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ABSTRACT

The vapor phase air oxidation of methane was investigated in an isothermal integral flow reactor at atmospheric pressure. Copper oxide on pumice and palladium on asbestos were the main catalysts studied. The effects of nitric oxide on pumice, copper oxide and palladium was also investigated at 600 to 670° C.

The effect of temperature, feed ratio,and weight ratio of modifier to feed on the conversion of methane and the product distribution was determined by gas chromatography.

It has been found that nitric oxide,a homogeneous catalyst for the partial oxidation of methane, does not have any inhibiting or promotional effect when used with copper oxide or palladium, and that the reaction with these catalysts takes place on the catalytic surface between the adsorbed fragments of reactants.

In the presence of small amounts of methylene chloride, the overall oxidation of methane is substantially inhibited. At the same time, however, this compound enhances the formation of formaldehyde.

It is suggested that the promotional effect of the modifier is mainly due to its interaction with adsorbed oxygen and adsorbed formaldehyde, supressing the further oxidation of aldehyde to the undesired products.

I INTRODUCTION

The catalytic oxidation of hydrocarbons is growing in importance as a method of synthesis. In principle, most oxygenated carbon compounds, as well as olefins and dienes, can be made by the partial oxidation of plentiful hydrocarbons. Equilibria in reactions with oxygen are usually very much in favor of the oxygenated or dehydrogenated products, and the major problem is that of obtaining a selective reaction. As knowledge grows, we find more examples of succesful oxidation processes. Reactions now carried out on a large scale include the oxidations of ethylene to acetaldehyde, ethylene to ethylene oxide, propylene to acrolein, benzene to maleic anhydride, and naphtalene to phthalic anhydride.

There are at present three fundamental directions of pursuit in the investigation of oxidative processing of hydrocarbons: (1) heterogeneous oxidation by molecular oxygen in the gas or liquid phase; (2) homogeneous oxidation by molecular oxygen in the gas or liquid phase; (3) radiation induced oxidation by molecular oxygen.

Methane is the most difficult hydrocarbon to oxidize and although it is the simplest hydrocarbon gas and would be expected to give formaldehyde uncontaminated with more complex organic products, its partial oxidation is extremely difficult and usually results in its complete conversion to carbon dioxide and water. Indeed the present incomplete understanding of the mechanism of such oxidation is largely attributable to the apparent absence of partial products which could throw some light on the routes followed by the overall reaction.

In the present work, an exploratory study has been made to find suitable catalysts to isolate intermediates in the catalytic oxidation of methane. This is a very important step to accomplish in the partial oxidation of methane, mainly due to the great lack of information available, and before going to a deeper insight into the kinetics of such reaction.

In order to determine the nature and role of these intermediates and to enable appreciable quantities of such compounds to be isolated, either the direct route for the complete oxidation of methane or the futher oxidation of the intermediate products must be inhibited.

Since the chemisorption of methane involves dissociation to labile adsorbed methyl or methylene groups, which may carry a slight positive charge, one method of improving the yields of partial products is to control appropriately the further reactions of these adsorbed species.

Particular attention has been paid to the influence of gaseous addidives and studies have also been made of the effect of an halogen compound which would be expected to increase the selectivity of conversion of the initial hydrocarbon to partial oxidation products.

An integral fixed bed flow reactor has been chosen in this study for the following reasons:

(a) From an industrial viewpoint one is more interested in yield and selectivity, using a mixture of air and methane over a heated stationary catalyst at approximately atmospheric pressure;

(b) Integral reactor is not restricted to small conversions and analytical accuracy is greater.

(c) Modifiers continuously escape from the catalyst surface and a batch reactor would not be suitable for catalyst modification study.

II. LITERATURE SURVEY

Direct oxidation of methane to formaldehyde would be economically very attractive if sufficiently high formaldehyde yields could be obtained. Many of the studies directed to this end have involved noncatalytic processes or the use of homogeneous catalysts. However some work has also been done on the use of heterogeneouscatalysts.

Norrish (1) introduced in 1948 a di-radical-chain scheme for methane oxidation involving active centres which were CH_2 radicals and oxygen atoms. Norrish considered that the first and evidently the only stable intermediate product was formaldehyde.

Bone and Gardner (2) found that the maximum concentration of formaldehyde and the maximum reaction rate were attained almost immediately after the end of the induction period and were maintained practically unchanged during the further course of the oxidation reaction.

The second important evidence of the special role of formaldehyde was the sharply accelerating effect of its addition to the methane oxidation. Thus, for example, Bone and Allum (3) found that small additions of formaldehyde to a methane-oxygen mixture can cause considerable reduction of, and even complete elimination of, the induction period and also a sharp decrease of the reaction period.

Vanpée (4) proved that if the quantity of formaldehyde added to the initial methane-oxygen mixture was exactly equal to the maximum quantity accumulated at the moment of attainment of maximum reaction rate without addition of formaldehyde, then the oxidation begins rapidly and takes place at the maximum rate.

There was little doubt regarding the close relationship between the concentration of formaldehyde and the rate of methane oxidation. Hence it was natural to suppose that this link was determined by the branching role of formaldehyde in the process of methane oxidation.

After the publication of Norrish's di-radical-chain scheme, one of the several problems confronting the investigators in the oxidation of methane was to find a satisfactory explanation for the displacement of the maximum rate of methane oxidation, and the conditions under which the reaction rate declines after its attainment and when it remains constant almost to the end of the transformation.

The second problem has been to find a satisfactory explanation regarding the role of formaldehyde in the process of methane oxidation. This has been now proved beyond doubt by the special significance of formaldehyde in the oxidation reaction of methane and led to the assumption that it is this intermediate product which is responsible for degenerate branching.

The third problem which had remained unexplained in the kinetics of methane oxidation concerned the orders of the reactions with respect to each of the reactants.

According to Norrish's scheme (5) the maximum reaction rate varied with the concentrations of methane and oxygen in the following manner $W_{max} \cong [CH_4]^m [O_2]^n$ where $m \cong 2$, $n \cong 1$. At low temperatures (up to 500°C), this relationship agreed well with experimental data. While the order of reaction with respect to methane decreased with increasing temperature it increased with respect to oxygen.

Another problem which could not escape the attention of the investigators was the problem of the magnitude of the total activation energy of methane oxidation. In the literature there are different experimental values for this important characteristic of the reaction. Thus Vanpée (6) for the temperature range 377-422°C obtained the value E= 93 Kcal/mole, Bone and Allum (3) for the range 423-487°C found E= 90 Kcal/mole and Fort and Hinsshelwood (7) for the range 447-487°C found E= 62 Kcal/mole. It has been thus concluded that decrease in temperature below 450°C leads to a significant increase (from 60 to 90 Kcal/mole) in the activation energy of methane oxidation.

Yenikolopyan (8) using Semenov's theory (9) of degenerate branching reactions, has examined the oxidation of methane in detail. However no mention has been made regarding the variation of the activation energy with temperature.

He showed theoretically that in degenerate branching reactions, up to the attainment of the maximum rate, and maximum concentration of the branching product, the rate of pressure increase and the accumulation of this active product always changed in the same sense.

Yenikolopyan examined also the question of the variation of reaction rate with respect to the extent of combustion. It was seen that the maximum rate, after which a sharp decrease always occurred was attained at the moment when fifty percent of the initial reactants have been converted. Another kinetic characteristic of the reactions under consideration which was given a theoretical explanation in the work of Yenikolopyan was the effect of the additions of an intermediate substance giving rise to degenerate branching on the reaction kinetics. Since this effect was felt mainly in the initial stages of the reaction, the author proposed that the concentration of initial reactants remained unchanged during the transformation. Thus it can be stated that Yenikolopyan was able to deduce from theory all the facts established much earlier by experiment concerning the effect of additions of the intermediate branching product on the kinetics of degenerate branching reaction. This also made it possible to establish criteria for examining the type of intermediate products which determine degenerate branching. They suggested that this was the complete elimination of the induction period of the reaction for additions of this intermediate product to the initial mixture, in quantities corresponding strictly to the maximum formed in reaction without additives under the given conditions. The reaction in this case should initiate the non-branching reaction and proceed from the very begining at a constant rate, equal in magnitude to the maximum rate obtainable under given conditions for reactants without additives.

The last problem which attracted the attention of Yenikolopyan (10) in the kinetics of methane oxidation was the problem of the variation in the order of this reaction with respect to the initial reactants as temperature is increased. Yenikolopyan has shown that the orders of reaction with respect to hydrocarbon and oxygen changed with temperature from second to first and from zero to second respectively.

Hoare and Walsh (11) established that the values of the order of the reaction and the magnitude of the total activation energy depended on the nature and state of the surface of the reaction vessel. The authors used in their experiments quartz vessels, the surface of each of them being subjected to different kinds of special treatment before being used for methane oxidation. They found that different surfaces induced different rates and it was possible to place them in the following decreasing order of decreasing rate: treated with hydrogen fluoride, old, heat treated and coated with lead oxide. The authors considered that this was undoubtedly caused by the oxidation of carbon monoxide formed during the reaction of methane with oxygen. This oxidation was encouraged by the treatment of the surface with hydrogen fluoride and the presence of excess oxygen. Further experiments showed that additions of carbon monoxide to the initial mixture caused a greater pressure decrease. From this the authors concluded that the oxidation of carbon monoxide under these conditions was induced by the oxidation of methane.

Semenov (12) proposed in 1958 the following radical-chain scheme for the process:

(0) $CH_4 + O_2 \longrightarrow \dot{C}H_3 + H\dot{O}_2$

(1) $\dot{C}H_3 + O_2 \longrightarrow HCHO + O_2$

(2) $\dot{O}H + CH_4 \longrightarrow \dot{C}H_3 + H_2O$

(2') $\dot{O}H + HCHO \longrightarrow H_2O + H\dot{C}O$

(3) $HCHO + O_2 \longrightarrow H\dot{C}O + H\dot{O}_2$

(4) $H\dot{C}O + O_2 \longrightarrow CO + H\dot{O}_2$

(5) $CH_4 + H\dot{O}_2 \longrightarrow H_2O_2 + \dot{C}H_3$

(5') $HCHO + H\dot{O}_2 \longrightarrow H_2O_2 + H\dot{C}O$

(6) $\dot{O}H \xrightarrow{\text{wall}}$ chain breaking

Using the method of quasi-stationary concentrations, he obtained the following expression:

$$-\frac{d[CH_4]}{dt} = \frac{2k_2 k_1}{A_6} \left(\frac{k_2 k_5}{k'_2 k'_5}\right)^{1/2} [CH_4]^2 [O_2]$$

where "A" is defined as being equal to the product of the rate constants and concentration of initial reactant participating in the given elementary process.

The value of the activation energy found from this equation was about 46 Kcal/mole, as compared to experimental value of 44-46Kcal/mole.

Literature dealing with the theoretical and experimental aspects of the reaction mechanism is quite comprehensive. Besides the explanation of the reaction mechanism there is another, but no less important aspect of the chemical transformation, viz. ways and means of controlling the reaction for the selective preparation of one of the products which is industrially valuable. An understanding of the mechanism can give a reason able choice of ways of influencing the reaction.

In the oxidation reactions, alcohols and acids undergo further oxidation only to a negligible extent and can therefore be considered as end products of reactions. In contrast to these formaldehyde enters readily into subsequent oxidations with the formation of water and oxides of carbon and is therefore an intermediate product.

From what has already been said it is clear that in so far as alcohols and acids are concerned the problem of increasing their yield reduces to the problem of increasing the proportion of the initial hydrocarbon. In the case of formaldehyde, for a given percentage of oxidation of the initial hydrocarbon, it is important to increase the yield of formaldehyde whilst suppressing further oxidation.

Attempts to achieve this gave rise to a whole series of relevant experimental studies. They all reduced to an endeavour to alter the concentration of active centers which can be achieved by action on the main types of elementary processes: initiation of active centers, degenerate branching and destruction of active centers. For this purpose many methods can be employed as small additions of substances capable of forming the radicals more readily than the initial reactant, addition of inert gas, variation of vessel diameter, treatment of vessel walls, etc.

Nevertheless the attempts to increase the yield of formaldehyde by this means proved to be unsuccessful. The reason for this lack of success was explained by Yenikolopyan (13).

Schematically

$$A \longrightarrow B \longrightarrow C \qquad\qquad B \text{ (intermediate product)}$$

Rate of accumulation of B:

$$\frac{d[B]}{dt} = \sum_{ij} a_{ij}\, n_j - \sum_{kl} b_{kl}\, n_l$$

The first term is the sum of elementary processes leading to B. The second is the sum of elementary processes leading to the consumption of B.

'aij' and bkl' are kinetic coefficients equal to the product of a constant and the concentration of initial reactant or intermediate product. 'n_j' and 'n_l' are concentration of active centers.

When $\frac{d[B]}{dt}$ becomes equal to zero, the concentration of B reaches a maximum. If the concentration of active centers n_j and n_l are directly proportional, then any effect on n_j leads to a corresponding change in n_l; that is the maximum concentration of formaldehyde remains unchanged.

Yenikolopyan (13) studied the effect of:

(1) Addition of inert gas decreasing chain breaking and therefore increasing concentration of active centers.

(2) Diameter of reaction vessel

(3) Treatments of wall and packing it

(4) Addition of homogeneous catalyst

He found that (1), (2), and (3) had no effect on yield of formaldehyde.

Thus the results of Yenikolopyan suggest that any variable that effects the reaction leading to a change in the concentration of active centers cannot increase (or decrease) the maximum concentration of intermediate formaldehyde. It should be stressed besides, that this conclusion refers to the case when the intermediate product is formed and consumed by chain means. Yenikolopyan also showed that if on the other hand the intermediate product, forming a chain, is consumed by molecular means, then its maximum concentration could be increased by increasing the concentration of active centers. Therefore if it could be possible by any means (homogeneous additives, surface changes) to obtain a non chain consumption of inter mediate product, then by increasing the concentration of active sites may increase the yield of the intermediate product.

Bibb and Lucas (14) have demonstrated that a low concentration of nitric acid vapor obtained by passing the gases to be oxidized through concentrated nitric acid at room temperature acts as an effective reaction catalyst.

Bone and his co-workers (15, 16) found that while the addition of small amounts of nitric oxide diminishes, amounts in excess of the optimal completely eliminates the oxidation induction period of methane. Thus they found that the addition of a 32 percent nitric oxide eliminated the induction period. Two modes of heating of the mixture have been mentioned. The authors assumed that the first maximum was produced by the rapid reaction of nitric oxide with methane with the formation of nitromethane, and the second was the result of the oxidation reaction of methane, catalysed by nitromethane.

A patent (17), relates a process of manufacturing formaldehyde by oxidizing methane with oxygen of air with small quantities of nitric oxide added in the presence of catalysts. According to the main patent the catalyst preferably used in the process was pumice. The best conditions are attained using Italian pumice at 670° C reaction temperature with 5:1 air to methane ratio and a residence time of up to 35 seconds.

According to Mayor (18) the best results have been obtained by the use of a solid catalyst in conjunction with an oxide of nitrogen.

Holm and Reichl (19) also describe another German bench scale methane oxidation process whereby 90% of formaldehyde could be obtained. This procedure employed oxygen containing approximately one percent ozone and a supported barium peroxide catalyst activated with approximately .5 per cent of silver oxide.

Patented process for the conversion of methane to formaldehyde cover a wide variety of techniques including the use of sonic gas velocities, fluid bed catalysts (20), ultraviolet light in the presence of mercury vapor and a motored engine reactor.

Schonfelder (21) reported 55 to 58 per cent conversions of methane to formaldehyde by the passage of a mixture of air, methane and steam over copper or silver at 500°C.

Campbell (22) investigated the use of a number of supported metal catalysts for methane oxidation. Formaldehyde was the principal intermediate product.

Ahuja and Mathur (23) investigated the kinetics of methane oxidation using a palladium catalyst. The conversions of methane were small and limited to about 10 per cent. The experimental results indicated that the reaction rate was controlled by surface reaction in which the adsorbed oxygen and adsorbed methane reacted to produce adsorbed carbon dioxide and adsorbed water.

Firth (24) studied the complete oxidation of methane on palladium-gold alloys using a microcalorimetric method, and suggested that the oxidation probably occurred through a series of reaction steps involving partially oxidized intermediates adsorbed on the catalyst. It also seemed likely that the slow step in the oxidation on palladium was the reaction of this adsorbed intermediate, and not the dissociative adsorption of methane The reaction was found to be first order with respect to methane under all the conditions studied.

Anderson and co-workers (25) found oxides of nickel,chromium, manganese, vanadium and cobalt quite effective for methane oxidation. From the recent work of Anderson (25), it has been concluded that catalytic activity of metals and their oxides decreases in the following order: palladium, platinum, chromium, manganese, copper, cerium, cobalt, iron, nickel and silver. This order of effectiveness was the same as previous reported by Cohn and Haley (26).

Atroshenko (27) studied the heterogeneous oxidation of natural gas, formaldehyde and methanol using different supported catalysts. He found the optimum amount of metal on pumice to be 2-10%, and the most active catalysts to be the oxides of: molybdenum, thorium, chromium, silver and mixtures of the oxides of silver and chromium.

Andrushkevich and co-workers (28) studied the catalytic properties of the metal oxides of period IV of the periodic table with respect to oxidation of methane. It has been established that the activity of the oxides, calculated on the basis of 1 g.m. of active metal decreased in the following order: chromium, manganese, copper, cobalt, iron, nickel. While the most active single component catalyst was cobalt oxide, the most active supported catalyst was chromium oxide. The activation energy of the active catalyst was in the range 15-25 Kcal/mole. The order of the reaction with respect to methane was sufficiently close to first order.

III. THEORY

Although the change with time in the degree of advancement of a reaction cannot be calculated from fundamental data with any accuracy, the systems of chemistry provide indications of the course of reactions and of the factors which affect their rate. Current concepts of catalysis by solids reemphasize the congruence with chemistry and suggest the application of its great factual and theoretical content to surface chemistry by means which are overtly or tacitly empirical e.g. by analogy, correlation.

The object of the design of a complex catalyst for a new process is to prescribe a set of solid phases of suitable specifity, the manner of their association,their physical form and methods of preparation and use. Thus major problems are encountered in the selection of the relevant data, the representation of essentials in comprehensible form and the manipulation of the findings.

Due to lack of experimental information on the nature of elementary steps in the catalytic oxidation of hydrocarbons it is difficult to establish the true mechanism of catalytic heterogeneous reactions. However it is also suggested by many scientists, by analogy with reactions occurring in the homogeneous phase, that catalytic oxidation of hydrocarbons proceeded via the generation and intereaction of radicals.

1. DERIVATION OF THE VIRTUAL MECHANISM

The true mechanism of a novel process will be necessarily based upon cognate chemistry, which is displayed in the "stoichiometric statement", a series of reactions of molecularity not exceeding two and of specified type e.g. dehydrogenation, condensation etc.

(A). The stoichiometric statement

The target transformation (T): shows the desired overall reaction (the molecularity may exceed 2).

The characteristic of various type of chemical reactions can be classified as:

(I) Primitive processes (P), reactions of single reactants molecules

(II) Self-interactions (S), reactions between identical reactant molecules

(III) Cross-interactions (CS), reactions between different reactants

(IV) Sequential reactions (SQ), between reactants and the products of their own primitive processes and self-interactions.

(V) Cross-sequential reactions (CSQ), between a reactant molecule and the products of the reactions (I), and (II), of other molecules, and so on.

(B) The Thermodynamic Theme

Thermodynamic methods are generally used to define approximate ranges of the operating variables for the target transformation and then, within these ranges, to assessthe probability of the chemical characteristics of the reactions. In addition to the usual physical and thermochemical information, likely parasitic reactions should be recognizable as well as intermediate steps in the significant reactions. All stable molecules must be considered as possible intermediates and products.

(C) The mechanism

The possible overall transformations, target and parasitic reactions are generally written in extended form as sequences of stoichiometric statements drawn from the characteristic chemistry and show in proper order the derivation of the products from the reaction steps. Steps which appear simple but are in fact complex must be expanded. There are usually more than one sequence and they may be interconnected. The sequences are to contain reactions of high and low equilibrium constant in varying order: the species shown as produced in steps with large equilibrium constants may appear as intermediate or final products; conversely small equilibrium constants indicate molecules which are not final products but may be virtual intermediates. Species which can undergo no further change must terminate a sequence, but unreactive substances are not usual targets, and termination must generally be effected by adjustment of reaction rates through appropriate choice of catalyst. Thermodynamic data are useful in predicting the likely course of a reaction at a branchpoint and in pin-pointing the slow steps of a sequence. If a reactant or an intermediate can decompose by more than one route of similar kind, it is found that the reaction tends to follow the path with the most favourable change in free energy. Also the step in a sequence with the most adverse free energy change will be the slowest and requires special attention in the catalyst design. For uncoupled endothermal reactions the activation energy cannot be less than the enthalpy increment.

The mechanism given by a small complete set of sequences of ordered stoichiometric statements comprising all the parallel and consequtive reactions thought to make major contributions, molecular fragments, radicals and ions, are excluded. The steps to be accelerated or inhibited, and their types, will be apparent.

2. CHEMICAL ASPECTS OF OXIDATION CATALYST

(A) Comparison with homogeneous oxidation reactions

The broader features of the mechanism of non-catalysed reactions of hydrocarbons and oxygen are now established, though in no case is there a complete understanding of all the aspects of the reaction. These oxidations are free-radical chain processes whose kinetics are dependent upon the interplay of four groups of elementary steps: initiation, propagation, branching and termination. The molecular species produced by oxidation of the hydrocarbon are frequently as reactive or more so than the hydrocarbon itself.

Homogeneous gas phase oxidations are frequently complicated by surfaces. For example a surface may cause the destruction of an intermediate, which would otherwise cause branching or destroy a radical thereby introducing a termination. Whereas in the homogeneous case, one reason for the complexity of the kinetics is the ability of propagating radicals to attack both reactant and partial oxidation product, in the heterogeneous case the competition between reactant and partial oxidation product for the active sites leads to a kinetic complexity.

(B) The multifunctional catalyst

The multifunctional catalyst is the one that contains more than one type of catalytic site and comprise a phase or phases (properly admixed) with selectivities appropriate only to the desired steps of the mechanism. A list of such solids is drawn up on the basis of known patterns of activity but remains precursory until the virtual mechanism has been reformulated with chemisorbed complexes as intermediates. In the chemisorbed state molecular fragments can now be used and the atoms of the solid are introduced in symbolic form or as electronic configurations, to allow a deeper insight into the mechanism and a refinement of the catalyst design.

Kinetic considerations: The efficient catalysts for the target transformation requires that the activity of the chosen component solids should be "consistent" in two ways- (I) the specifity of a solid necessary for a later step must not be such as to misdirect an earlier step ,(II) the total activity of each phase must be adjusted, by choice of specific area and specific activity, to avoid accumulation of undesirable intermediates. The inexactness of these judgements usually leads to the formulation of a small group of similar catalysts rather than to a single catalyst.

Catalyst formulation: It is important to observe that the solid phases must be "compatible" which means that juxtaposition of the solids, in preparation or in situ, must not lead to chemical changes which produce phases which are different from the ones specified in the design.

(C) Partial oxidation catalysts: activity and selectivity

The nature of the catalytically active phase, or where there is more than one phase, their nature and proportion, normally varies with operating conditions. This is especially so if the catalyst contains variable valence metal oxides, as is nearly always the case. An important factor in influencing this change is the ratio of hydrocarbon (reducing) to oxygen in the reaction mixture. Oxides with high activity towards hydrocarbon oxidation are generally p-type semiconductors (Mn, Co,Ni, Cr) but by themselves they generally show little or no selectivity to particular products. The non-transition oxides of the long periods, and especially the oxides of the short periods, show little activity in hydrocarbon oxidation. Transition oxides of moderate activity which frequently show good selectivity are n-type semiconductors (W, Mo, U, V). It seems that the activity of transition metals within a group decreases as atomic number increases e.g. Cr $>$ Mo $>$ W $>$ U. Although of low activity when used alone sub-groupe B oxides (especially In, Tl, Sn, Pb As, Sb, Bi, Se, Te) are frequently used in conjunction with a transition metal to give catalyst of moderate activity and high selectivity (e.g. Bi + Mo, V + Sn). In general it does not appear possible to achieve high selectivity and high activity by combining one of the very active transition oxides of the p-type with a low activity, but selective, n-type oxide. It is likely that in many of these mixed catalyst compound formation or solid solution occurs, so that the lattice is different in structure and/or dimensions from that of either single oxide. Phosphorus and boron are also frequent major components, they may act in a similar way or they may confer a dehydration function on the catalyst system, permitting the dehydration of a non-isolatable intermediate. However the transition metal oxides themselves are quite efficient dehydration catalysts at the temperatures normally necessary for oxidation. It has been suggested that lattice modifications change the transition metal oxygen bond strength, and that this should be within a range which permits, both rapid interactions of this oxygen with the hydrocarbon, and at the same time rapid re-oxidation of the metal ion by molecular oxygen. It is sometimes postulated that catalysts which cause non-selective oxidation are those which chemisorb oxygen as single atom species, the latter being assumed to be highly reactive and non-selective. Then if it is further supposed that for dissociative chemisorption of oxygen there is required a juxtaposition of metal ions, one may ascribe the increase in selectivity accompanying the addition to a catalysts of phosphorus etc., to the separation, by dilution, of active centres.

The idea that the nature of the distribution of limited groups of oxygen atoms on the surface governs the competition between parallel reactions, and so the selectivity, has recently been suggested. Frequently components are added to catalysts in much smaller proportion than the "modifiers" described above. They may change the activity and/or selectivity of the catalysts. The mechanisms by which these additives ("promoters") function must be different from those suggested above for "modifiers". The stable valency of the promoter is normally different from that of the main component.

(D) Modified catalyst and the electron theory of catalysis

There have been numerous attempts to correlate catalytic properties of oxides with their semiconducting properties. The correlations have been demostrated particularly for the basis oxide doped with small proportions of additives. Since conductivity is a bulk property and catalysis is a surface property a successful correlation will depend on the changes in chemical composition producing changes both in the conductivity and in the Fermi level at the surface. However experimental results show that the relationship between conductivity and catalytic activity is much more complex. This is probably due to the fact that the conductivity of polycrystalline semiconductors often is not affected by changes in the Fermi-level of the surface. Thus there must be another connection between changes in electron work functions of modified catalysts and their adsorptive and catalytic activities.

The effects exerted by surface impurities, and by impurities located in the adjacent to surface layer at a depth exceeding the Debye length, on electrical conductivity and in the electron work function will be different. In other words, modification of semiconductors makes possible a wide range of variations in the electron work function ($\Delta \phi$). On the other hand it was found that $\Delta \phi$ was a linear function of the activation energy for chemisorption of oxygen.

3. THE PARTIAL OXIDATION OF METHANE

The homogeneous reaction is a chain reaction in which chain branching arises from the oxidation of the initial products, HCHO, the final products being CO, CO_2 and H_2O.

The heterogeneous catalysis of methane oxidation is very much less understood. Complete oxidation to CO_2 and H_2O is the most frequent, though small amounts of HCHO and less often CH_3OH and HCOOH have often been reported.

(A.) The stoichiometric statement

The target transformation of this study is the partial oxidation of methane to formaldehyde

$$CH_4 + O_2 \;=\; HCHO + H_2O$$

The characteristic chemistry is developed below. After each equation is shown the free energy for the reaction at 700° K (Kcal/mole), and the type of reaction, abbreviated as DH = dehydrogenation, OI = oxygen insertion, O = oxidation, DW = dehydration, A = addition. Oxygen insertion refers specifically to the insertion of oxygen into a C-H bond to give a C-OH bond.

