING TO COFFIN'S HYPOTHESIS.

Khitrin's (20) work was based on first-order rate equations of the heterogeneous reactions (2) and (3) at the surface while the homogeneous gas-phase reaction, a second order reaction, was represented by two first-order expressions $R_3 = k [\text{CO}]$ when $[\text{CO}] < [\text{O}_2]$ and $R_3 = k [\text{O}_2]$ when $[\text{O}_2] < [\text{CO}]$. However, he did not consider the energy equation.

Van der Held (21) conducted some research based on the film theory. These were (i) the case when the temperature is so high that the combustion of carbon monoxide to carbon dioxide takes place in a reaction zone which is thin against the thickness of the laminar layer and (ii) the case when the temperature is not so high but still high enough so that the partial pressure/concentration of oxygen at the surface maybe taken as zero. In both cases, the Boudouard reaction was assumed to be in equilibrium. In the first case, no oxygen reaches the surface, hence no formation of mono-

- xide by carbon oxidation. Also, no carbon monoxide reaches beyond the gas-phase reaction zone toward the boundary layer edge. With the reaction zone in the centre of the gas film, the stagnant film has been divided into three zones. For both the zones adjacent to the surface and the boundary, bulk flow terms were included while in the reaction zone, carbon monoxide combustion reaction rate was expressed with a $3/2$ order rate equation, and the solutions were also presented for second and third order rate equations.

In the second case, the reaction zone is bounded by the carbon surface, i.e. the entire boundary layer is the reaction zone and there is a negligible temperature maximum in the gas. The equations have been solved using only the second-order rate expression for the reaction zone. Contrary to case 1, oxygen does reach the surface but the CO_2 concentration there is nearly zero.

Wicke and Wurzbacher (22) provided some experimental evidence by measuring the temperature and concentration distributions of CO_2 , CO and O_2 within the film. They showed a maximum in the concentration profile of carbon dioxide.

Hugo and Wicke (23) in their work on carbon particle combustion has considered only the gas-phase reaction (4) and used a rate expression that is first order with respect to carbon monoxide and zero order with respect to oxygen. They assumed an isothermal film to justify carbon monoxide concentration profiles described by Wicke and Wurzbacher. De Graaf (24) measured the temperature within the boundary layer and found that the temperature in the reaction zone was higher than the temperature of the burning carbon, the highest temperature being measured at the outside of the blue visible part of the zone. Kish (25) who also made temperature measure-

ments also found temperature maxima several hundred degrees above the surface temperature. Field (27) in his model used a first-order expression for $C + \frac{1}{2}O_2 = CO$, and have not considered the Boudouard reaction. Theirs was an isothermal model. Kurylko et al (28) developed an unsteady state model considering intraparticle diffusion, a zero order rate expression for reaction (2), a first-order expression for (3) and a second-order rate expression for carbon monoxide oxidation.

Last but not least is the model developed by Amundson et al. which is also the basis of this work. This model has been described in later pages.

TABLE 2
SUMMARY OF REVIEW

	<u>Heterogenous Reaction</u>		<u>Homogenous reaction</u>	Observations
	$2C+O_2=2CO$	$C+CO_2=2CO$	$2CO+O_2 = 2CO_2$	
Rhead & Wheeler (2)	Intermediary solid product C_xO_y decomposes to CO and CO_2 .			Only chemical kinetics studied.
Nusselt(1-film) (7)	Diffusion controlled	Not considered	Not considered	
Hougen & Watson(1-film) (8)	Diffusion controlled	Diffusion controlled	No reaction in film	Used to study fuel beds. CO burns in bulk.
Burke & Schumann (2-film) (9)	Not considered (No O_2 reaches the surface)	Ratio CO/CO_2 at surface is model parameter.	Very fast. Flame thickness neglected	Based on need of explaining the effect of presence of steam on coal combustion.
Hottel et al. (10)		Not considered		Rate studies with change from kinetic control to diffusion control. CO_2 formed at surface.
Sebastian & Mayers(11)		Not considered		CO_2 formed at surface. Rate changes from kinetic control to diffusion control.
Grodzovskii & Chukhanov (12)	Diffusion controlled	Not considered	Relatively slow rate of combustion.	CO is the primary product.

	Heterogenous Reaction		Homogenous reaction	Observations
	$2C+O_2=2CO$	$C+CO_2=2CO$	$2CO+O_2 = 2CO_2$	
Rhead and Wheeler (16)		Studied reaction rate.		Rapid increase in rate between 1500 1700°K.
Drakeley (14)		Studied reaction rate only.		Rate expression includes reverse reaction.
Broom & Travers (15)		Studied mechanism		Intermediate complex formed.
Mayers (17)		Reaction rate in kinetic control		Arrhenius type rate expressions.
Spalding (18)	Equilibrium	Equilibrium	Equilibrium	Requires equilibrium conditions at bulk. Predicts amooth 2-film model.
Spalding (18)	No O_2 at surface	No CO_2 at surface	Nothing is assumed	Assuming equal diffusivities of all species, rate of combustion and surface temp. is independent of reactions in boundary layer.
Coffin & Brokaw (19)	Equilibrium	Equilibrium	Equilibrium	Diffusion equations more rigorous than Spalding.
Khitrin (20)	First order kinetics	First order kinetics	$R_3=k[CO], [CO] < [O_2]$ and $R_3=k[O_2], [CO] < [O_2]$	Energy equation not included.
Van der Held (21) (2 models)	1.No O_2 reaches surface 2. O_2 reaches surface but $[CO] \approx 0$	1. CO_2 at surface is model parameter 2. CO/CO_2 in equilibrium at surface.	1.Reactions of order 3/2 and 2., in thin isothermal flame 2.Reaction zone includes all b.l.	1.B.layer divided into 3 zones. No O_2 is zone I near surface; No CO in Zone III near bulk; thin isothermal flame in Zone II. 2.Low temp. model. Product mostly CO. Little CO to be burned.

	<u>Heterogenous Reaction</u>		<u>Homogenous reaction</u>	Observations
	$2C+O_2=2CO$	$C+CO_2=2CO$	$2CO+O_2 = 2CO_2$	
Wicke & Warzbacher (22)				Profiles of CO_2 , CO and O_2 obtained experimentally.
Hugo & Wicke (23)	Not considered	Not considered	First order w.r.t. CO and zero order w.r.t. O_2	Isothermal film. Used to justify CO profiles by Wicke & Wurzbacher
De Graaf (24)				Temperature profile measured. Maxima obtained.
Field (26)	First order	Not considered	Upper bound used to check critical size after which it becomes important.	Non-isothermal model.
Kurylko et al.(27)	Zero order and intraparticle diffusion	First order	Second Order $R_3 = k [CO] \cdot [O_2]$	Unsteady state model considering intraparticle diffusion. Finite element model. Extremely slow to run.

2.3 RATES OF REACTIONS

Field (26) correlated the results of several investigations of the rate per unit area of carbon surface for the reaction $2C + O_2 = 2CO$. In the temperature range of 1000-2000°K, it can be written as,

$$\begin{aligned} R_1 &= 726 \exp(-35,700/RT) P_{O_2} \quad \text{gmols of } O_2/\text{cm}^2 - \text{s} \\ &= 3.007 \times 10^5 \exp(-17966/T) \frac{\rho_3 g_3}{M_3} \quad \text{kgmols of } O_2/\text{m}^2 - \text{s} \end{aligned}$$

There is much less information for the reaction between carbon and carbon dioxide. The rate seems to depend on the type and degree of conversion of the carbon considered. For the study, a first-order kinetic relation is used,

$$\begin{aligned} R_2 &= k_2' \exp(-59,200/RT) C_1 \\ &= k_2 \exp(-29790/T) \frac{\rho_1 g_1}{M_1} \quad \text{kgmols of } CO_2/\text{m}^2 - \text{s} \end{aligned}$$

where the value of k_2 has been taken as 4.1×10^9 . Although analysis showed that this value should be considerably less, the use of this figure does not undermine the validity of approach as the range of char reactivity is quite large.

The correlation used for the homogenous gas-phase combustion $CO + \frac{1}{2}O_2 = CO_2$ is the one proposed by Howard et al (28) for the temperature range 840-2360°K.

$$R_3 = k_3' \exp(-15090/T) C_2 C_3^{\frac{1}{2}} C_{H_2O}^{\frac{1}{2}} \quad \text{kg-mols of } CO/\text{m}^3 - \text{s}$$

where k'_3 is taken as 1.3×10^{11} and is used for moist conditions. or where the water content is small to act as catalyst for the homogenous reaction.

For dry conditions, as assumed in this study, the equation is (obtained from (29)),

$$R_3 = 8.016 \times 10^8 \exp(-15090/T) \frac{\rho g_2}{M_2} \cdot \left(\frac{\rho g_3}{M_3} \right)^{\frac{1}{2}}$$

2.4 THE SURFACE TEMPERATURE (T_s) AND ITS INFLUENCE

A rise in particle temperature shifts the process towards the physically controlled limit; a lowering of T_s tends to make kinetics control. But what controls T_s itself? A qualitative understanding is as follows:

The particle temperature is controlled by the rate of exothermic combustion at the surface and by the rate of heat loss by conduction and radiation.

As conduction, like diffusion, is inversely proportional to the distance (radius) while radiation is independent of it, the latter becomes unimportant as the particle radius diminishes. As a result, the temperature of the particle tends to increase as burning proceeds.

Radiation plays a vital role in igniting injected coal particles. Mere dependence on heat conduction would be inadequate. If radiative heat loss is too intense, the chemical reaction may be extinguished because a reduction of the surface temperature leads to reduction of the reaction rate which in turn reduces heat generation and further diminishing of surface temperature.

Combustion may also be extinguished by either excessive flow or by deficient flow. In the first case the reaction is quenched by convection and in the second case by heat losses.

3.1 THEORETICAL MODEL OF CARBON PARTICLE COMBUSTION

The fundamental consideration in the development of a model for combustion of carbon particle is the reactions that occur at the particle surface. In the present model, which is due to Caram and Amundson, it is assumed that the main product of the reaction between carbon and oxygen at high temperatures is carbon monoxide. Research to determine the validity of this assumption has been discussed in the literature review. The strongest point in favour of this assumption is the experimental evidence of carbon dioxide maximum in the boundary layer surrounding a particle and the homogenous combustion of carbon monoxide in the boundary layer (often visible as a blue flame surrounding the particle). Another important experimental evidence whether carbon monoxide or dioxide is formed at the particle surface is due to Arthur (30) who found after eliminating the masking effect caused by the homogenous combustion of carbon monoxide, that above a surface temperature of 1273°K , the main product of reaction was CO. To complete the picture and explain the concentration profiles, we include further the Boudouard reaction at the surface. Thus the following reactions occur:



a heterogenous and exothermic reaction occurring at the surface, its rate being denoted by R_1 kgmols of $\text{O}_2/\text{m}^2 - \text{s}$.



a heterogenous and endothermic reaction also occurring at the surface, its rate being denoted by R_2 kgmols of $\text{CO}_2/\text{m}^2 - \text{s}$ and



an exothermic and homogenous reaction occurring at the boundary layer of the gaseous film, its rate being denoted by R_3 kgmols of $\text{CO}/\text{m}^3\text{-s}$.

In the present model we will consider a carbon particle as being a part of a large population burning under the same conditions. For reasons of simplicity the carbon surface will be taken as flat and neglect any convection. Since the present objective is to study diffusion and reaction in the boundary layer, we will assume that the carbon particle is impervious to diffusion, though in practice this may not be the case. We will further assume constant physical properties inside the boundary layer, dissociation of carbon dioxide to be negligible and radiation equilibrium.

