KINETIC ASPECTS OF THE TREATMENT OF COPPER ORES BY THE SEGREGATION PROCESS

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DEDICATION

To the greatest man I've ever met ..... my father.

ABSTRACT

A study has been made of the kinetic and thermodynamic aspects of cuprous chloride reduction on a coke surface by hydrogen. The steam-carbon reactions were studied in order to discover if the adsorbed hydrogen generated during the reaction could be responsible for the reduction of cuprous chloride vapour at the coke surface. The nature and characteristics of the deposited copper were also studied.

The most efficient method of reducing gaseous cuprous chloride to copper is by gaseous hydrogen and according to the kinetics and thermodynamics of the reaction, this process will proceed faster and to a greater degree of completion, the higher the reaction temperature. However when cuprous chloride is reduced by gaseous hydrogen, copper will deposit on any convenient substrate; there is no preferential deposition on carbonaceous materials when reduction is solely by gaseous hydrogen. The most effective method of depositing copper on a carbonaceous material is by hydrogen contained on that material surface. On coke and charcoal this hydrogen exists mainly as metastable hydrocarbon groupings on the surface and the quantity and apparent activity of these groupings increases with a decrease in the maximum temperature to which the carbon material has been subjected.

Although reaction with water vapour will create adsorbed hydrogen on a degassed coke or charcoal surface, the quantity generated is small compared to that inherently contained by either carbon material (1/100). However of the two, charcoal can adsorb four times as much hydrogen, gram for gram, than can coke. Any beneficial effect that water vapour has, generating adsorbed hydrogen, is offset by the fact that gaseous hydrogen is also generated leading to non specific deposition.

If the partial pressure of hydrogen is lower than that of cuprous chloride vapour then a dendritic type of growth is favoured, if the reverse is true then crystal and filament growth is more predominant. Copper can be deposited on the copper deposited on the coke, if the partial pressure of hydrogen is low, and the nature of this deposited growth is platelets and filiform.

The effect of water vapour in the system has a negligible effect on hydrogen production, compared to the amount of hydrogen produced by the thermal treatment of coke in heating to 850°C. However it does increase the amount of methane present in the system by 15% by its reaction with the coke at temperatures below 850°C. Thus from this work it is suggested that a coal coked at a temperature not exceeding 850°C would be a better segregation agent than coal for copper reduction.

It was found from the steam-carbon reactions that the surface oxide Co is stable on a coke surface at temperatures upto 1000°C and that there are several types of Co each exhibiting a different degree of thermal stability. The amount of hydrogen on coke as hydrocarbons decreases rapidly with temperature and there are two basic types of hydrocarbon. At temperatures higher than 850°C only adsorbed hydrogen generated by water vapour reaction would be the sole source of hydrogen for cuprous chloride reduction at the coke surface. Thus since charcoal can adsorb four times as much hydrogen than can coke during reaction with water vapour, then it would be a better segregation agent at temperatures higher than 850°C.

The mechanism accepted for water vapour reduction by carbon is that it is a gas/solid interaction to give gaseous hydrogen and a surface oxide Co. Hydrogen sets up an adsorption-desorption state with active sites and the surface oxide degenerates into adsorbed carbon monoxide which is desorbed. There was no evidence to support the theory that the surface oxide reacts with gaseous carbon monoxide to produce carbon dioxide , on the contrary it was found that the surface oxide reacts with water vapour to produce carbon dioxide. It was proposed that when copper replaces hydrogen on the coke surface, this disrupts the π-bonding of the carbon matrix which releases adsorbed gases and activates the breakdown of the surface oxide to carbon monoxide and of the hydrocarbons to hydrogen. This can be regarded as catalysis of the steam carbon reaction since the vacation from the surface by the adsorbed gases frees active sites for further reaction.

The cuprous chloride trimer was indirectly found to be the most prominent

species in the vapour phase in the temperature range 500 to 700°C and its vapour pressure was calculated to be :-

$$\log_{10} P_{Cu_3Cl_3} \text{ (mm Hg)} = -5,540 / T^{\circ}K + 6.3 \pm 0.1$$

and subsequently the value of ΔH_v over the same temperature range was found to be 25 ± 2 Kcal/mole trimer.

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SUMMARY OF SYMBOLS USED

( )	adsorbed species
[ ]	concentration or number of
a	activity
a_c	apparent activity of carbon
a_{C_f}	apparent activity of the free active sites
a_H	apparent activity of hydrogen on a coke surface
C	carbon
C_f	free active site
'Co'	surface oxide
ΔG	Gibbs free energy
ΔH_m	Enthalpy of melting or fusion
ΔH_s	Enthalpy of sublimation
ΔH_v	Enthalpy of vapourisation
k	reaction rate constant
K	equilibrium constant
P	pressure of
R	gas constant 4.575 cal/deg when converting ln to $\log_{10}$
T	temperature ^oC or ^oK
τ	gas residence time

Note ppm in this work refers to volume parts per million

INTRODUCTION

The extraction of metallic copper from its ores usually involves a smelting or a leaching process. Flotation can improve the concentrate grade but is impractical if the copper mineral is difficult to liberate from the gangue or when the copper minerals are mainly silicates. A smelting process is usually used if the ore is sulphidic in nature; this involves an initial roasting of the ore concentrate to remove excess sulphur, a smelting step to produce a matte of copper(I) sulphide, iron(II) sulphide and a siliceous slag, and a conversion step in which air or oxygen-enriched air is blown through the molten matte to produce metallic copper and iron oxide which combines with the slag.

Non-sulphidic ores are usually leached, copper oxide ore is leached with dilute acids or ammoniacal ammonium carbonate, followed by electrolysis or cementation. However, leaching is inneffective for copper carbonates (malachite or azurite both invariably associated with dolomite and limestone), silicates (dioptase or chrysocolla) or mixed sulphide/oxide ores, therefore carbonates and silicates require calcining to copper oxide which is easier to process.

These ores which are difficult to treat are known as 'refractory', the word is used in its original sense i.e. from the french 'réfractaire' meaning 'resistant'. These ores are aptly named as such, partially because the copper is finely disseminated throughout the ore matrix and thus difficult to concentrate, and also because of their high melting points. Thus at normal metallurgical temperatures these ores would have to be treated by a gas/solid or a liquid/solid reducing reaction to produce liquid copper. However it is well known that the metal chloride melting and boiling points are lower than those of their oxides (see table 1). Thus chloridisation of an oxide or silicate ore can produce a compound more amenable to metallurgical extraction.

TABLE 1 (61-63)

	Melting Point °C		Boiling Point °C	
Metal	Oxide	Chloride	Oxide	Chloride
Cu_I	1336	430	dec	1690
Cu_{II}	1212	500	dec	1000(?)
Sn_{IV}	1630	-33	-	115
Sn_{II}	-	247	-	652
Fe_{II}	1307	677	3414	1074
Fe_{III}	1465	304	dec	334
Mg_{II}	2825	417	3200	1416
Pb_{II}	900	495	1516	950
Co_{II}	1808	730	dec	1050
Cr_{III}	1990	-	3000+	1300

dec = decomposes

There are very few new pyrometallurgical processes which can treat refractory ores successfully, some of these appear promising[1] but the only recent major advance in copper production is the development of the segregation process[2-18].

In this process , the ore (1-5% Cu) is heated together with small amounts of alkali chloride (0.1-1.5%) and a carbonaceous material (0.25-1.0%) such as coal or coke. After a few minutes at 700-800°C the coke is covered with particles of copper which can then be recovered by flotation. The process was discovered by accident in 1923 by Moulden and Taplin who were trying to reduce in situ a Chilean copper oxide ore to make it amenable to an ammonia leach. They found that when the ore was mixed with coal and heated to 600-800°C, the copper migrated to the coal surface. They explained this from the presence of sodium chloride in the ore.