Primitive (P): None

Self interactions (S): $2\,CH_4$	$= C_2H_6 + H_2$:	+ 20	:DH
	$= C_2H_4 + 2H_2$:	+ 32	:DH
Cross interactions (CS):			
$CH_4 + 1/2\ O_2$	$= CH_3OH$:	- 22	:OI
	$HCHO + H_2$:	- 37	:OI + DH
	$CO + 2H_2$:	- 37	:OI+DH
$CH_4 + O_2$	$= HCHO + H_2O$:	- 70	:OI+DH+O
	$HCOOH + H_2$:	- 67	:2xOI+DH
	$CO + H_2 + H_2O$:	- 87	:OI+DH+O
	$CO_2 + 2H_2$:	- 90	:OI+DH+O
$CH_4 + 3/2\ O_2$	$= HCHO + H_2O$:	- 31	:OI+DH+O
	$HCOOH + H_2O$:	- 116	:2xOI+DH+O
	$CO + 2H_2O$:	- 136	:OI+DH+O
	$CO_2 + H_2 + H_2O$:	- 139	:OI+DH+O
$CH_4 + 2O_2$	$= HCOOH + H_2O$:	- 98	:2xOI+DI+O
	$CO + H_2O_2 + H_2O$:	- 118	:OI+DH+O
	$CO_2 + 2H_2O$:	- 189	:OI+DH+O

Sequential reactions (SQ):

$CH_4 + C_2H_6$	= $C_3H_8 + H_2$	:	+16	DH+A
$+C_2H_4$	= C_3H_8	:	+4	A
$+CH_3OH$	= $C_2H_5OH + H_2$	:	+13	DH+A
	$(CH_3)_2O + H_2$	:	+27	DH+A
$+HCHO$	= C_2H_5OH	:	+10	A
	$(CH_3)_2O$	:	+24	A
$+H_2O_2$	= $CH_3OH + H_2O$	:	-56	OI
$+HCOOH$	= $CH_3CHO + H_2O$	:	+4	A+DW
$+CO$	= CH_3CHO	:	+24	A
$+CO_2$	= CH_3COOH	:	+35	A

Cross-sequential reactions (CSQ)

$C_2H_6 + O_2 = C_2H_5OH$, CH_3COO_4etc cf CS

$H_2 + 1/2O_2 = H_2O$: -50 :O

$$\left.\begin{array}{l} CH_3OH + O_2 \\ HCHO, \text{ etc} \end{array}\right\} = \text{products as under CS}$$

(B) The thermodynamic theme

Though the free energy change for the target transformation is large and negative

$$CH_4 + O_2 \longrightarrow HCHO + H_2O \quad : \quad \Delta G = -70 \text{ Kcal/mole}$$

The free energy changes given in section (A) show that complete oxidation is even more favoured and also that formaldehyde is thermodynamically unstable with respect to decomposition.

The partial oxidation of methane to formaldehyde is therefore a kinetic problem, in that the simultaneous reactions of formaldehyde oxidation and of direct methane oxidation to carbon oxides must be supressed.

Section (A) emphasis the complexity of many apparently simple reactions.

(C) The Mechanism

Breakdown of the favoured reactions in section (A) into those of single types yields the virtual mechanism.

$CH_4+1/2\ O_2$	$\longrightarrow$	CH_3OH	oxygen insertion
CH_3OH	$\longrightarrow$	$HCHO+H_2$	Dehydrogenation
HCHO	$\longrightarrow$	$CO+H_2$	Dehydrogenation
$HCHO+\ 1/2O_2$	$\longrightarrow$	HCOOH	Oxygen insertion
$H_2+1/2O_2$	$\longrightarrow$	H_2O	Oxidation
H_2+O_2	$\longrightarrow$	H_2O_2	Oxidation
$CO+1/2O_2$	$\longrightarrow$	CO_2	Oxidation

The functionsrequired of the catalyst are therefore

1. Dehydrogenation
2. Oxygen insertion

The first is provided by metals or by semiconducting oxides of transition metals. These components are also oxidation catalysts, the selectivity increasing roughly in the order: metals, p-type oxides, n-type oxides.

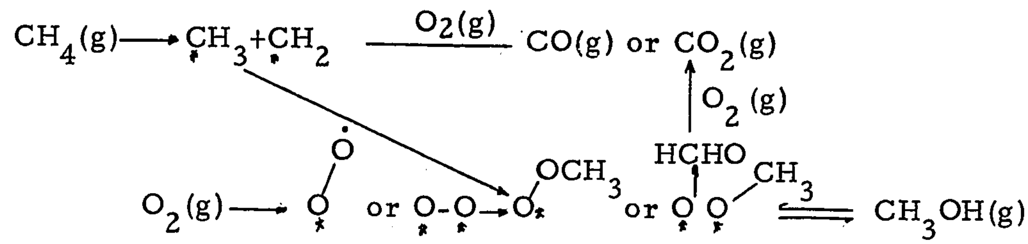
By applying the reaction to the surface of such catalysts, it will be seen that successful catalyst will probably be an n-type transition metal oxide.

Methanedehydrogenation: Methane deuterium exchange and other experiments have shown that chemisorption involves the dissociation of methane either to methyl groups or to labile methylene groups, which bear a slight positive charge. Some very limited evidence suggests that only methyl group are obtained on oxides. The rate of chemisorption and the strength of the surface-to-carbon bond, may be gauged from the rates of the deuterium-exchange reaction and of the oxidation reaction, which are in accord with the prediction of crystal field theory. From the transition metal ions having a favourable d-electron configuration may be selected those having some oxidative ability, to assist the development of a positive charge, on the methyl group.

Oxygen insertion: By analogy with other catalysed insertion reactions, the reaction would be expected to occur by the migration of a methylene or more probably, of a methyl group onto an adsorbed oxygen species (molecular or atomic) to form, therefore a methoxide or methyl peroxide group. The former will yield methanol by hydrolysis or formaldehyde by a further dehydrogenation while the latter will yield formaldehyde by simple decomposition.

This forms the mechanism for the target transformation. Parasitic reactions are the direct formation of carbon oxides by the dehydrogenation and oxidation of methylene or methyl groups, and further oxidation of formaldehyde.

The surface scheme may therefore be summarised as:



(D) Kinetic considerations

Supression of the parasitic reactions corresponds first of all to supression of the dehydrogenation of methyl or methylene groups, in favour of the migration reaction. Since the methylene is either bound more firmly to the surface than the methyl group or has more labile protons, or both, the problem would be cased by using an oxide rather than a metal, catalyst to prevent methylene formation altogether. The surface-to-methyl bound must then be made weaker than the surface to oxygen bond to favour methyl migration onto oxygen over the opposite reaction, and sufficiently weak to allow the rate of migration to compete with the rate of reaction of the methyl group with gaseous oxygen.

These requirements suggest that the dehydrogenation function should be quite weak (d^{o}, d^{1}, d^{5}, d^{10} or perhaps d^{4} configuration) while the oxygen insertion function should be that of an n-type oxide (T_iO_2, V_2O_5, MoO_3, Fe_2O_3, ZnO).

A rapid migration reaction further requires that the adsorption sites for methane and for oxygen should be crystallographically adjacent, and that the catalyst should therefore consist of a single phase. If the dehydrogenation and oxygen insertion functions are to be provided by different components, these must therefore exist together in a single complexe oxide. The other half of the kinetic problem is to decrease the ratio of the rate of formaldehyde oxidation to that of methane oxidation.

It is likely that the slow step in methane oxidation will be methane dehydrogenation. Since the necessary dehydrogenation components will catalyse the dehydrogenation of formaldehyde at least as effectively. Another step than this must be made the slow step for formaldehyde oxidation.

It is known that formaldehyde, in the form $CH_2(OH)_2$ is only very slowly attacked in aqueous solution by oxidants such as Cu^{+2}, Ag^{+}, or Fe^{+3} ie oxidants only capable of accepting one electron per ion. Thus the conversion of the diode to the aldehyde on the surface of the catalyst could be made the slow step of the reaction by incorporating a hydration function into the catalyst, and by restricting the other components to "single electron" oxidants.

Amongst the most succesful hydration catalysts are those containing phosphate or tungstate often in conjunction with a transition metal ion (Zn^{+2}, Fe^{3+}, or V^{5+}). Thus the ions selected earlier are not inconsistent with hydration activity, nor with the need for "single electron" oxidants.

The presence of a hydration component may enhance the hydrolysis of methoxide groups, as opposed to their oxidation, and thus increase the production of methanol relative to formaldehyde.

(E) The multifunctional catalyst

To summarise the conclusions of the preceding sections, the functions required are:

(I) dehydrogenation

(II) oxygen insertion, to effect the target transformation

and (III) hydration, to inhibit the oxidation of formaldehyde

The dehydrogenation function must yield specifically methyl groups, held more weakly to the surface than is the adsorbed oxygen. Further, the catalyst should not contain cations which in oxidizing a subtrate, accept more than one electron at a time. These requirements restrict the possible transition metal cations to V^{5+}, Mn^{3+}, Fe^{3+}, Ni^{3+}, Cu^{2+}, Ce^{4+}.

The oxygen insertion function must cause oxygen to be chemisorbed more strongly than methyl groups. V^{5+} and Fe^{3+} occur in n-type oxides (V_2O_3, Fe_2O_3) and so could conseivably execute this function, but the other ions would have to be supplemented by ions such as V^{5+}, Fe^{3+}, Zn^{2+}, Cd^{2+}, Mo^{6+}, Ti^{4+}. For these ions rather than those in the list above, to function as the oxygen adsorption sites, the redox potentials of different cations in the same lattice must be such that it is the lower oxidation states of these latter ions which are present rather than those of the former. This requirement probably rules out Mn^{3+}, Ni^{3+} and Ce^{4+}, unless these highly oxidizing ions can be stabilized in the mixed oxide lattice, by the addition of basic oxides such as ZnO for example. This in turn must be judged against the posibility that methyl groups formed by the dehydrogenating cations may preferentially migrate to non-transition metal cations, with which they form stronger bonds.

The ions remaining:
V^{5+}, Fe^{3+}, Cu^{2+}
and V^{5+}, Fe^{3+}, Zn^{2+}, Mo^{6+}, Ti^{4+} are all consistent with a hydration function, which could be provided by incorporating tungstate or phosphate into the catalyst.

IV. EXPERIMENTAL

A. REACTANTS AND CHEMICALS

(1) Air

Air was supplied by the Linde Company in compressed cylinders at a pressure of 2500 psig. The gas chromatographic analysis of the air gave the following composition: 20.95% oxygen, 79.00% nitrogen, and some traces of carbon dioxide.

(2) Methane

Methane C.P. grade, with a minimum purity of 99.00% was supplied by Matheson Co., in cylinders at a pressure of 2265 psig. (70 F).

(3) Chromatographic materials

The substrate used in the vapor chromatographic analysis was sucrose octa-acetate, $C_{28}H_{38}O_{19}$, M,W, 678.59 (supplied by Fisher Scientific catalogue no. 4026-P) and the support Columpak T 40-60 mesh (Fisher Scientific no. C-587). Methylene chloride (reagent grade. Fisher Scientific Co.) was used as a solvent for the substrate.

In the gas partitioner the columns used were packed with two substances: Di-2-ethylhexylsebacate on 60-80 mesh columpak, which is in a liquid phase, and is known as DEHS, and Molecular sieve 5A. (Fisher Scientific catalogue no. 11-134-63A and 11-129-520 respectively).

(4) Formaldehyde 37% by weight.

Formaldehyde used was supplied by Fisher Co. (no. F-79) and had an assay as HCHO 36·0-38·0%. It was stabilized with 10-15% methanol. The quantitative analysis of the formaldehyde solution gave the following composition: 37.25% as HCHO and 13.9% as CH_3OH. See appendix B.

B. CATALYST AND MODIFIERS

(1) Palladium on asbestos 5% (Fisher Scientific no. P-5)

(2) Nitric oxide

Matheson technical grade with a minimum purity of 98.5% at a cylinder pressure of 500 psig (70 F).

(3) Methylene chloride (Fisher Scientific Co. D-123). 99 mol% pure.

(4) Copper oxide on pumice 16% by weight.

C. EXPERIMENTAL APPARATUS

The partial oxidation of methane was investigated in a flow system. A schematic diagram of the experimental apparatus used in this study is given in Figure 1.

The experimental apparatus itself may be divided into three main sections:

(1) Feed Section

(2) Reactor Assembly

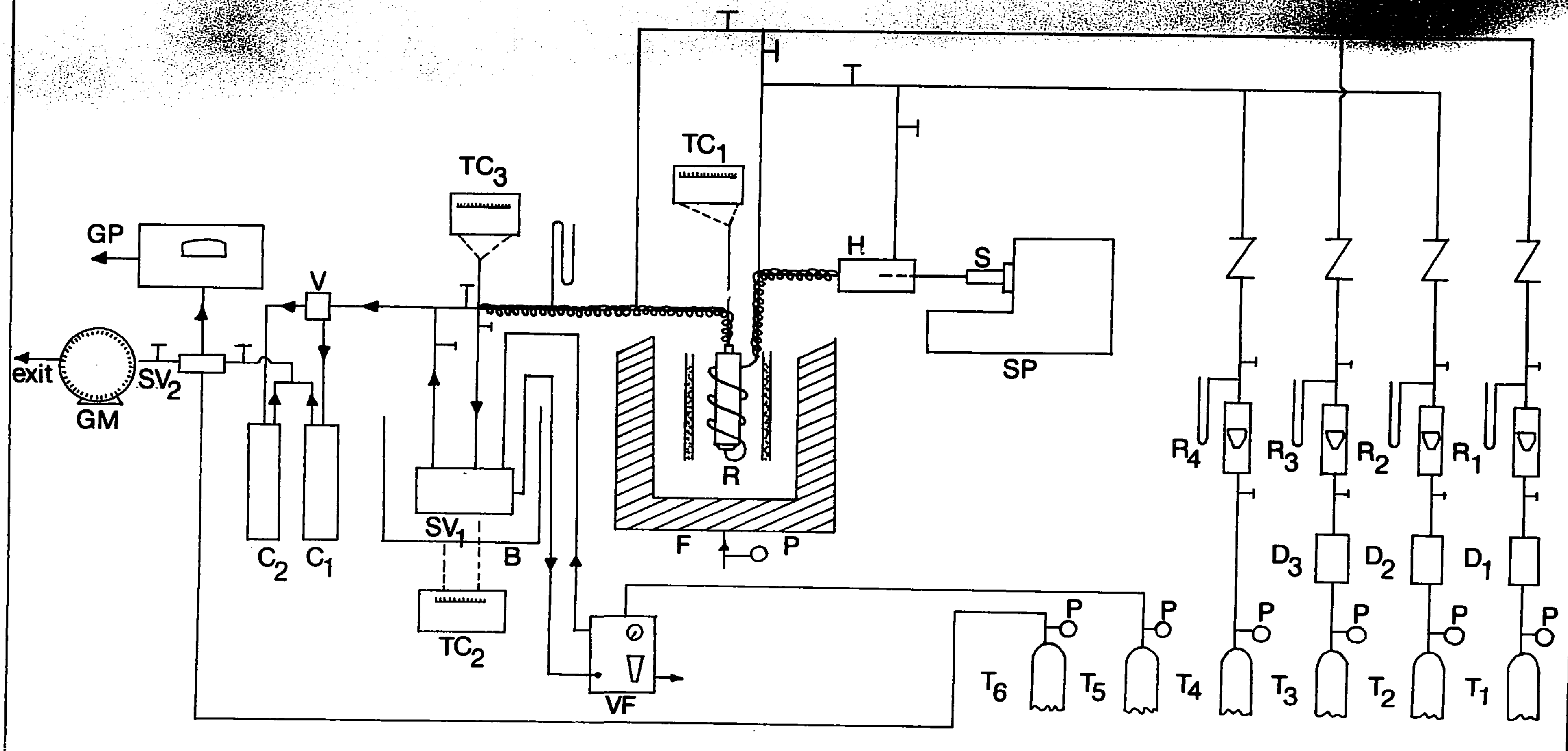
(3) Product Analysis Section

(1) Feed Section

The feed section consisted of six gas streams, the first and second of which transported helium, used as a carrier for the chromatographic analysis. These two lines were made out of 1/4 in O.D., standard copper. The pressure and volume flow rate of these two gas streams were controlled by means of a two-stage pressure regulators (Model 8, Con no. 580, Matheson of Canada, Ltd., Whitby, Ontario).

The third line carried air to the fluidizing sand bath which was used for heating the reactor.

The fourth and fifth line transported the air and methane used as reactants. Both gases were obtained from high pressure cylinders, through a series of high pressure diaphram type regulators (Model 8, Conn no. 590 and 350, Matheson of Canada, Ltd.,) whereby the pressure of air and methane were reduced to 20 psig. The compressed gases were passed through tubes containing indicating drierite to

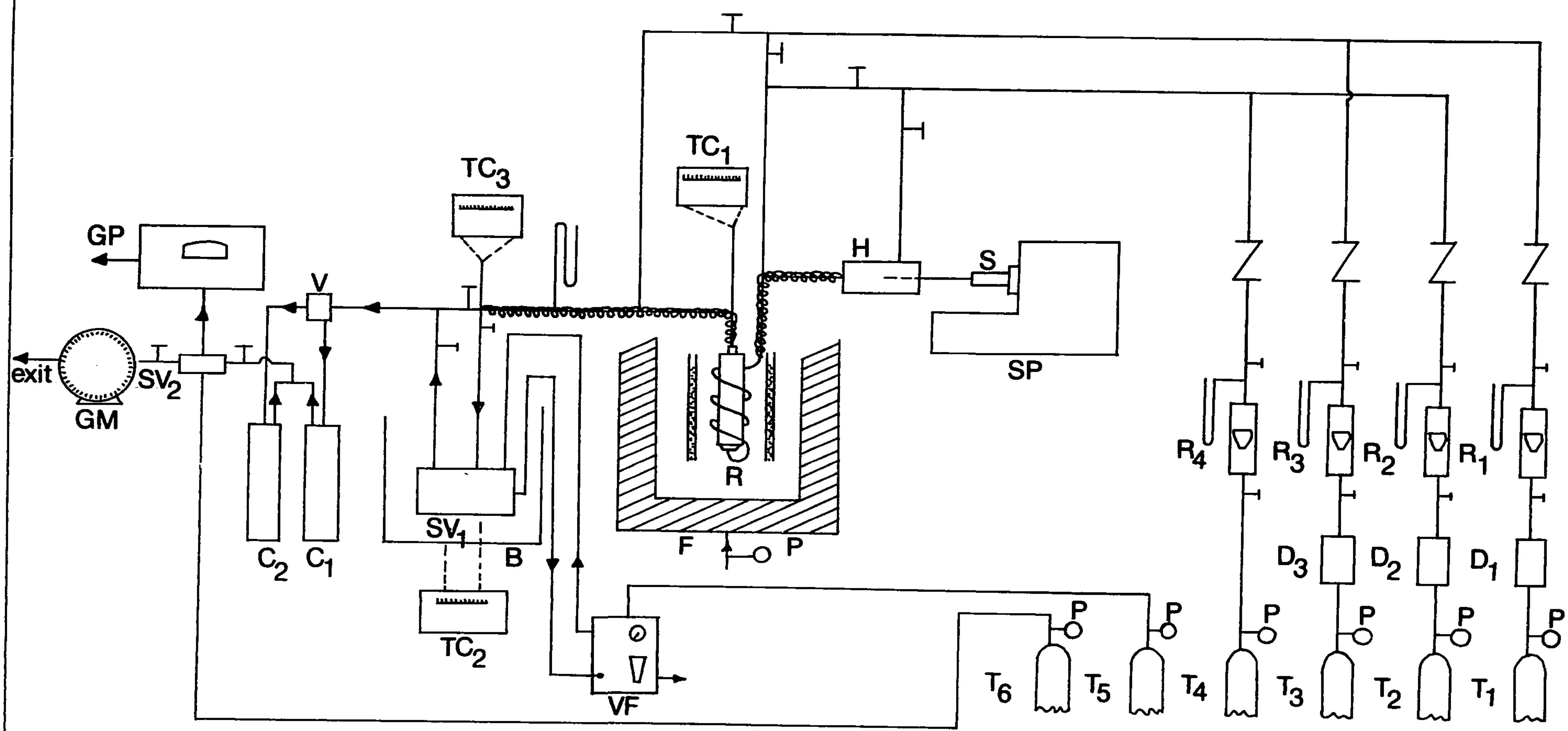


B : oil bath
C_1-C_2 : traps
F : furnace
GM : gas test meter
GP : gas partitioner
H : hot inlet
D_1-D_3 : drying tubes

P : pressure controllers
R_1-R_4 : rotameters
R : reactor
S : syringe
SP : syringe pump
$SV_{1,2}$: sampling valves
V : three way valve

T_1 : methane tank
T_2 : air tank
T_3 : nitric oxide tank
T_4 : CO or CO_2 tank
T_5,T_6 : helium tank
TC_1-TC_3 : temperature controllers
VF : vapor fractometer

Figure 1 Schematic Diagram of the Apparatus.



- B : oil bath
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- TC_1-TC_3 : temperature controllers
- VF : vapor fractometer

Figure 1 Schematic Diagram of the Apparatus.

remove any possible trace amount of moisture. The gas lines, made out of 1/8 in O.D. 316 stainless steel tubing, passed through, Matheson Company rotameters with needle valve (body series, 622, flowmeter tubes and float series 601-602) where the flow rate of each of the gas streams were measured.

Two streams of air were used; one stream, preheated, was passing through a HAMILTON'S INLET (Part no. 86800 HAMILTON CO., Whittier, California) used as a vaporizer for the liquid modifier and the other was bypassed and mixed with the other two streams before they entered the preheating section. The Hamilton's Inlet's heavy aluminum outer body evenly distributed the heat from the cartridge heater and eliminated cold spots.

The sixth line carried nitric oxide and may be used to transport any kind of modifiers in gas form. A two stage corrosion resistant regulator including check valve (Model 151, flowmeter tube 610, Matheson Co.) was used to measured accurately very low flows. This line was mixed with the methane gas stream before entering the preheating section.

Each rotameter was connected with a mercury manometer so that the pressure effect on the gas flow rates could be corrected.

Methylene chloride used as modifier, was introduced continuously and precisely from a Yale Luer-Lok hypodermic syringe driven by a motorized syringe pump (Harvard Apparatus Inc., Mills, Mass.) into the Hamilton's Inlet, where it was vaporized and carried away by the hot air stream. The syringe pump was equipped with synchronous motor and a gear train with knob for selecting twelve exact speeds.

(2) Reactor Assembly

The reactor was made from a 6 x 1/2 inch piece of stainless steel tubing (Figure 2). A porous stainless steel plate which served as a support for the catalyst, was installed at the bottom of the tube. A Swagelok reducer was used below the porous plate and attached to the preheating section.

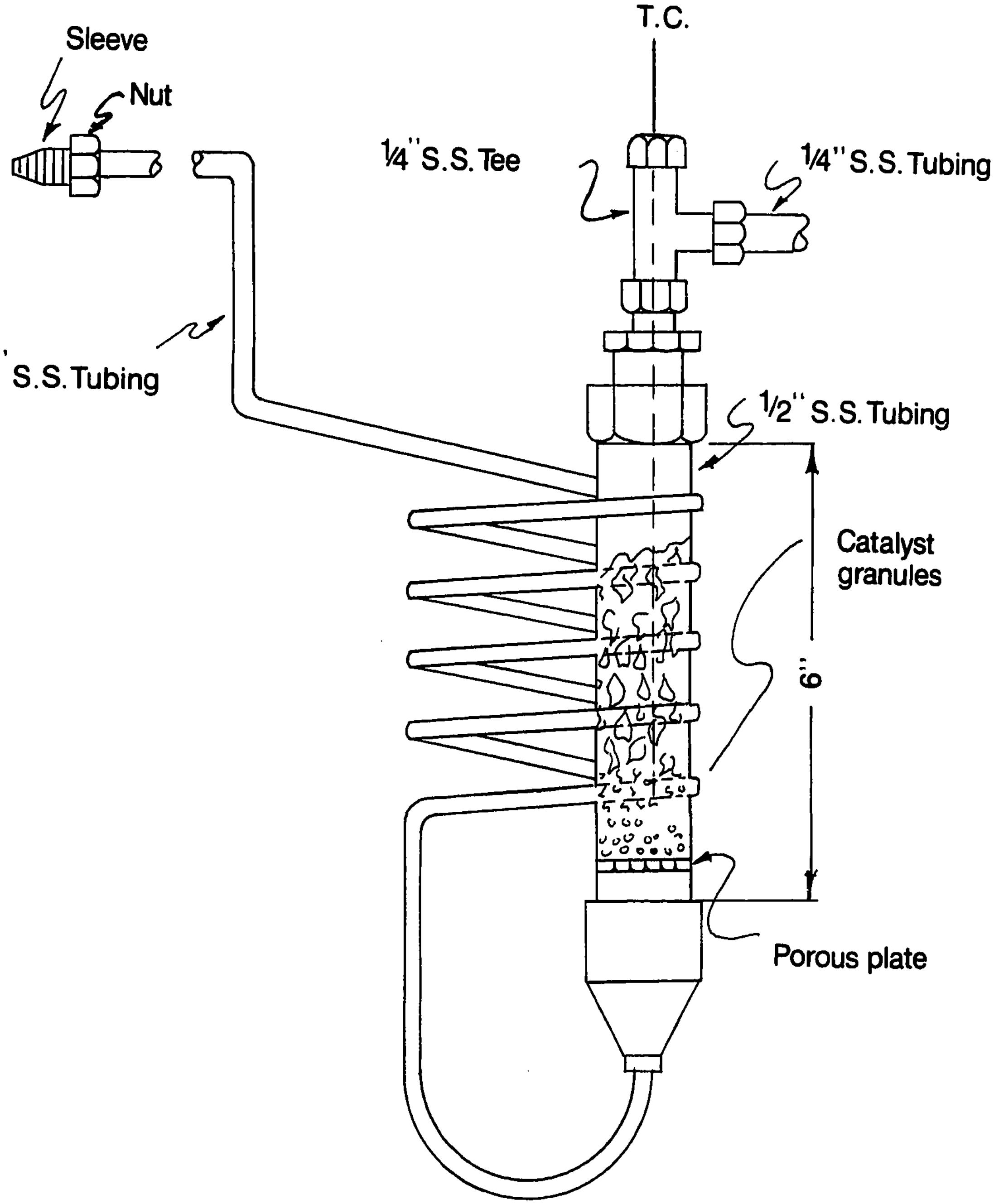


Figure 2 Reactor and Preheater.

The top of the reactor was fitted with a Swagelok "T" connection. A stainless steel protected thermocouple, 1/16" O.D., 12" immersion length, with metallic armored lead, was inserted into the reactor, to a level just above the top of the porous plate and was connected with temperature controller number 1 (Thermo Electric Potentiometer circuit controller) to control the temperature inside the reactor.

A potentiometer (Honeywell, Model 2745) was connected in parallel with the temperature controller, so that the temperature of the reactor could be recorded during the reaction.

The container for the fluidized sand bed (Figure 1) was made from a 5 in. O.D., steel cylinder, with a porous stainless steel plate inserted at the botton, and a steel funnel, welded to the base of the cylinder below the porous plate, and attached to compressed air line. Around the steel cylinder was wrapped a beaded heating wire with a resistance of 15 ohms which was connected to a 10 ampere powerstat and left on all the time.

A layer of clean Ottawa sand, was placed in the container on top of the porous plate and a 10 in. long 2.5 in O.D. ceramic core with a resistance wire wrapped around it, was held in the center of the bed. This heating wire had a resistance of 40 ohms and was connected to the temperature Controller 1, through a 10 ampere powerstat. Asbestos powder mixed with water was applied in a 1/2" to 1" thick layer to the heating wires for insulation and also to fix the wires in position.

The reactor was placed upright in the center of the ceramic core, while the vessel was completely filled with sand.