3.2 THE MASS AND ENERGY BALANCES

Under the conditions stated above, the mass balances equations are

$$\text{CO}_2 : \quad \frac{d}{dx} \left(\rho D_1 \frac{dg_1}{dx} \right) = -M_1 R_3 \quad (1)$$

$$\text{CO} : \quad \frac{d}{dx} \left(\rho D_2 \frac{dg_2}{dx} \right) = M_2 R_3 \quad (2)$$

$$\text{O}_2 : \quad \frac{d}{dx} \left(\rho D_3 \frac{dg_3}{dx} \right) = \frac{1}{2} M_3 R_3 \quad (3)$$

and the energy balance equation is,

$$\frac{d}{dx} \left(\lambda \frac{dT}{dx} \right) = - \frac{W_1}{2} R_3 \quad (4)$$

Combining equations (1) and (2), (1) and (3), (1) and (4), we get, and using the the assumption that ρD_i remains constant, we get,

$$\frac{\rho D_1}{M_1} \frac{d^2 g_1}{dx^2} + \frac{\rho D_2}{M_2} \frac{d^2 g_2}{dx^2} = 0 \quad (5)$$

$$\frac{\rho D_1}{M_1} \frac{d^2 g_1}{dx^2} + \frac{2 \rho D_3}{M_3} \frac{d^2 g_3}{dx^2} = 0 \quad (6)$$

$$\frac{\rho D_1}{M_1} \frac{d^2 g_1}{dx^2} - \frac{2 \lambda}{W_1} \frac{d^2 T}{dx^2} = 0 \quad (7)$$

which on integration becomes,

$$\frac{\rho D_1}{M_1} \frac{dg_1}{dx} + \frac{\rho D_2}{M_2} \frac{dg_2}{dx} = A' \quad (8)$$

$$\frac{\rho D_1}{M_1} \frac{dg_1}{dx} + \frac{2 \rho D_3}{M_3} \frac{dg_3}{dx} = A'' \quad (9)$$

$$\frac{\rho D_1}{M_1} \frac{dg_1}{dx} - \frac{2 \lambda}{W_1} \frac{dT}{dx} = A''' \quad (10)$$

Integrating once again and using the boundary conditions that at $x=0$, the surface of the carbon particle

$$g_1 = g_{1s} \quad (11)$$

$$g_2 = g_{2s} \quad (12)$$

$$g_3 = g_{3s} \quad (13)$$

$$T = T_s \quad (14)$$

We obtain,

$$\frac{\rho D_1}{M_1} (g_1 - g_{1s}) + \frac{\rho D_2}{M_2} (g_2 - g_{2s}) = Ax' \quad (15)$$

$$\frac{\rho D_1}{M_1} (g_1 - g_{1s}) + \frac{2 \rho D_3}{M_3} (g_3 - g_{3s}) = A''x \quad (16)$$

$$\frac{\rho D_1}{M_1} (g_1 - g_{1s}) - \frac{2 \lambda}{W_1} (T - T_s) = A'''x \quad (17)$$

The constants A' , A'' , A''' can be found out using the boundary conditions that at $x = 0$,

$$-\frac{\rho D_1}{M_1} \left(\frac{dg_1}{dx} \right)_{/x=0} = -R_2 \quad (18)$$

$$-\frac{\rho D_3}{M_3} \left(\frac{dg_3}{dx} \right) = -R, \quad (24)$$

$$-\frac{\rho D_2}{M_2} \left(\frac{dg_2}{dx} \right)_{/x=0} = 2(R_1 + R_2) \quad (19)$$

$$-\lambda \left(\frac{dT}{dx} \right)_{/x=0} = (-\Delta H_1)R_1 + (-\Delta H_2)R_2 \quad (20)$$

to obtain

$$A' = -(2R_1 + R_2) \quad (21)$$

$$A'' = (2R_1 + R_2) \quad (22)$$

$$\begin{aligned} A''' &= \frac{2(-\Delta H_1)R_1}{W_1} + \left(1 - \frac{2\Delta H_2}{W_1}\right)R_2 \\ &= \frac{-\Delta H_1}{W_1} (2R_1 + R_2) \end{aligned} \quad (23)$$

By using the kinetic expressions they become,

$$A' = -(2k_1 \frac{\rho g_{3s}}{M_3} + k_2 \frac{\rho g_{1s}}{M_1})$$

$$A'' = (2k_1 \frac{\rho g_{3s}}{M_3} + k_2 \frac{\rho g_{1s}}{M_1})$$

$$A''' = \frac{(-\Delta H_1)}{W_1} \left(2k_1 \frac{\rho g_{3s}}{M_3} + k_2 \frac{\rho g_{1s}}{M_1} \right)$$

where $k_1 = k_1(T_s)$, $k_2 = k_2(T_s)$. Using the following dimensionless variables

$$\alpha_1 = \frac{M_1 D_2}{M_2 D_1}, \quad \alpha_2 = \frac{M_1 D_3}{M_3 D_1}, \quad \alpha_3 = -\frac{2\lambda M_1 T_b}{W_1 \rho D_1}$$

$$\beta_1 = \frac{k_1 M_1 b}{D_1 M_3}, \quad \beta_2 = \frac{k_2 b}{D_1}, \quad \gamma = \frac{-\Delta H_1}{W_1}$$

$$s = \frac{x}{b}, \quad \tau = \frac{T}{T_b}, \quad \tau_s = \frac{T_s}{T_b}$$

We get,

$$(g_1 - g_{1s}) + \alpha_1(g_2 - g_{2s}) = -s(2\beta_1 g_{3s} + \beta_2 g_{1s}) \quad (24)$$

$$(g_1 - g_{1s}) + 2\alpha_2(g_3 - g_{3s}) = s(2\beta_1 g_{3s} + \beta_2 g_{1s}) \quad (25)$$

$$(g_1 - g_{1s}) + \alpha_3(\tau - \tau_s) = s\gamma(2\beta_1 g_{3s} + \beta_2 g_{1s}) \quad (26)$$

Using the known boundary values at $s=1$, viz.

$$g_1 = g_{1b} \quad (27)$$

$$g_2 = g_{2b} \quad (28)$$

$$g_3 = g_{3b} \quad (29)$$

$$T = T_b \quad (30)$$

equations (24) to (26) can be brought down to the form

$$g_{1s} = \frac{g_{1b} + 2\alpha_2 g_{3b} - (g_{1b} + \alpha_3(1 - \tau_s))(\alpha_2 + \beta_1)/\gamma\beta_1}{1 + \beta_2 - (1 + \gamma\beta_2)(\beta_1 + \alpha_2)/\gamma\beta_1} \quad (31)$$

$$g_{3s} = (g_{1b} - g_{1s} + \alpha_3(1 - \tau_s) - \gamma\beta_2 g_{1s})/2\gamma\beta_1 \quad (32)$$

$$g_{2s} = (g_{1b} - g_{1s} + \alpha_1 g_{2b} + 2 \beta_1 g_{3s} + \beta_2 g_{1s}) / \alpha_1 \quad (33)$$

Now we have three equations (31,32,33) with four unknowns (g_{1s} , g_{2s} , g_{3s} , τ_s).

Hence in order to obtain the fourth equation, it becomes essential to integrate directly one of the equations (1), (2), (3) or (4), which is made difficult by the presence of the highly non linear term $R_3 = R_3(g_{2s}, g_{3s}, \tau_s)$.

Let us suppose that R_3 is represented by a third-order polynomial of the form

$$R_3 = A_0 + A_1 x + A_2 x^2 + A_3 x^3 \quad (34)$$

The boundary conditions applicable for the rate expression R_3 are,

$$\text{at } x = 0, \quad R_3 = R_{3s} \quad (35)$$

$$x = b, \quad R_3 = 0 \quad (36)$$

(at the edge of the boundary layer, the concentration of carbon is nearly equal to zero. $R_3 = f(T, g_{2s}, g_{3s}) = 0$)

$$\text{at } x=b, \quad \left(\frac{dR_3}{dx} \right)_{x=b} = 0 \quad (\text{as } R_3 \text{ at } x=b \text{ is zero}) \quad (37)$$

$$x = 0, \quad \left(\frac{dR_3}{dx} \right)_{x=0} = B$$

$$\text{where } B = k_3 \cdot \exp\left(-\frac{E_3}{RT}\right) \cdot \frac{\rho^{3/2}}{M_2 M_3^{1/2}} \left[\frac{2M_2}{\rho D_2} (R_1 + R_2) g_{3s}^{1/2} + \frac{M_3}{\rho D_3} \cdot R_1 \frac{g_{2s}}{2g_{3s}^{1/2}} + \frac{E_3}{T^2} (h_1 R_1 + h_2 R_2) g_{2s} g_{3s}^{1/2} \right]$$

$$\dots \dots \dots \quad (38)$$

Using these boundary conditions, the constants in eq. (34) are found to be as

$$A_0 = R_{3s} \quad (39)$$

$$A_1 = B \quad (40)$$

$$A_2 = -\frac{1}{b^2}(3R_{3s} + 2 \cdot B \cdot b) \quad (41)$$

$$A_3 = \frac{1}{b^3}(2R_{3s} + B \cdot b) \quad (42)$$

and equation (34) becomes,

$$R_3 = R_{3s} + B \cdot x - \frac{1}{b^2}(3R_{3s} + 2B \cdot b)x^2 + \frac{1}{b^3}(2R_{3s} + B \cdot b)x^3 \quad (43)$$

$$\text{where } R_{3s} = k_3 \exp\left(-\frac{E_3}{RT}\right) \frac{\rho^{3/2}}{M_2 M_3} \cdot g_{2s} g_{3s} \quad (44)$$

To obtain the fourth equation required for solving the unknowns (g_{1s} , g_{2s} , g_{3s} , T_s), let us integrate eq. (4) by substituting the polynomial (43) in (4).

$$\frac{d^2 T}{dx^2} = -\frac{W_1}{2\lambda} R_3 = -\frac{W_1}{2\lambda} (A_0 + A_1 x + A_2 x^2 + A_3 x^3)$$

$$\frac{dT}{dx} = -\frac{W_1}{2\lambda} (A_0 x + A_1 \frac{x^2}{2} + A_2 \frac{x^3}{3} + A_3 \frac{x^4}{4}) + C_1$$

$$\text{At } x = 0, \quad \left(\frac{dT}{dx}\right)_{x=0} = h_1 R_1 + h_2 R_2 \quad \text{where } h_1 = \frac{-\Delta H_1}{\lambda}, \quad h_2 = \frac{-\Delta H_2}{\lambda}$$

$$C_1 = h_1 R_1 + h_2 R_2$$

$$\frac{dT}{dx} = -\frac{W_1}{2\lambda} (A_0 x + A_1 \frac{x^2}{2} + A_2 \frac{x^3}{3} + A_3 \frac{x^4}{4}) + (h_1 R_1 + h_2 R_2) \quad (45)$$

$$T = -\frac{W_1}{2\lambda} (A_0 \cdot \frac{x^2}{2} + A_1 \cdot \frac{x^3}{6} + A_2 \cdot \frac{x^4}{12} + A_3 \cdot \frac{x^5}{20}) + (h_1 R_1 + h_2 R_2) \cdot x$$

Using the boundary condition that, at $x=b$, $T=T_b$, we get,

$$T=T_b - \frac{W_1}{2\lambda} \left[\frac{A_0}{2}(x^2-b^2) + \frac{A_1}{6}(x^3-b^3) + \frac{A_2}{12}(x^4-b^4) + \frac{A_3}{20}(x^5-b^5) \right] + (h_1 R_1 + h_2 R_2)(x-b) \quad (46)$$

Applying this equation at $x=0$, $T=T_s$ and using the values of A_1 , A_2 , A_3 , A_4 from eqns. 39-42, we obtain,

$$T_s = T_b + \frac{W_1 b^2}{40\lambda} (7R_{3s} + B \cdot b) - (h_1 R_1 + h_2 R_2) \cdot b \quad (47)$$

Now we have four equations (31, 32, 33 and 47) to solve for the four surface conditions viz. g_{1s} , g_{2s} , g_{3s} and T_s .