Their original patent[2] described a two stage reactor, a directly heated rotary kiln to raise the temperature of the ore which then passed into an insulated secondary kiln, together with salt and coal, where segregation took place. A later patent[3] described a rotary hearth type reactor, to the lower part of which the reagents were added to initiate segregation. The mixture was then passed into a soaking pit to complete segregation. The first pilot plant[4,5] was put into operation at the Alaska mine in Southern Rhodesia in 1929. It operated until June 1931 when the low price of copper forced the mine to close. The reactor was a rotary kiln, the top three-quarters of which were used to heat the ore, at this point the reagents were added and the lower quarter then acted as the segregation zone. The Union Miniere du Haut Katanga plant[6] operated with difficulty from August to November 1931 using rotary kilns in a two stage process, but it eventually had to close down, again due to low copper prices.

The closure of these two plants seemingly terminated the commercial exploitation of the segregation process and over the next twenty-five years no plants were built to operate any sort of segregation process although a certain quantity of research work was being published giving a clearer insight into the mechanisms involved[19,20]. However, in 1958 a pilot plant was built in Mauritania to treat the gold bearing Akjoujt copper ore[7], but again the operative difficulties of rotary kilns in a two stage process were too great and the plant closed down. A new plant is today treating the same ore[8] but it is using a new style one stage reactor. In 1960 a one stage rotary kiln was built by Transarizona Resources at the Lake Shore mine[9,10,11] which successfully treats a copper silicate ore. A shaft furnace was constructed in 1960 as a one stage reactor to treat the Berenguela copper-silver ore in Peru[12]. The Anglo American Corporation built a pilot plant at Rhokana in Zambia[13,17] which incorporates an outer fluidised bed heating reactor which overspills hot ore into a central segregation chamber into which the reagents are added. The commercial plant[14-18]

separates the two chambers and has the fluidised heating chamber feeding hot ore continuously into the segregation reactor by its side.

Since its discovery the process has been investigated in many laboratories in order to find suitable reagents, optimum temperature, suitable apparatus and also to understand the mechanism and the thermodynamics of the reactions involved[19-45].

The mechanism now generally accepted was first put forward by Rey[19,20] and is divided into three major steps:-

1. Initiation A halide, usually salt, is hydrolysed by water in the presence of the ore constituents such as silica, alumino-silicates etc. to produce hydrogen chloride gas;

$$x.SiO_2 + 2.NaCl + H_2O = Na_2O.x.SiO_2 + 2.HCl \quad \ldots\ldots(1)$$

2. Extraction The hydrogen chloride attacks the copper mineral (represented as the oxide) to produce volatile cuprous chloride;

$$n.Cu_2O + 2n.HCl = 2.(CuCl)_n + n.H_2O \quad \ldots\ldots\ldots\ldots\ldots(2)$$

3. Reduction and Segregation The hydrogen associated with the carbonaceous material reduces the cuprous chloride to form segregated copper which deposits on the carbon particles;

$$(CuCl)_n + \frac{n}{2}.H_2 = n.Cu + n.HCl \quad \ldots\ldots\ldots\ldots\ldots\ldots(3)$$

One of the advantages of the segregation process is that hydrogen chloride is regenerated and so can react further with more ore. Thus salt additions theoretically account merely for hydrogen chloride losses by leakage and fume extraction. This process works well with siliceous ores (recovery 90-95%) however the recovery from calcerous ores is still low (80%).

Segregation is being developed and extended to include other refractory ores but the major work being done is for nickel recovery[48-60].

In this thesis a study has been made of the nature of the reduction of cuprous chloride vapour on coke and its effect on the water vapour-coke reactions.

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CHAPTER I

Previous Work on Reactions Associated with the Segregation Process

(a) Hydrolysis of sodium chloride in the presence of ore constituents

The decomposition of sodium chloride by water vapour was found to be increased if an acid oxide was present, by Brewer and Roth[64]. They found that silica and alumina both increased the production of hydrogen chloride by factors of 2 and 5 respectively. However their work also showed that a mixture of alumina and silica in the proportions 1:2 increased the sodium chloride hydrolisation by a factor of 30 at a temperature of 850°C. de Keyser and Deguelde[65] studied salt hydrolysis in the presence of kaolin ($Al_2O_3 . 2SiO_2$) and isolated the product phase $Na_2O.Al_2O_3.2SiO_2$ and a compound of this phase and salt $3(Na_2O.Al_2O_3.2SiO_2).NaCl$. Cirkov[66] found a range of silicate compositions when salt was hydrolysed in the presence of silica; below 840°C Na_2SiO_3, $Na_2Si_2O_5$ between 870 and 900°C and $Na_2Si_3O_7$ between 940 and 980°C.

This reaction, studied with special reference to the segregation process, was assumed by Rey[19] to produce sodium silicate Na_2SiO_3. Diaz[32] believes the ortho-silicate $Na_2Si_2O_5$ is formed. Rampacek et al.[27] however, state that "... the yield of hydrochloric acid from quartz-salt or opal-salt mixtures was no greater than that obtained by heating the salt alone in the presence of moisture". They believe that kaolinite $Al_2O_3.2SiO_2.2H_2O$ reacts with salt to produce the alumino-silicate $Na_4Al_2O_3.2SiO_3$ and that moisture is not a neccessary reagent. Rey[67] has stated that alumino-silicates are more active than silica and that the presence of iron and manganese oxides also help because of the formation of sodium ferrite and manganate respectively.

More recent studies by Hanf and Sole[68,69] of the hydrolysis of salt in the presence of silica, conclude that above a temperature of approximately 700°C, the primary end product of the reaction was a glass of approximate composition $Na_2O.2SiO_2$ which contains some dissolved NaCl. They found that

the partial pressures of hydrogen chloride generated during the initial stages of reaction are much higher than those predicted from equilibrium constant values, and they reason that this is because the sodium silicate formed is soluble in the quartz to a small extent thus lowering its activity. Thus they state that the reaction:-

$$2NaCl + x.SiO_2 + H_2O = Na_2O.x.SiO_2 + 2HCl \quad \ldots\ldots\ldots(1)$$

where x is equal to two, is the most prominant, and the establishment of equilibrium is extremely rapid (< 1 sec.). This has an important implication for the segregation process since, as rapidly as hydrogen chloride is consumed by the chloridisation of the copper in the ore it is immediately replenished by the hydrolysis reaction.

(b) Chloridisation of metal oxides and ores

Chloridisation of metal ores is a well known metallurgical process and is well reviewed[70,71]. However the previous and some present[48,72] aims of chloridisation are to produce a solid chloride which can then be leached, or to extract the gaseous chloride and condense it[46,47]. It is only a segregation process which aims to reduce the chloride to the metal not in situ, because this severely hinders further extraction, but on the coal particles.

In all copper segregation plants salt is used as the chloride generating agent mainly because of its low cost. Some ores, due to their included chloride, such as atacamite ($Cu_2Cl.(OH)_3$) need no salt additions for segregation to take place[21]. A mixed copper oxide/sulphide ore was subject to segregation tests with various halogen bearing reagents and it was found[31] that with a siliceous ore $CaCl_2$, $MgCl_2$, NaF, $KClO_3$ all gave as good results as did salt, however with calcerous ores only $CaCl_2$ performed as well as salt. Sziklavari[36] chloridised both Cu_2O and CuO with calcium chloride in the presence of a ferric salt and/or silica. He found that the presence of either Fe_{III} or silica, or better still both, gave much

improved copper recoveries. Neumann and Schlechton[73] studied the chloridisation of various metal oxides by $CaCl_2$ at 800°C and found that additions of Al_2O_3, SiO_2 and B_2O_3 each increased the degree of chloridisation. $COCl_2$ has been suggested[52,74,75] as a possible intermediary for chloridisation reactions, but its thermal instability must exclude it from serious consideration. Therefore, as a chloridising agent for copper segregation salt has many equals but in commercial production economics insist on its use. In nickel segregation, although chlorides of Ca, Na, Mg and Fe_{III} can give good results[54], many workers[49,51,53,60,78] agree that $CaCl_2$ is a better segregation agent than salt; this does not preclude the use of salt in nickel segregation[55-57,76-80]. Indeed some workers[58,59] use hydrogen chloride as a chloridising agent.