The fluidized bed was placed in an outer aluminum cylinder, one foot long in diameter, resting on a piece of asbestos board, in the center of which a hole had been drilled for the compressed air line. The space between the aluminum cylinder and the bed was packed with vermiculate. The surface of the outer cylinder was coated with a layer of asbestos cloth 3" thick for further insulation.

(3) Product Analysis Section

The exit line from the reactor, was made out of 1/4 in O.D. 316 stainless steel tubing, heated by means of a 90 ohms heating tape and leading the gases from the reactor to a constant temperature oil bath. The temperature in the exit stream was controlled by means of temperature controller TC_3 (Model 63, Thermistemp, Fisher Scientific).

A high temperature sampling valve supplied by Perkin Elmer Corp., New Jersey, was made of stainless steel with a teflon rotor which can stand a temperature up to 200°C and a 50 p.s.i.g. pressure without any leakage. A sampling loop (4.5 ml volume) was attached to the valve. The bath oil was heated by an immersion heater (Fisher Catalogue 11-463-18V4) with a Variac powerstat. A constant bath temperature was maintained by temperature controller TC_2 (a Yellow Springs thermistor temperature controller model 71). The liquid bath 10" x 10" O.D. (Pyrex-Corning glass Works, Corning, New Jersey) was well insulated with asbestos cement and glass wool to reduce the heat losses to the surroundings. The pressure of the sampling gas, essentially the reaction pressure, was controlled at 915 mm Hg by adjusting the needle valve in the exit line.

The Perkin-Elmer model 154 vapor fractometer equipped with thermal conductivity cell detector, D.C., power supply and electronic temperature controlling system was used to separate formaldehyde, methanol and water. Helium was used as a carrier gas and was introduced into the sample injection block, after passing it through the high temperature sampling valve (Figure 3).

The exit gases from the high temperature sampling valve were led to a condenser and ice-cooled trap, where the heavier reaction products were condensed. The uncondensable gases were led into a Fisher Gas Partitioner, through a drying tube, where the traces of moisture were removed.

The Fisher Hamilton Model 29 gas Partitioner employing dual-column dual detector chromatographic system was used to separate and

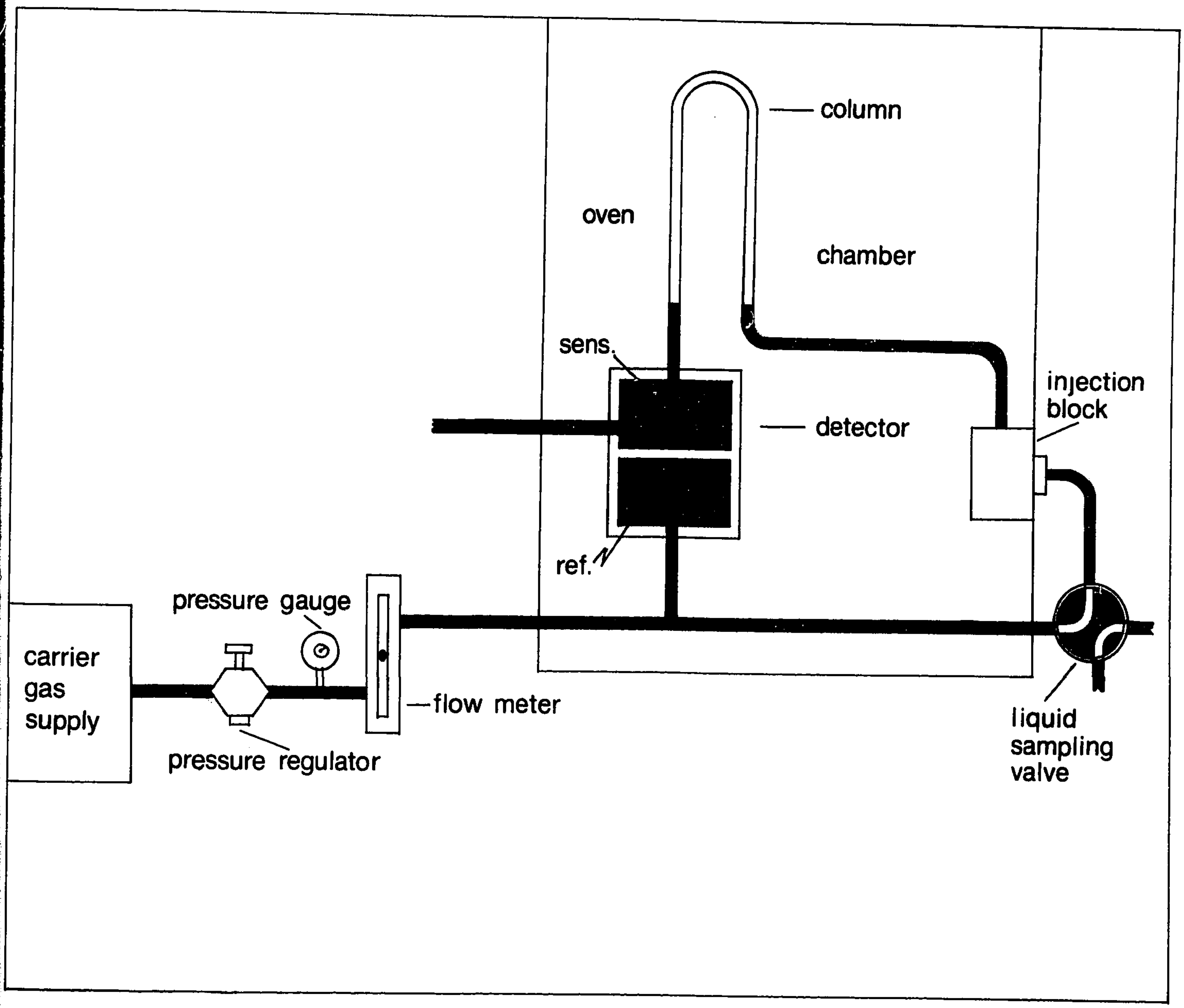


Figure 3 Schematic Flow of Vapor Fractometer.

measure carbon dioxide, oxygen, nitrogen, methane and carbon monoxide, in the exit gas. Samples were introduced into the instrument through the use of a specially designed thermal conductivity cell which employed four matched Gow Mac W2 hot wire filaments.

A zero supressor (supplied by Fisher Scientific Co.) 0-10 mv, was used to connect the gas partitioner or the vapor fractometer with the chart recorder (Texas Instrument Inc., Texas Model Servo/riter II) from which the recorder input signal exceeded 1/m.v. could be suppressed.

D. EXPERIMENTAL PROCEDURE

(1) Leakage Test

The system was tested at 20 psig for any possible leaks in the following way:

(i) There was no indication of the gas flow through the rotameter as the valves in the downstream were closed.

(ii) Every connection in the equipment was tested with snoop.

(2) Calibration of equipment

Flow rates of the gas streams were measured by calibrated rotameters. The pressure for the reactants was maintained at 1538 mm Hg by the manual adjustament of the fine metering valves in the exit rotameters. The temperature of the inlet gases was the corresponding room temperature (24^{o}-28^{o} C). Flow rates were corrected for the temperature fluctuation. The volumetric flow rates were checked by both the soap bubble method and the wet test gas meter supplied by American Instrument Co. Calibration curves for the flow rates of air, methane, carbon dioxide, carbon monoxide and nitric oxide are given in Appendix A.

The feed rates of chlorine modifier were controlled by the speed of the syringe pump, which in turn was calibrated by weighing the distilled water pumped for a certain time. The calibration chart for the syringe pump is given in Appendix A.

The thermocouples were calibrated by inserting them into the fluidized bed furnace and an ASTM thermometer (0-400°C) was attached to it. A calibration curve of temperature against millivolts is given in Appendix A.

The gas samples were separated on the Fisher Gas Partitioner. Mixtures of air, methane, carbon monoxide and carbon dioxide in varying proportions were accordingly made for separation by the Gas Partitioner. Mixtures of water, methanol and formaldehyde of known composition were injected into the Perkin-Elmer Model 154 Vapor Fractometer from the feed preparation unit or by injecting the samples directly into the injection block heater. The time and order of elution of the components was based on previous injections of the pure components. The quantitative analysis was based on the relative peak height ratio. The calibration curves, both for the Gas Partitioner and Vapor Fractometer are given in Appendix A.

(3) Analysis procedure (29), (30)

(i) Formaldehyde, methanol and water

The hot effluent from the reactor was directly introduced into the Perkin-Elmer Vapor Fractometer through a high temperature sampling valve.

The column used for separation was a 18 foot length 1/4 in O.D. standard copper, packed with 15% wt sucrose octa-acetate on Columpak T. A typical gas chromatogram obtained from Vapor Fractometer is shown in Figure 4. Water was used as the key component for its chemical stability and low volatility.

(ii) Gases

The inlet feed and the product gases were analyzed for carbon dioxide, oxygen, nitrogen, methane and carbon monoxide by periodic injection into the Fisher Gas Partitioner containing two columns joined in series. The first column was packed with a 13 foot long by 1/4 inch diameter DEHS and the second was a 12 foot long by 5/16 inch diameter 42-60 mesh Molecular sieve. A typical analysis of the products from the Gas Partitioner is shown in Figure 5. Nitrogen gas was used as the key component for its chemical inertness.

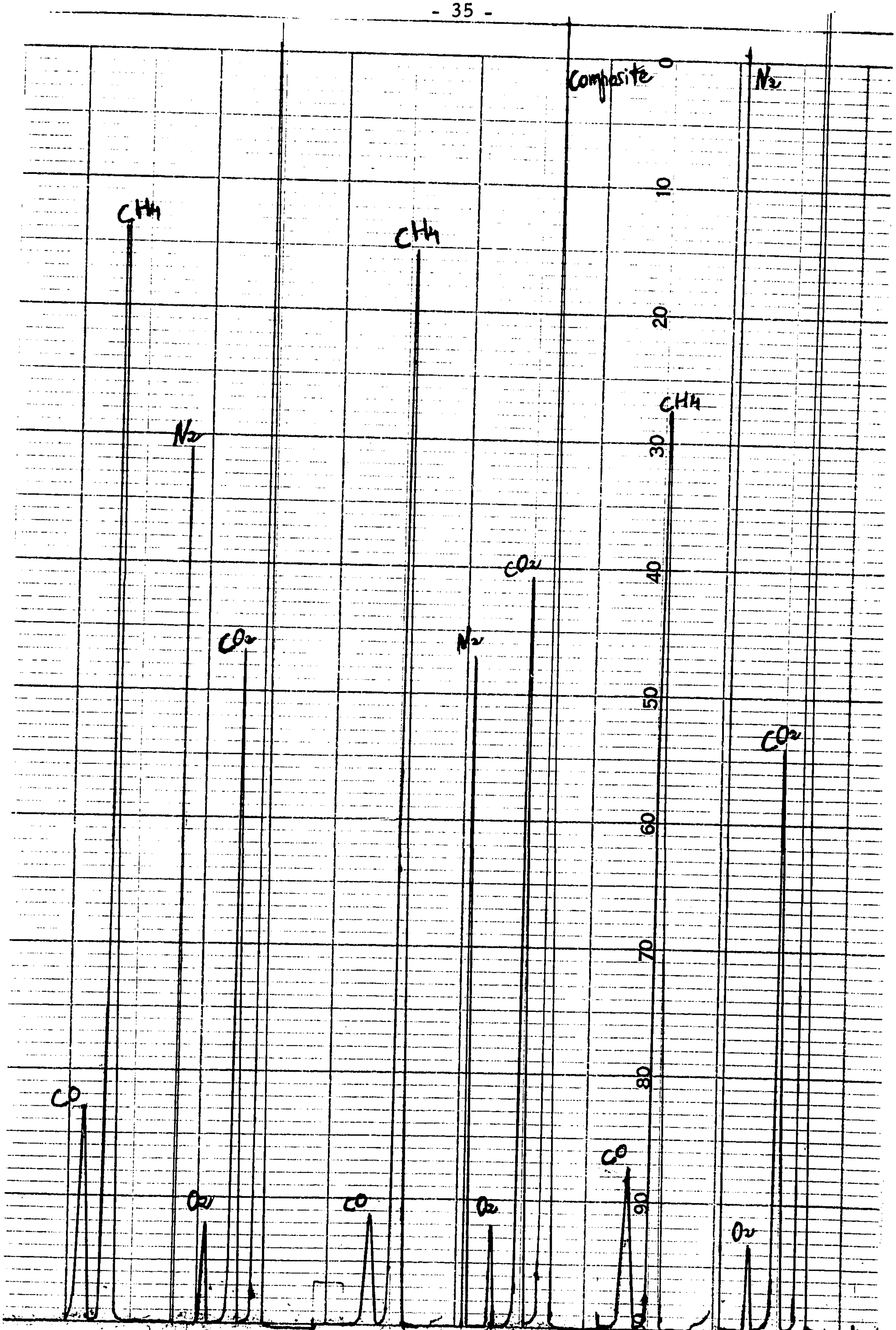


Figure 4 Typical Analysis of the gaseous Products.

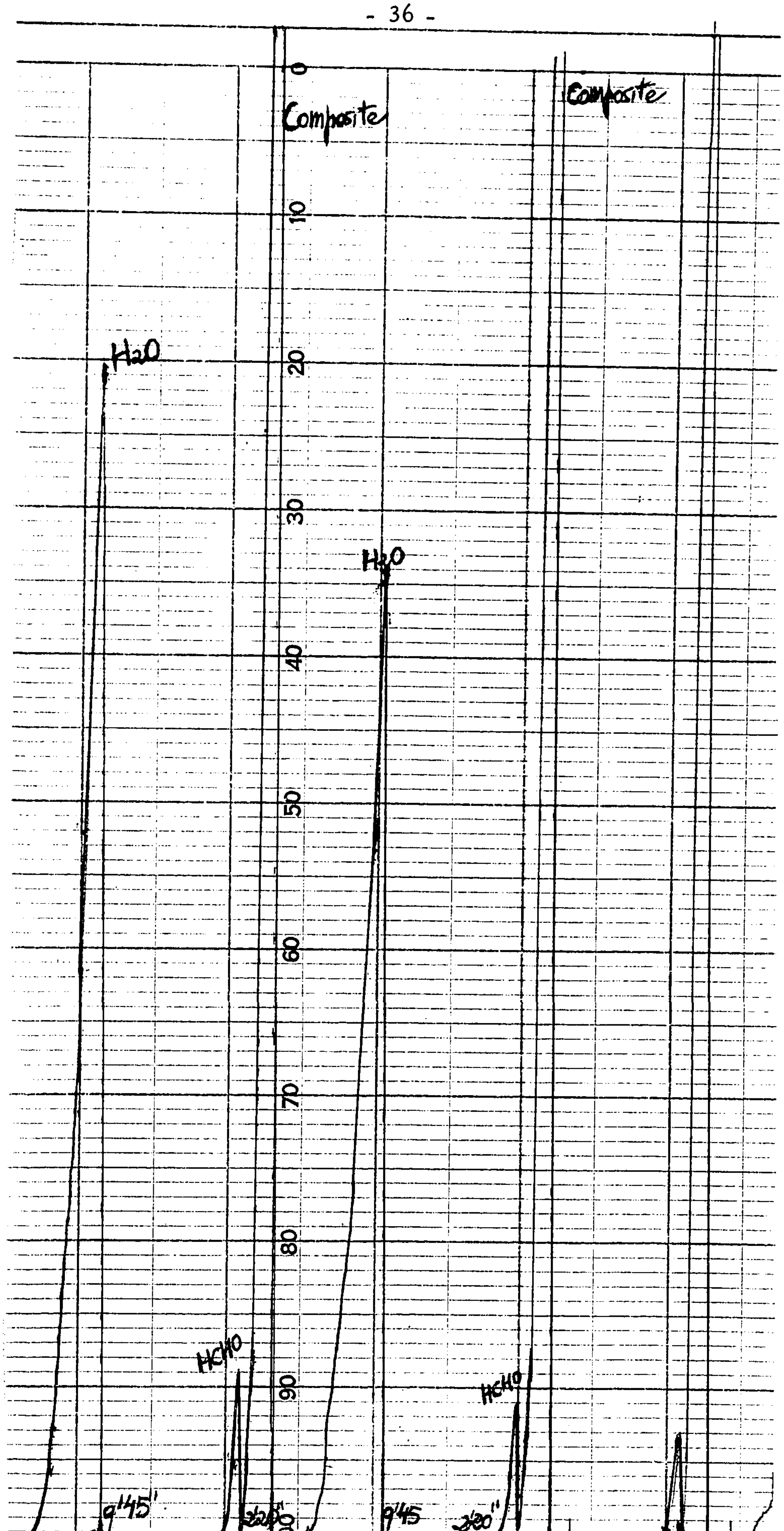


Figure 5 Typical Analysis of the Liquid Products.

(4) Operating procedure

Details of the experimental procedure for making an initial run with a specific weight of catalyst are described in this section.

(i) Start-up

(a) Purge the feed line and reactor with compressed air at 20 psig.

(b) Test the system for any leaks.

(c) Turn on the departmental compressed air to fluidize the furnace bed at 15 psig.

(d) Turn on the helium gas streams and temperature for the gas partitioner and vapor fractometer.

(e) Switch on the "variac" powerstats and temperature controllers for the various heating tapes in the inlet and outlet streams, fluidized bed furnace and constant temperature oil bath.

(f) Switch on the detectors and recorders for gas chromatographs in order to allow the base line to become straight and stable.

(ii) Run

(a) When the required temperature in the reactor was attained, methane was added to the feed and the flow rates of air and methane were adjusted so as to give the desired total flow rate and molar ratios in the feed.

(b) The modifier was introduced into the feed line. The amount of modifier was controlled by adjusting the speed of syringe pump and the size of syringe.

(c) Maintain the feed gases and the modifier at the specified flow rates for one hour to obtain steady state conditions at the particular temperature desired.

(d) Introduce the hot effluent gases from the reactor into the vapor fractometer via the high temperature sampling valve and the uncondensable gases from the ice-cooled trap into the gas partitioner.

(e) Take samples in both analytical instruments, until the two gas chromatograms show no change in composition thereby indicating that a steady-state has been reached.

(f) Measure the total flow of the uncondensable gases with the wet test meter before each sample is taken.

(g) Shut off the methane feed and keep air flowing through the catalyst bed for one hour before the start of another run.

(h) Drain the condensate from the trap.

(i) Periodically the gas chromatographs calibration were checked to assure stability of the columns.

V RESULTS AND DISCUSSION

Experimental data were collected by means of a quasi-isothermal fixed-bed reactor at atmospheric pressure. Flow rates were calculated on the basis of the rotameter readings, previously calibrated. The effluent rates were computed on the basis of the total flow rate of the feed and from total gas flow rate and composition of the product stream. The steady state was realized not only from the operating conditions but also from the products analysis. Results were obtained from the various runs, where type of catalyst, feed compositions, temperature and amount of modifier were varied. The mass of the catalyst in grams is denoted by W, the rate of flow of the total feed in gram moles per hour by F, the air to methane ratio by $\bar{R}$ and the ratio of gram moles of modifier fed per hour to the total flow by Z. While conversion is referred to as the moles of methane consumed (reacted per hour) to the moles of methane fed per hour, the rate of formation is referred to as the moles of various products formed per hour. The ratio of gram-moles of formaldehyde formed to the gram-moles of methane reacted is defined as selectivity, S.

Copper oxide on pumice and palladium on asbestos were used as the main catalysts. They were also used in conjunction with nitric oxide and methylene chloride as modifiers.

1. The methane oxygen reaction in the absence of gaseous additives

Copper oxide has not extensively been used in methane oxidation but is a very common catalyst in other partial oxidation reactions. Though the kinetics of methane oxidation, on palladium catalyst, has been studied in some detail, both over microcatalic beads (24) and in a pulsed flow reactor (25, 31) and a tubular reactor (23), no partial oxidation products have been identified.

Ahuja and Mathur (23) proposed the rate controlling step in methane oxidation to be the surface reaction between the adsorbed oxygen and methane. The oxygen may be adsorbed molecularly in a single or double sites.

The rate of reaction (r) has been expressed as:

$$r = \frac{C[P_{CH_4} P^2_{O_2} - P^2_{H_2O} P_{CO_2} / K]}{[1 + K_{CH_4} P_{CH_4} + K_{O_2} P_{O_2} + K_{CO_2} P_{CO_2} + K_{H_2O} P_{H_2O}]^3}$$

the corresponding initial rate equation being:

$$r_o = a\pi^3 / (1 + b\pi)^3$$

Cullis and co-workers (31) found the reaction rate at 300^{o}C. to be proportional to the square root of initial methane concentration and to be independent of initial oxygen concentration for methane/oxygen ratios between 0.125 and 1.0. These measurements carried out at total conversions from 10 to 50%, were extended up to 400^{o}C. to give an apparent activation energy of 19$\pm$1 K cal mole^{-1} for a $CH_4 + 2O_2$ mixture.

In the present work, the kinetics of the reaction was investigated over a range of temperature (350^o-525^{o}C.), air: methane ratio (6 to 1) and weight of catalyst (4 gr. Cu O on pumice and 0.3 gr. Pd on abestos). Copper oxide a p-type semiconductor was found to be not very active and very unstable. Similar results have been reported previously by several Russian scientists (32). The reaction was also studied over an "equilibrium" palladium catalyst (i.e., catalyst conditioned to constant activity). There is evidence that during methane oxidation experiments, oxygen adsorbed on the catalyst surface may react further with the catalyst to produce bulk palladiumoxide. At 450^{o}C. the extent of such oxidation, was found to be a function of the air: methane ratio. Similar results have been reported by Cullis (31). The oxidation of the catalyst was found to be rapid when this ratio was greater than 5, and a repeated passage of pulses containing the same amounts of methane and oxygen, caused decreasing amounts of catalyst oxidation, until the catalyst approached a constant level of activity.

Palladium catalyst used in the present work was conditioned to constant activity and should therefore be considered to consist largely of palladium oxide.

Over the whole range of experimental conditions, carbon dioxide and water accounted for over the 85% of methane consumed and were the only final products in the oxidation over copper oxide.
Carbon monoxide could not be detected at temperatures below 400°C.

The results are summarized in Figures no. 6 to 11.

2. The methane oxygen reaction in the presence of nitric oxide as gaseous additive

Nitric oxide has widely been used in conjunction with other catalysts in the preparation of formaldehyde from methane. In the present work the oxidation of methane to formaldehyde has been studied at 600 to 670°C. with 0.1 to 0.5 per cent nitric oxide in the reactant feed, in the absence and presence of the catalyst.

Karmilova and co-workers (33) paid special attention to the rate of formation of formaldehyde in the oxidation of methane. The formation of formaldehyde has been interpreted as a branching reaction. Treating formaldehyde as a chain centre, and assuming:

$$\frac{d[CH_2O]}{dt} = a_o + \phi[CH_2O]$$

and on integrating,

$$[CH_2O] = \frac{a_o}{\phi}\left(e^{\phi t} - 1\right)$$

It was found that $\phi \propto [O_2]$ and $a_o \propto [O_2]$, ϕ decreases as $[NO]$ increases, but a_o increases linearly with $[NO]$.

They proposed as initiating steps:

$$NO + O_2 \longrightarrow NO_2 + {}^{\cdot}O^{\cdot}$$

$${}^{\cdot}O^{\cdot} + CH_4 \longrightarrow CH_3^{\cdot} + OH^{\cdot}$$

and as branching step the reaction between CH_2O and O_2 (page 7). They assumed that nitric oxide can inactivate an intermediate radical ($CH^{\bullet}_3$ or $CH_3O^{\bullet}_2$). They then derived:

$$a_o \propto [O_2][NO]/(1+b[NO]) \text{ and } \phi \propto [O_2]/(1+b[NO])$$

Figure 12 shows that a conversion of up to 30% is obtained with carbon monoxide, carbon dioxide, water, formaldehyde and methanol as oxidation products. In the presence of pumice (a non catalytically active substance), under similar temperature range and air to methane ratio, the conversion diminished and proportionally the selectivity increased. No methanol was detected. It is also noticed that as the air to methane ratio increased the conversion also increased and the selectivity decreased.

In the presence of catalytically active substances only complete oxidation products could be detected. Adsorption, desorption and surface reaction control the reaction instead of a radical chain process.

An increase in the amount of nitric oxide favoured the formation of complete oxidation products, due to the branching reaction and propogation of formaldehyde oxidation.

3. The methane oxygen reaction in the presence of an halogenated additive

Experiments were carried out in the tubular flow reactor to determine the effect exerted by a halogenated compound on the oxidation of methane.

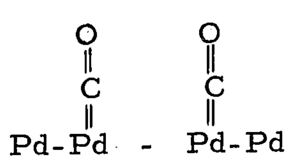
Previous results have been reported by Cullis and co-workers (31) on the action of some partial products of methane oxidation in the reaction. It was seen that methanol and formaldehyde both retard the oxidation of methane but are themselves completely oxidized. It is also known that some halogen-containing additives facilitate the isolation of intermediate products during the heterogeneous catalytic oxidation of other hydrocarbons, e. g., ethylene (34) and propylene (35). Cullis and co-workers (31) studied also the influence of some halogen-containing additives in the oxidation reaction of methane. A comparative survey of the effects of a number of halomethanes was made over a palladium catalyst bead at 450° C. Experiments with the four chloromethanes showed, that although at inhibitor concentration sufficient to give $I < 0.5$ ($I = \frac{\text{inhibited initial reaction rate}}{\text{uninhibited initial reaction rate}}$). The inhibiting efficiency of these compounds depended on both the number of chlorine atoms in the molecule and their reactivity, at lower concentrations of inhibitor, the effects of the different compounds were not very different. The inhibiting efficiency at higher concentrations of the four chloromathanes increased in the following order: CH_2Cl_2, CH_3Cl, $CHCl_3$, CCl_4. Comparison of the effect of dichloromethane with some other halomethanes showed that this compound had about the same inhibiting efficiency as difluoromethane but was a considerably less powerful inhibitor than dibromomethane or diiodomethane.

In the present work it was considered, however, that the underlying mechanism of oxidation could be better elucidated by the use of an additive which did not cause too complete inhibition, and for this reason methylene chlorine, which had the least powerful inhibiting effect of the four chlorine compounds was selected.

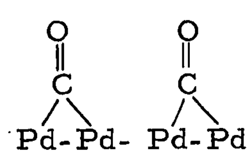
Figures 19 to 22 show the effects of 0.1 to 0.8 mole % of methylene chloride which strongly inhibits the overall oxidation of methane. At the same time, however, this compound promotes the formation of formaldehyde. The introduction of methylene chloride did not produce detectable amounts of any other partial oxidation products of methane.

Figure 23 show a less inhibiting effect in the oxidation of methane over palladium catalyst.

Concerning the mode of binding of carbon monoxide on palladium in the I.R. study of this chemisorption system 36 (36), has been observed two major bands "linear" and "bridged".



linear



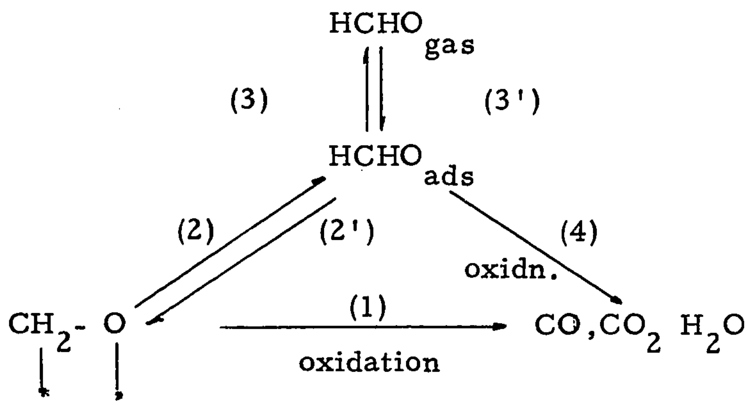
bridged

Bridged is the more strongly bonded and 50% must be present in linear and 50% in bridged. Deposition of carbon on the surface has the effect of blocking selectively those sites which favor bridge-bonding. Chemisorption of methane is known to be dissociative, the production of either methyl or methylene radicals involving an activation energy of 100 Kcal mole (37). It seems likely, however, that methane is most strongly chemisorbed on the "bridge sites" as bridge-bonded methylene radicals and that oxidation involves primarily the reaction of less stable linearly-bonded radicals with surface lattice oxygen. As reported by Cullis (31) the results in the presence of non-halogenated additives suggest that these compounds inhibit reaction simply by competing successfully with methane for surface sites.