3.3 THE METHOD OF SOLUTION

The problem encountered in obtaining the concentration and temperature profiles in the boundary layer is the values of the surface conditions. Let us deal with it first. The equations available for the purpose are:

$$g_{1s} = \frac{g_{1b} + 2\alpha_2 g_{3b} - [g_{1b} + \alpha_3(1-\tau_s)](\alpha_2 + \beta_1)/\gamma\beta_1}{1 + \beta_2 - (1 + \gamma\beta_2)(\beta_1 + \alpha_2)/\gamma\beta_1} \quad (31)$$

$$g_{3s} = (g_{1b} - g_{1s} + \alpha_3(1 - \tau_s) - \gamma\beta_2 g_{1s}) / (2 - \gamma\beta_1) \quad (32)$$

$$g_{2s} = (g_{1b} - g_{1s} + \alpha_1 g_{2b} + 2\beta_1 g_{3s} + \beta_2 g_{1s}) / \alpha_1 \quad (33)$$

and rewriting eq. (47) as

$$F(T_s) = T_s - T_b - \frac{w_1 b^2}{40\lambda} (7R_{3s} + B.b) + (h_1 R_1 + h_2 R_2).b \quad (48)$$

Given the bulk conditions,

for any value of T_s , the values of g_{1s} , g_{2s} and g_{3s} may be obtained from eqns. 31 to 33. If the values of the letter are positive, it is indicative that the value of T_s selected lies in a region of feasible solution. Should any of the mass fractions (g_{1s} , g_{2s} , g_{3s}) be negative no further efforts need or can be made as no solution is obtainable. For each value of T_s in the feasible region, the function $F(T_s)$ can be calculated. The solution obviously lies where $F(T_s) = 0$ or $F(T_s) = \epsilon$ (the acceptable error) and the corresponding values of T_s , g_{1s} , g_{2s} and g_{3s} are the required surface conditions. In this work, the function was evaluated for T_s within the range 900-1800⁰K at fixed intervals. The regions of feasible solutions were then scanned at smaller intervals to get the root where $F(T_s) \approx 0$.

With the surface conditions known the mass fractions and temperature within the boundary layer can be obtained directly from equations 46, 26, 25 and 24.

The solution of the surface conditions also permitted the calculation of other useful parameters. These are the Rate of combustion, q ; the Heat generated at the surface, HS ; the Total Heat Generated, HT ; and the Ratio of CO/CO_2 produced. These were calculated as follows:

$$q = 12(2R_1 + R_2) \quad \text{kg/m}^2 \quad (49)$$

$$HS = - \left(\frac{dT}{dx} \right)_{/x=0} \quad (50)$$

$$HT = - \left(\frac{dT}{dx} \right)_{/x=b} \quad (51)$$

$$\begin{aligned} \frac{CO}{CO_2} &= \frac{- \left(\frac{D_2}{M_2} \right) \left(\frac{dg_2}{dx} \right)_{/x=b}}{- \left(\frac{D_1}{M_1} \right) \left(\frac{dg_1}{dx} \right)_{/x=b}} \\ &= \frac{2R_1 + R_2}{\frac{H_1}{W_1} (2R_1 + R_2) - \frac{2}{W_1} \left(\frac{dT}{dx} \right)_{/x=b}} - 1 \quad (52) \end{aligned}$$

4.1. RESULTS AND DISCUSSION

The equations have been solved for normal carbon (where the values of the rate constants are as given in section 2.3) and reactive carbon (where the char is considered to be 100 times more reactive to oxygen and 10 times more reactive to carbon dioxide than the one considered in normal carbon), using boundary conditions of $g_{1b}=0$, $g_{2b}=0$, and $g_{3b}=0.1126$ (10% by volume) at the edge of the boundary layer. These solutions have been compared with the numerical solutions of Caram and Amundson which will be referred to as exact solution. It must, however, be mentioned here that the present solutions are not obtained with the same value of the reaction rate constant for the homogenous reaction as used by Caram and Amundson and hence exact agreement of the results for the two cases may not be expected. In the exact solution the authors considered the presence of small amount of water vapor and used the first expression for R_3 (p. 15) but they did not report the value of its concentration and hence it was not possible to carry out the calculations under identical conditions. In the present case, any presence of water vapor has been neglected and the reaction rate constant has been obtained from the second expression for R_3 (given in p. 16). However, it is expected that the solution with no water vapor and the exact solution of Caram and Amundson for trace level water would be close although the kinetic expression for the homogenous reaction is different in the two cases.

Examples of the curve $F(T_g)$ vs. T_g , needed to obtain the roots of eq. 48, are given in Figs. 6, 7 and 8. In Fig. 6, the solution for normal carbon at $T_b = 500^\circ\text{K}$ is shown. Here we see that two roots exist and a single curve passes through both the roots without any discontinuity.

However, discontinuity of the solution curve may exist at other values of T_b . Though the figure shows only two roots, there is in fact still another root for T_s below 1000°K , but this has not been reported as the kinetic expressions are valid at temperatures above 1000°K . With the present kinetic expressions, the third root for T_s (below 1000°K) is very close to T_b i.e., $T_s > T_b$, and this would suggest that the rate of oxidation is small enough to be insignificant. A typical case for this is when a carbon particle is left at normal ambient temperature. In the following discussions we will ignore this case and consider the cases for T_s above 1000°K only. A noteworthy feature of the curve in Fig. 6 is that the slope of the curve changes very rapidly as T_s increases. This is because of the presence of exponential terms in eq. 47, (B) which increases rapidly as T_s increases.

Figs. 7 and 8 are for reactive carbon at ambient temperatures of 200°K and 300°K respectively. Although this range of bulk temperature may not be of practical interest, solutions are sought for these cases because of the possibility of existence of more than two roots at lower temperatures, as reported by Caram and Amundson. These authors found as many as four solutions (excluding the solution for $T_s < 1000^{\circ}\text{K}$) between 268 - 348°K . In the present case, for 200 to 240°K two roots have been obtained, and a solution for $T_b = 200^{\circ}\text{K}$ is shown in Fig. 7. Again the function, $F(T_s)$ is continuous between the two roots and the slope of the curve is very steep at higher T_s . An expanded view of the region at higher T_s is shown in Fig. 7. For $T_b = 300^{\circ}\text{K}$, there is only one solution as against four reported for the exact solutions. The curve in Fig. 8 exists in segments and yields only one root though it misses another near 940°K

by a slight margin. The points where the segments disappear are the boundaries of the feasible region and beyond that $F(T_s)$ is imaginary because negative values of the mass fractions lead to non-feasible regions of solution.

Figs. 9 & 10 both contain the locus of solutions for the base case (normal carbon, 10 percent oxygen in the bulk and a film thickness of 0.005 m.) together with the exact solutions and it is evident that the agreement of the solutions obtained in this work and the exact solutions may be considered satisfactory, particularly at the higher values of T_b . At the lower ambient temperatures the curve for exact solutions shows that at 220°K, the two roots coincide. But this is not found to be so in the present work; the two segments would meet at a lower T_b than the range considered here. The deviation of the curves are more pronounced at lower T_b for the lower temperature solution.

The surface mass fractions and other useful parameters such as the heat generated at the surface, HS and the ratio of the fluxes of CO/CO₂ at the edge of the boundary layer have also been calculated and these have been plotted in Fig. 12 and these may be compared with the exact solutions shown in Fig. 11, by superimposing the exact solutions. As T_s predicted here is found to agree well with the exact solution it follows that the surface mass fractions would also agree since these are obtained using eqs. (31, 32 and 33). However, the HS and CO/CO₂ curves do not show as good agreement although the upper part of the HS curve agrees fairly well. The reason for this may be due to the approximate nature of the solution. Both the expressions for HS and CO/CO₂ involve derivatives of the temperature and this indicates that although use of the polynomial

surves well in predicting the surface conditions, it is less satisfactory in obtaining their derivatives. This limitation of the approximate method is common with other cases of momentum, heat and mass transfer problems. Although these deviations are large, the trends in the pattern of the curves are similar, as indicated by the presence of the maxima of the HS and the minima and maxima of the CO/CO_2 curves.

Let us now study the conditions at the surface using Figs. 9.11 & 12. For the lower temperature solution at a low surface temperature (high T_b) the concentration of oxygen at the surface is close to the ambient value suggesting that diffusional resistance is not important and hence the process is controlled by the chemical reaction rate. The dominant process is the oxidation of carbon to carbon monoxide as can be seen by comparing values of R_1 and R_2 where it will be found that $R_1 > R_2$. As T_s increases (T_b decreasing), the domination of the carbon oxidation to CO is decreased. Yet we see that oxygen concentration falls. This is due to increased rate of the carbon oxidation reaction as well as the carbon monoxide combustion in the film. But still the rate of CO production at the surface is higher than CO_2 reduction. At still higher T_s , the CO_2 reduction reaction begins to show its effect and can be seen from the HS curve which passes through a maximum and finally through zero to where it is the endothermic CO_2 reduction reaction which is the dominant process. Thus the surface receives heat where reduction reaction dominates (higher T_s) while releasing it where the oxidation reaction dominates (lower T_s). But it is interesting to note that at high surface temperatures the CO_2 concentration is high and this is because of the high rate of CO_2 formation in the film and hence its availability at the surface.

The locus of the second roots rise as the bulk temperature rises (Fig. 9). Fig. 12 shows that there will be practically no oxygen at the surface and the CO_2 reduction reaction is the only reaction occurring at the surface. In the film almost all the oxygen is used up for the oxidation of CO. This process is essentially diffusion controlled and the T_s vs T_b curve becomes asymptotic to a straight line of unit slope. In this case there is a fixed difference between the ambient and surface temperature.

The effect of changing the ambient oxygen concentration and film thickness are shown in Figs. 9 and 10 respectively together with the exact solutions and again a satisfactory agreement is obtained. The effect of decreasing the bulk concentration is to shift the $T_s - T_b$ curve to the right indicating that a higher bulk temperature is required to prevent quenching of the combustion process. The effect of decreasing the film thickness (Fig. 10) is to decrease the diffusional resistance. This follows from the figure where the kinetic control region extends to a much higher surface temperature than the base case. The curve is also found to shift to the right. As resistance to diffusion decreases the product formed at the surface, which is mainly CO, is immediately swept out into the bulk, the main product of combustion being CO. At high bulk temperatures the process becomes diffusion controlled and hence the curves become asymptotic to a straight line of unit slope, for both low bulk oxygen concentration and lower value of the film thickness.

For reactive carbon the $T_s - T_b$ curve is shown in Fig. 13. In this case the agreement between the present solution and the exact solution

is close only at higher surface temperatures. At lower temperatures, the agreement is unsatisfactory. As mentioned earlier, the exact solution predicts four solutions between 268-348°K whereas the present case predicts only one solution for T_b above 240°K. The sigmoid region of the exact solutions covers a narrow range and collapsing of this region may lead to a single solution. It is not clear whether this is a limitation of the method of solution or it is due to a difference in the value of the rate constant used for the homogenous reaction. The equations are sensitive to the values of parameters used and one needs to investigate further before a definite conclusion can be made.

Typical temperature and concentration profiles for normal carbon are shown in Figs. 14, 15 and 16. The temperature profiles for both solutions have been shown for $T_b = 300^\circ\text{K}$ and $T_b = 700^\circ\text{K}$. For the higher temperature solutions in both cases there are clear maxima and these are obtained nearly at the same location. From the curves it is evident that for higher temperature solutions the surface receives heat due to the higher rate of the endothermic reaction at the surface as mentioned earlier. For the lower temperature solutions the profiles are nearly straight. As expected the CO_2 profiles for the higher temperature solutions pass through maxima but the CO_2 maxima and temperature maxima are not located at the same point in the film as double film theory suggests. The higher temperature solutions also exhibit a very high concentration of CO and zero O_2 concentration at the surface.

The temperature and concentration profiles for reactive carbon at $T_b = 300^\circ\text{K}$ have been shown in Fig. 16. As mentioned before, only one

solution has been obtained for this value of the bulk temperature and so only one set of profiles is presented. Because of high reactivity, the surface reactions are quite high resulting in low O_2 and CO_2 concentrations and high CO concentration at the surface. By the same token the rate of the homogenous carbon monoxide combustion is also high resulting in temperature and CO_2 maxima within the boundary layer.