In copper segregation however, it is accepted that hydrogen chloride which is produced by salt hydrolysis, reacts with the copper mineral (represented as Cu_2O) to form gaseous cuprous chloride :-

$$n.Cu_2O + 2n.HCl = 2.(CuCl)_n + n.H_2O \quad \ldots\ldots\ldots\ldots (2)$$

Chaleroux et al[79] contend that cupric chloride ($CuCl_2$) can be formed by the reaction of hydrogen chloride with cupric oxide, but Ivanshentsev[80] et al found that above 500°C cupric chloride decomposes into cuprous chloride and chlorine.

Brittan[44] however contends that in a segregation chamber, with sufficient carbon monoxide present, any cupric oxide is reduced to cuprous. In the absence of carbon monoxide however, he found that a stoichiometric equivalence exists between the copper reacted and the amount of hydrogen chloride consumed. This is in agreement with previous work[81] and corresponds to the reaction:-

$$2CuO + 2HCl = 2.CuCl_{(liquid)} + H_2O + \tfrac{1}{2}O_2$$

Even so, by whatever mechanism, the end product of chloridisation is gaseous cuprous chloride, unless of course, the equilibrium partial pressure

of cuprous chloride is exceeded, in which case some liquid cuprous chloride would be expected.

(o) Thermodynamics of gaseous copper chlorides

Solid cupric chloride ($CuCl_2$) is unstable and decomposes to cuprous chloride $(CuCl)_n$ and chlorine. According to the figures quoted by Wicks and Block[82] this reaction generates one atmosphere of chlorine at 810°K. Hammer and Gregory[83] made an effusion study of the equilibrium pressures of cuprous and cupric chlorides and chlorine over solid and liquid cupric chloride; they found that at equilibrium:-

$$\text{Log}_{10} P_{Cl_2} \text{ (mm Hg)} = 12.741 - 8672.T^{-1} \quad (T \text{ in } ^\circ K)$$

and $$\text{Log}_{10} P_{CuCl_2} \text{(mm Hg)} = 12.941 - 10,119.T^{-1} \text{ (T in } ^\circ K)$$

They assumed that cupric chloride vapour exists as the monomer, however Polyachenok[85] states that oupric chloride vapour exists as dimerio molecules.

Cuprous chloride vapour was long regarded as dimeric on the basis of early vapour density measurements, but in 1948 Brewer and Lofgren[84] by studying the chloridisation of copper by hydrogen/hydrogen chloride gas mixtures discovered the existance of a trimer Cu_3Cl_3. For the reaction:-

$$x.HCl + x.Cu = (CuCl)_x + \frac{x}{2}.H_2$$

they calculated the equilibrium constants K_1, K_2, K_3 for x = 1,2 and 3. They found that as K_2 was negative, Cu_2Cl_2 was not a prominant species, and therefore for the reversible reaction:-

$$3CuCl_{(g)} = Cu_3Cl_3 \text{ (g)}$$

they found that;-

$$\Delta G = -126,400 - 12.51 \text{ T logT} + 104.7 \text{ T}$$

Thus at lower temperatures the equilibrium will be shifted to favour the the formation of the trimer molecules, whereas at high temperatures, the

monomer becomes the species of importance. Wong and Schomaker[86] proposed a planar six-membered ring structure for the trimer on the basis of their diffraction studies.

However, the existence of a tetramer (Cu_4Cl_4) in the vapour phase below the melting point[87,88] and above[85] has been verified, and Mielcarski[89] found that in transpiration experiments with argon, the molecular weight calculated corresponded to a hexamer (Cu_6Cl_6), which he proposed existed as a dimerised trimer $(Cu_3Cl_3)_2$. Even so, when the carrier gas was changed to nitrogen the molecular weight values indicated that a tetramer was the vapour species. Federov and Shakhova[90] concluded from their saturation and boiling point experiments that above 475°C cuprous chloride forms triple molecules in the vapour, and below this temperature there is further association with the formation of the six-fold molecule Cu_6Cl_6. Hilden and Gregory[91] in their vapour phase absorbance work acknowledge the existance of a tetramer, but confine their work to the trimer as this is the absorbing species in the near ultra-violet. They also verified the transition of cuprous chloride from the zinc blende structure at 407°C to a wurtzite structure which then persists to the melting point at 424°C.

Thus experimental work concerning the structure of cuprous chloride vapour $(CuCl)_x$ suggests that the polymer coefficient x varies mainly with temperature, but can also vary with other reaction parameters.

The vapour pressure plots for cuprous chloride as reported by various workers and calculated for the trimer, are shown in figure 1. and were obtained as follows :-

(1) Polyachenok[85] in 1969 quotes $\text{Log } P(\text{torr}) = 5.046 - 4403.T^{-1}$ (T in °K)

(2) Federov[90] in 1961, linear regression of his results gave in the temperature range 673-1073°K $\text{Log } P(\text{torr}) = 6.408 - 5209.T^{-1}$

(3) Hammer and Gregory[83] in 1964 quote $\text{Log } P(\text{torr}) = 10.290 - 7574.T^{-1}$ in the temperature range 500-700°K

(4) Brewer[84] in 1950 quotes $\Delta G = 37{,}870 + 36.85.T.\log T - 140.83.T$ and $\text{Log } P(\text{atmos}) = -\Delta G/2.303.R.T$ which reduces to , in the temperature