The addition of halomethanes also strongly inhibits the oxidation of methane and the effectiveness of inhibitors increases with the lability of the carbon-halogen bond.

Adsorption of alkyl chloride (38) resulted in rupture of all carbon-chlorine bonds before any carbon-hydrogen bonds were broken and, as a result, the catalyst will tend to become covered by negatively charged halogen species. However one striking effect of the halomethanes is to increase dramatically the yields of formaldehyde (Figures 19 to 23). The finding that formaldehyde can be formed in quite high yields indicates that this compound is an important intermediate in certain circumstances. The observed dependence of rate on reactant concentrations (Figures 9 to 11) suggests that the rate-determining step is a surface reaction between adsorbed methane fragments and adsorbed oxygen, the latter being present in excess. It seems likely that the immediate precursor of formaldehyde is a complex: $\underset{|}{CH_2} - \underset{|}{O}$ formed by the interaction of linearly bonded methylene redicals with some oxygen-containing species.

The observation that the addition of methylene chloride has an effect which is initially cumulative and that the catalyst only slowly returns to its original state when the halogen compound is no longer introduced suggests that the additive acts primarily by modifying the electronic properties of the catalyst surface. The introduction of halo-compounds would be expected to lead to the formation of dipoles with the negative charge facing outwards, and the presence of these will tend to decrease the coverage by oxygen ions



Since the direct conversion of the methylene-oxygen complex to final products reaction (1) , probably involves interaction with adsorbed oxygen, the extent of this reaction relative to reaction (2) would be expected to be decreased by halogen-containing additives. Furthermore, if formaldehyde, like other oxygenated intermediates, acts as an electron acceptor, the presence of negative dipoles should enhance desorption reaction (3) rather than further oxidation reaction (4) of this partial oxidation product.

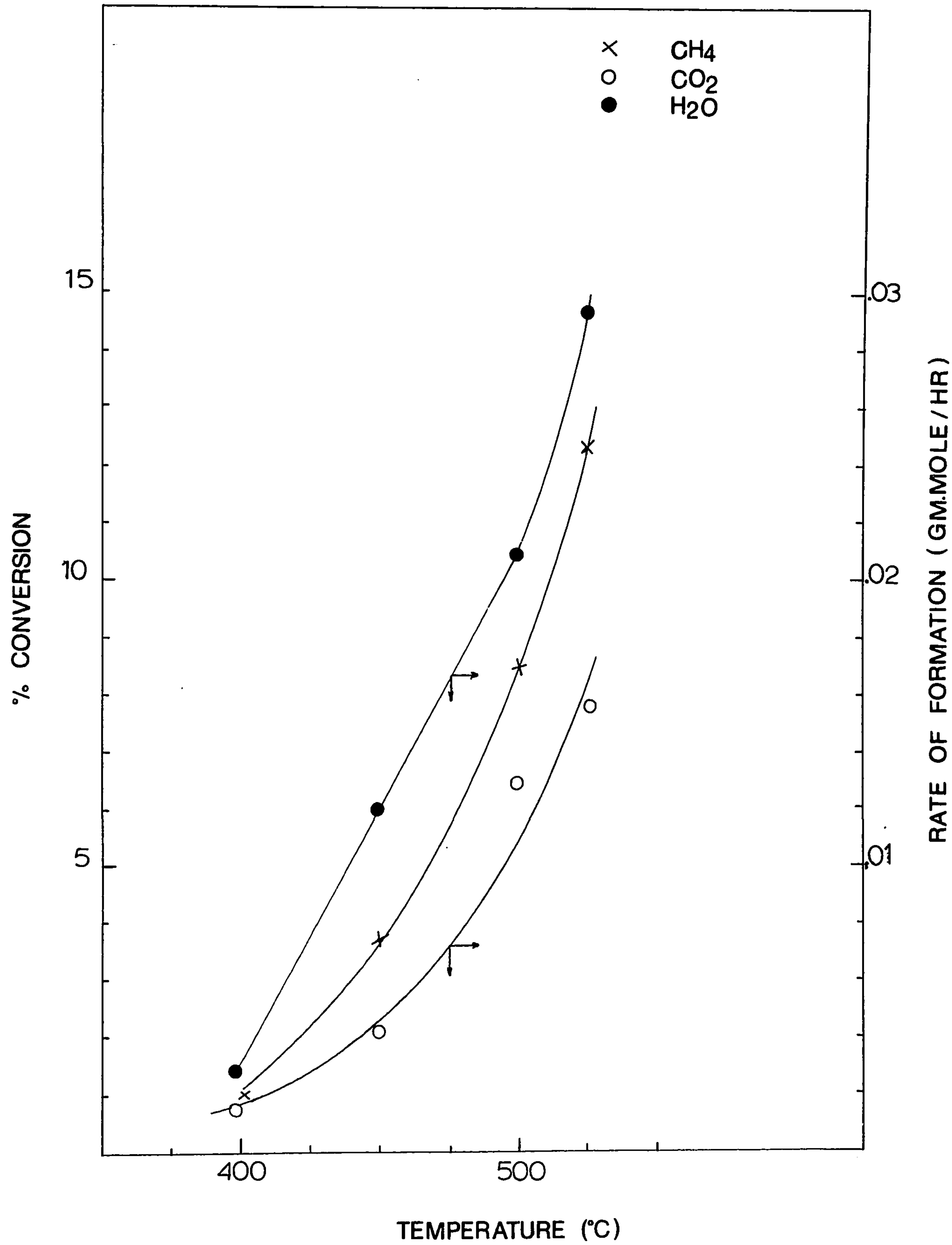


Figure 6 Effect of Termperature on Conversion and Rate of Formation using a Copper Oxide Catalyst for R = 6.

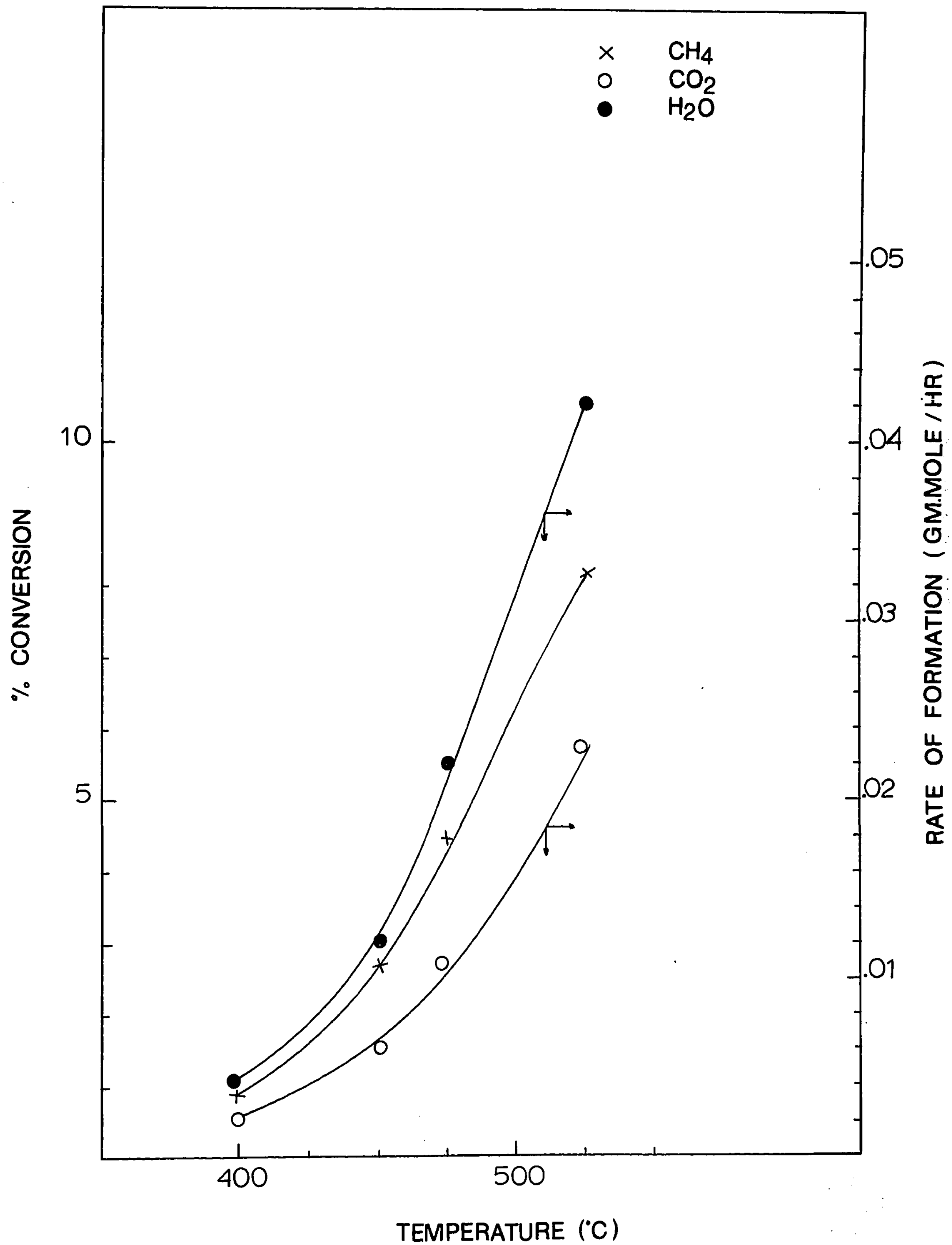


Figure 7 Effect of Temperature on Conversion and Rate of Formation using a Copper Oxide Catalyst for R = 3.

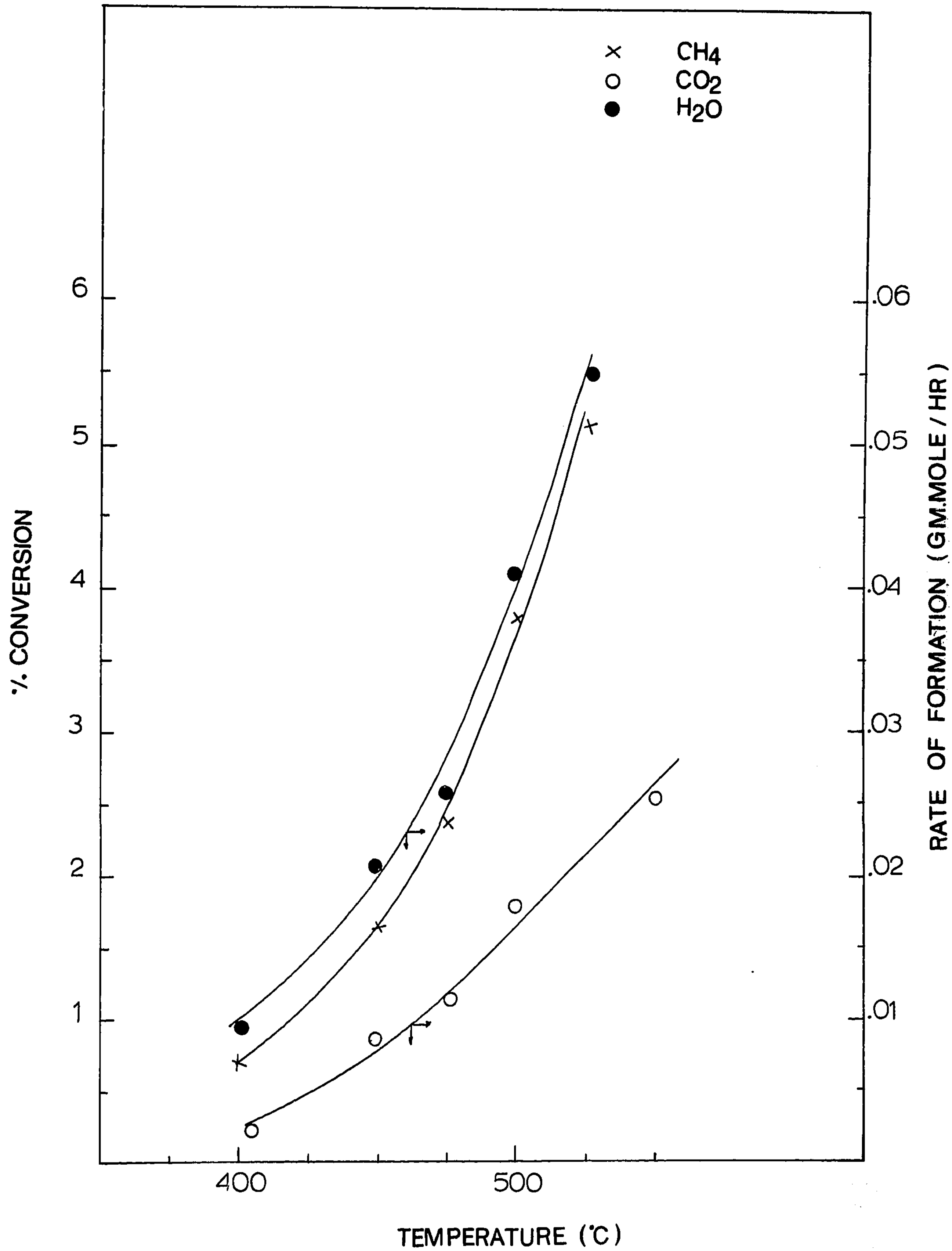


Figure 8 Effect of Temperature on Conversion and Rate of Formation using a Copper Oxide Catalyst for R = 1.

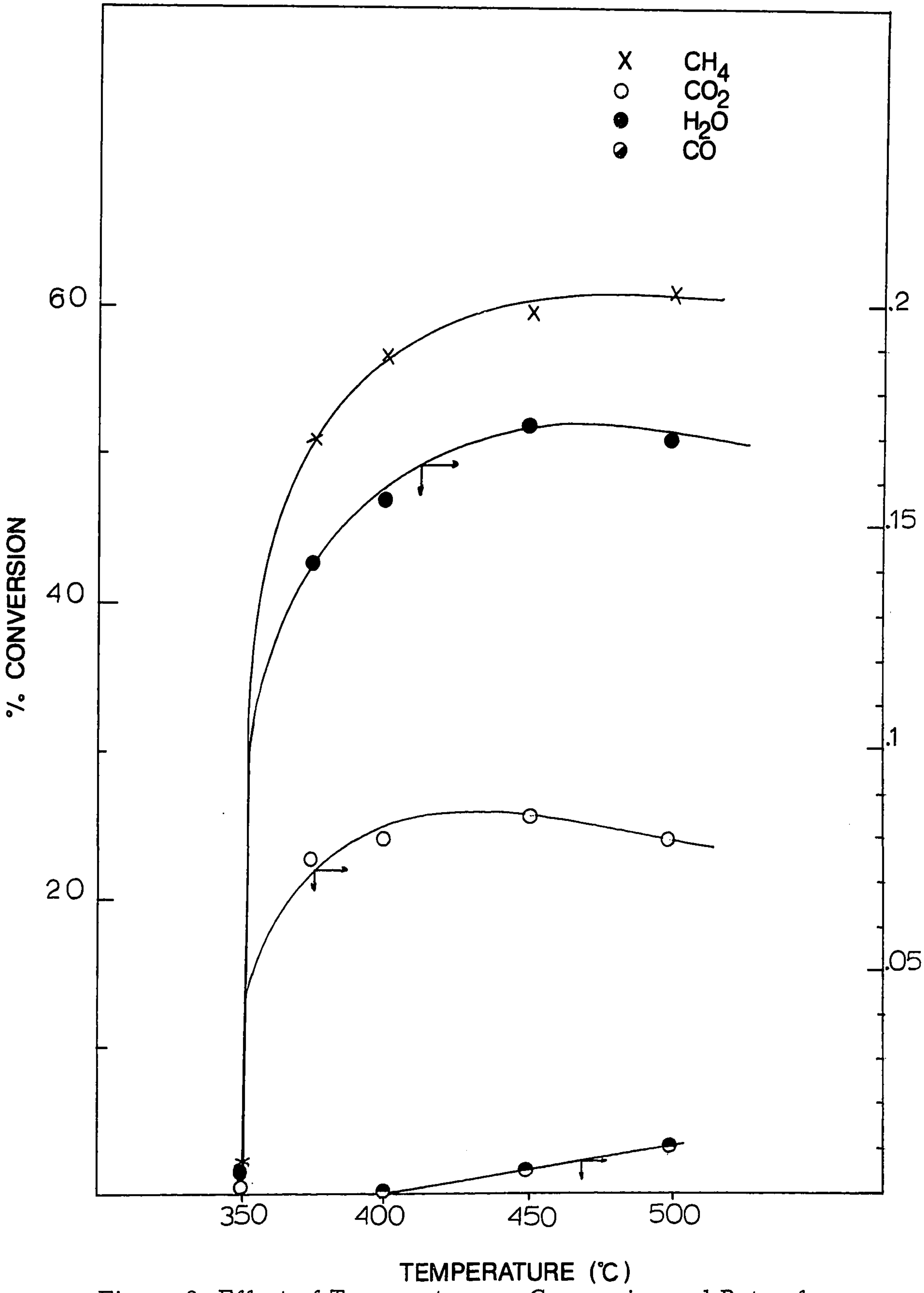


Figure 9 Effect of Temperature on Conversion and Rate of Formation using a Palladium Catalyst for R = 6.

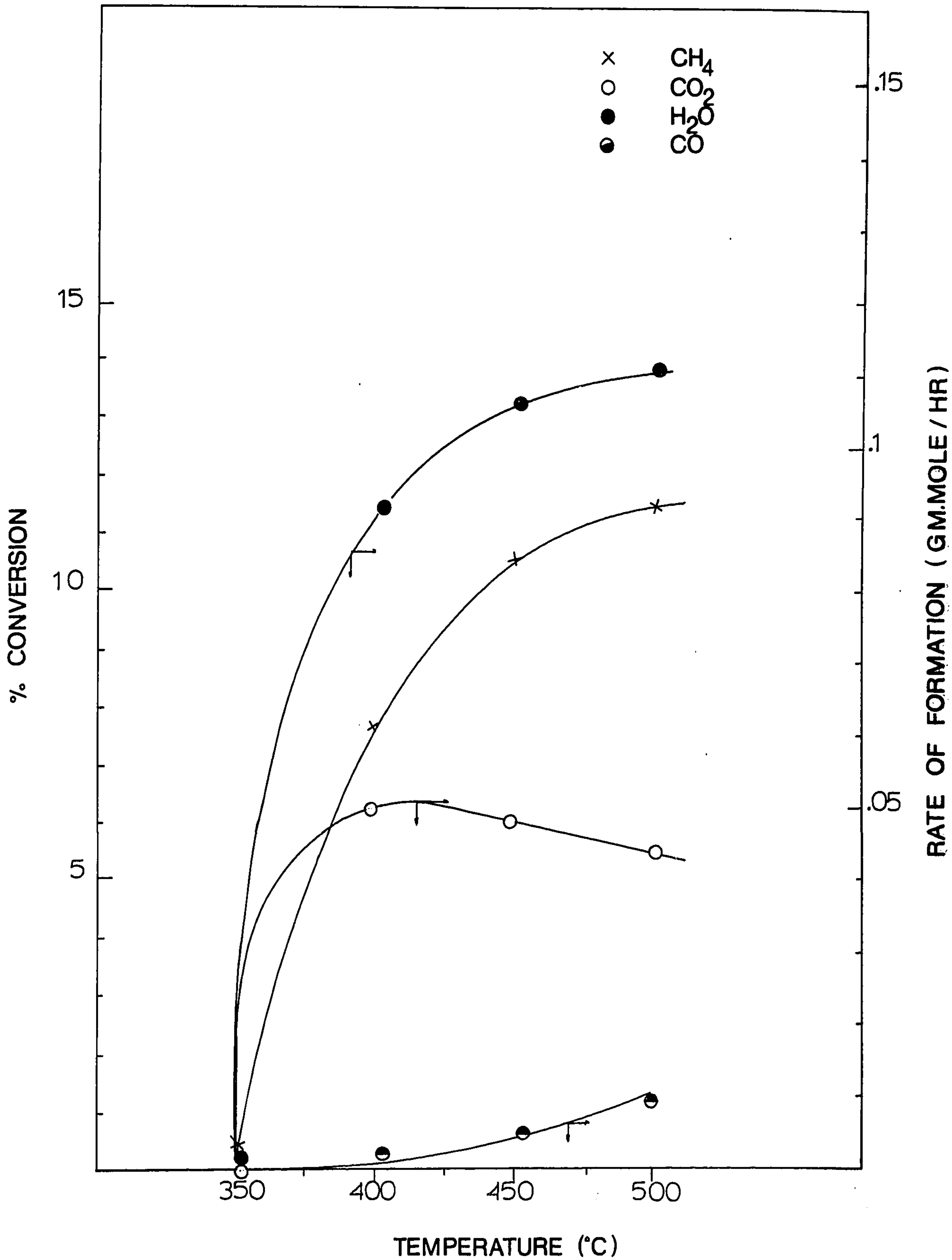


Figure 10 Effect of Temperature on Conversion and Rate of Formation using a Palladium Catalyst for R = 1.

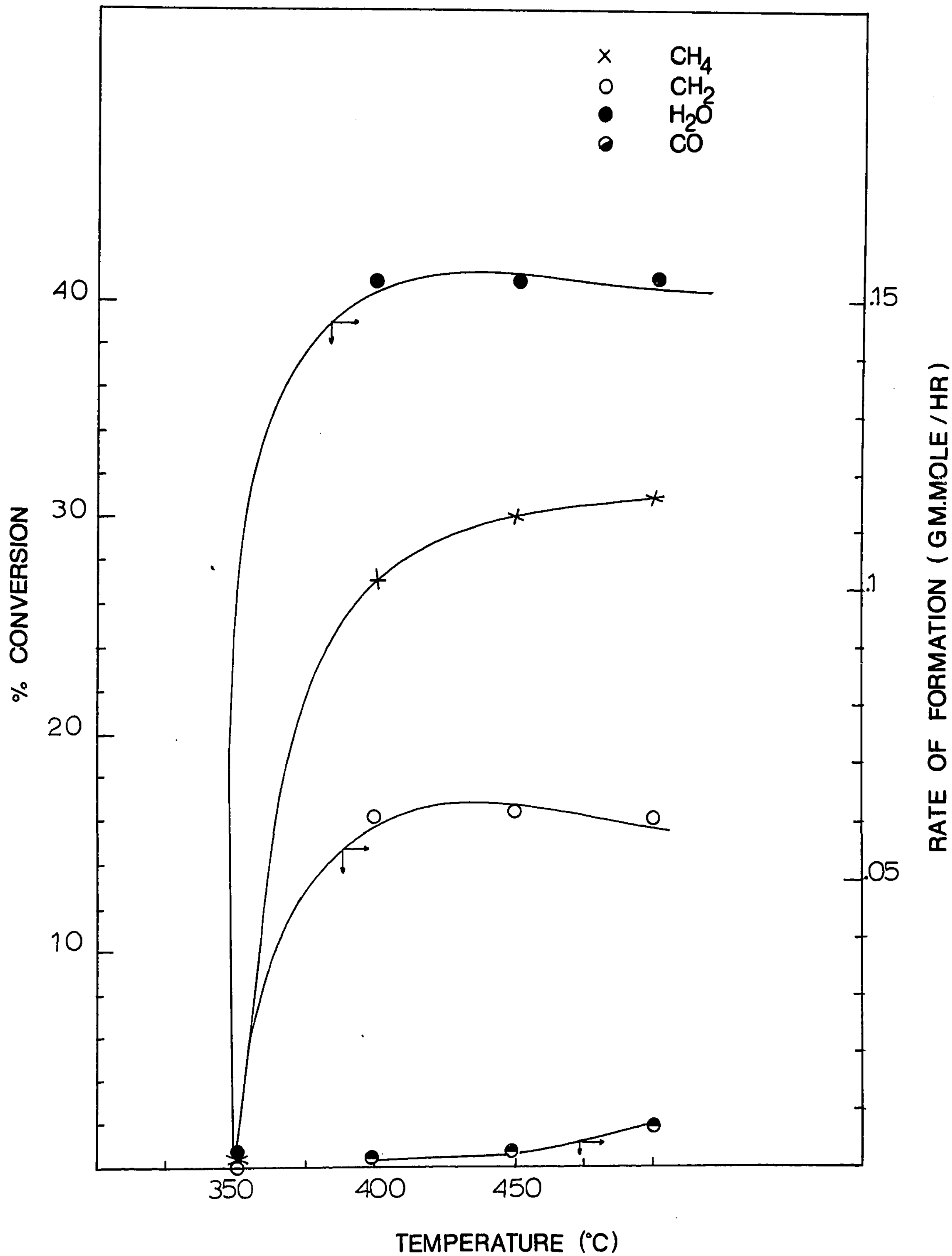


Figure 11 Effect of Temperature on Conversion and Rate of Formation using a Palladium Catalyst for R = 3.

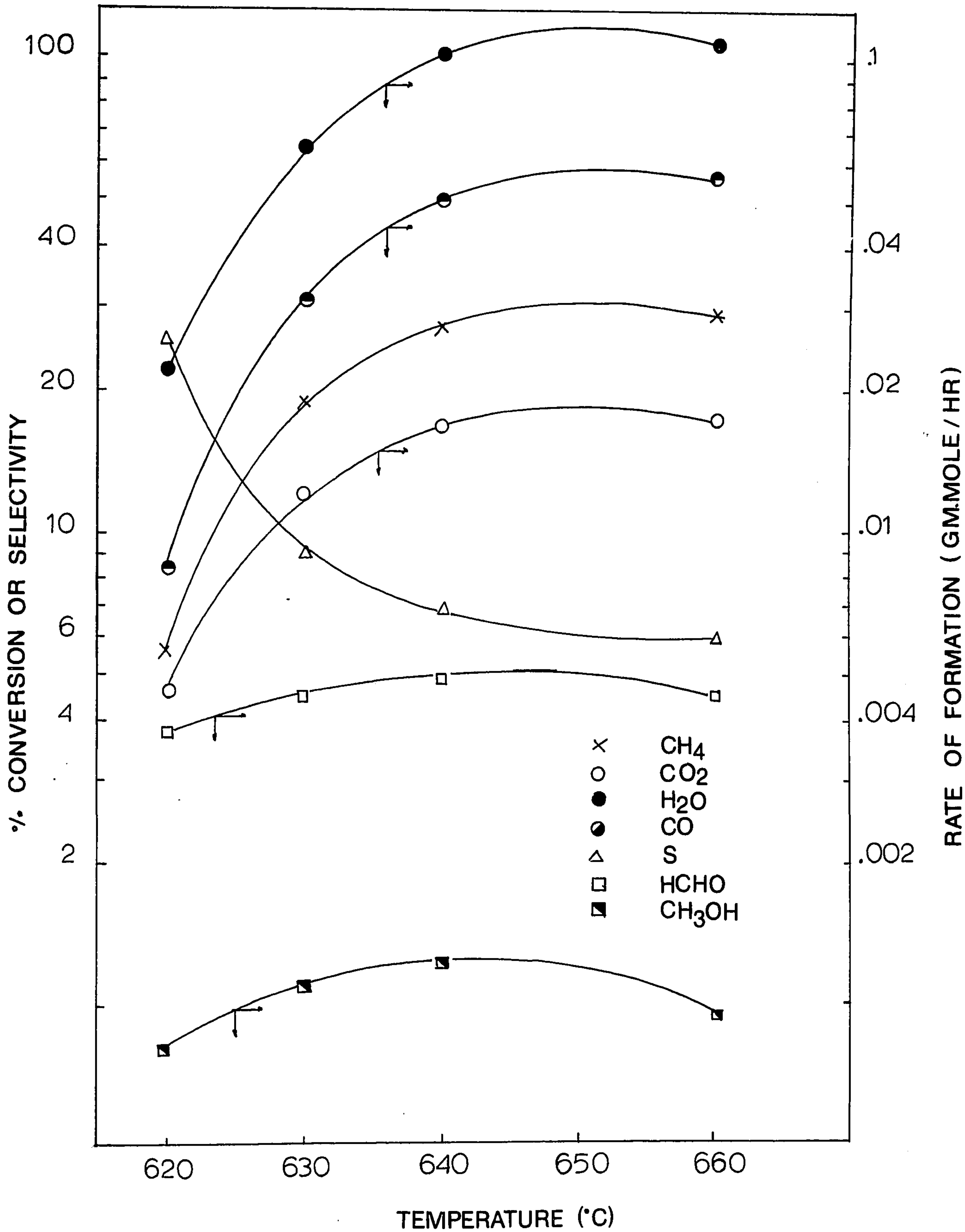


Figure 12 Effect of Temperature on Conversion, Rate of Formation and Selectivity using 0.1% Nitric Oxide as a Catalyst for R = 3.