The rate of combustion of carbon, q , has been plotted for both normal and reactive carbons in Fig. 18. The short stub corresponds to the lower section of the solutions in Fig. 13 and the arm for the normal carbon reaching downwards is the lower part of the solutions in Figs. 9. The other two curves represent the upper part of the solutions for normal and reactive carbon. The two top curves indicate that as the ambient temperature rises (and T_g with it) the rate of combustion also rises, the reactive carbon combusting more rapidly at lower bulk temperature. At high temperatures both the curves flatten out but at a certain point the curve for the normal carbon rises above that for reactive carbon and then flattens. We may recall that Sebastian & Mayers reported that the effect of the reactivity falls off with increase in temperature. The cause for this is that beyond certain critical temperature the effect of R_1 becomes negligible and then it is R_2 which determines the rate of combustion and which is greater for normal carbon. The reason for the flattening off ^{of} the curves obviously is due to the transition to diffusion control. The q curve for the lower solution temperatures for normal carbon may be explained thus: as T_b rises, T_g falls (Fig. 9 and 10) and as a result both R_1 and R_2 decrease - hence the negative slope of the curve. An interesting feature is the location of the short stub for

the lower solution of reactive carbon. The q -curve for the lower solution is found to be above that for the higher solution. In this case higher q results because of its greater value of R_1 which has a greater weightage in the expression for q .

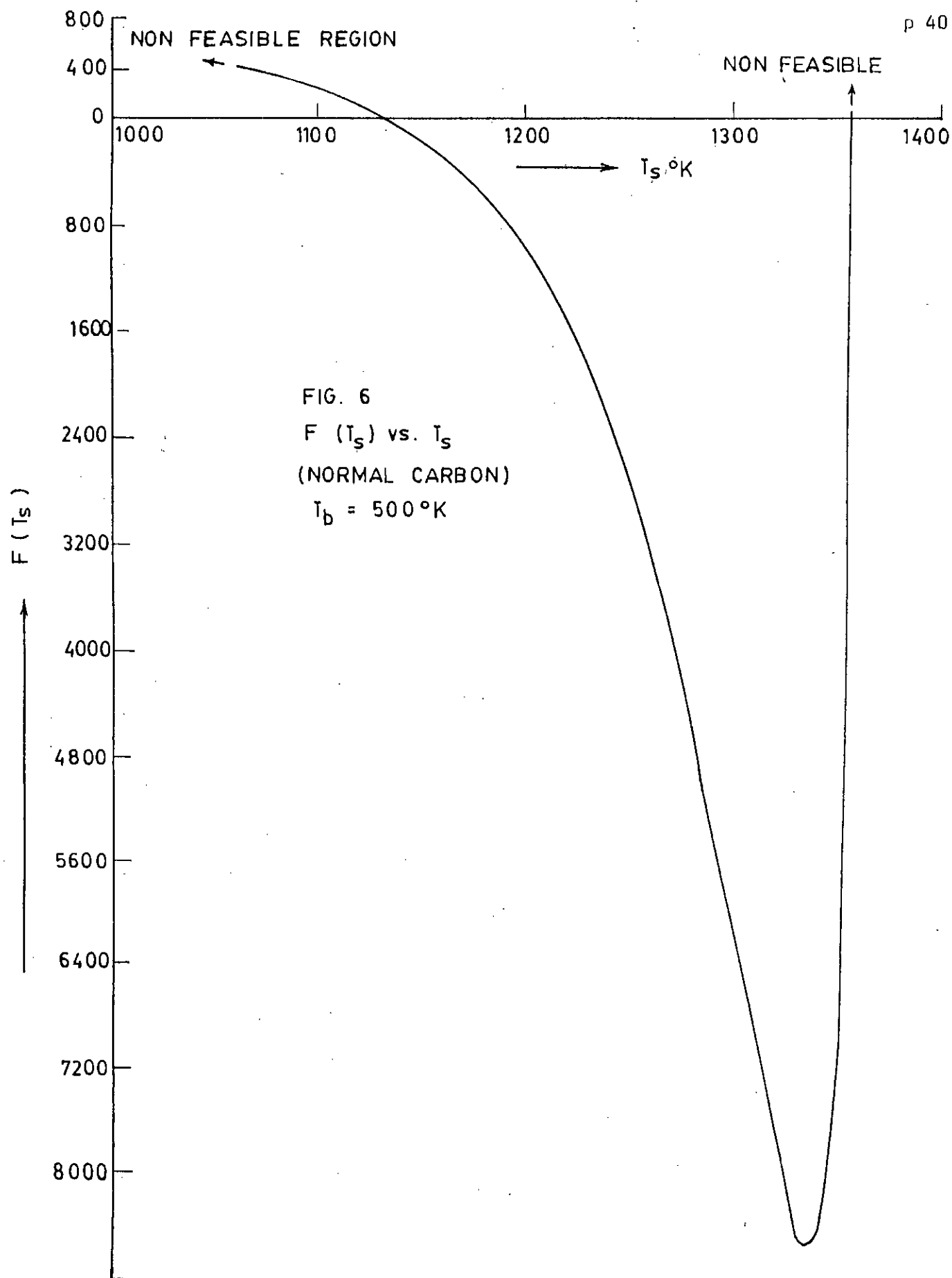
The heat generated at the surface, HS and the total heat generated, HT are shown in Fig. 19 for both normal and reactive carbons. Starting with the higher temperature solutions, it is seen that for both normal and reactive carbons the surface is receiving heat while HT is positive and the change is small, the change being due to more CO_2 reduction at the surface and higher rate of CO combustion in the film. This change is slightly more pronounced for the reactive carbon. For the lower solutions of the reactive carbon both HT and HS are seen to be positive (at the temperatures the roots were available) because of the domination of the oxidation reaction at the surface. The same is true for the normal carbon except to a varying degree.

In the present case, for reasons of simplicity, solution has been obtained with $R_{3b} = 0$. Here this is automatically satisfied because of the choice of boundary conditions. When both g_{1b} and g_{2b} are not zero, the analysis must consider a non zero value of R_{3b} keeping all other conditions unaltered.

4.2 CONCLUSION

The use of the polynomial greatly reduces the extensive numerical method required for obtaining a solution. However, the success of the method has not been fully established since, the method failed to predict

multiple solutions for reactive carbon. This point needs to be further investigated. The information that can be compiled from the solution, is immense and can enable us to look more deeply the events and transitions involved in the combustion of a carbon particle. Hopefully the present analytical solution, albeit approximate, would serve as basis for carrying out a more detailed analysis of a combustion reactor.