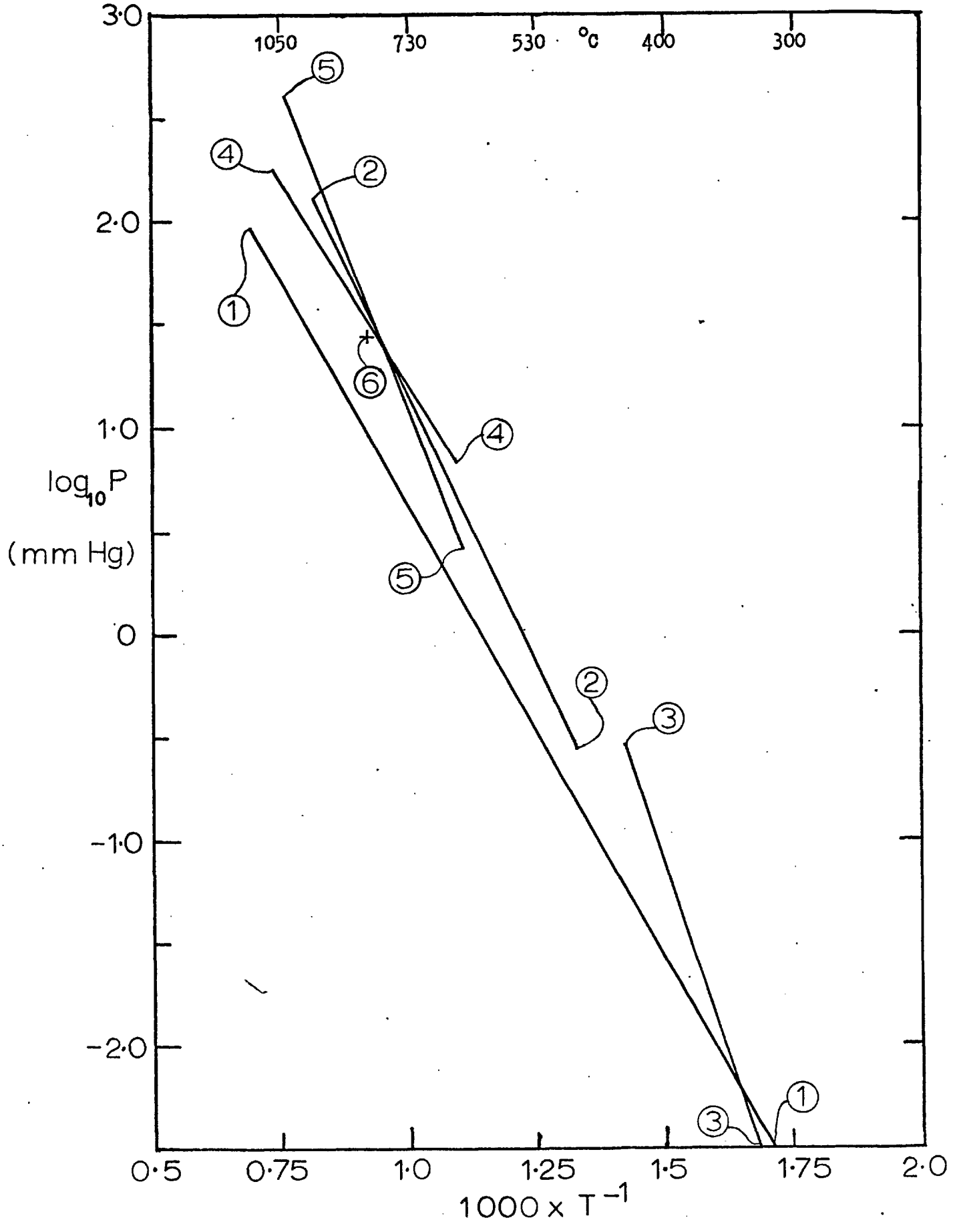


FIG I. VAPOUR PRESSURE OF CUPROUS CHLORIDE TRIMER

(1) Polyachenok (3) Hammer (5) Tarazenkov

(2) Federov (4) Brewer (6) Mielcarski

range 1000-1350°K Log P(torr) = 33.66 - 8.053.log T - 8275.T^{-1}

(5) Tarazenkov[92] in 1935, linear regression analysis of his results for the temperature range 900-1300°K gives Log P(torr) = 7.587 - 6459.T^{-1}

(6) Mielcarski[89] measured at 1073°K $P_{(CuCl)_3}$=30.2 torr

Three points have been taken from each of these workers results at the upper, middle and lower part of their temperature ranges, and a linear regression analysis was performed on all these results to give :-

$$\text{Log}_{10} P(\text{torr}) = 6.354 - 5276.T^{-1} \pm 0.25 \quad \ldots\ldots\ldots\ldots\ldots(30)$$

This value will be taken as the vapour pressure of trimeric cuprous chloride.

(d)Reactions of cuprous chloride with other reagents of the segregation process

(1) Sodium chloride In general if copper recovery is plotted against the percentage of salt added, the resulting plot would show increasing recoveries up to a certain level of salt concentration, then a plateau of constant copper recovery over a range of salt concentration , then recovery would fall off with increasing salt additions. This effect has been noted and studied[78,81,93,94] and is thought to be due to the solution of cuprous chloride in liquid sodium chloride which thus reduces the vapour pressure of cuprous chloride.

(2) Carbon and carbon monoxide Diaz[32] found no reaction of cuprous chloride on degassified graphite at 750°C. Hadjiat[81] also found that for pure graphite and even for degassified charcoal in a dry, inert gas flow, there was no reduction of cuprous chloride vapour by carbon atoms in the temperature range 600-800°C. This is only to be expected, due to the thermal instability of carbon tetrachloride. Similarly, $COCl_2$ exhibits thermal instability although it is considered by some to play some sort of role as a possible chloridisation agent[52,74,75].

(3) Water Vapour Hadjiat[81] found that there was a certain amount of reaction between gaseous or liquid cuprous chloride and water vapour to give

hydrogen chloride and cuprous oxide. However he was not able to draw any firm conclusions about the degree of completion of the reaction. From the JANAF tables[62] however it can be calculated that the equilibrium constant for the reaction at 700°C is about 1×10^{-4}.

(4) Hydrogen Several authors[95-101] have studied the growth of copper from a vapour phase reaction. Bagdasarian[95] noticed that a fairly large proportion of cuprous chloride was volatilised and reduced inthe gaseous state by hydrogen. He observed also that besides the formation of equi-axial crystals, hair-like crystalline aggregates developed on the copper surface at temperatures higher than 700°C. The structure of the copper deposited from cuprous halide vapour reduction by hydrogen, has been extensively studied by Huber[96]. A copper deposit was obtained by using two experimental techniques :-

(I) Hydrogen was reacted with cuprous chloride vapour transported through a tuyere by an inert gas.

(II) Hydrogen was passed over cuprous chloride contained in a boat.

With the first method Huber investigated the nature of the deposit on a substrate (glass,copper or silver) placed normally to the axis of the cuprous chloride jet. In the mixing zone the substrate was covered with a mirror-like coat of copper. In the outer part of the mixing zone, copper dendrites were observed, while in the inner portion filaments and crystals with round shapes appeared. The inner portion was larger at lower hydrogen partial pressures.

With the second method, no dendrites were formed immediately above the melt but always filiform growth occured. Most of the melt was transformed into a spongy mass of copper crystals. The zone above the melt corresponds to the inner portion of the mixing zone. In both cases the filaments of copper were of two kinds :-

1. Fine filaments often very much ramified,the diameter of these individual filaments was a few microns.

2. Rod shaped, straight or bent sometimes screw shaped copper crystals, their lengths ranged upto 1 cm. and their thickness 1/10 mm.

The first type were more frequent, the filaments are always monocrystals and their longitudinal axis was always (001). According to Huber round shaped crystals are formed because the endothermic heat of the reduction of the salt vapour is extracted from the copper surface at which the reaction occurs. Brenner [97,98] found that the whiskers always occured on deposited copper and the initial substrate had no effect. He observed the growth of copper whiskers through an optical microscope and concluded that these whiskers grow from their tips. He showed that if the whiskers grow by the condensation of copper vapour produced by the vapour phase reduction, then the supersaturation of the copper vapour has to be 10^4 to 10^6 near the surface to account for the observed axial growth rates. Since the rate of two dimensional nucleation would be extremely large at this value of supersaturation, no whiskers would have been formed. Coleman and Sears[99] therefore suggested that the transport of the copper halide vapour to the whisker surface and subsequent reduction at the tip might be the mechanism. Brenner[97,98] deduced from the assumption of vapour condensation at the tip, that the axial growth rate should then be proportional to the rate of arrival of the copper halide vapour at the tip of the whisker. He verified that at least below the halide melting point, the growth is primarily controlled by the halide vapour pressure. Coleman and Sears[99] suggested that growth was projected by a screw dislocation along the axis of a whisker which should then be a perfect crystal apart from the one screw dislocation. However Allan and Webb[100] did not detect any screw dislocation with X-ray diffraction studies, and Yamamoto et al[101] did not detect this either with their transmission electron microscopy. Although growth from the tip is clearly shown, growth from the base cannot be ruled out. Allan and Webb[100] observed both types of growth from a CuCl melt reduced with hydrogen. Hadjiats work[81] on cuprous chloride reduction gave similar results to

Huber[96] in as much as he observed two distinct zones of copper deposits when cuprous chloride vapour is jetted towards a substrate over which hydrogen is flowing. In the inner zone two types of growth were noticed; I, fine crystals forming a thin coating and II, branching filaments perpendicular to the surface. The filaments were about 5 microns in diameter and up to 1 mm. in length. In the outer zone, dendrites had grown outwards from the surface with their main axes perpendicular to the substrate surface. Their lengths reached 1 mm. near the inner zone boundary but quickly decreased with distance away from this boundary. Hadjiat explains the two zones from the P_{H_2} / P_{HCl} ratio, when P_{H_2} is low, i.e. P_{H_2} / P_{HCl} is very small the nature of copper growth is filaments and fine crystals, when P_{H_2} is high i.e. P_{H_2} / P_{HCl} is very large , dendritic growths are favoured.