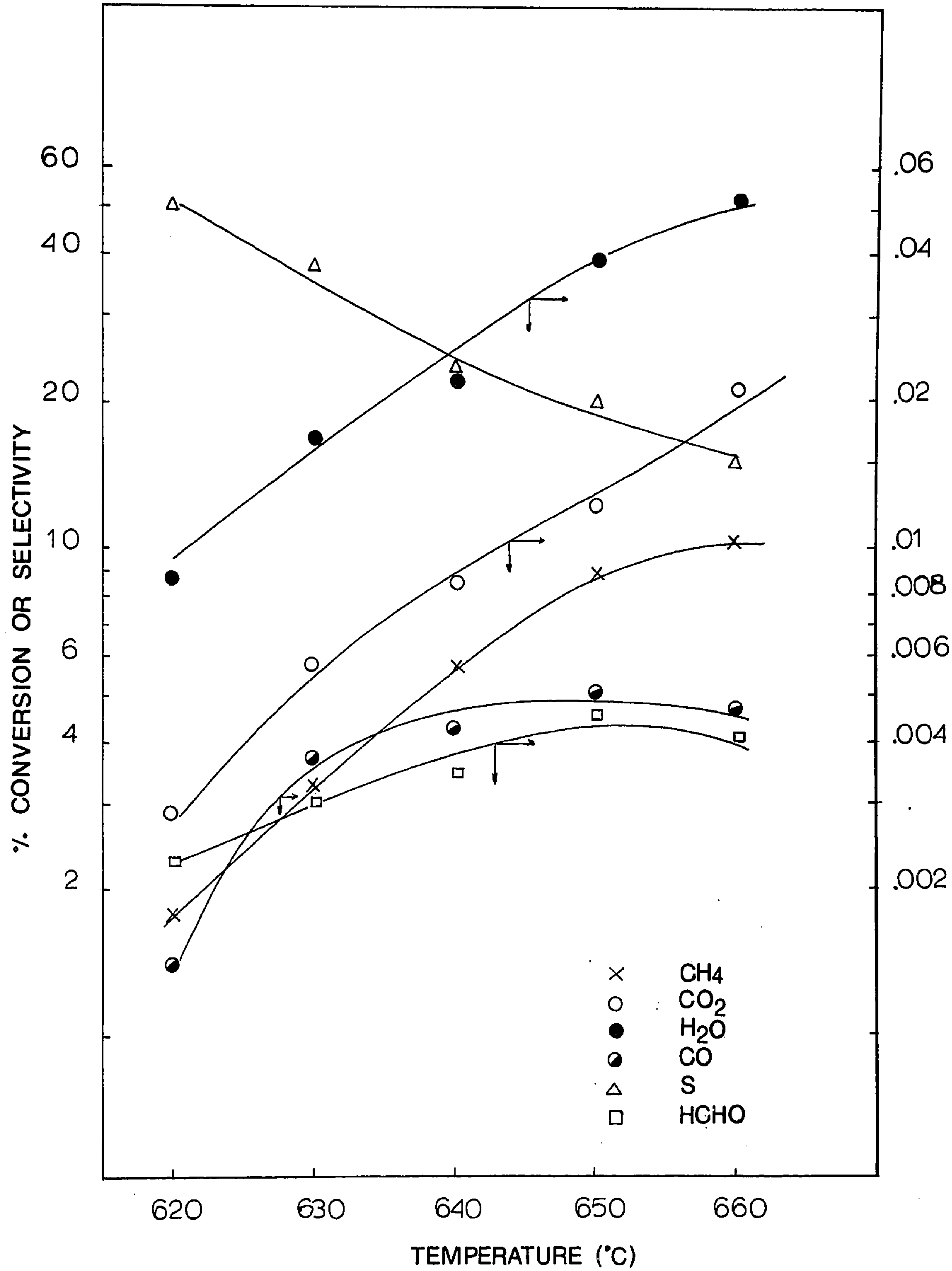


Figure 13 Effect of Temperature on Conversion, Rate of Formation and Selectivity using 0.1% Nitric Oxide with Pumice as a Catalyst for R = 3.

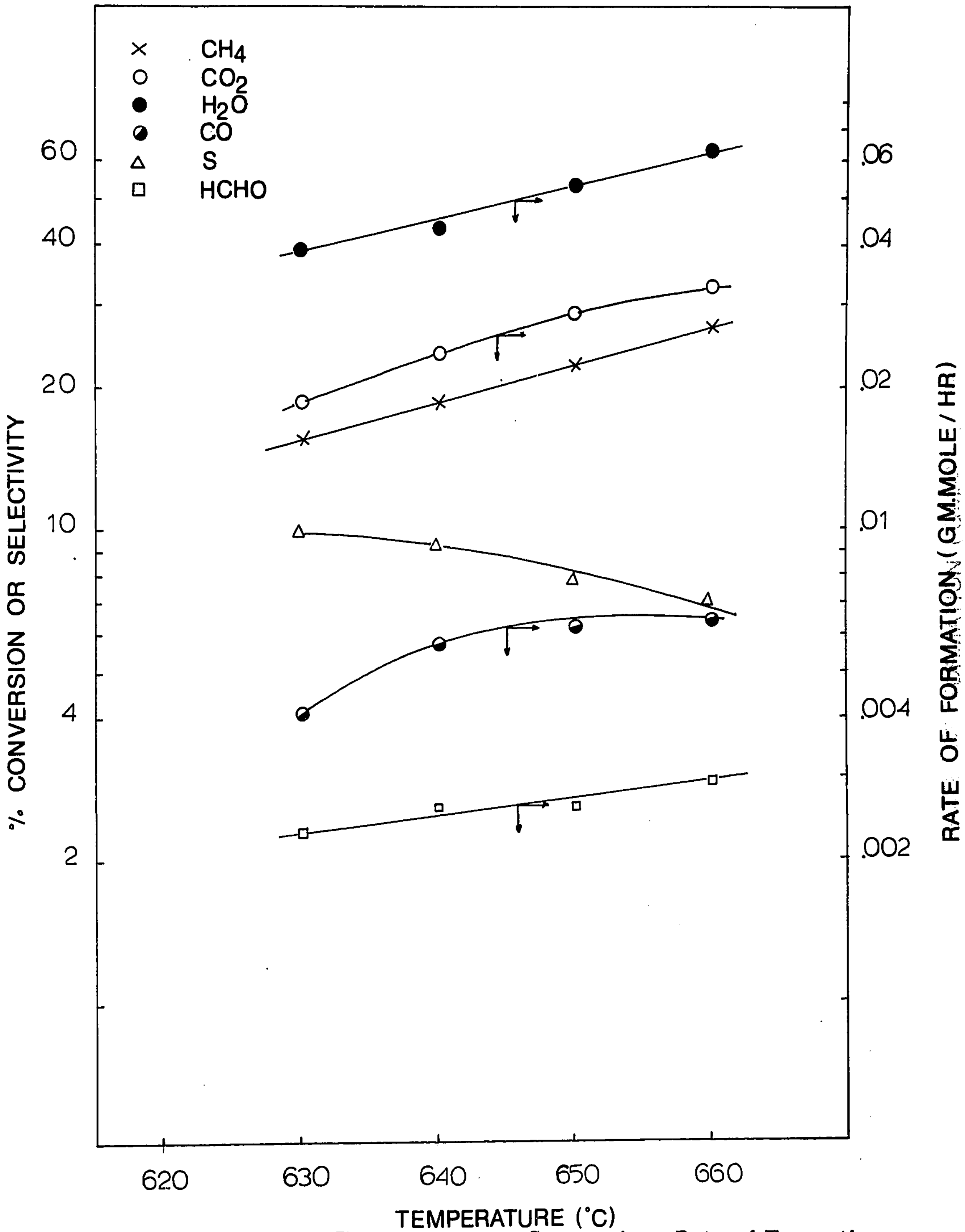


Figure 14 Effect of Temperature on Conversion, Rate of Formation and Selectivity using 0.1% Nitric Oxide with Pumice as a Catalyst for R = 6.

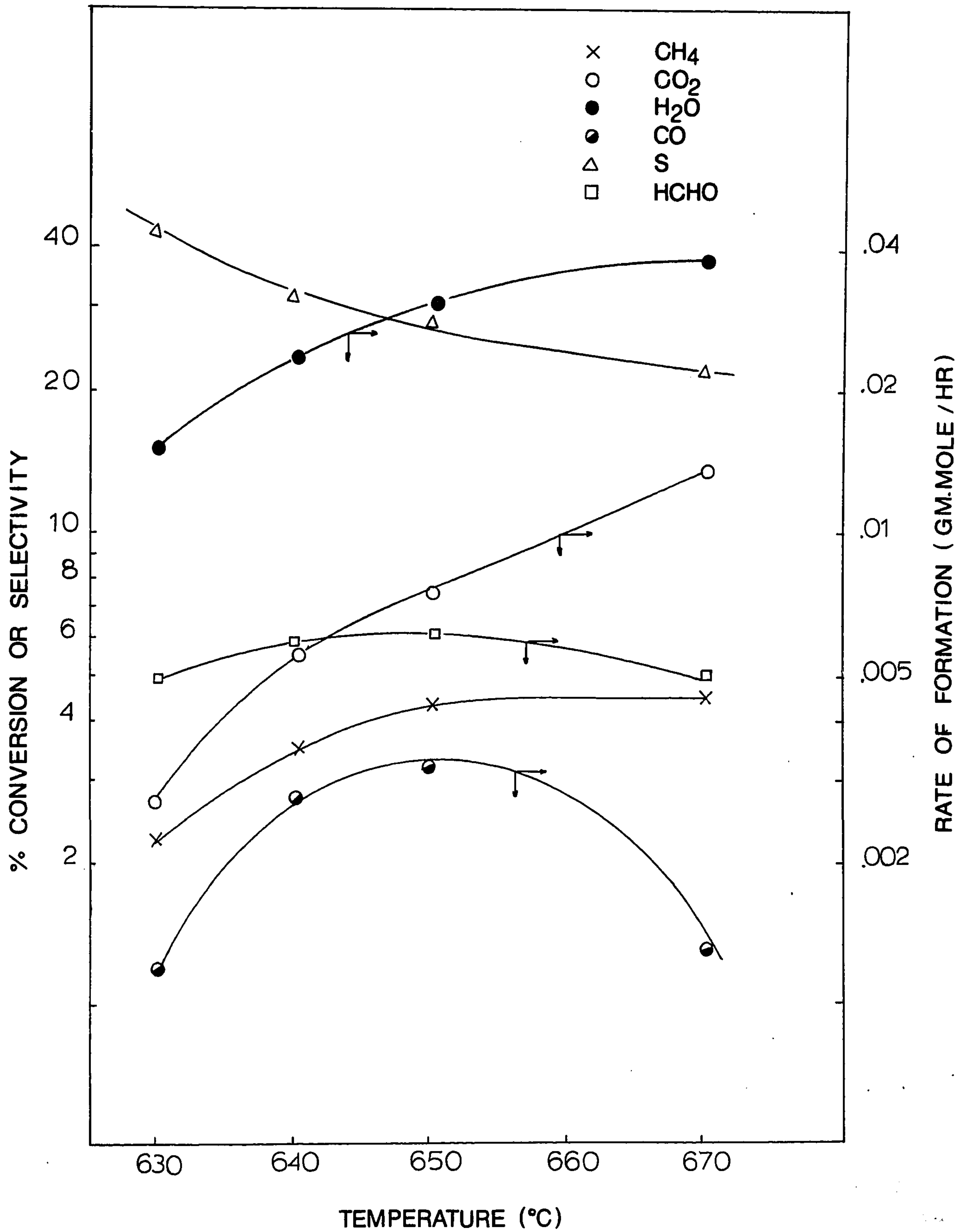


Figure 15 Effect of Temperature on Conversion, Rate of Formation and Selectivity using 0.1% Nitric Oxide with Pumice as a Catalyst for R = 1.

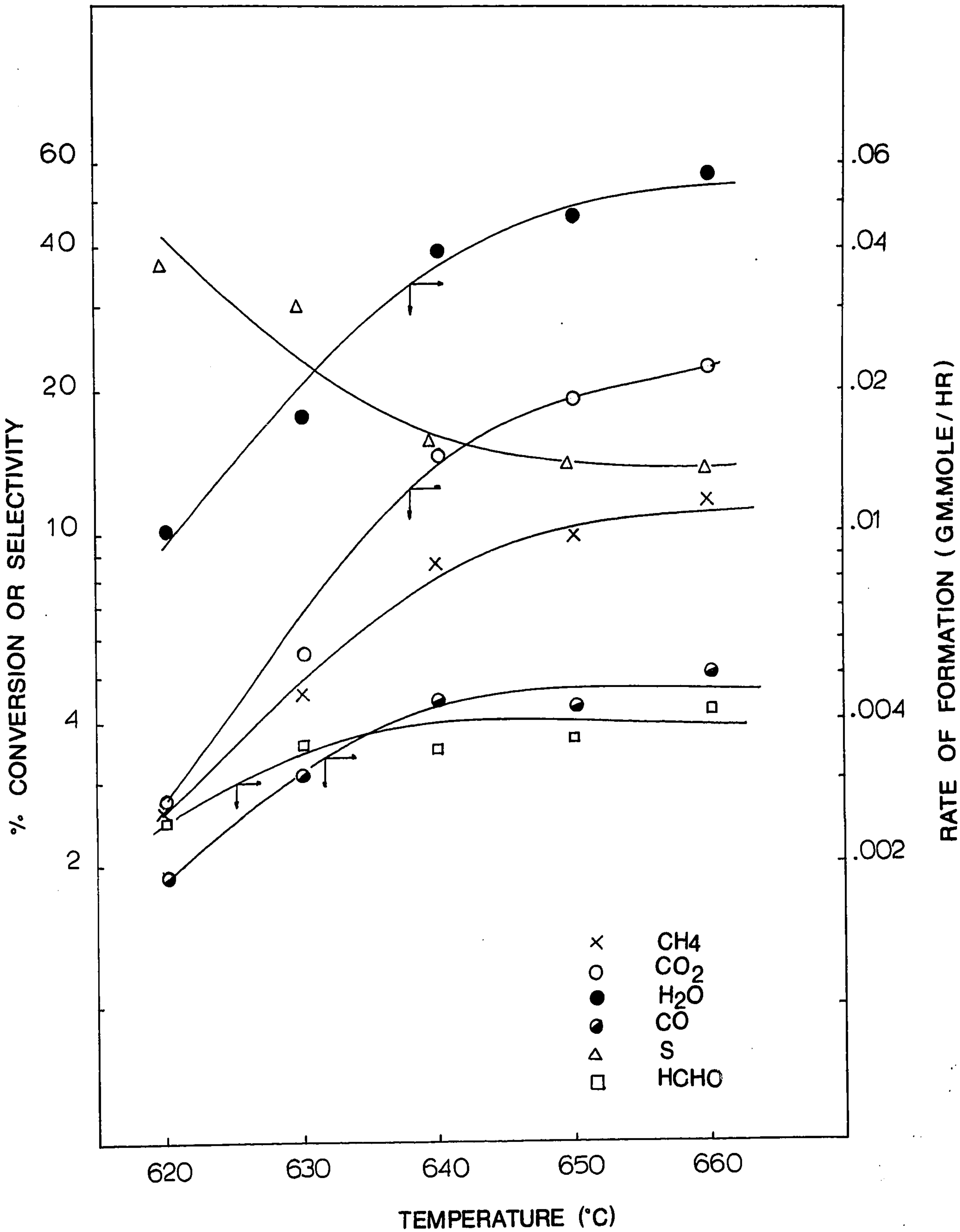


Figure 16 Effect of Temperature on Conversion, Rate of Formation and Selectivity using 0.5% Nitric Oxide with Pumice as a Catalyst for R = 3.

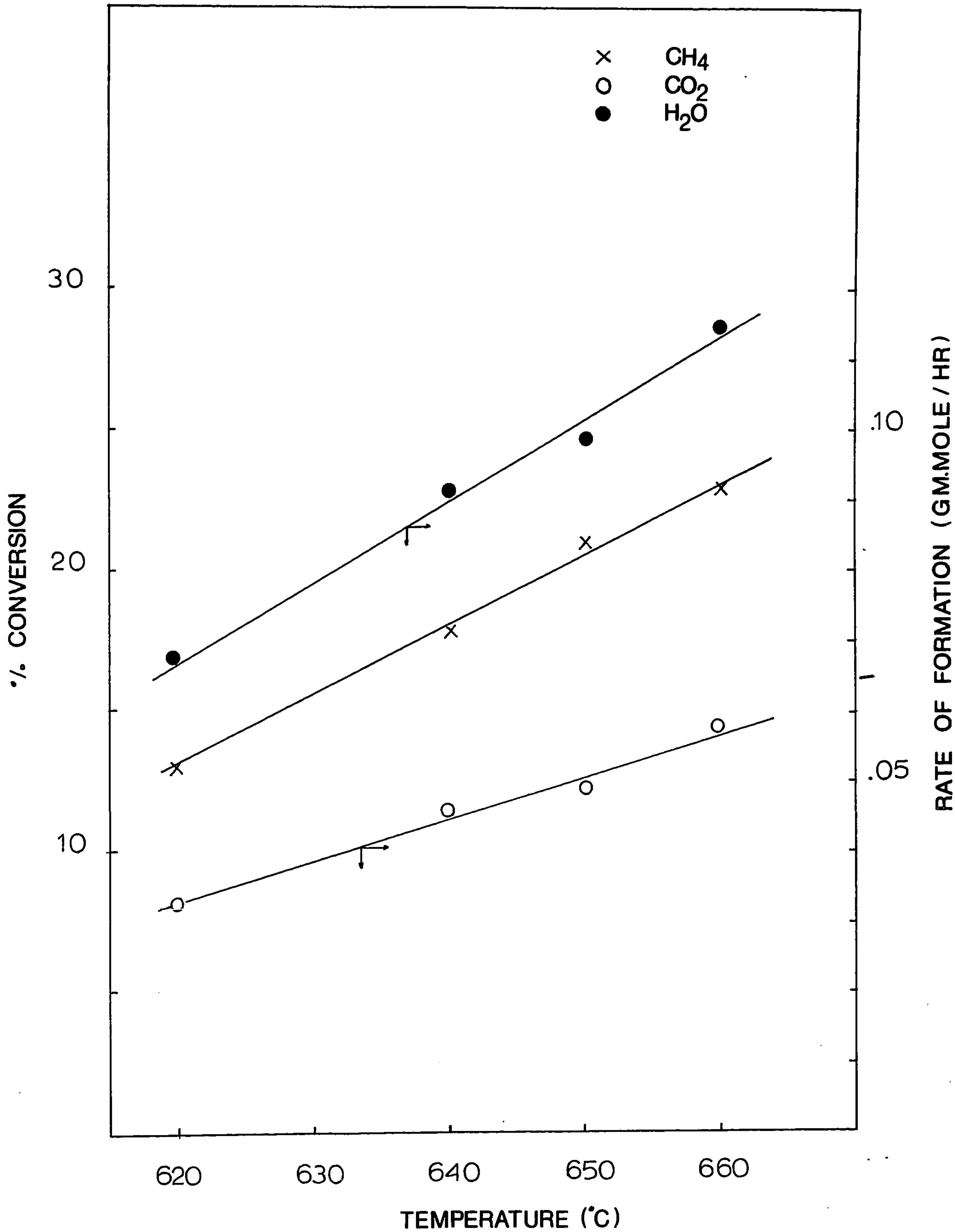


Figure 17 Effect of Temperature on Conversion, Rate of Formation and Selectivity using 0.1% Nitric Oxide with Copper Oxide as a Catalyst for R = 3

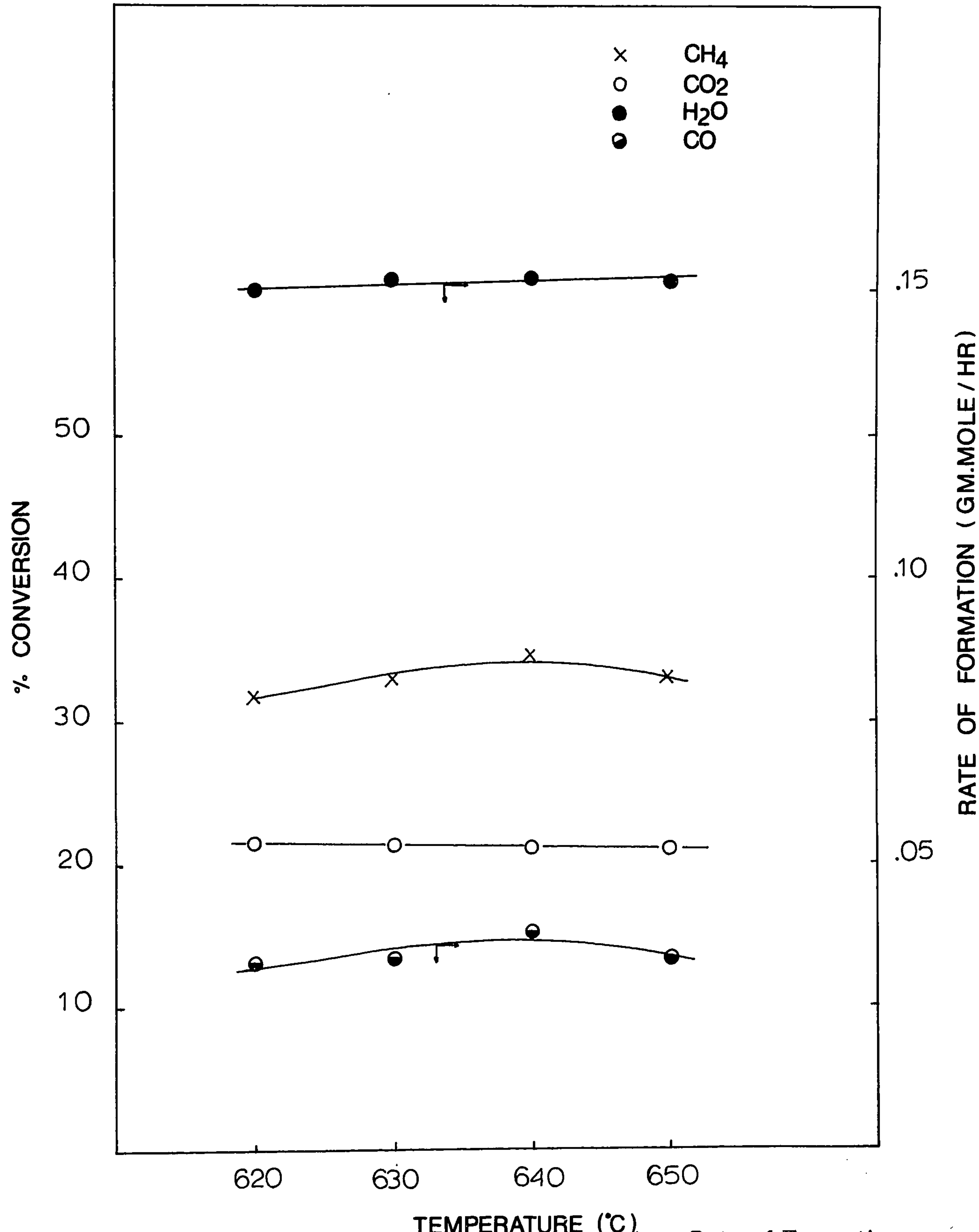


Figure 18 Effect of Temperature on Conversion, Rate of Formation and Selectivity using 0 1% Nitric Oxide with Palladium as a Catalyst for R = 3.

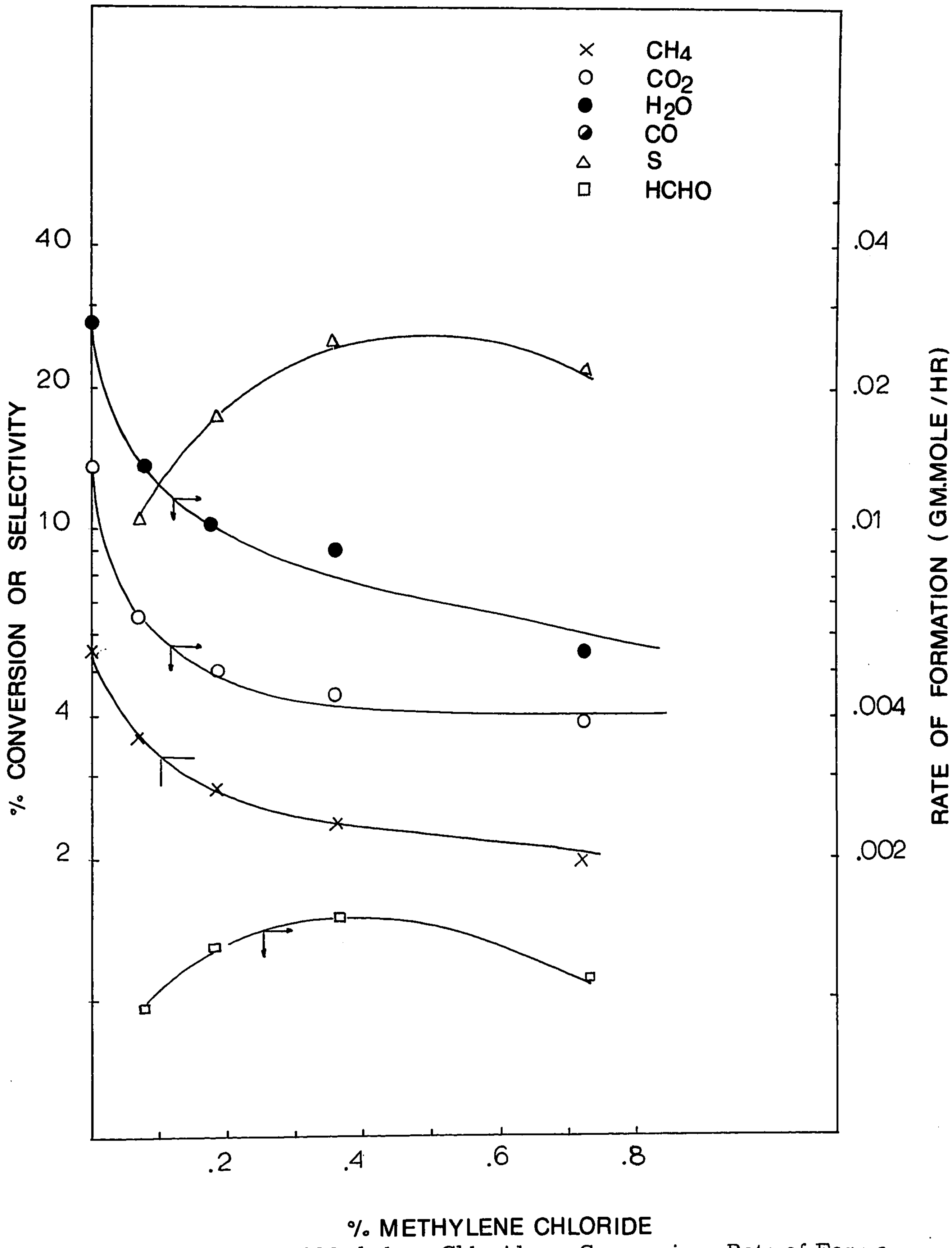


Figure 19 Effect of Methylene Chloride on Conversion, Rate of Formation and Selectivity using a Copper Oxide Catalyst at 525°C for R = 3.