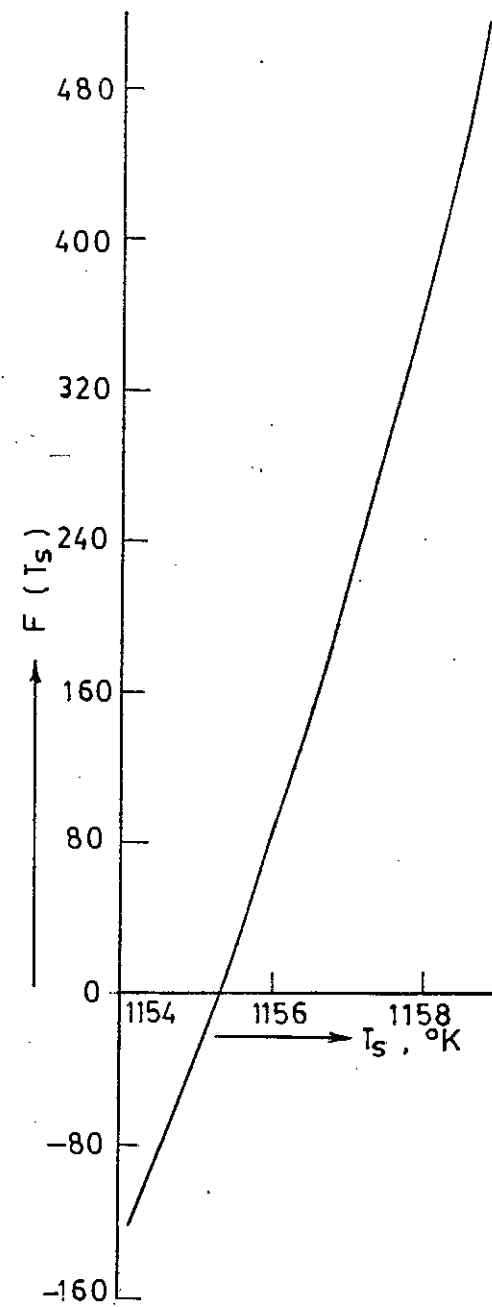
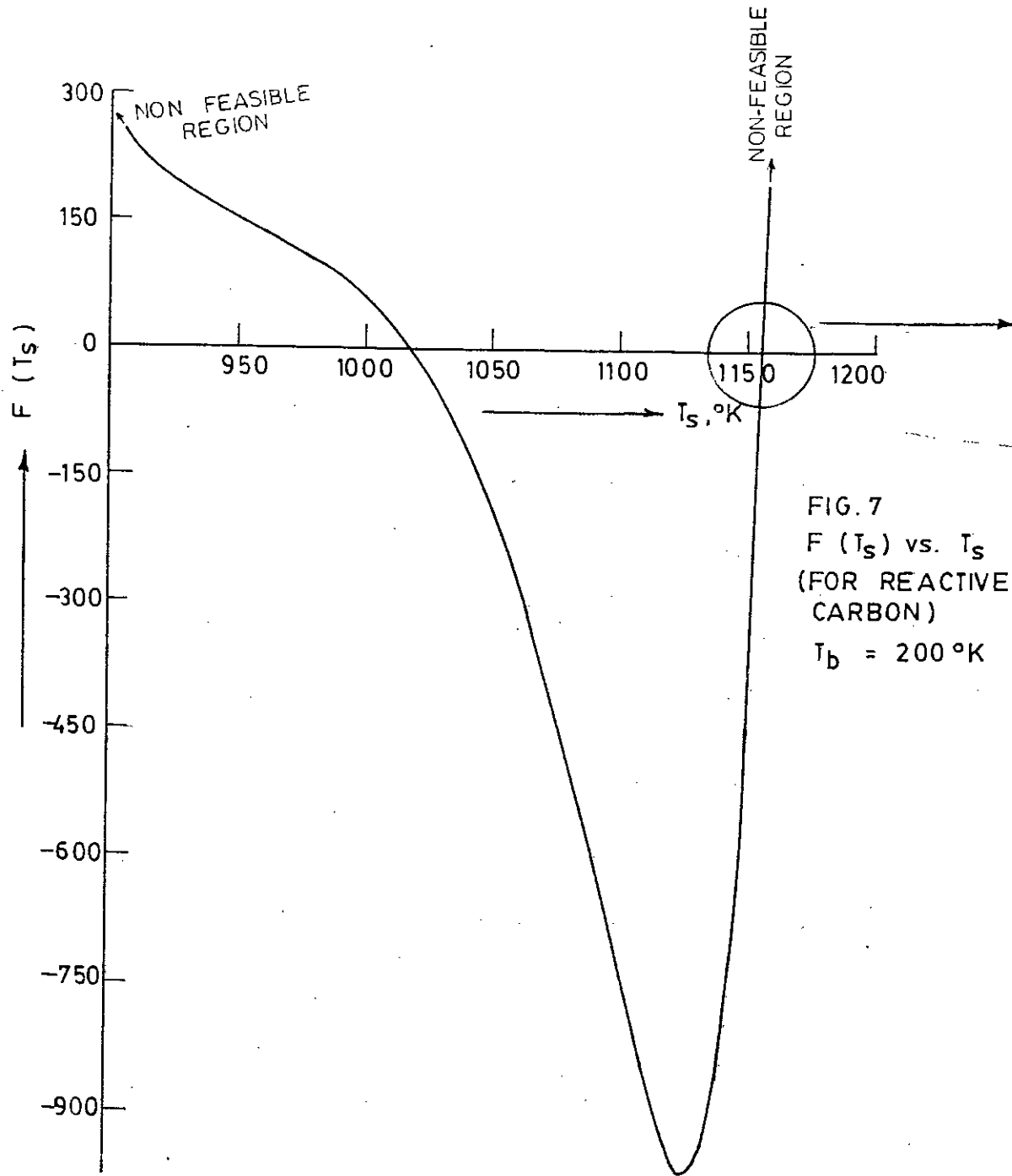
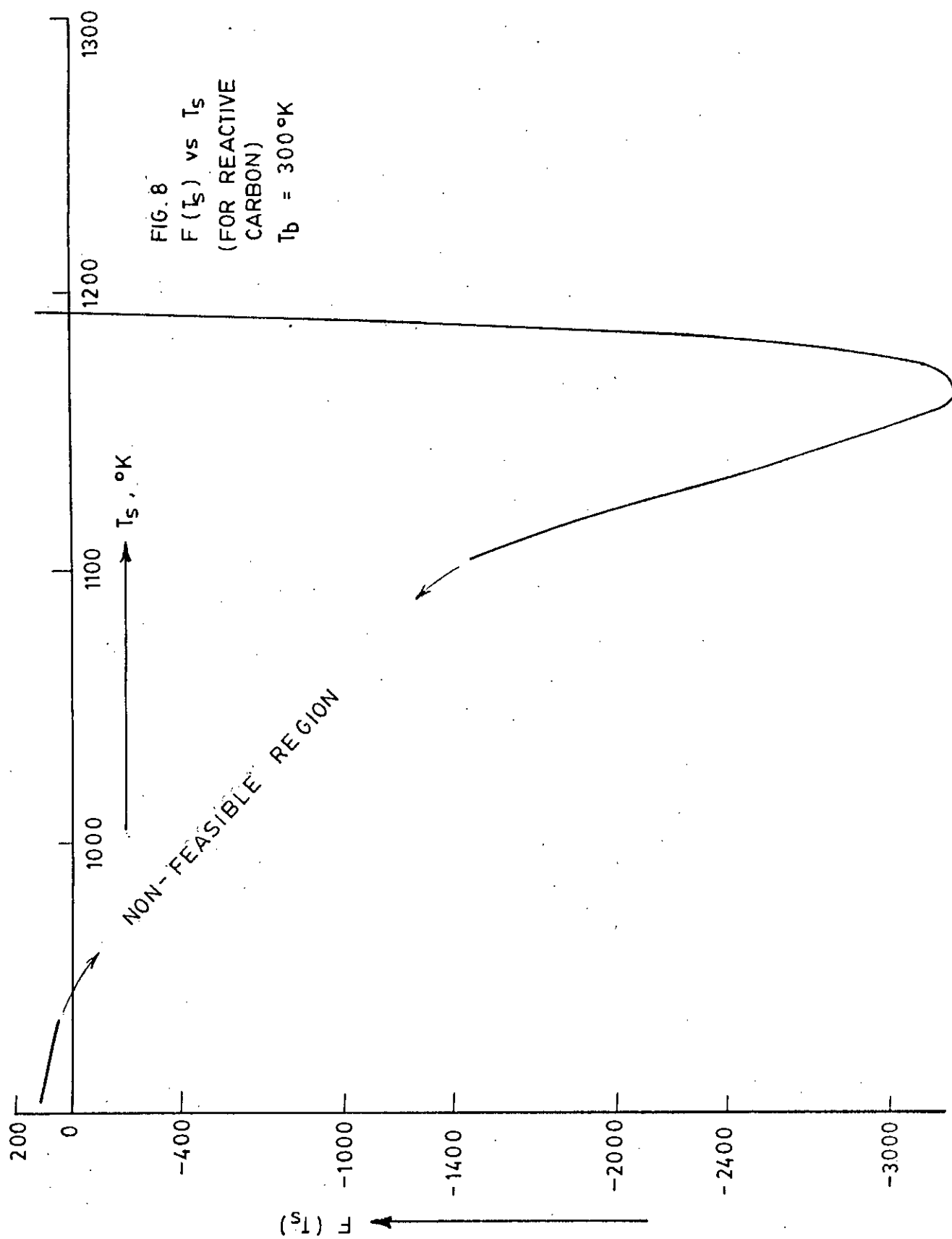