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It is considered that the cuprous chloride vapour in a TORCO segregation chamber is reduced by hydrogen. This hydrogen is thought to be derived from the volatile content of the carbonaceous material and from the action of water vapour upon the carbonaceous material. As the purpose of this work is to discover the source and nature of the hydrogen that is responsible for the cuprous chloride reduction, there follows a brief summary of the present knowledge of some carbonaceous materials, of their volatile content and of their reactions with water vapour.

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CHAPTER II

Previous Work on the Reactions of Various Gases with Carbons

(1) The effect of thermal treatment on carbons

(a) Gas Evolution Konchesky and Stewart[102] passed coal and steam in varying proportions into a reaction coil held at various temperatures and analysed the gaseous products. They found that coal volatilises rapidly and about 70% of the volatile matter evolves within 0.6 seconds at 854°C. Devolatilisation then continues at a slower rate while the fixed carbon component in the char or in the partially devolatilised coal, begins to take part in the steam carbon reaction. They calculate that of the material volatilised, 57% is hydrogen, 17.5% is carbon monoxide, 19.5% is carbon dioxide, 4.4% is methane and 1.6% is unsaturated hydrocarbons. These values vary with the residence time and with the temperature of the coil. Emmett[103], when degassing various coals and charcoals by heating them to 1200°C, found that 0.5-1.5% by weight of hydrogen was evolved and that for a steam activated coconut charcoal, the volatile matter consisted of 38.5% hydrogen, 58% carbon monoxide, 0.6% methane, 0.7% carbon dioxide and 2.2% H_2O and for a steam activated coal, the volatile matter consisted of 30% hydrogen, 65% carbon monoxide, 1.8% methane, 1.1% carbon dioxide and 2.1% H_2O. He also found that coal and charcoal only produce significant quantities of CO_2 (20%) on heating to 1200°C when they have first been extracted with HF. His experiments show that the amounts of gas evolved when coal or charcoal is heated from room temperature to 900°C expressed as a percentage of the amount evolved when heated from room temperature to 1200°C are as follows:- for steam activated charcoal, hydrogen 27%, carbon monoxide 59%, carbon dioxide 95%, methane 1%, and for a steam activated coal, hydrogen 23%, carbon monoxide 10%, carbon dioxide 82%, and methane 4%. Interesting work has been done by Sharkey and co-workers[107,108] who irradiated samples of coal, with laser pulses which heated the sample to several thousand degrees, and analysed the product gases. They also studied the effect

of various atmospheres on this reaction. The results of their work on various coals showed that acetylene,not hydrogen, was the principal gaseous product. Also, they found that the inert atmosphere had a considerable effect on the composition of gaseous products from any one coal type.

Research has been carried out on the effect of various coal types[78] on copper segregation and it was found that in general that the volatile content should be between 6-20% and the coal should have a high specific surface area.

(b) Surface Area. Razouk et al[104] found that the specific surface area of coking coals increased with carbonisation temperature and reached a maximum at about 600°c. Cokes prepared at temperatures above 800°C possess a much lower surface area , probably due to the sealing off of the micropore system. They also discovered that coals and cokes prepared below 900°C exhibit a molecular sieve effect in as much as the specific surface area calculated from the adsorbtion of methanol was very much higher than that derived from the adsorbtion of benzene and cyclo-hexane. Toda[105] also found this effect when heat treating coals above 850°C. He found that the micropore volume began to decrease at about 900°C when calculated from the measurements made with carbon tetrachloride, but when carbon monoxide was used, the micropore volume apparantly stayed constant until about 1100°C when it began to decrease with increasing heat treatment temperature.

The change in charcoal pore size distribution and specific surface area with increasing heat treatment temperature was researched by Gutsze and Jarecka[106]. They found that the specific surface area of charcoal rapidly decreased when the heat treatment temperature reached 700°C. On the evidence of microscopic studies they stated that the smaller pores are eliminated preferentially,which probably explains why these heat treated carbons exhibit molecular sieve effects.

(2) Gas Chemisorption on Carbon Bangham and Stafford[109] when studying the adsorption of hydrogen on graphite observed that large amounts of hydrogen

atoms and not molecules were adsorbed at room temperature. They also found that hydrogen-treated graphite became a good adsorbant for oxygen. Barrer and co-workers[110,111] also observedthat hydrogen is adsorbed as atoms and that the same atoms always desorb to give back the hydrogen molecule. The activation energy for hydrogen chemisorption was found to be between 22 and 33.8 kcal/mole as the fractional surface coverage was increased from zero to 0.3. Kingman[112] in his studies on highly purified charcoal found that hydrogen was not adsorbed at a measurable rate below 200°C. Over the temperature range from 340 to 395°C the activation energy for chemisorption was 30 kcal/mole in the range of 0 - 0.3 cc hydrogen per gram of charcoal. Thomas[113] observed that the adsorption of hydrogen on outgassed graphite was an activated process in the temperature range 600-750°C and the activation energy for adsorbtion varied from 10 - 33 kcal/mole for fractional coverage of 0.1 - 0.6.

McCarroll and McKee[114] studied the reactivity of graphite towards hydrogen, oxygen and nitrogen they found that only oxygen at 1000°C was reactive in the undissociated state. However dissociated hydrogen was reactive at 700°C upwards and nitrogen at 1000°C. It has been known for many years that dissociative or non-dissociative chemisorption of gases on carbon surfaces can only account for a small fraction of the total surface area. Chemisorption involves a covalent or ionic bond between the adsorbed species and the surface carbon atom or atoms. It is well known that the properties of carbons are highly anisotropic and there is every indication that chemisorption does not occur at the ideal regions of the basal planes,but only occurs on the basal plane edges and at basal plane imperfections :- vacancies,edge and screw dislocations, and vacancy clusters. Therefore in adsorbtion experiments only the reactivity of strong or active sites is measured. The existance of active sites on carbon surfaces has been suggested by many workers. Rideal and Wright[115] while studying the oxidation of carbon suggested that there were three types of surface site on carbon which behave differently in oxidation reactions. Long and Sykes[116] considered

that the same charcoal contained two different types of site, one of which reacts with steam and the other with carbon dioxide. Taylor[117] and co-workers, in their studies on the chemisorption of gases on a wide variety of solid surfaces, found that their Elovitch plots $\left\{q = \frac{1}{\alpha}.\ln(1 + a\alpha t)\right.$ where q is the amount of gas absorbed in time t and a and α are constants$\left.\right\}$ of their results , showed breaks and abrupt changes of slope. They attributed this behaviour to absorbtion on different types of site.

Walker and co-workers[118,119], while studying the chemisorption of oxygen on carbon between 100 and 575°C, observed that chemisorption involved more than one type of site. Also in their studies using graphon (a highly purified form of carbon)[120,121] in the temperature range -78 to 160°C, they concluded that chemisorption takes place on five different types of active site. However in their work with hydrogen[122] on graphon in the temperature range 100 to 600°C, they observed only four types of site but they state that as the rate of chemisorption of hydrogen is much slower than that of oxygen, the fifth group of sites would only be observed if chemisorption was carried out at a much higher temperature eg. 700+°C. They conclude that as a carbon surface presents several carbon-carbon distances to the incoming hydrogen molecule, an activated complex formed between hydrogen and two surface carbon atoms would be expected to have different potential energy configurations dependent on these spacings between carbon atoms.