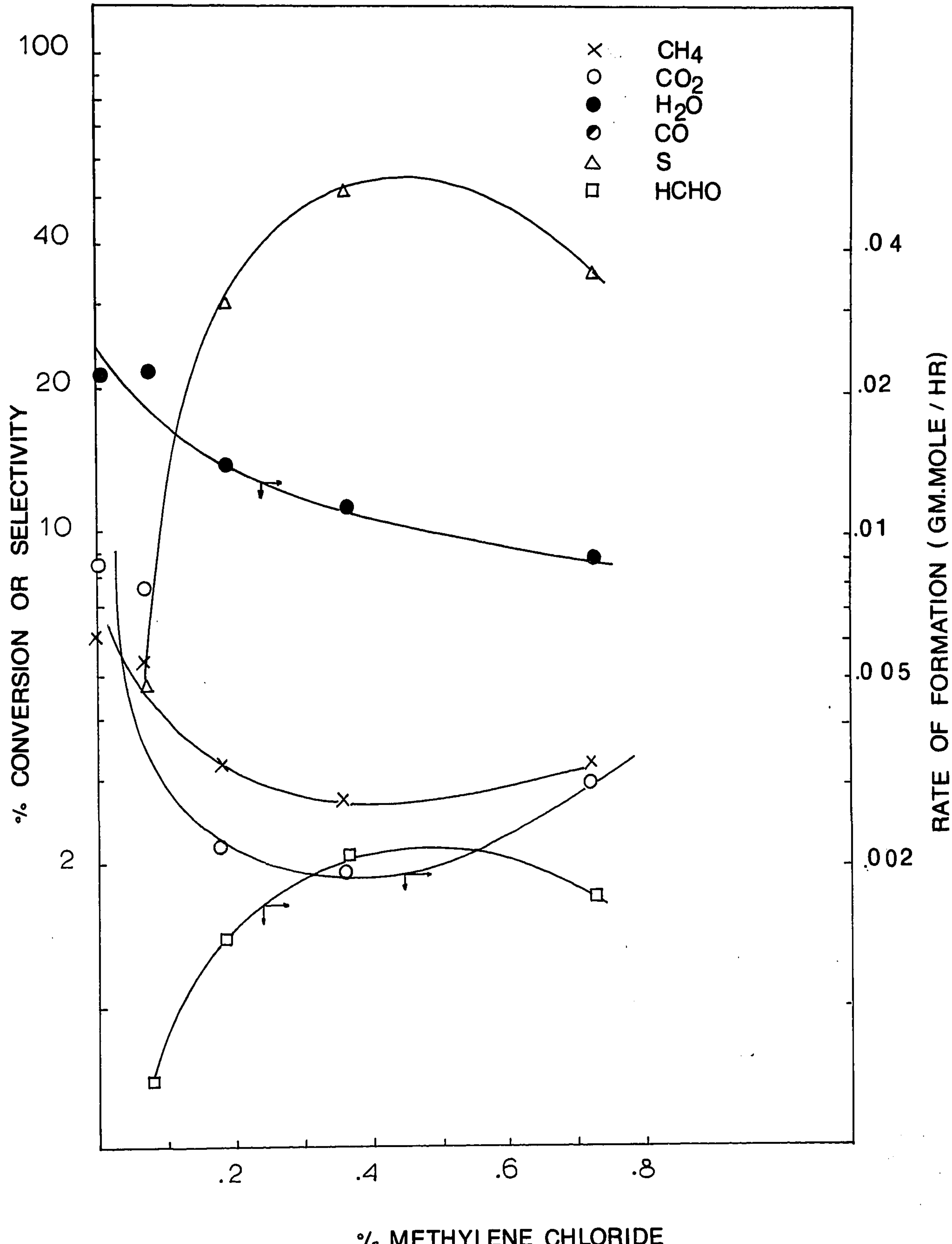


Figure 20 Effect of Methylene Chloride on Conversion Rate of Formation and Selectivity using a Copper Oxide Catalyst at 525°C for R = 6.

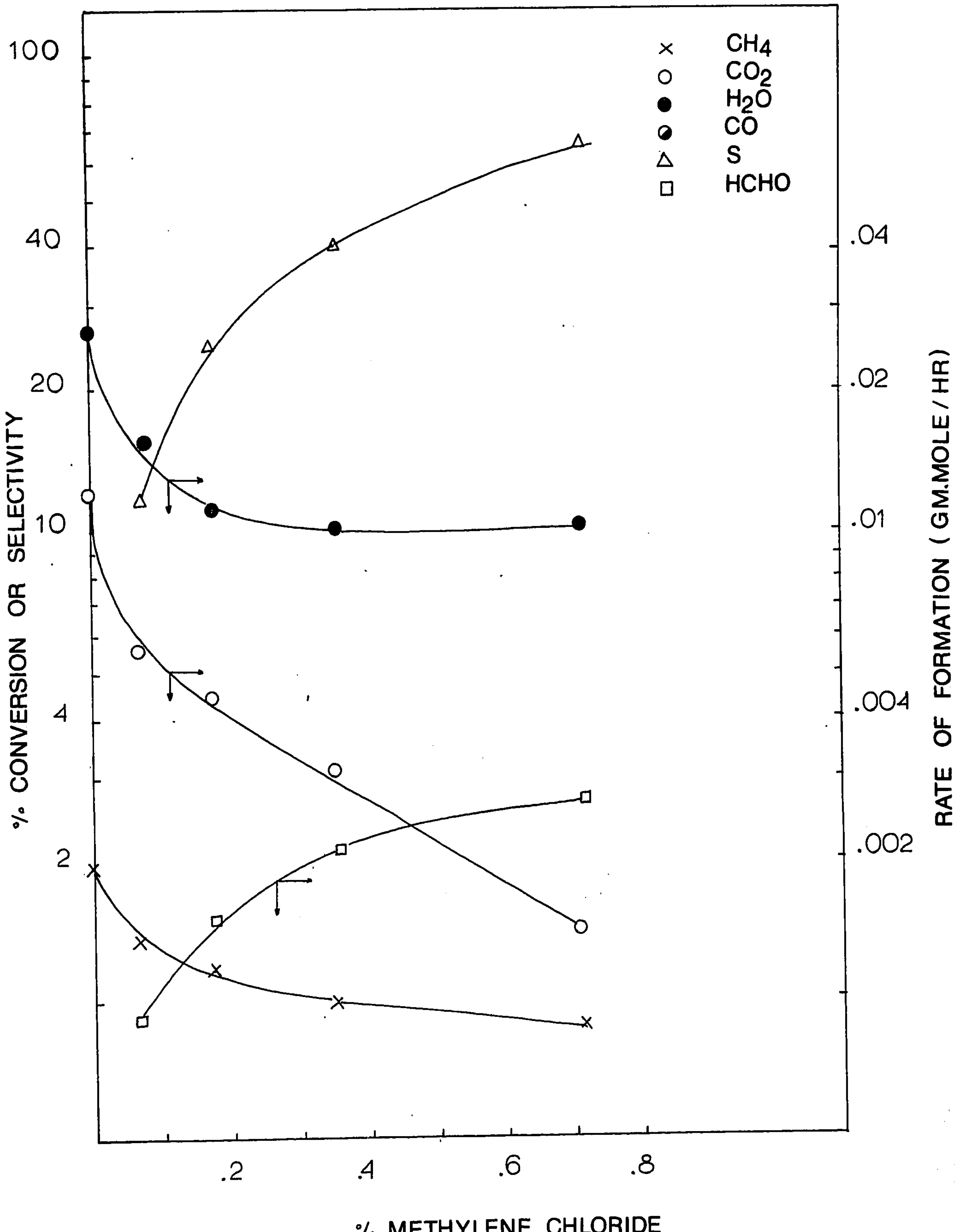


Figure 21 Effect of Methylene Chloride on Conversion Rate of Formation and Selectivity using a Copper Oxide Catalyst at 525° C for R = 1.

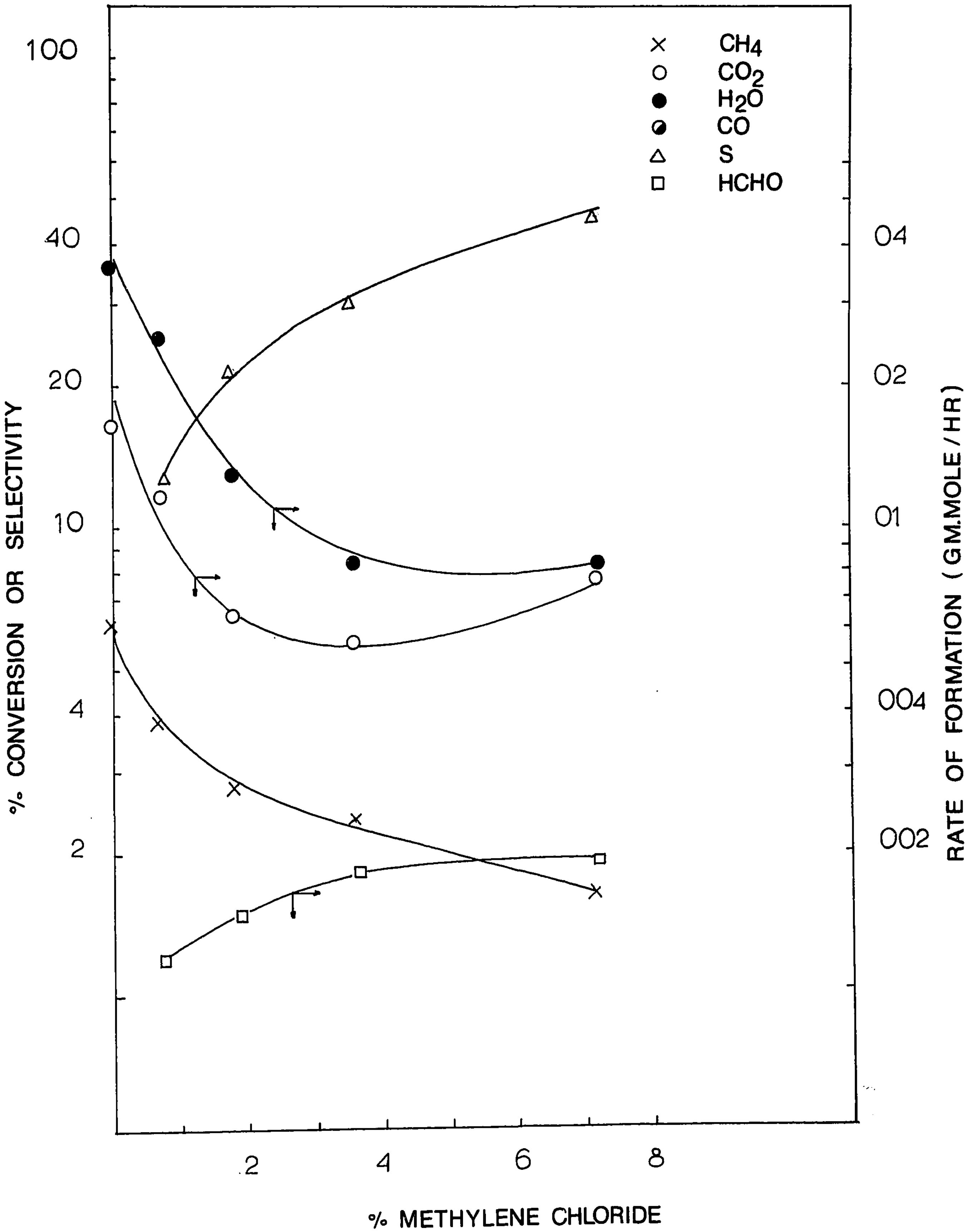


Figure 22 Effect of Methylene Chloride on Conversion, Rate of Formation and Selectivity, using a Copper Oxide Catalyst at 525° C for R = 3.

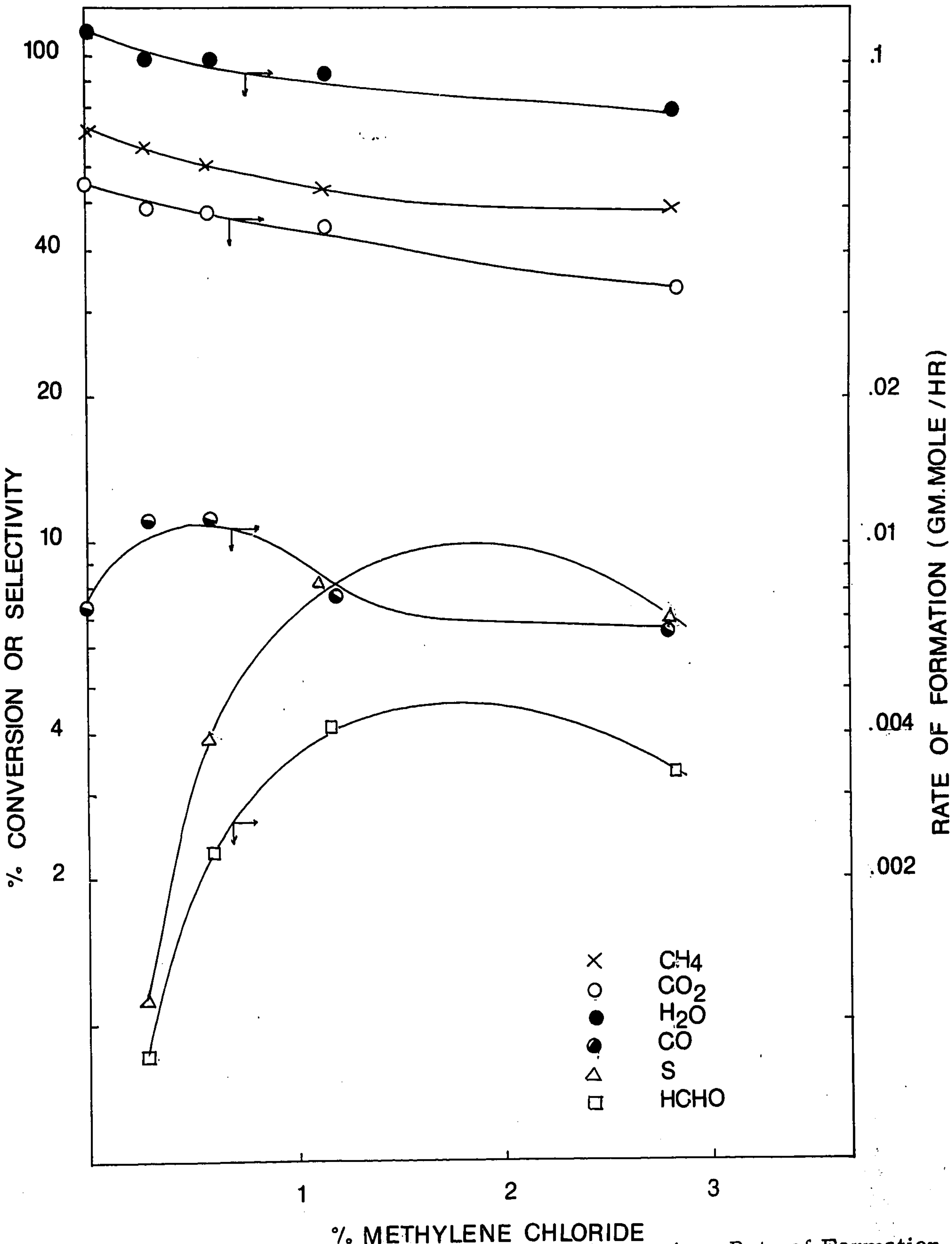


Figure 23 Effect of Methylene Chloride on Conversion, Rate of Formation and Selectivity, using a Palladium Catalyst at 525°C for R = 6.

VI CONCLUSIONS AND RECOMENDATIONS

The catalytic oxidation of methane was investigated with different catalysts and gaseous additives in order to determine the most favourable conditions under which formaldehyde could be isolated and also to determine the role of this intermediate.

An experimental system, facilitating precise rate measurements and analytical technique to measure accurately and continuously even traces of formaldehyde without polymer formation, was developed. This technique facilitated the detection of short-lived species and had a great advantage over the collection-sample injection technique especially in this particular reaction, due to the low solubility and stability of formaldehyde in the presence of water alone.

The following conclusions are drawn from the experimental data:

1. The reaction rate depended on reactant concentrations, the rate determining step to be a surface reaction between adsorbed methane fragments and adsorbed oxygen.

2. Nitric oxide is an homogeneous catalyst, and acted as an initiator in the radical chain process.

3. The presence of pumice caused probably the destruction of an intermediate radical in the homogeneous catalysis affecting the propagation of the radical chain process by introducing a termination.

4. An increase in the amount of nitric oxide promoted the initial steps in the radical chain process (initiation, propagation and chain reaction) affecting the selectivity of the reaction.

5. Nitric oxide did not affect the rate of reaction on catalytically active substances like palladium and copper oxide, proceeding the reaction as without addition of such additive.

6. The additions of methylene chloride as modifier strongly inhibited the overall oxidation of methane and promoted the formation of formaldehyde.

7. A continuous supply of a constant amount of modifier to the catalyst was essential to maintain the selectivity of the catalyst.

8. The molar per cent ratio of modifier to the feed was the most important factor in selective oxidation. A smaller amount of modifier improved the selectivity for the aldehyde, but larger amounts tended to decrease it.

9. Methylene chloride is an acceptor type which has higher electronegativity than that of the skeleton catalyst. The introduction of this halo-compound is expected to lead to the formation of dipoles, and the presence of these will tend to decrease the coverage by oxygen ions. It is for this reason the extent of the direct conversion of the methylene-oxygen complex to final products, decreased relatively as compared to the partial oxidation to formaldehyde. At the same time those dipoles enhance the desorption of formaldehyde rather than its further oxidation.

It is recommended that

1. Further work on the oxidation of methane over other single and multifunctional catalyst such as (V^{5+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, Mo^{6+}, Ti^{4+}, and $PO_4^{\equiv}$) be studied.

2. In order to obtain a better understanding of the reaction other gaseous additives giving rise to negative dipoles on the surface should be studied.

VII APPENDIX

APPENDIX A

Calibration of Equipment

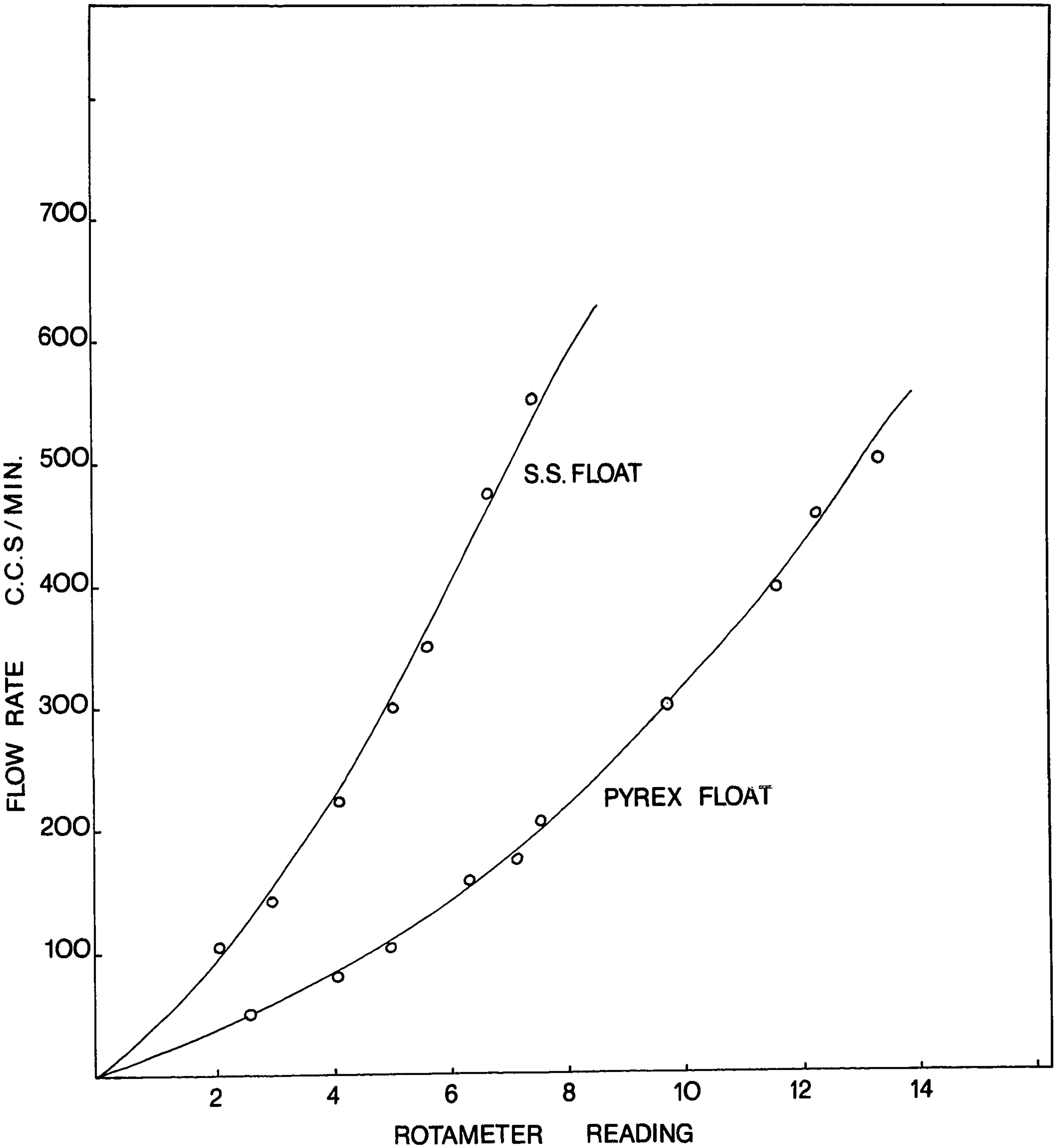


Figure 24 Rotameter Calibration for Air.

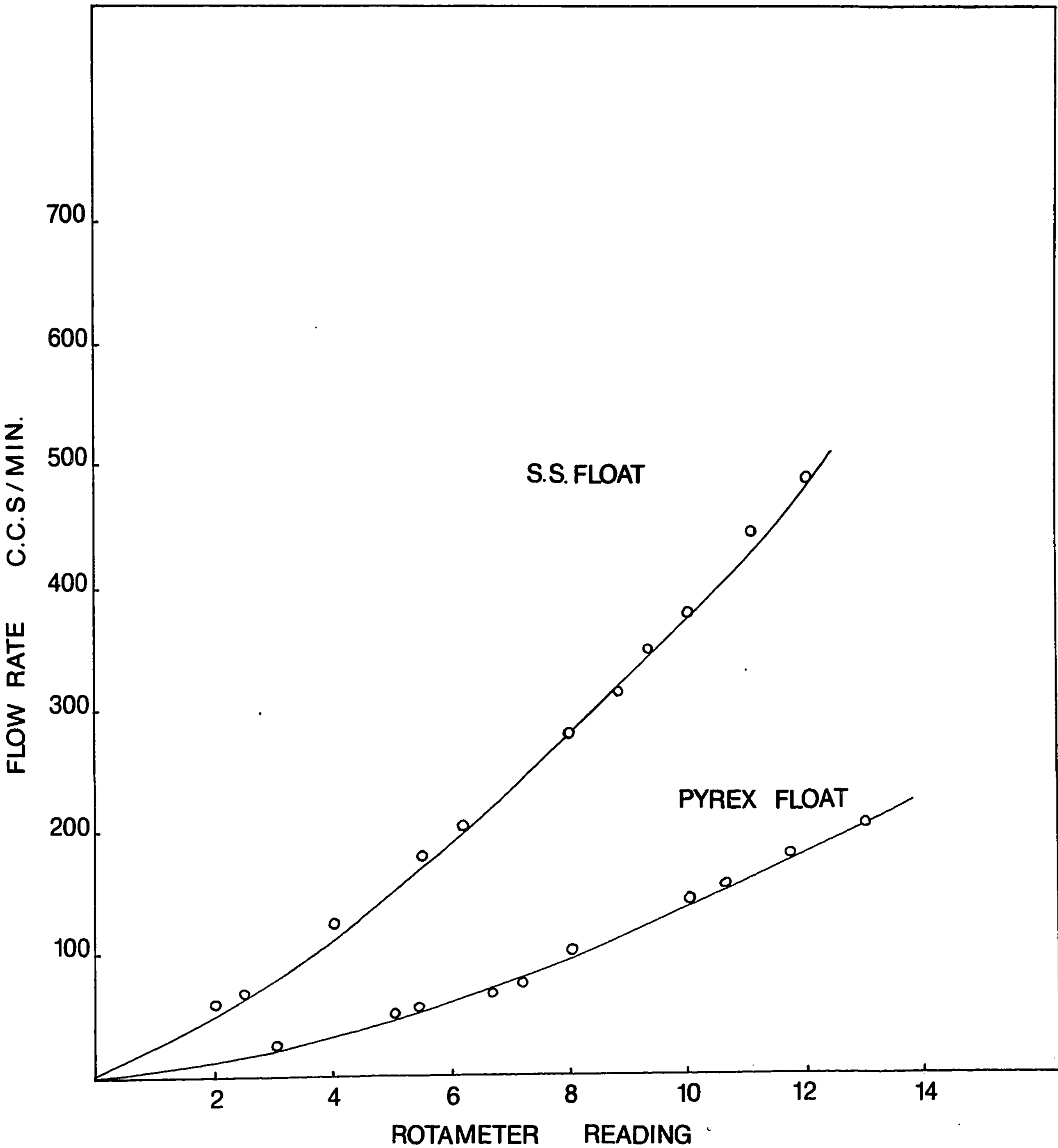


Figure 25 Rotameter Calibration for Methane.