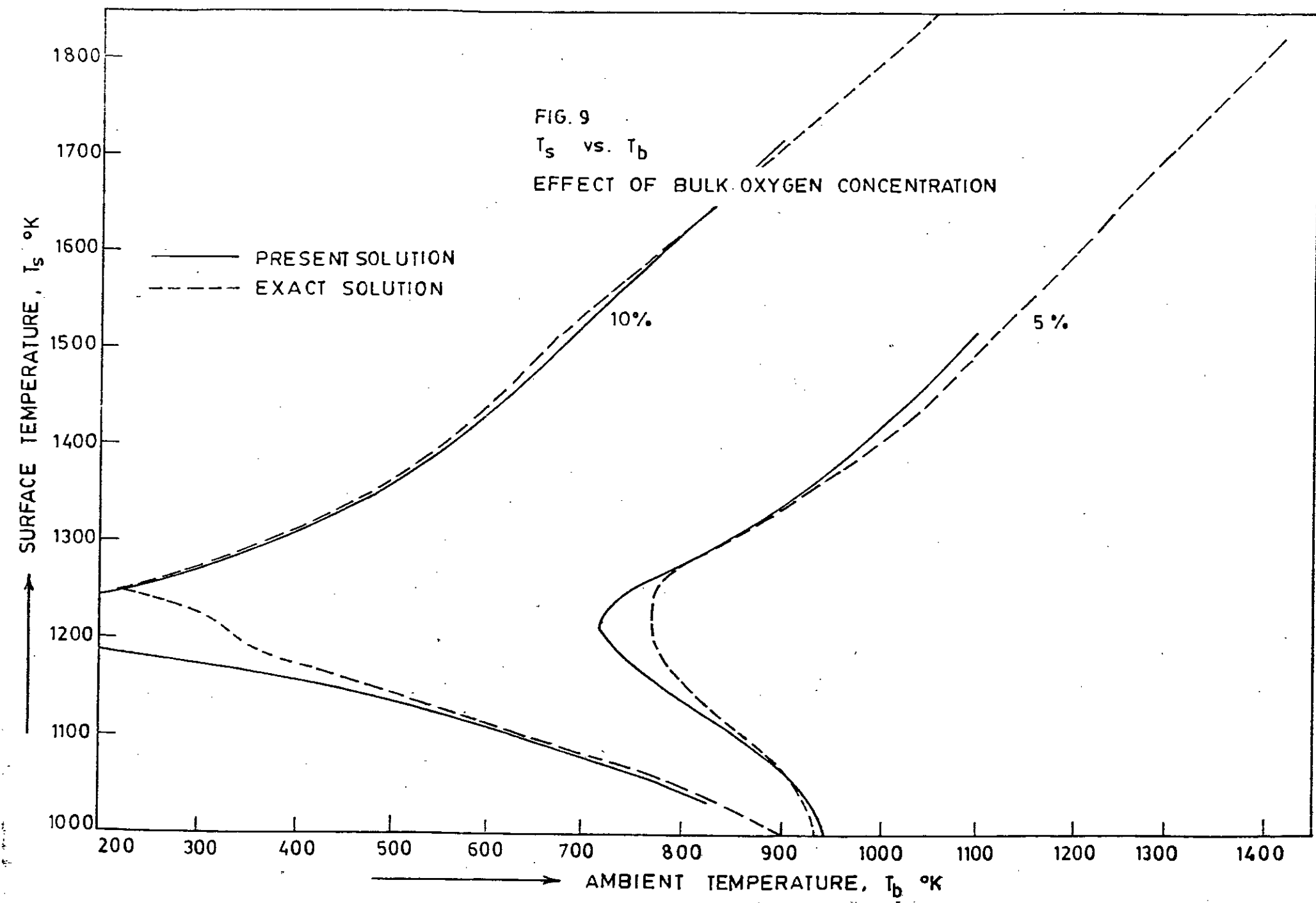
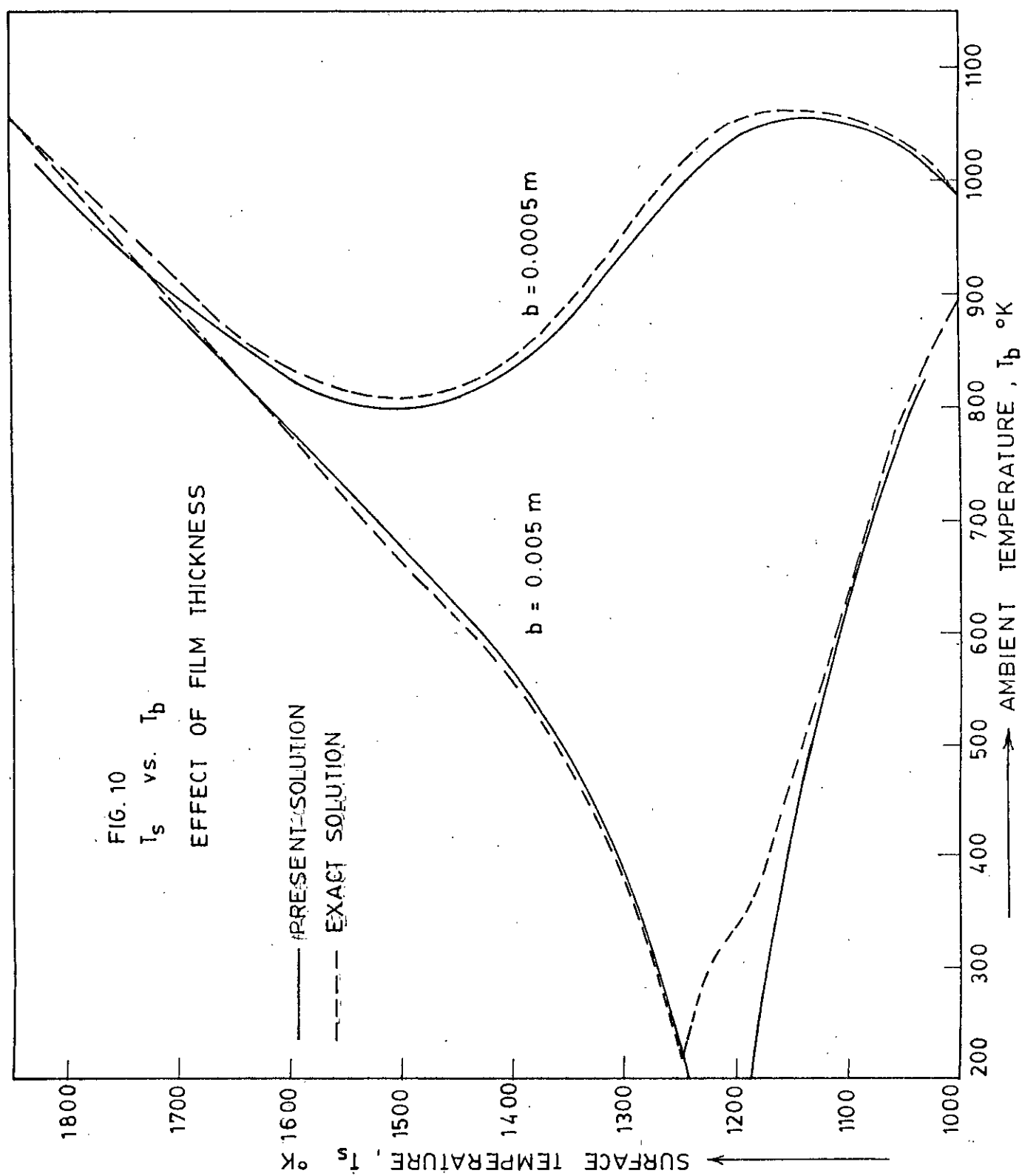
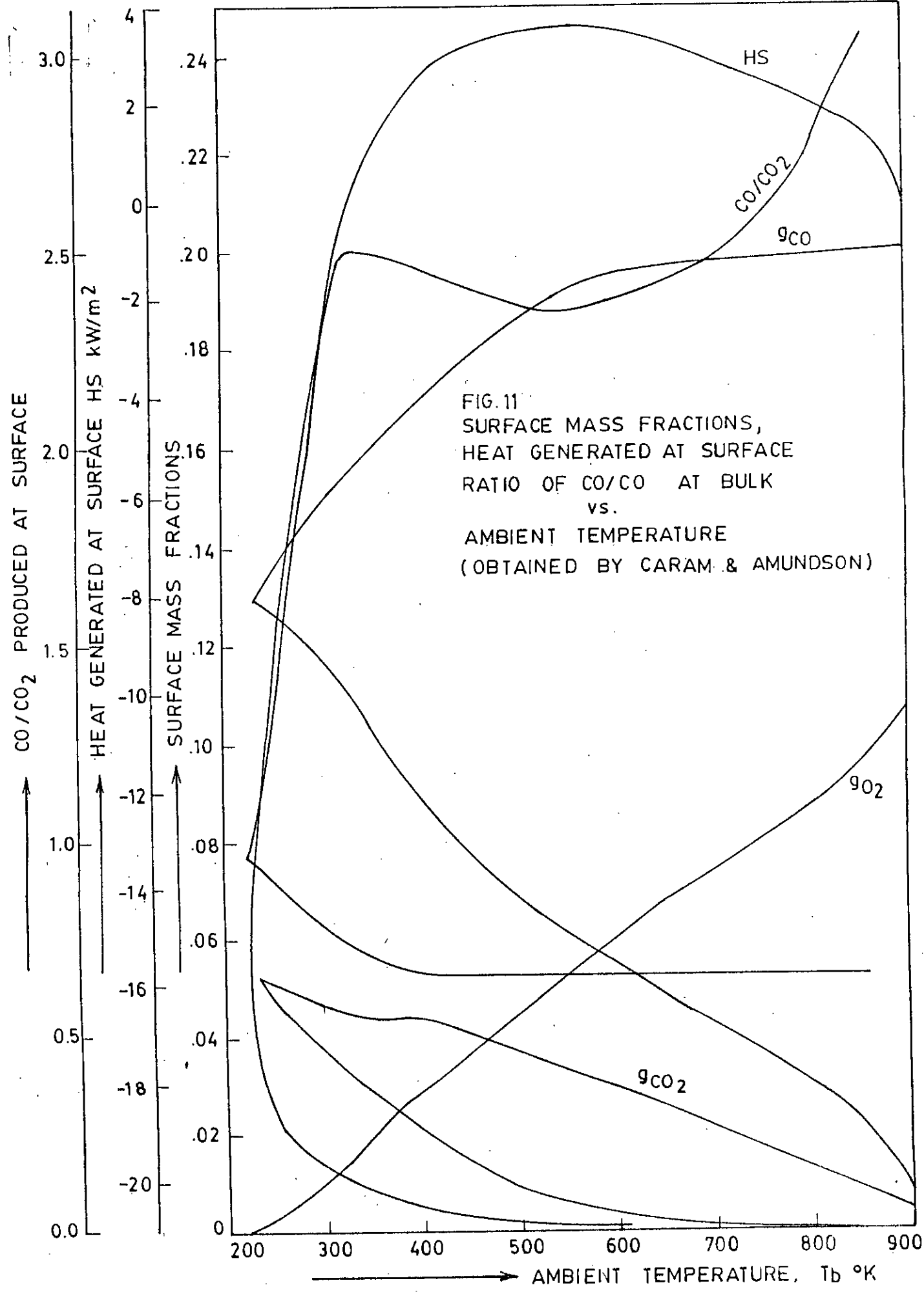