Puri and co-workers[123,124] found that hydrogen from charcoals when being driven off between 30 and 1200°C is eliminated in steps, again they attribute this to different energy levels of hydrogen bonding.

Chemisorption of hydrogen on coke is very important in segregation reactions because it is thought that this hydrogen is responsible for the reduction of the cuprous chloride vapour and subsequent deposition of copper on the coke. It is well known that coke,coal and charcoals can hold many times their own volume of gas. Emmett[103] has shown that when steam activated coal is heated from 900 to 1000°C, typioally 35.3 cc measured at NTP of hydrogen are evolved per gram of sample.

(3) Reactions of steam with carbon

Konchesky and Stewart[102] in their experiments of heating coal and steam found that the following reactions are involved :-

1.Devolatilisation (FC is fixed carbon and VM is volatile matter)

COAL (FC & VM) ⟶ (Thermal decomposition) CHAR (FC & residual VM) + Volatile Components (tar, light oil, H_2O, H_2, CO, CO_2, H-C Gases)

1a.Thermal cracking

Volatile components + H_2O ⟶ (Thermal cracking) $CO + CO_2 + H_2 + H_2O$ + H-C Gases

2.Steam-Carbon Reaction

CHAR (FC & residual VM) + $H_2O \longrightarrow CO + H_2$ + residue of gasification (residual FC & VM) .....(4)

3.Water Gas Shift Reaction

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad \text{.....(6)}$$

Many workers[125-138] have found that the primary reaction products of steam and various forms of carbon were hydrogen and carbon monoxide produced by :-

$$C + H_2O \longrightarrow H_2 + CO \quad \text{.....(5)}$$

They also found that excess water vapour can react by :-

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad \text{.....(6)}$$

This reaction was thought[125] to occur heterogeneously on the carbon surface and the carbon dioxide so produced could react with the carbon by :-

$$CO_2 + C \longrightarrow 2.CO \quad \text{.....(7)}$$

(4) Mechanism of Steam-Carbon Reactions

Long and Sykes[116] proposed, that when a water molecule comes into contact with a carbon surface it forms an adsorbed hydrogen atom and an adsorbed hydroxyl radical, which subsequently breaks down into an adsorbed oxygen atom and another adsorbed hydrogen atom. The hydrogen atoms then combine to form

an adsorbed hydrogen molecule which can then desorb. The adsorbed oxygen atom leaves the carbon surface much more slowly but when it does it leaves as a carbon monoxide molecule. Johnstone[128] proposed a similar mechanism but with the condition that the hydrogen and hydroxyl group do not necessarily adsorb on neighbouring sites.

The natures of hydrogen and oxygen on a carbon surface are totally different, oxygen is chemically combined with a carbon atom and forms carbon monoxide on desorbtion, whereas hydrogen adsorbs and desorbs as hydrogen. This does not preclude the formation of a carbon hydrogen molecule, but Thomas[137] in his review of carbon reactivity states that at 800°C the rate of reaction of carbon and oxygen is some 10^8 times faster than the rate of reaction of hydrogen with carbon. Thus it is the formation of a surface complex between oxygen and a surface carbon atom that is the initial major product of steam-carbon reactions. This was first postulated by Rhead and Wheeler[138] in 1912. However it is the work of Ergun[134] which gives a more modern account of the steam-carbon reaction mechanism.

A reactive site on the surface of the carbon C_f reduces water vapour to give hydrogen and a site occupied by oxygen C_o :-

$$H_2O + C_f \rightleftharpoons H_2 + C_o \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

$$\text{Equilibrium constant } K_2 = (H_2).(C_o) \,/\, (H_2O).(C_f)$$

The actual carbon gasification occurs when the occupied site leaves the solid phase as carbon monoxide and in doing so generates more free sites :-

$$C_o \longrightarrow CO + n.C_f \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

where n is an integer of value 0, 1 or 2 when an individual site is considered, statistically n can have any value between 0 and 2. If $n > 1$ the number of reaction sites increases with gasification and the solid becomes more reactive, if $n = 1$ the reaction rate will remain constant during an experiment and a steady state can be maintained, if $n < 1$ the solid will become less active with gasification.

Carbon dioxide can also react with an unoccupied site generating a molecule of carbon monoxide and an occupied site:-

$$CO_2 + C_f \rightleftharpoons CO + C_o \quad \text{.......................................(10)}$$

Equilibrium constant $K_1 = (CO).(C_o) / (CO_2).(C_f)$

It will be noticed that reactions 8 and 10 are reversible, therefore in the steam-carbon system the reverse reaction of 10 is the source of carbon dioxide. This is more easily seen if equation 10 is subtracted from equation 8, then the water gas reaction is obtained :-

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad \text{.......................................(6)}$$

Equilibrium constant $K_6 = (CO_2).(H_2) / (CO).(H_2O)$

Thus $K_2 = K_6.K_1$ ....(11)

Ergun[134] measured K_2 values for steam-coke reactions and found that these values agreed quite well with K_2 values obtained from calculations based on carbon dioxide and carbon reactions (K_1) and the water gas reaction (K_6). Thus Ergun reasoned that the same surface oxide complex was involved in both the steam-carbon and the carbon dioxide-carbon reactions. Ergun[132] also measured K_1 values for three different types of carbon and found that the agreement was very good. Since his theory unifies the mechanisms of both reactions it is named the 'Unified theory'.

The problem confronting most workers is the nature of this surface oxide, i.e. the nature of C_o. Shelef and Walker[139], having discovered five types of chemisorbtive behaviour for oxygen[118,119], postulate that there are two basic types of surface oxide, the first is formed on sites which are exceedingly sensitive to contamination and posses a high reactivity ie. a relative short lifetime on the surface which gives a high rate of gasification, and the second is a more stable intermediate of steady state gasification. Thus they explain their initial high rates of reaction.

Mentser and Ergun[140] studied the kinetics of oxygen exchange between carbon dioxide and carbon monoxide on a carbon surface and found that the

rate was a few orders of magnitude higher than the rate of gasification (reaction 9). They conclude that the surface oxide complex consisted of two-thirds of a double bond between an oxygen atom and a surface carbon atom.

(5) Kinetics of Steam-Carbon Reactions

The empirical rate equation first postulated by Gadsby et al.[125] in 1946 was that :-

$$\text{Rate} = \frac{k_1 P_{H_2O}}{1 + k_2 P_{H_2} + k_3 P_{H_2O}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (22)$$

where k_1, k_2, k_3 are constants and P signifies pressure .

This equation is most versatile in as much that if the pressures of steam and hydrogen are replaced by pressures of carbon dioxide and carbon monoxide then the rate equation obtained describes the oxidation of carbon by carbon dioxide. The equation is still being used at present[135,137] to adequately describe rates of carbon gasification reactions. However more sophisticated equations are used by Turkdogan et al.[141-145] in their work on the kinetics of carbon-carbon dioxide reactions using coke, charcoal and graphite. Turkdogan[142] proposes that the difference in reaction rate of the carbon types is due almost entirely to the difference in internal area. Ergun[132,134] in his unified theory, argues that the surface oxide, Co, formed during the water vapour reaction is exactly the same as that formed from CO_2. Thus present workers can develop sophisticated equations to deal satisfactorily with their results and most are agreed that the gasification of carbon involves the formation of a surface oxide. Ergun refers to this oxide as C_o a carbon site occupied by oxygen, Turkdogan however refers to it as C_2O_2, a carbon dioxide molecule combined in some way with a surface carbon atom. The Arrhenius plots of log rate versus reciprocal temperature give a gradient which is the activation energy for a reaction. Workers[146,147] have observed maxima in Arrhenius plots for carbon gasification whereas other

normal reactions give linear plots. Strickland-Constable[146] attributes this phenomenon to an oxide which can exist on the carbon surface beyond 1000°C whereas the commonly accepted oxide is only stable up to about 900°C. Thus the nature of carbon gasification is by no means fully understood.