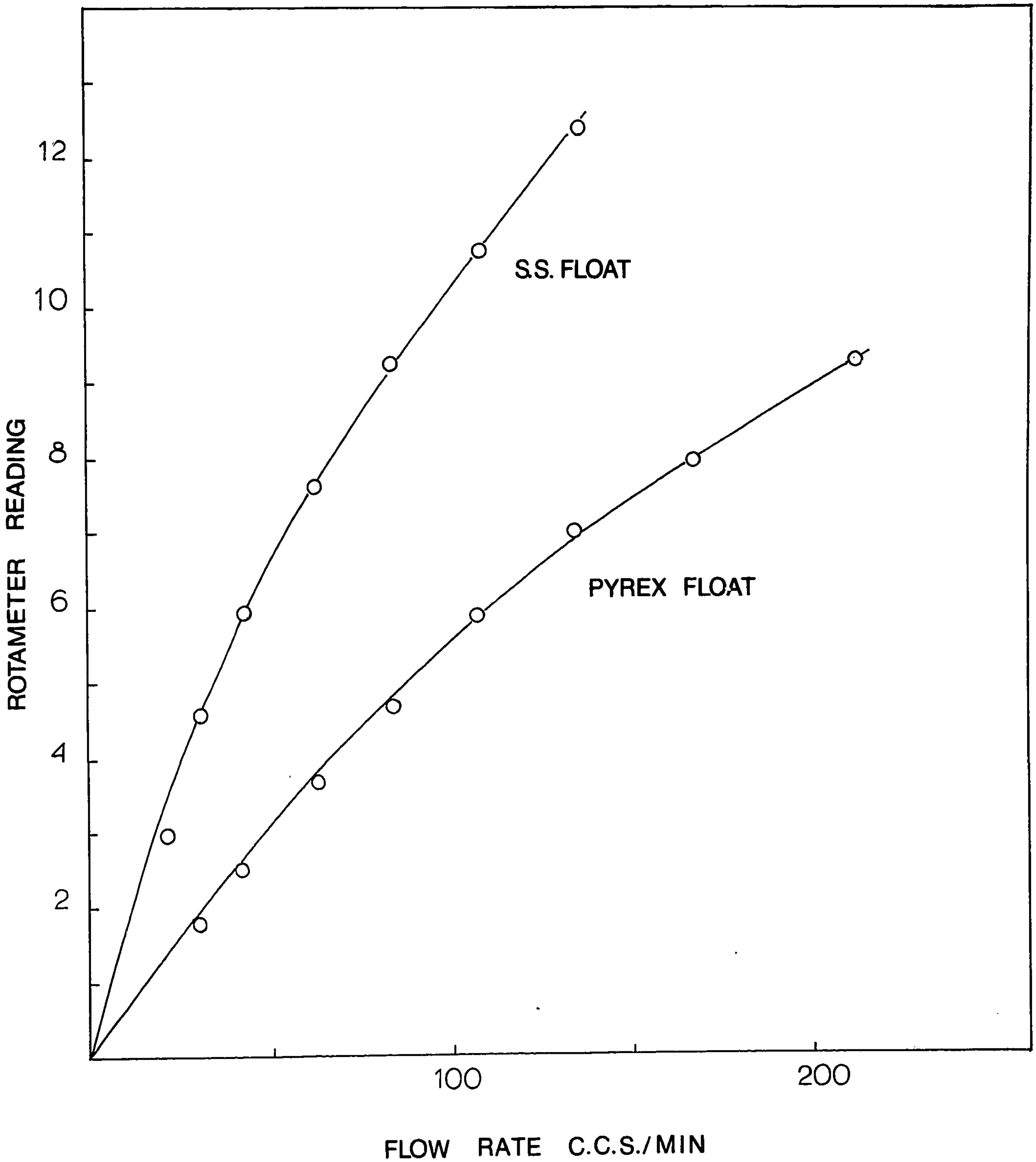


Figure 26 Rotameter Calibration for Carbon Dioxide.

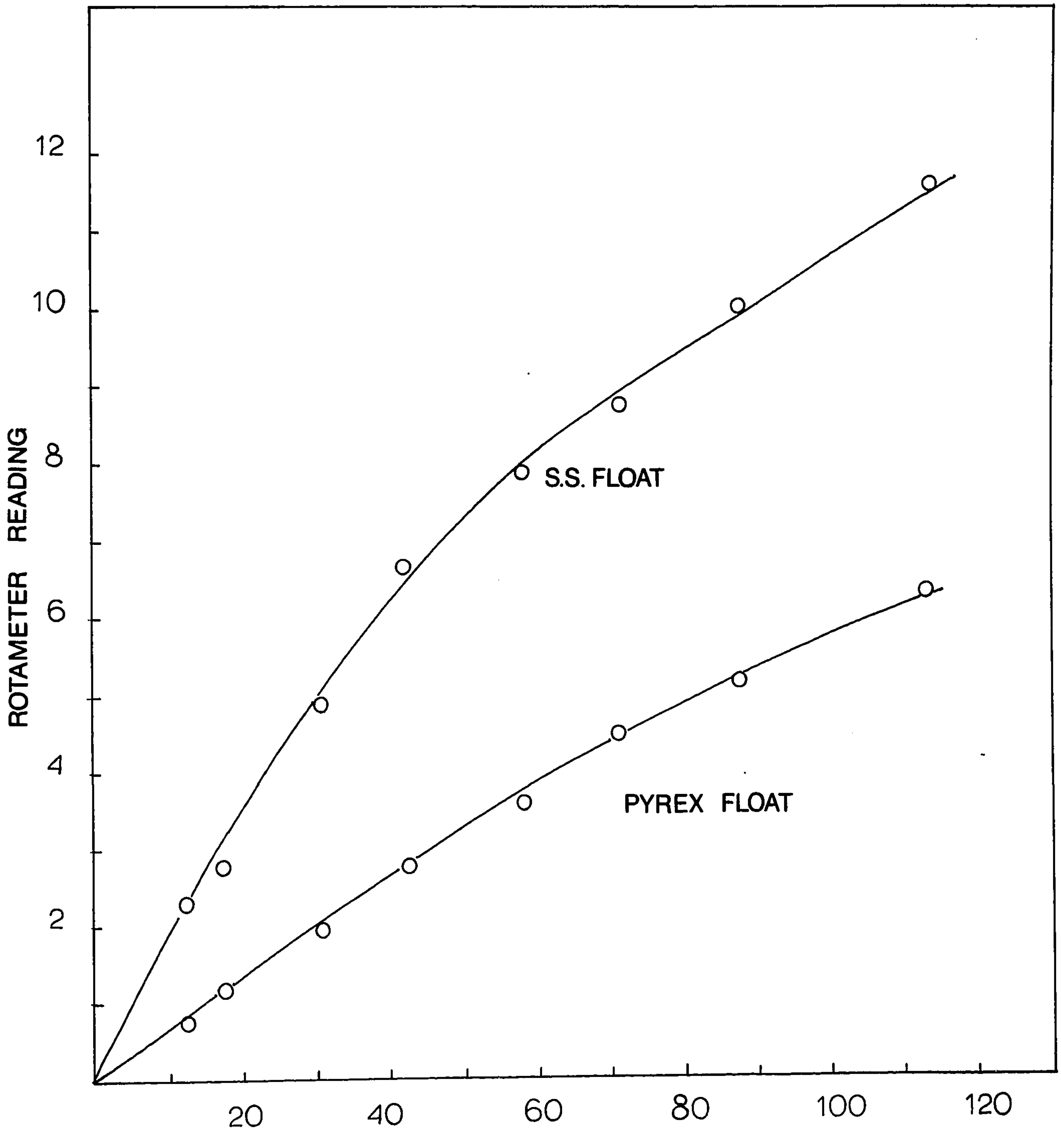


Figure 27 Rotameter Calibration for Carbon Monoxide.

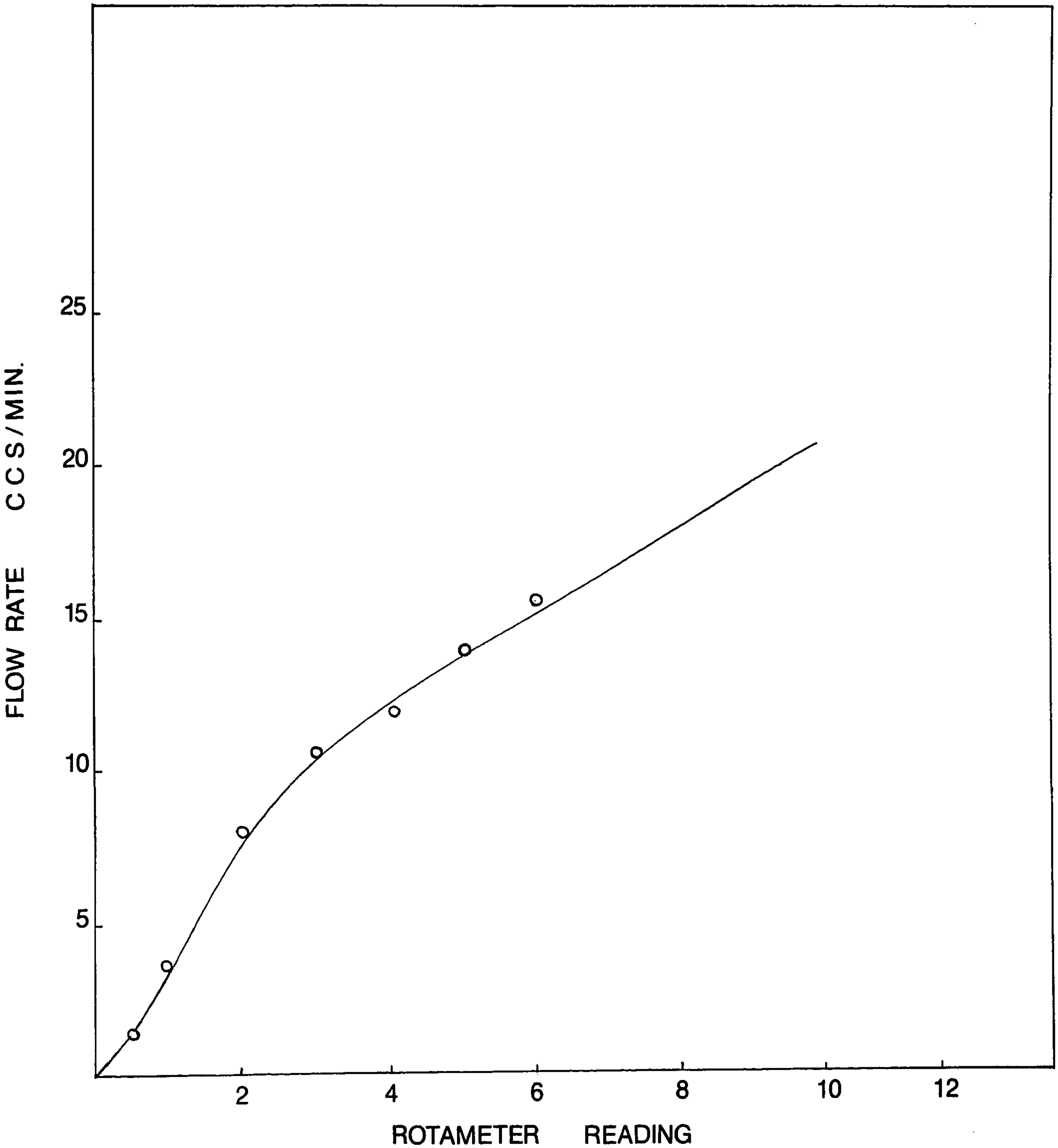


Figure 28 Rotameter Calibration for Nitric Oxide.

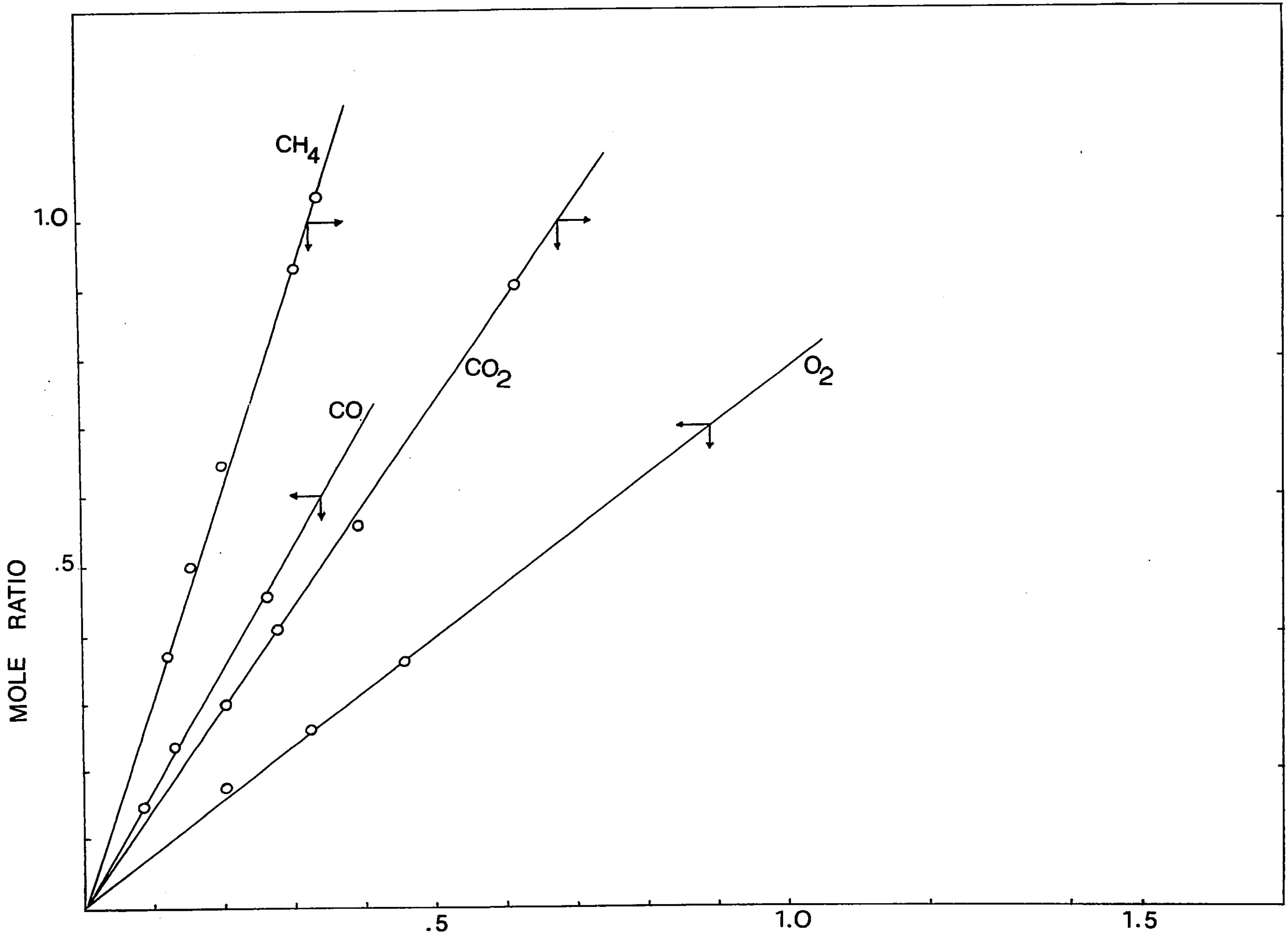


Figure 29 Calibration of Fisher gas Partitioner.

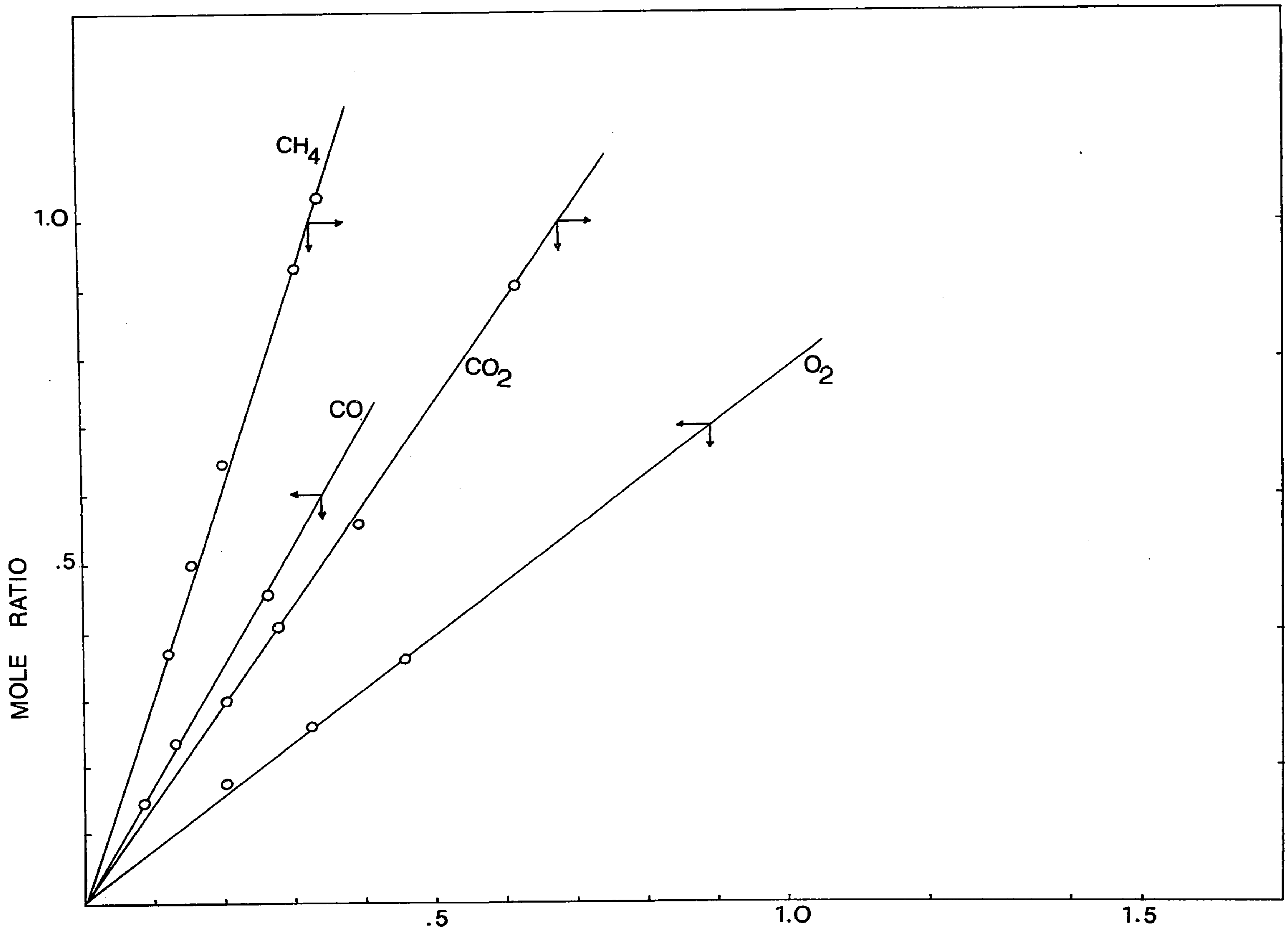


Figure 29 Calibration of Fisher gas Partitioner.

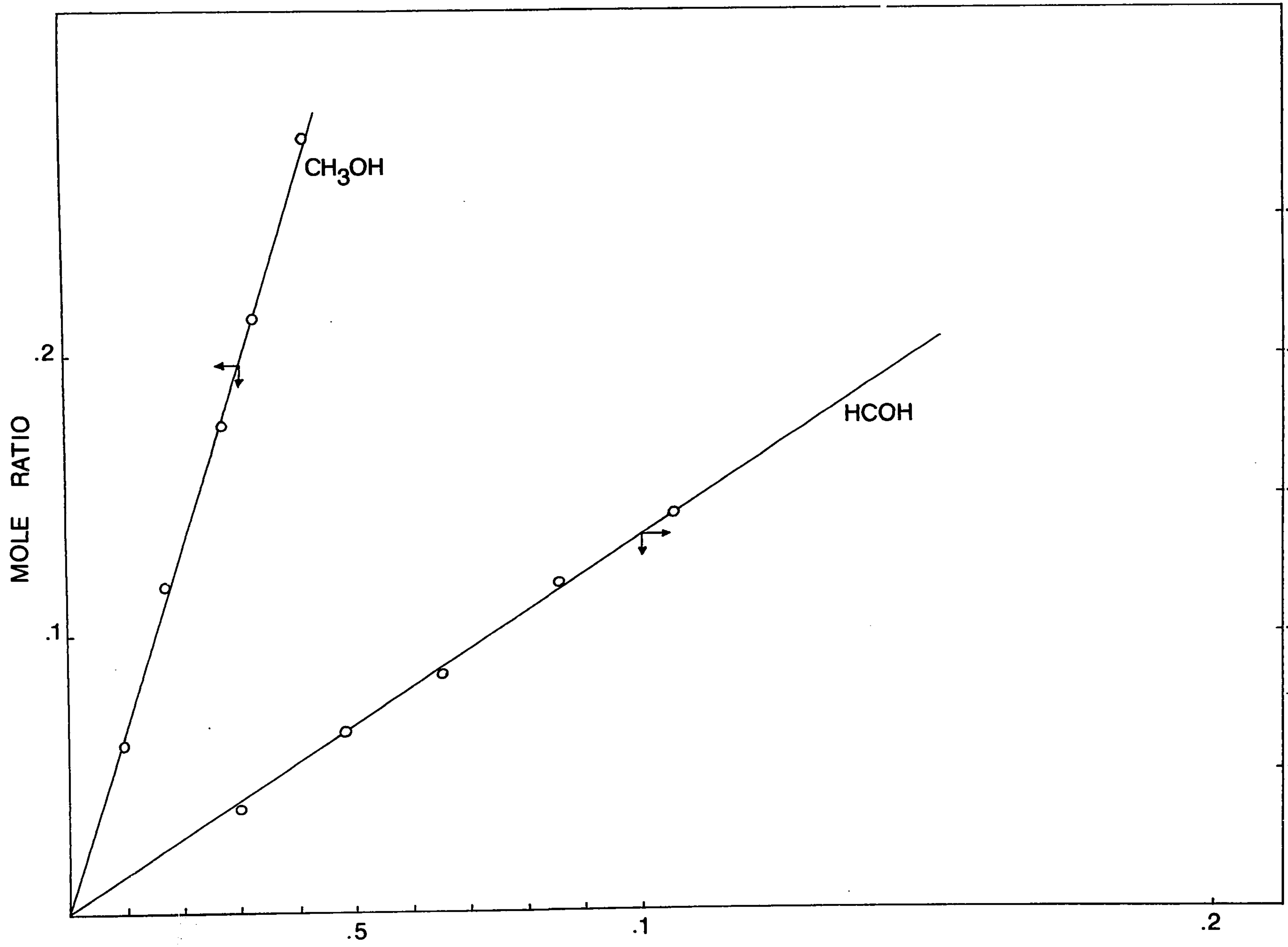


Figure 30 Calibration of Perkin-Elmer Vapor Fractometer

Calibration of Syringe Pump for Methylene Chloride Injection

Syringe: 2 ml Yale Luer Lok hypodermic syringe

Pump Setting Position	Flow rate ml/min	Flow rate ml/hr	Flow rate = mols/hr $= \dfrac{F(\frac{ml}{hr}) \times 1.31314\ (\frac{gr}{ml})}{85(\frac{gr}{mols})}$
12	0.00079	0.0474	0.000733
11	0.00197	0.1182	0.00183
10	0.00393	0.2358	0.00364
9	0.0079	0.4740	0.00733
8	0.0197	1.1820	0.0183
7	0.0393	2.3580	0.0364
6	0.079	4.7400	0.0733

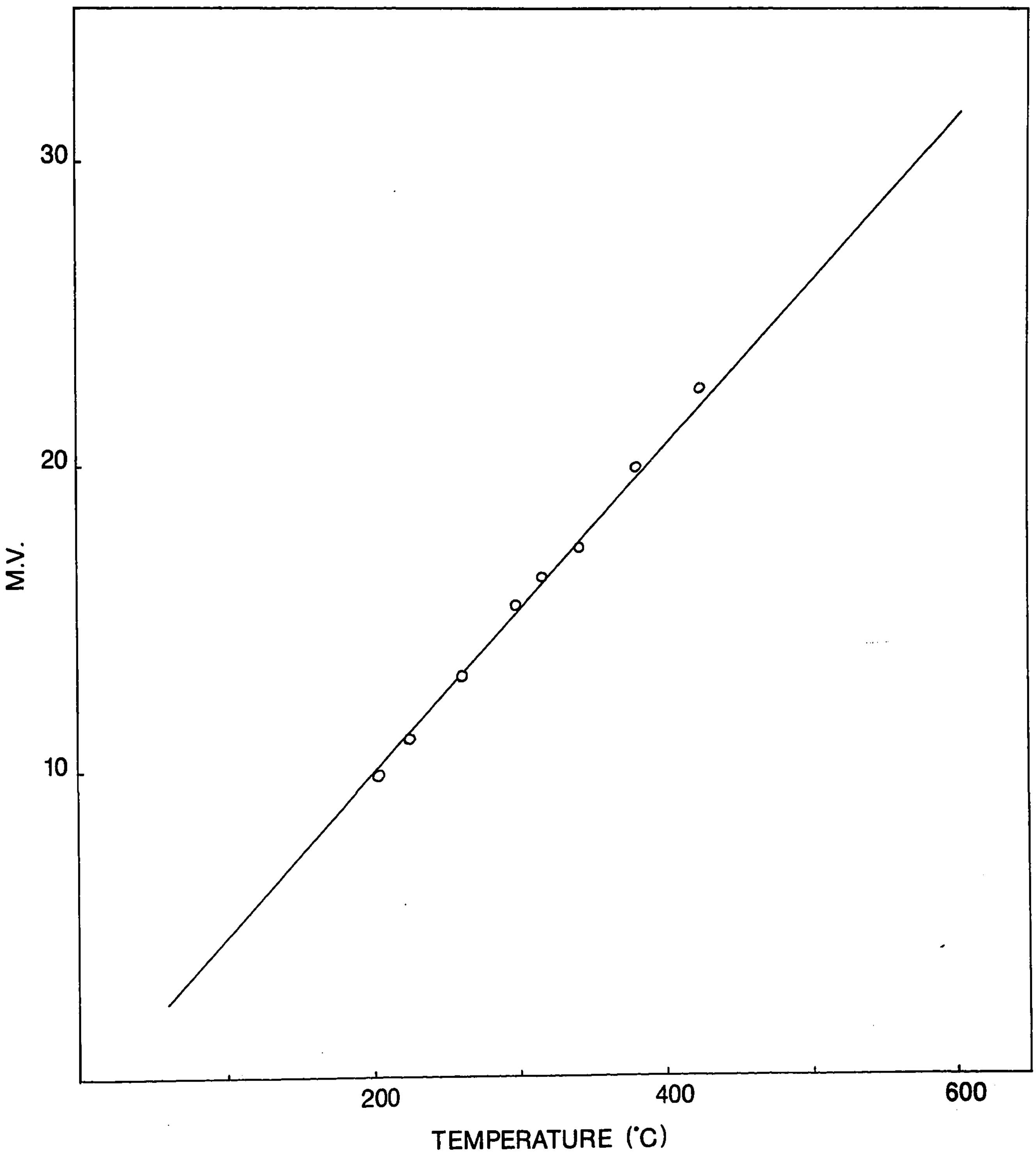


Figure 31 Calibration of Thermocouple

APPENDIX B

Analysis Formaldehyde Solution

39

The analysis of formaldehyde was based on the following reaction (39):

$$HCHO + Na_2SO_3 + H_2O \longrightarrow OHNa + CH_2(NaSO_3)OH$$

and the sodium hydroxide was titrated with N HCl being then applied:

$$\% \, HCHO \, (sol) = \frac{\text{Acid titer x Normality of acid x } 3.003}{\text{Weight sample}}$$

HCl (cc)	0	6	10	15	20	25	27
pH	12.72	12.46	12.23	11.99	11.74	11.25	10.86

28	28.5	28.6	29	30	32	35	40	45	50
10.38	9.41	9.07	8.39	7.81	7.39	7.30	6.57	5.99	2.90

2.2976 gms. HCHO solution were neutralized with 28.5 cc HCl.

$$\% \, HCHO = \frac{28.5 \times 3.003}{2.2976} = 37.25\%.$$

Density determination:

Temperature

Weight of Pychometer (dry)	= 80.5425
Weight of Pychometer with water	= 130.5289
Weight of Water	= 49.9864
Density of water at 24°C	= 0.9974
Volume of Pychometer = $\frac{49.9864}{0.9974}$	= 50.1167
Weight of Pychometer with HCHO formaldehyde	= 134.5991
Weight of formaldehyde	= 54.0566

Density of formaldehyde

at $24^{o}C = \dfrac{54.0566}{50.1167} = 1.07861$

For a 37.25% HCHO this density corresponds to a 13.9% CH_3OH in
37
the solution (39).