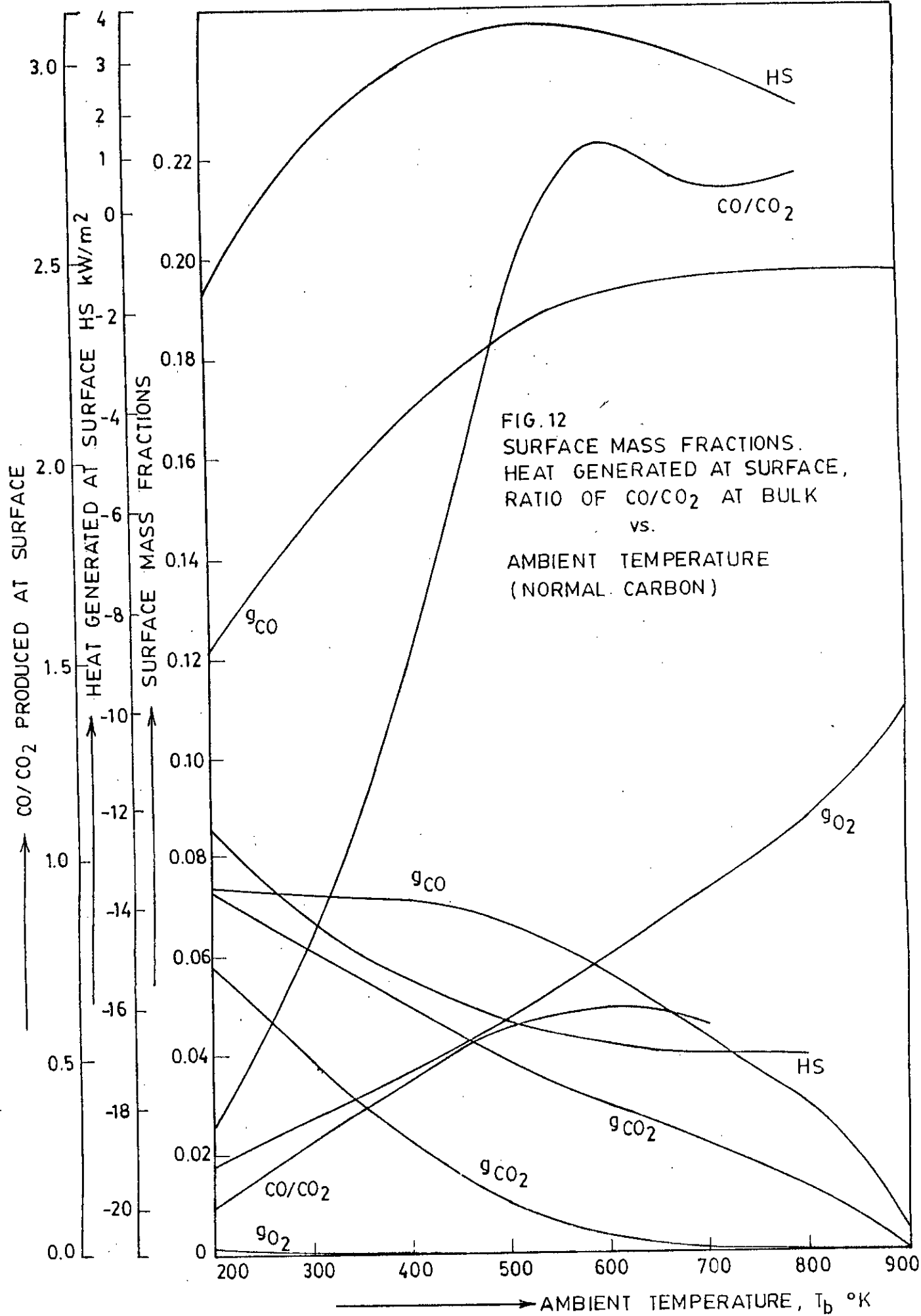
Fig. 7

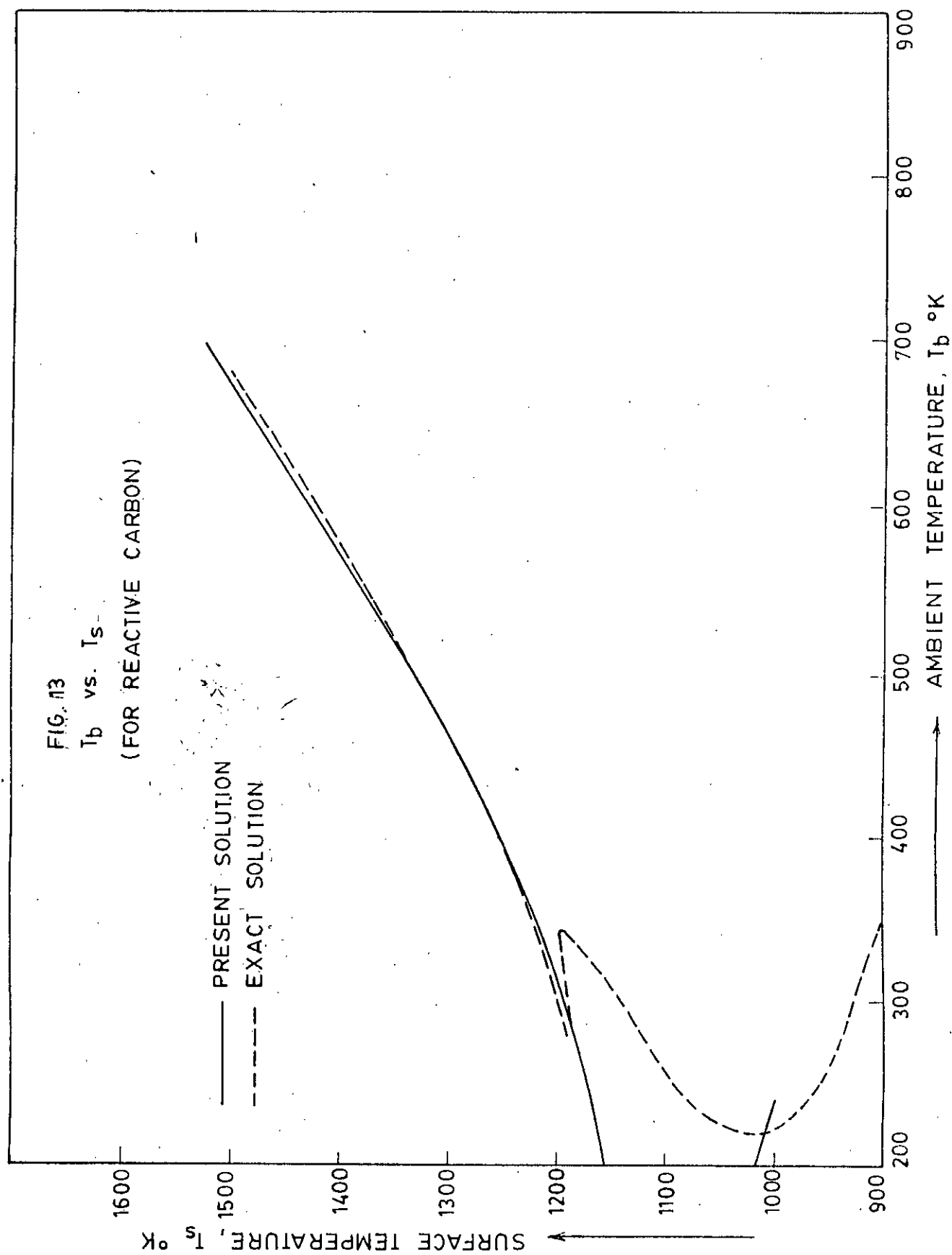


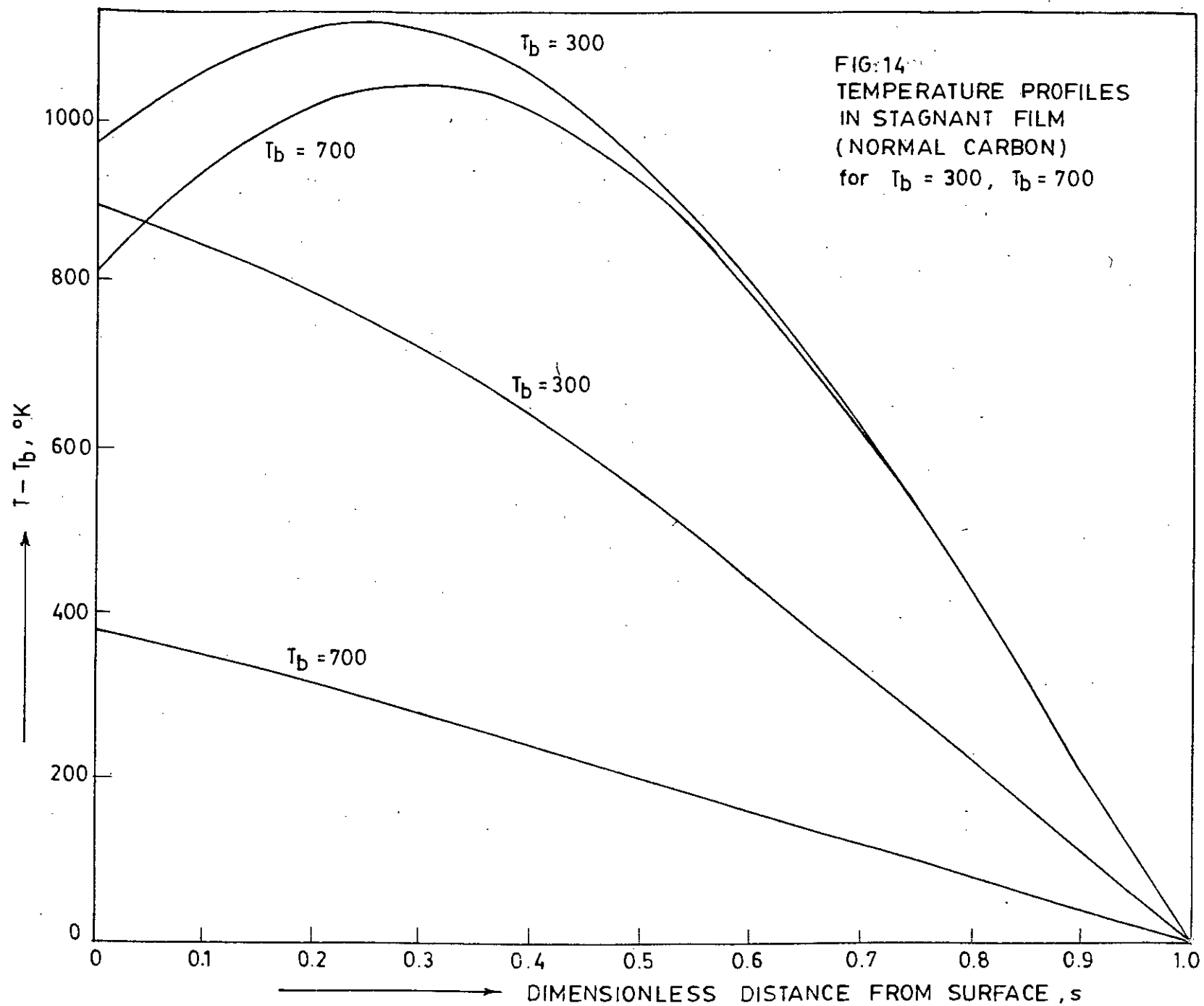


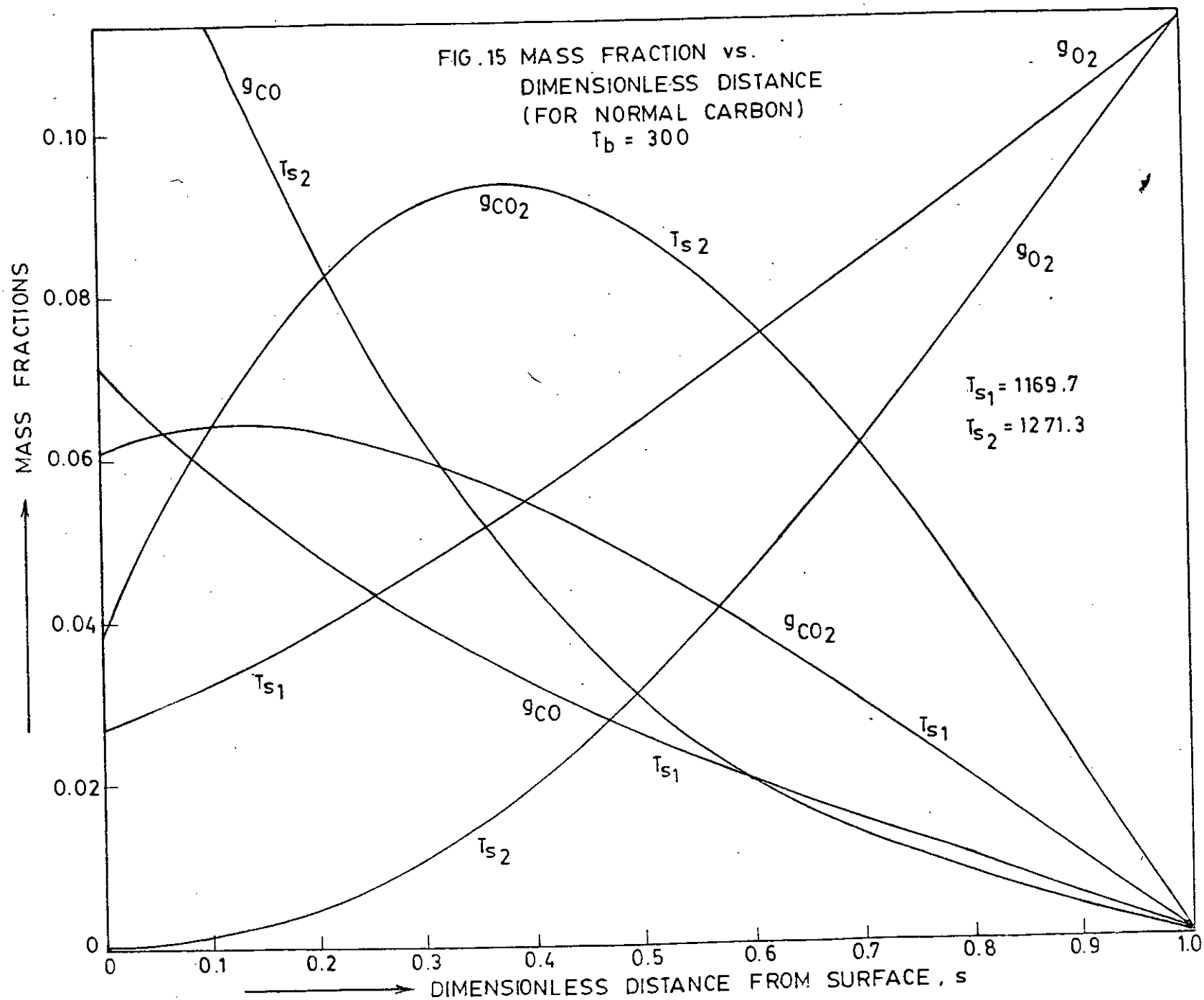


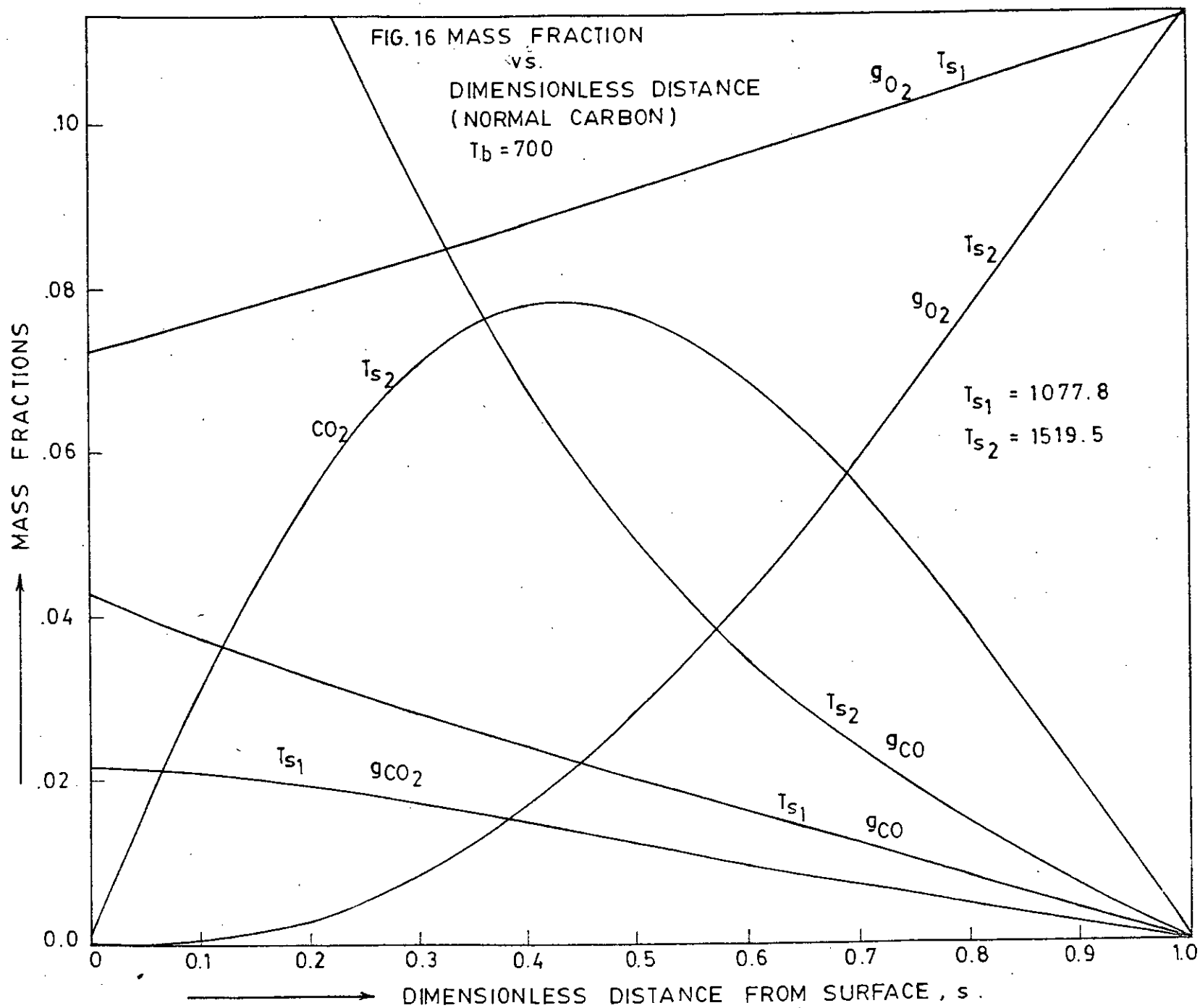


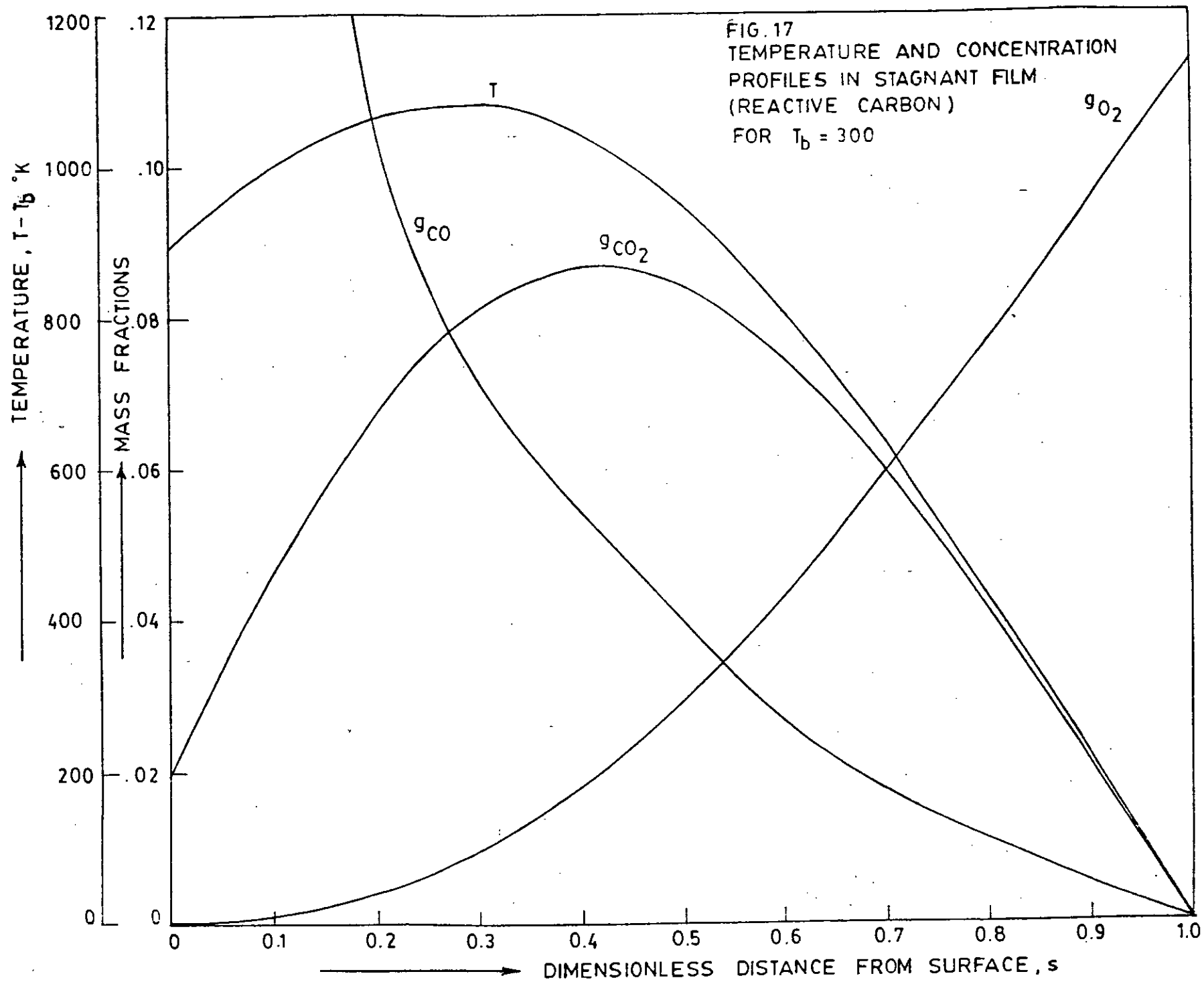


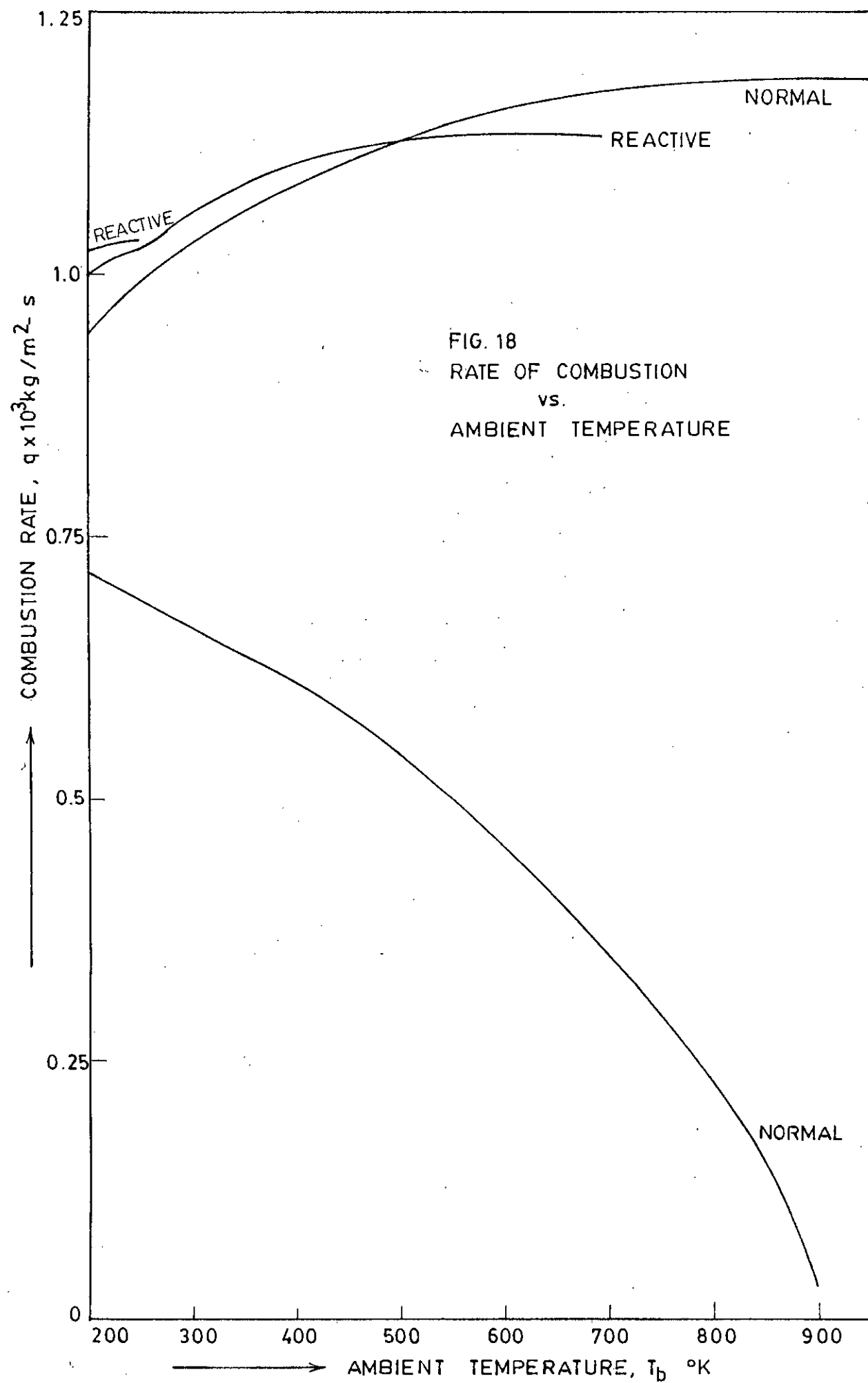


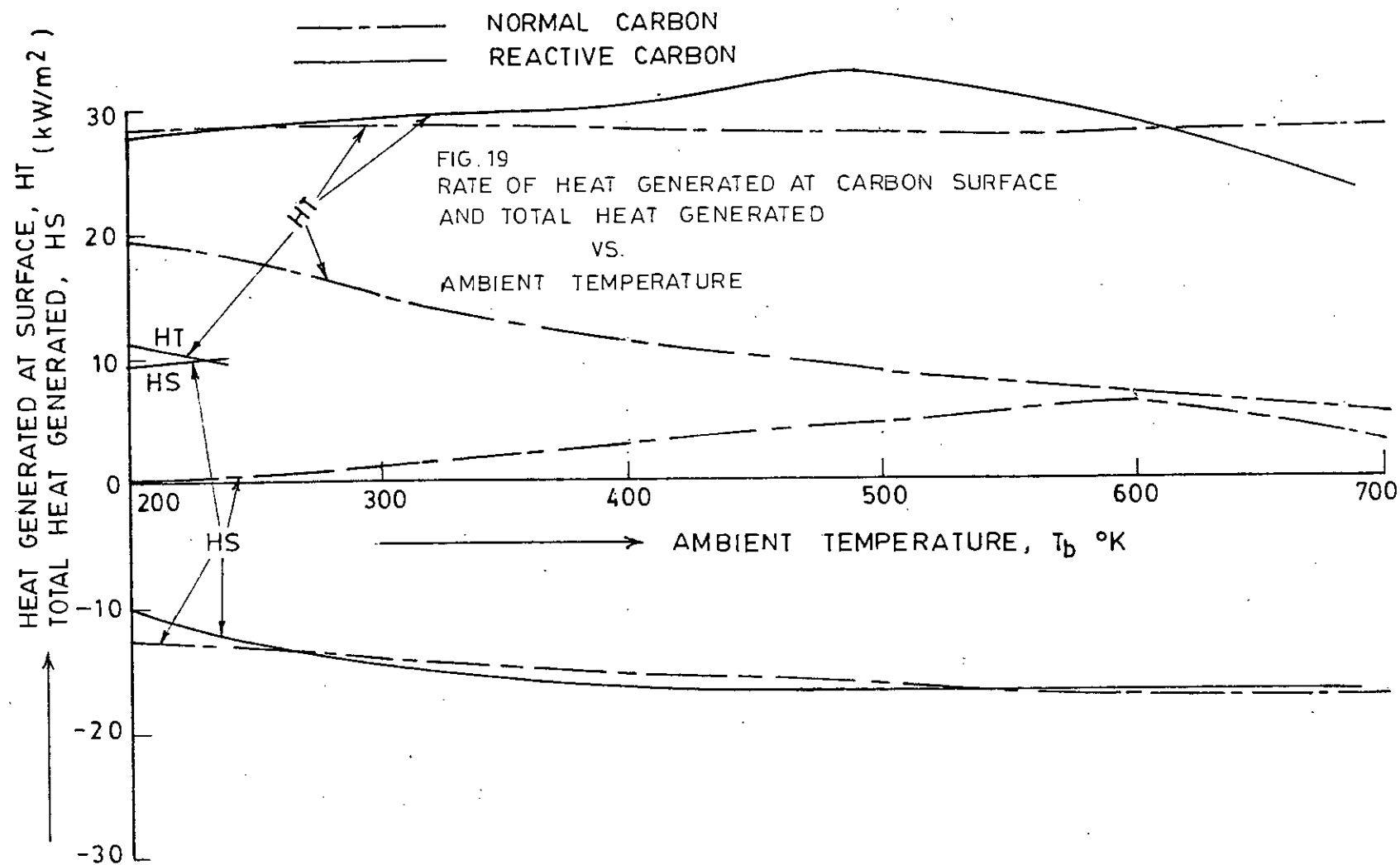












5. NOMENCLATURE

- A', A'', A''' = constants defined in equations 21, 22 and 23.
 A_0, A_1, A_2, A_3 = constants defined in equations 39, 40, 41 and 42.
 b = Thickness of boundary layer, m.
 B = Constant defined in equation 38.
 D_i = Diffusivity of i th component, m^2/s .
 E_i = Activation Energy of i th reaction, kcal/kgmol.
 g_i = Mass Fraction of the i th component.
 h_i = $\frac{\Delta H_i}{\lambda}$
 HS = Heat generated at the surface, W/m^2 .
 HT = Total heat generated, W/m^2 .
 k_1 = Rate constant for the $2C+O_2$ reaction, m/s.
 k_2 = Rate constant for the $C+CO_2$ reaction, m/s.