(6) The Catalysis of Carbon Gasification

In the previous section it was shown that the nature of carbon gasification was not yet completely understood, therefore it comes as no surprise to find that the catalysis of this reaction is even less well understood.
The reviews[148-150] are summations of previous work, without any real attempt to make definite statements on proposed mechanisms. Walker et al.[150] however, do place the theories of carbon gasification catalysis into two groups, the oxygen transfer and the electron transfer groups.

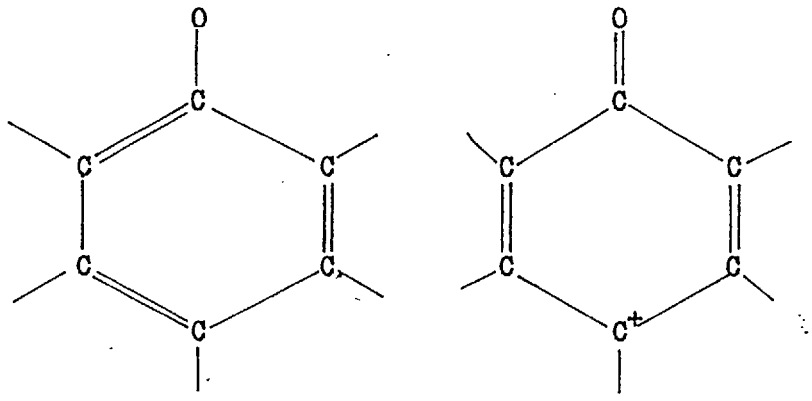
a. Oxygen transfer. This mechanism was first advanced by Neumann et al.[151] in 1931 and can be represented as :-

$$RO + CO_2 \longrightarrow RO.CO_2 \quad \text{then} \quad RO.CO_2 + C \longrightarrow RO + 2CO$$

where RO represents a metallic oxide. Even so this chemical mechanism does not explain in what way the non-catalysed mechanisms are bypassed. This mechanism more or less tacitly assumes that the limiting step of the non-catalysed reaction is the chemisorptive step and that a catalyst particle serves as an active chemisorptive centre.

b. Electron transfer. Long and Sykes[127,152] made the first and most detailed attempt to formulate an electron transfer theory. They summarise the mechanism as follows :-

1. The catalysts influence the general energy levels of the reacting sytems.
2. The active sites are considered to be the less firmly bound carbon atoms situated at the edges of graphitic lattice planes.
3. When an oxygen atom is adsorbed at such a site, two types of distribution of the π-electrons may be distinguished as seen in figure 2. Type (b) needs less energy to break the carbon-carbon bonds to release a CO molecule.



(a) (b)

Figure 2. Two types of distribution of π electrons (from Long and Sykes[127])

4. The action of the catalyst is thought to be such as to induce type (b) distribution of the π electrons; therefore, the activation energy of the last stage of gasification will be decreased by the catalyst.

5. If the last stage is the rate controlling step, the overall activation energy will be reduced.

6. The first stage of gasification will also be facilitated if the oxygen is attached to the carbon atom by a double bond.

7. The mobility of π electrons provides a means whereby catalysts situated at various points in the carbon lattice may influence events at the active sites.

8. The probable mode of action of a catalyst is explained by its accepting electrons from the carbon planes in order to facilitate both adsorption by increasing the carbon-oxygen bond strength and desorption by weakening the adjoining carbon-carbon bonds.

9. It is immaterial from which part of the conjugated system the electron is removed. The catalyst need not be situated at an active site; it need only be in contact with the same plane of the carbon lattice from which the electron is removed.

10. The ability of the transition metal oxides to accept electrons is explained by arguments of catalysis on semiconductors. Thus wustite should be a catalyst because of its metal deficit structure, while the metal itself (Fe)

is not supposed to have any catalytic activity.

Therefore, the Long and Sykes theory predicts a decrease in the activation energies of both the adsorption and desorption steps. It limits the number of active sites, even in the case of catalysed reaction, only to those corresponding to edge carbon atoms. It does not explain the effect of catalysts on the basal planes. It excludes metals as the active catalysts. Rakswarski[153] however, extends the apparent validity of the Long and Sykes theory to include metals, his arguement is that the transition metals with unfilled d bands do satisfy the basic requirements of serving as electron acceptors and hence are capable of forming surface carbon-metal type bonds.

The experimental evidence supporting both theories is large; however below are summarised the principal catalysts for the gasification reactions,

Reaction 5 :- Na and K carbonates[130,127], CuO[154], $CuCl_2$[155].

Reaction 6 :- Fe_2O_3, CaO and Na_2CO_3[130,127].

Reaction 7 :- Fe_2O_3[127,156], Fe_3O_4[156], Cu[130], Cr[157], Fe[150,157,158] Co and Ni[150,157,158].

Inhibitors of reaction 7 are B and P found by Raksawski et al.[159]. The only result here of real importance is the work of Kislykh and Shishakov who found that the uncatalysed activation energy of activated charcoal in the temperature range 680-730°C was 48.7 kcal/mole and when the charcoal was impregnated with 1% $CuCl_2$ solution this value was lowered to 44.2 kcal/mole. Kroger and Melhorn[154] found that of the metal oxides, CuO had the greatest catalytic effect on the oxidation of graphite by water vapour; followed, in decreasing order of activity, by the oxides of Cr,Ni,Fe,U,Tl,Mn, Co and Al. Alkali carbonates were the most active of all catalysts and, in decreasing order of activity were :- K,Na,Rb,Cs and Li.

In terms of auto-catalysis previous results[125] show that hydrogen strongly retards the forward reaction of 5, and CO strongly retards the forward reaction of 7. The forward reaction of the water gas reaction 6 is retarded by hydrogen and to a lesser extent by CO_2, the reverse reaction is retarded by steam but is unaffected by CO. Montet and Myers[135] found that the app-

arent activation energyof the steam-carbon(graphite) reaction varied with water vapour concentration, they also found that at a water vapour concentration of 22,000 ppm, the activation energy E_a was -68 kcal/mole, but when the water vapour concentration was lowered to 250 ppm then E_a increased to -109 kcal/mole. Blyholder and Eyring[129] found that the rate determining steps were the adsorption of water vapour onto a graphite surface and the desorption of molecular hydrogen away from the surface; they also found that the adsorbed species had a limited mobility on the surface.

Montet and Myers[136] discovered that a concentration of hydrogen of less than 1 vpm inhibits the water vapour reaction to an appreciable extent and they attribute this to the dissociative adsorption of hydrogen, thus the apparent activation energy increases with hydrogen concentration since it is hydrogen which blocks the active sites.

Thus, as regards the segregation process, it would seem that the ore and ash constituents if containing alkali carbonates would catalyse the steam-coke reactions. Also the deposition of copper metal would not only catalyse the reaction by its presence on the coke surface, but the reduction of cuprous chloride would remove hydrogen from the active sites.

As far as is known hydrogen chloride has no effect on steam-carbon reactions. Iapalucci and co-workers[160] in their work on chlorine containing coals conclude that the chlorine content of a coal is practically all evolved as hydrogen chloride, only at temperatures above 2000°K does Cl (not Cl_2) become a contending species. Also, whatever its nature, the chlorine has no effect on the burning properties of a coal but does have a serious effect on the corrosive nature of the stack gases.

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CHAPTER 3

EXPERIMENTAL WORK

This chapter is divided into five sections. Firstly there is an introduction which explains the aims of this work as a whole and its relevance to the TORCO process. Together with this there is a brief résumé of the experiments performed with an explanation of the reasoning behind, and objectives of each experiment. There follows a summary of all the experiments and major results in a tabulated form.