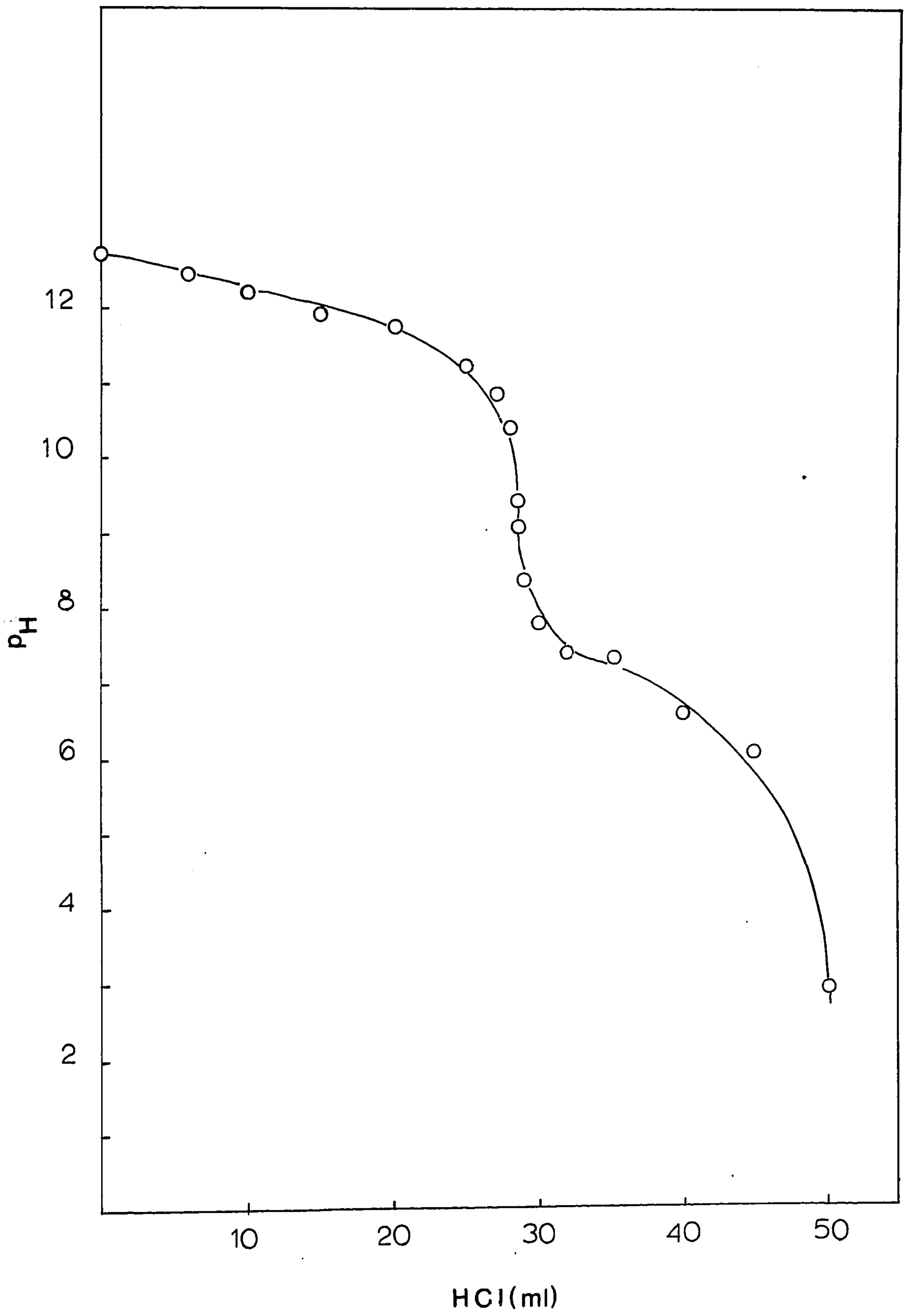


Figure 32 Sodium hydroxide titration in the Analysis of Formaldehyde Solution.

APPENDIX C

Tabulated Experimental Data

TABLE C-A-1

Experimental Data for Oxidation of Methane over Copper Oxide Catalyst

W=4gr. $\bar{\bar{R}}$=6

Run no.	Temperature (°C)	Feed moles/hr CH_4	Feed moles/hr O_2	Feed moles/hr N_2	% Conversion X_{CH_4}	% Selectivity S_{HCHO}
69	400	.1475	.1860	.6980	1.00	-
65	450	.1475	.1860	.6980	3.70	-
64	500	.1475	.1860	.6980	8.50	-
84	525	.1475	.1860	.6980	12.40	-

Run no.	Products moles/hr						
				Rate of Formation moles/hr.			
	CH_4	O_2	N_2	CO_2	CO	H_2O	HCHO
69	.1460	.1833	.6980	.0015	-	.0028	-
65	.1420	.1754	.6980	.0042	-	.0119	-
64	.1350	.1650	.6980	.0128	-	.0207	-
84	.1312	.1575	.6980	.0154	-	.0293	-

TABLE C-A-2

W=4gr. $\overline{R}$= 3

Run no.	Temperature (^oC)	Feed moles/hr CH_4	Feed moles/hr O_2	Feed moles/hr N_2	% Conversion X_{CH_4}	% Selectivity S_{HCHO}
74	400	.2580	.1630	.6130	.78	-
77	450	.2580	.1630	.6130	2.71	-
78	475	.2580	.1630	.6130	4.45	-
85	525	.2580	.1630	.6130	8.14	-

Run no.	Products moles/hr			Rate of Formation moles/hr.			
	CH_4	O_2	N_2	CO_2	CO	H_2O	HCHO
74	.2560	.1585	.6130	.0021	-	.0044	-
77	.2510	.1515	.6130	.0062	-	.0123	-
78	.2465	.1418	.6130	.0106	-	.0221	-
85	.237	.1192	.6130	.0227	-	.0421	-

TABLE C-A-3

W= 4 gr. $\overline{R}$=1

Run no.	Temperature (^{o}C)	Feed moles/hr CH_4	Feed moles/hr O_2	Feed moles/hr N_2	% Conversion X_{CH_4}	% Selecitivity S_{HCHO}
92	400	.5165	.1085	.4075	.68	-
93	450	.5165	.1085	.4075	1.65	-
89	475	.505	.1085	.4075	2.38	-
94	500	.5165	.1085	.4075	3.78	-
95	525	.5165	.1085	.4075	5.13	-

Run no.	Products moles/hr.			Rate of formation moles/hr.			
	CH_4	O_2	N_2	CO_2	CO	H_2O	HCHO
92	.5130	.1005	.4075	.0021	-	.0094	-
93	.5080	.0882	.4075	.0083	-	.0205	-
89	.4930	.0837	.4075	.0114	-	.0254	-
94	.4970	.0693	.4075	.0178	-	.0409	-
95	.4900	.0548	.4075	.0255	-	.0548	-

TABLE C-B-1

Experimental Data for Oxidation of Methane over Palladium Calatyst

W=0.3gr. $\overline{R}$=6

Run no.	Temperature (^oC)	Feed moles/hr CH_4	Feed moles/hr O_2	Feed moles/hr N_2	% Conversion X_{CH_4}	% Selectivity S_{HCHO}
103	350	.1475	.1860	.6980	1.45	-
105	375	.1475	.1860	.6980	51.2	-
104	400	.1475	.1860	.6980	56.7	-
102	450 450	.1475	.1860	.6980	59.7	-
101	500	.1475	.1860	.6980	61.0	-

Run no.	Products moles/hr CH_4	Products moles/hr O_2	Products moles/hr N_2	Rate of Formation moles/hr. CO_2	Rate of Formation moles/hr. CO	Rate of Formation moles/hr. H_2O	Rate of Formation moles/hr. HCHO
103	.1454	.1803	.698	.0021	-	.0057	-
105	.0720	.0434	.698	.0755	-	.1426	-
104	.0638	.0303	.698	.0812	.0012	.1569	-
102	.0594	.0122	.698	.0835	.0050	.1734	-
101	.0575	.0148	.698	.0802	.0105	.1705	-

TABLE C-B-2

$W = 0.3$ $\overline{R} = 1$

Run no.	Temperature (^oC)	Feed moles/hr CH_4	Feed moles/hr O_2	Feed moles/hr N_2	% Conversion X_{CH_4}	% Selectivity S_{HCHO}
106	350	.5165	.1085	.4075	.23	-
108	400	.5165	.1085	.4075	7.65	-
109	450	.5165	.1085	.4075	10.58	-
110	500	.5165	.1085	.4075	11.52	-

Run no.	Products moles/hr			Rate of Formation moles/hr.			
	CH_4	O_2	N_2	CO_2	CO	H_2O	HCHO
106	.5153	.1061	.4075	.0012	-	.0024	-
108	.4770	.0053	.4075	.0502	.0013	.0912	-
109	.4620	.0054	.4075	.0477	.0043	.1055	-
110	.4570	.00508	.4075	.0435	.00947	.1099	-

TABLE C-B-3

W=0.3 $\overline{R}$=3

Run no.	Temperature (^oC)	Feed moles/hr CH_4	O_2	N_2	% Conversion X_{CH_4}	% Selectivity S_{HCHO}
112	350	.2580	.1640	.6170	.36	-
113	400	.2605	.1640	.6170	27.6	-
114	450	.2580	.1630	.6130	30.2	-
115	500	.2620	.1653	.6220	31.1	-

Run no.	Products moles/hr CH_4	O_2	N_2	Rate of Formation moles/hr. CO_2	CO	H_2O	HCHO
112	.2570	.1605	.617	.0012	-	.0033	-
113	.1886	.0084	.617	.0697	.0032	.1546	-
114	.1800	.0084	.613	.0720	.0042	.1564	-
115	.1805	.0083	.622	.0686	.0142	.1557	-

TABLE C-C-1

Experimental Data for Oxidation of Methane with 0.1% Nitric Oxide as a Catalyst

$\overline{R}=3$

Run no.	Temperature	Feed moles/hr			% Conversion	% Selectivity
	(^oC)	CH_4	O_2	N_2	X_{CH_4}	S_{HCHO}
182	620	.255	.161	.605	5.73	25.60
181	630	.255	.161	.605	19.00	9.27
183	640	.255	.161	.605	27.50	6.87
184	650	.255	.161	.605	29.20	5.95

Run no.	Products moles/hr							
				Rate of Formation moles/hr				
	CH_4	O_2	N_2	CO_2	CO	H_2O	$HCHO$	CH_3OH
182	.247	.1366	.605	.0046	.0085	.0225	.0038	.0006
181	.2065	.0970	.605	.0120	.0310	.0650	.0045	.0011
183	.1898	.0573	.605	.0170	.0503	.1032	.0050	.0012
184	.1855	.0522	.605	.0172	.0565	.1061	.0046	.0009

TABLE C-D-1

Experimental Data for Oxidation of Methane with .1% Nitric Oxide over Pumice as a Catalyst

W=2 gr. $\overline{R}$=3

Run no.	Temperature (°C)	Feed moles/hr CH_4	Feed moles/hr O_2	Feed moles/hr N_2	% Conversion X_{CH_4}	% Selectivity S_{HCHO}
158	620	.258	.163	.612	1.75	50.00
159	630	.258	.163	.612	3.10	38.50
160	640	.258	.163	.612	5.65	23.40
161	650	.258	.163	.612	8.92	20.20
180	660	.258	.163	.612	10.40	15.15

Run no.	Products moles/hr CH_4	Products moles/hr O_2	Products moles/hr N_2	Rate of Formation moles/hr. CO_2	Rate of Formation moles/hr. CO	Rate of Formation moles/hr. H_2O	Rate of Formation moles/hr. HCHO
158	.2535	.1520	.6120	.0028	.0014	.0087	.0023
159	.2501	.1418	.6120	.0057	.0037	.0167	.0031
160	.2435	.1388	.6120	.0082	.0043	.0228	.0034
161	.2350	.1258	.6120	.0122	.0051	.0403	.0046
180	.2330	.1090	.6120	.0217	.0047	.0506	.0041

TABLE C-D-2

W=2gr. $\overline{R}$=6

Run no.	Temperature (^oC)	Feed moles/hr CH_4	Feed moles/hr O_2	Feed moles/hr N_2	% Conversion X_{CH_4}	% Selectivity S_{HCHO}
164	630	.1477	.1855	.7000	15.63	10.[illegible]
165	640	.1477	.1855	.7000	18.42	9.45
166	650	.1477	.1855	.7000	22.55	7.90
167	660	.1477	.1855	.7000	26.86	7.18

Run no.	Products moles/hr CH_4	O_2	N_2	Rate of Formation moles/hr. CO_2	CO	H_2O	HCHO
164	.1246	.1445	.7000	.01862	.0041	.0391	.0023
165	.1205	.1370	.7000	.0236	.0058	.0438	.0026
166	.1144	.1273	.7000	.0282	.0062	.0535	.0026
167	.1080	.1190	.7000	.0327	.0066	.0641	.0029

TABLE C-D-3

W=2 gr. $\overline{R}$= 1

Run no.	Temperature (^oC)	Feed moles/hr CH_4	Feed moles/hr O_2	Feed moles/hr N_2	% Conversion X_{CH_4}	% Selectivity S_{HCHO}
170	630	.5165	.1085	.4075	2.25	42.70
171	640	.5165	.1085	.4075	3.58	31.60
172	650	.5165	.1085	.4075	4.17	28.60
173	670	.5165	.1085	.4075	4.56	22.20

Run no.	Products moles/hr			Rate of Formation			
	CH_4	O_2	N_2	CO_2	CO	H_2O	HCHO
170	.5050	.0975	.4075	.0027	.0012	.0151	.0049
171	.4980	.0892	.4075	.0056	.0027	.0236	.0059
172	.4950	.0842	.4075	.0074	.0032	.0301	.0061
173	.4940	.0721	.4075	.0134	.0013	.0382	.0050

TABLE C-E-1

Experimental Data for Oxidation of Methane with0.5% Nitric Oxide over Pumice as aCatalyst

W=2gr $\overline{R}$=3

Run no.	Temperature	Feed moles/hr			% Conversion	% Selectivity
	(°C)	CH_4	O_2	N_2	X_{CH_4}	S_{HCHO}
175	620	.268	.163	.612	2.61	36.40
179	630	.268	.163	.612	4.48	30.00
176	640	.268	.163	.612	8.70	15.00
177	650	.268	.163	.612	9.86	14.20
178	660	.268	.163	.612	11.75	13.65

Run no.	Products moles/hr						
				Rate of Formation moles/hr.			
	CH_4	O_2	N_2	CO_2	CO	H_2O	HCHO
175	.2610	.1525	.6120	.0027	.0019	.01035	.0026
176	.2447	.1242	.6120	.0151	.0045	.0390	.0035
177	.2416	.1163	.6120	.0189	.0043	.0461	.0037
178	.2365	.1050	.6120	.0226	.0051	.0575	.0043
179	.2560	.1450	.6120	.0056	.0031	.0177	.0036

TABLE C-F-1

Experimental Data for Oxidation of Methane with .1% Nitric Oxide over Copper Oxide Catalyst

W= 4 gr $\overline{R}$= 3

Run no.	Temperature (^{o}C)	Feed moles/hr. CH_4	Feed moles/hr. O_2	Feed moles/hr. N_2	% Conversion X_{CH_4}	% Selectivity S_{HCHO}
198	620	.2570	.1623	.609	13.00	-
199	640	.2570	.1623	.609	17.90	-
201	650	.2570	.1623	.609	21.00	-
200	660	.2570	.1623	.609	22.90	-

Run no.	Products moles/hr CH_4	O_2	N_2	Rate of Formation moles/hr. CO_2	CO	H_2O	HCHO
198	.2235	.0956	.6090	.0329	-	.0673	-
199	.2110	.0721	.6090	.0458	-	.0904	-
201	.2030	.0692	.6090	.0484	-	.0987	-
200	.1981	.0495	.6090	.0572	-	.1145	-

TABLE C-G-1

Experimental Data for Oxidation of Methane with 0.1% Nitric Oxide over Palladium Catalyst

$W=0.3 \quad \overline{R}=3$

Run no.	Temperature	Feed moles/hr			% Conversion	% Selectivity
	(^{o}C)	CH_4	O_2	N_2	X_{CH_4}	S_{HCHO}
214	620	.258	.163	.612	31.7	-
216	630	.258	.163	.612	32.9	-
219	640	.258	.163	.612	34.5	-
215	650	.258	.163	.612	32.9	-

Run no.	Products Moles/hr.						
				Rate of Formation moles/hr.			
	CH_4	O_2	N_2	CO_2	CO	H_2O	HCHO
214	.1762	.0087	.612	.0537	.0322	.1502	-
216	.1680	.0085	.612	.0532	.0334	.1529	-
219	.1690	.0087	.612	.0523	.0382	.1528	-
215	.1730	.0089	.612	.0526	.0339	.1526	-

TABLE C-H-1

Experimental Data for Oxidation of Methane over Chlorine Modified Coper Oxide Catalyst

W= 2gr. $\overline{R}$= 3 T= 525 (^oC)

Run no.	Z(%)	Feed moles/hr CH_4	Feed moles/hr O_2	Feed moles/hr N_2	% Conversion X_{CH_4}	% Selectivity S_{HCHO}
239	0	.2550	.1610	.6050	5.50	-
242	.0719	.2550	.1610	.6050	3.53	10.40
240	.179	.2550	.1610	.6050	2.82	17.50
241	.357	.2550	.1610	.6050	2.36	25.00
243	.718	.2550	.1610	.6050	1.96	22.00

Run no.	Products moles/hr			Rate of Formation moles/hr.			
	CH_4	O_2	N_2	CO_2	CO	H_2O	HCHO
239	.2410	.1343	.6050	.0136	-	.0271	-
242	.2460	.1493	.6050	.0064	-	.01341	.0009
240	.2478	.1519	.6050	.0049	-	.0102	.0013
241	.249	.1525	.6050	.0045	-	.0090	.0015
243	.250	.1553	.6050	.0039	-	.0057	.0011

TABLE C-H-2

W= 2 gr. $\overline{R}$= 6 T = 525 (^oC)

Run no.	Z (%)	Feed moles/hr			% Conversion	% Selectivity
		CH_4	O_2	N_2	X_{CH_4}	S_{HCHO}
244	0	.1458	.1832	.6920	6.05	-
245	.0719	.1458	.1832	.6920	5.35	4.75
246	.1790	.1458	.1832	.6920	3.22	30.45
247	.3570	.1458	.1832	.6920	2.75	52.40
248	.7180	.1458	.1832	.6920	3.29	35.50

Run no.	Products Moles/hr						
				Rate of Formation moles/hr.			
	CH_4	O_2	N_2	CO_2	CO	H_2O	HCHO
244	.1370	.1622	.6920	.0086	-	.0212	-
245	.1380	.1608	.6920	.0077	-	.0221	.0004
246	.1411	.1715	.6920	.0022	-	.0135	.0014
247	.1418	.1715	.6920	.0019	-	.01102	.0021
248	.1410	.1743	.6920	.0030	-	.0087	.0017

TABLE C-H-3

W= 2 gr. $\overline{R}$= 1 T = 525 (^{o}C)

Run nc.	Z (%)	Feed moles/hr.			% Conversion	% Selectivity
		CH_4	O_2	N_2	X_{CH_4}	S_{HCHO}
249	0	.5100	.1072	.4025	1.96	-
250	.0719	.5100	.1072	.4025	1.37	11.60
251	.1790	.5100	.1072	.4025	1.17	24,50
252	.3570	.5100	.1072	.4025	.98	40.6
253	.7180	.5100	.1072	.4025	.79	67.0

Run no.	Products moles/hr.						
				Rate of Formation moles/hr.			
	CH_4	O_2	N_2	CO_2	CO	H_2O	HCHO
249	.500	.0788	.4025	.0121	-	.0263	-
250	.503	.0925	.4025	.0056	-	.0153	.0008
251	.504	.0963	.4025	.0044	-	.0111	.0015
252	.505	.0958	.4025	.0031	-	.0103	.0021
253	.506	.0966	.4025	.0014	-	.0105	.0027

TABLE C-H-4

$W = 3.5$ $\overline{R} = 3$ $T = 525$ (^{o}C)

Run no.	Z (%)	Feed moles/hr.			% Conversion	% Selectivity
		CH_4	O_2	N_2	X_{CH_4}	S_{HCHO}
254	0	.252	.1588	.5970	6.15	-
255	.0719	.252	.1588	.5970	3.79	12.6
256	.1790	.252	.1588	.5970	2.78	21.3
257	.3570	.252	.1588	.5970	2.38	30.0
258	.7180	.252	.1588	.5970	1.59	47.0

Run no.	Products moles/hr.						
				Rate of Formation moles/hr.			
	CH_4	O_2	N_2	CO_2	CO	H_2O	HCHO
254	.2365	.1222	.5970	.0167	-	.0354	-
255	.2425	.1300	.5970	.0115	-	.0256	.0012
256	.2450	.1450	.5970	.0065	-	.0129	.0015
257	.2460	.1491	.5970	.0056	-	.0083	.0018
258	.2480	.1450	.5970	.0077	-	.0083	.0019

TABLE C-I-1

Experimental Data for Oxidation of Methane over Chlorine Modified Palladium Catalyst

W = .3 gr. $\overline{R}$ = 6 T = 525 (^{o}C)

Run no.	Z (%)	Feed moles/hr CH_4	Feed moles/hr O_2	Feed moles/hr N_2	% Conversion X_{CH_4}	% Selectivity S_{HCHO}
230	0	.0935	.1175	.4430	69.60	-
231	.280	.0935	.1175	.4430	66.80	1.10
232	.558	.0935	.1175	.4430	62.50	3.97
233	1.125	.0935	.1175	.4430	53.60	8.33
234	2.800	.0935	.1175	.4430	51.30	7.00

Run no.	Products moles/hr.			Rate of Formation moles/hr.			
	CH_4	O_2	N_2	CO_2	CO	H_2O	HCHO
230	.0285	.0061	.4430	.0552	.0073	.1139	-
231	.0311	.0134	.4430	.0493	.0112	.1055	.0007
232	.0350	.0144	.4430	.0488	.0112	.0993	.0023
233	.0434	.0184	.4430	.0442	.0076	.0933	.0042
234	.0454	.0211	.4430	.0374	.0250	.0788	.0034

APPENDIX D

Sample Calculation and Material Balance

RUN: 242 DATE: 11-6-71 CATALYST: C-H-1

TEMPERATURE	Troom: 27°C	Tcont.	Treactor: 525°C	
INLET VOLUMETRIC FLOW	AIR 315 $\frac{cc}{min}$	N2 248.75 $\frac{cc}{min}$	0.605 $\frac{mols}{hr}$	3
		O2 66.25 $\frac{cc}{min}$	0.161 "	
	CH_4 105 $\frac{cc}{min}$		0.255 "	1
OUTLET GASES TOTAL FLOW	$\frac{1000}{2'26''} = 409 \frac{cc}{min} = 1.00712$			

GAS ANALYSIS	CO_2	O_2	N_2	CH_4	CO
PEAK HEIGHT	5.4	114.8	383.7	102.6	—
PEAK HEIGHT RATIO	0.0141	0.2995	1	0.2675	
MOLAR RATIO	0.01049	0.247	1	0.407	
OUTLET GASES MOLAR FLOW	0.00635	0.1493	0.605	0.246	

LIQ. ANALYSIS	H_2O	HCHO	CH_3 OH
PEAK HEIGHT	126	33	—
PEAK HEIGHT RATIO	1	0.262	—
MOLAR RATIO	1	0.0707	—
OUTLET LIQ. MOLAR FLOW	0.01341	0.00094	

MATERIAL BALANCE in MOLS/HR			
	CH_4 0.255	CH_4 0.246	TOTAL GAS 1.00712 (check)
	O_2 0.161	O_2 0.1493	TOTAL CARBON 0.25329 (outlet)
	N_2 0.605	N_2 0.605	ERROR +0.66%
	TOTAL 1.021	CO_2 0.00635	CONVERSION 3.53%
		CO	SELECTIVITY 10.40%
		TOTAL GAS 1.00665	
		H2O	
		HCHO	
		CH3OH	

Sample Calculation:

This calculation is based on the experimental data of Run No. 242

(1) Moles in:

moles O_2/ hr

$$= \frac{66.25 \frac{cc}{min} \times 60 \frac{min}{hr}}{22.400\ cc/g\ mole \times \frac{300}{273} \frac{oK}{oK}} = .161$$

moles N_2/hr

$$= \frac{248.75 \frac{cc}{min} \times 60 \frac{min}{hr}}{22,400\ cc/g\ mole \times \frac{300}{273} \frac{oK}{oK}} = .605$$

moles CH_4/hr

$$= \frac{105 \frac{cc}{min} \times 60 \frac{min}{hr.}}{22,400\ cc/g.mole \times \frac{300}{273} \frac{oK}{oK.}} = .255$$

(2) Moles out

Analysis

(A) From gas Partitioner

Component	Peak height	Peak height ratio component $/N_2$
CO_2	5.4	0.0141
O_2	114.8	.2995
N_2	383.7	1
CH_4	102.6	.2675

(B) From Vapor Fractometer

Component	Peak height	Peak height ratio ($HCHO/H_2O$)
H_2O	126	1
HCHO	33	.262

Since the moles of nitrogen in the feed and in the effluent stream were the same, the effluent rates were computed on the basis of the nitrogen fed and on the peak height ratios of nitrogen to the reaction products.

moles CO_2/hr = 0.605 x .743 x 0.141 = 0.00635 g-moles/hr

moles O_2/hr = 0.605 x 0.825 x 0.2995 = 0.1493 g-moles/hr

moles CH_4/hr = 0.605 x 1.52 x 0.2675 = 0.2460 g. moles/hr

moles N_2/hr = 0.605 g-moles /hr

$$
\begin{aligned}
W_{HCHO} + W_{H_2O} &= 30\,(N_{HCHO}) + 18\,(N\,H_2O) \\
&\quad + 32(o\,N_O) + 16\,(oN_H) \\
&\quad - 32\,(N_O) - 16\,(N_H) \\
&\quad - 44\,(N_C) \\
&= 32 \times 0.161 + 16 \times 0.255 \\
&\quad - 32 \times 0.1493 - 16 \times 0.246 \\
&\quad - 44 \times 0.00635 \\
&= 0.2390 \text{ gms /hr} \qquad (1)
\end{aligned}
$$

$$W_{HCHO}/W_{H_2O} = 0.262 \times 0.27 \times \frac{30}{18} = 0.1179 \qquad (2)$$

Solving equation (1) and dividing by the corresponding molecular weight

moles HCHO/hr = .0009

moles H_2O/hr = 0.1341

Material balance-

Based on atomic oxygen

Component	in feed moles hr	in product moles/hr
O_2	2 x 0.1610=0.3220	2 x 0.1493 = 0.2986
CO_2		2 x 0.0064 = 0.0128
HCHO		0.0009
H_2O		0.0134
Total	0.3220	0.3257

$$\% \text{ Deviation} = \frac{0.3220 - 0.3257}{0.3220}$$

$$= -1.1\%$$

Based on atomic hydrogen

Component	in feed moles/hr	in product moles/hr
CH_4	4 x 0.2550 = 1.0200	4 x 0.2460 = 0.9840
H_2O		2 x 0.0134 = 0.02680
HCHO		2 x 0.0009= 0.0018
total	1.0200	1.0126

$$\% \text{ Deviation} = \frac{1.0200 - 1.0126}{1.0200} = 0.7\%$$

Based on atomic carbon

Component	in feed mole /hr	in product moles/hr
CH_4	0.2550	0.2460

CO_2		0.00635
HCHO		0.0009
Total	0.2550	0.25325

$$\% \text{ Deviation} = \frac{0.2550 - 0.2533}{0.2550} = 0.6\%$$

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