 k_3 = Frequency factor for the $CO+\frac{1}{2}O_2$ reaction, $(m^3)^{3/2}/(kgmol)^{1/2} s$.
 M_i = Molecular Weight of i th component.
 q = Rate of combustion, kg/s.
 R = Universal gas constant.
 R_1 = Rate of $2C+O_2$ reaction, $kgmols/m^2 s$.
 R_2 = Rate of $C+CO_2$ reaction, $kgmols/m^2 s$.
 R_3 = Rate of $CO+\frac{1}{2}O_2$ reaction, $kgmols/m^3 s$.
 S = Dimensionless distance from surface.
 T = Temperature, $^{\circ}K$.
 W_1 = Heat of combustion of two moles of CO, J/2 kgmol of CO.
 x = Distance from surface, m.

Subscripts: s = surface.
 b = ambient or bulk.
 1 = carbon dioxide.
 2 = carbon monoxide.
 3 = oxygen.

Greek Letters:

α = defined in page 24.
 β = defined in page 25.
 $(-\Delta H_1)$ = Heat of reaction for $2C+O_2$ reaction J/kgmol of O_2 .
 $(-\Delta H_2)$ = Heat of reaction for $C+CO_2$ reaction, J/kgmol of CO_2 .
 γ = defined in page 25.
 ρ = Density of gas, kg/m^3 .
 λ = Thermal Conductivity, J/m s K..

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