The second, third and fourth parts give descriptions of the apparatus used, the accuracies obtained from the analytical equipment and a list of the materials used in the experiments. The final section is a detailed description of the experimental procedures followed and the results obtained from each experiment together with a detailed discussion of each experiment within its own context.

(a) Introduction

The primary objective of a TORCO process is to remove copper from the ore matrix, via a gaseous chloride, and to accumulate the reduced copper into discrete particles which can be recovered from the gangue material by flotation. To facilitate recovery, the cuprous chloride must first be reduced on the coal particles where further reduction and agglomeration can take place. Therefore the successful operation of the process depends on the amount of copper that can be deposited on the coal particles, if the copper were to be reduced in situ in the ore matrix or if it were reduced on the gangue material, recovery by flotation would be low.

The object of this work was to discover the optimum conditions for copper nucleation on a carbonaceous material (coke) from cuprous chloride reduction. It was decided to study the reaction of water vapour with some carbonaceous materials and subsequently to study the nature of cuprous chloride reduction on coke.

An apparatus was built to provide an inert gas flowing through a packed bed

of charge material and a water vapour saturator was built into the system to provide a known partial pressure of water vapour. In a TORCO system the measured partial pressure of water vapour is of the order of 1% and so this was the main value of water vapour partial pressure used. From the previous work it is found that the principal reaction products of the steam carbon reactions are gaseous and that the reduction of cuprous chloride produces hydrogen chloride vapour. Therefore a gas chromatograph together with an automatic titrimeter were placed on line for continuous analysis of the exhaust gases. For maximum sensitivity of the chromatograph towards most of the product gases, helium was used as the inert gas;however this did mean that the instruments sensitivity towards hydrogen was reduced.

An initial experiment A, was performed with coke as the charge material, to discover the range of magnitude of the reaction products when the steam-carbon system was followed and to find out what effect the sudden introduction of cuprous chloride vapour had on this same system. The effect of the latter action was to suddenly,but briefly,liberate adsorbed gases from the coke surface. It was also found that to achieve a steady state, the coke bed had to be heat treated at 1000°C for several hours to reduce the amounts of hydrogen and carbon monoxide being evolved to a minimum. Thus degassing at 1000°C was a standard pre-treatment for the various carbons studied in the B series of experiments. In these, the effect of temperature was studied with reference to the steam-carbon reaction and it was found that each system achieved a steady state,but that this state was far removed from true thermodynamic equilibrium. The order of reactivity of the carbon types was found to be graphite,coal, coke and the most reactive towards steam was charcoal. The mass balances in each case indicated that the product gas analyses were consistent with the stoichiometric reduction of water vapour. Also it appeared that gas residence time was an important reaction parameter. The C series of experiments were performed to study the effect of temperature on the steam-coke system at a longer gas residence time than was used in the B series. It was found that at a slower flow rate and with a deeper bed, at each temperature

the system approached thermodynamic equilibrium more closely than at a low residence time. To gauge the effect of residence time on the steam-carbon reactions , the D series of experiments were performed with coke, charcoal and with graphite at one specific temperature but at various gas residence times. It was discovered that as the system approached almost static conditions the reaction equilibrium constants tended towards steady values, but that these values were still far removed from true thermodynamic equilibrium.

Thus it was apparent that the steam-carbon reactions in this apparatus did not achieve thermodynamic equilibrium. It was now decided, in the E series of experiments, to consider the initial reaction of water vapour with coke at a fixed temperature and to facilitate the study of this effect the coke was again degassed at 1000°C. The principal results were that the steam-coke reaction was slow to achieve a steady state condition and that there were sub-reactions involved in the process since the instantaneous mass balances were inconsistant with the stoichiometric reduction of water vapour. Therefore it was surmised that the reaction products ,hydrogen and carbon monoxide, were being adsorbed to a certain extent but at different rates during the initial reaction with water vapour. The ratio of hydrogen to carbon monoxide adsorbed was measured at 1:4.2 . Since copper particles exist in a TORCO segregation chamber, copper powder was introduced into the steam-coke system in experiment F to discover if it had any major effect on the reactions of water vapour. It was found that copper physically admixed with coke had no significant effect on the initial or steady state reactions of water vapour and coke.

For comparison with the other types of carbon studied, the G series of experiments were performed duplicating the procedure of experiment E but the bed materials used were charcoal and graphite. The results together with the E results indicated that each carbon type could adsorb the reaction products (hydrogen and carbon monoxide) and that the amounts of, and the ratio between these gases varied considerably with carbon type. The ratio of hydrogen to carbon monoxide adsorbed was 1:8.5 for graphite and 1:0.1 for charcoal as compared to 1:4.2 for coke.

Having considered the steady state and the initial reactions of water vapour with coke and two other carbon types of different reactivity, it was decided to try and simulate conditions inside a TORCO reactor which involves neither the steady state nor degassified coke. In experiments H and I coke was initially heated to 150°C to duplicate the drying operation of a TORCO plant and then the temperature of the coke was rapidly raised to 850°C as in the top of the segregation chamber. The effect of salt and water vapour on this process was studied by performing the experiments with all the combinations of :- with salt, without salt, with water vapour and without water vapour. The results indicated that the principal source of gaseous hydrogen was from the volatile content of the coke and that the presence of water vapour or salt had little effect on the quantity of hydrogen so produced. However both carbon monoxide and methane were produced from heating coke to 850°C and these quantities were small compared to those of hydrogen, but the presence of water vapour increased these quantities of carbon monoxide and methane by reaction with the coke. The presence of salt in the system catalysed to a small extent these carbon monoxide and methane producing reactions.

For purposes of comparison, charcoal was treated in a similar manner in experiment J but in the absence of salt and water vapour. It was found that charcoal produced more hydrogen per gram of sample than did coke. Two and a half hours after temperature rise initiation, charcoal produced, per gram of charge, 10 ml of hydrogen, 2.6 ml of carbon monoxide and 0.6 ml of methane; coke under the same conditions produced 5.5 ml of hydrogen, 1.5 ml of carbon monoxide and 0.8 ml of methane.

An interesting , but not significant result of experiments H and I was that nitrogen was evolved on heating a coke bed to 850°C. The K series of experiments were performed by subjecting the coke bed to various pre-treatments prior to the temperature rise to 850°C. From these experiments it was found that the nitrogen existing in coke was mainly chemical in nature. Another result of the H and I experiments was that the presence of salt in the system apparently reduced the quantity of hydrogen produced to a small extent. In

experiment L salt was reacted with hydrogen in the presence of silica and it was found that hydrogen chloride was produced,but that the amount was insignificant.

Having discovered that the volatile content of a coke is the major source of hydrogen in a TORCO system which contains 1% of water vapour,it was decided to introduce cuprous chloride into this system. The M experiments showed that the ampule designed,such that the helium gas flow was directed at liquid cuprous chloride and the resulting vapour was then directed towards the coke bed, was the most suitable source of a known partial pressure of cuprous chloride in the apparatus used. By using this apparatus in experiment N to generate various partial pressures of cuprous chloride in a steam/degassified coke system , it was discovered that no cuprous chloride was reduced on the coke surface. Instead the cuprous chloride had been reduced by gaseous hydrogen on the nearest surface to the ampule which was the reaction vessel's walls. By analysis of the product gases it was found that there was a discrepancy between the amount of hydrogen generated from water vapour, calculated from an oxygen balance, and the amount of hydrogen actually measured leaving the system. However there was a direct correlation between this 'lost' hydrogen and the amount of cuprous chloride generated and measured by the titrimeter. Thus in a water vapour containing system using a degassified coke, the hydrogen consumed in the reduction of cuprous chloride was derived from the water vapour reduction reaction. When this occurs,it was discovered that the deposition of copper is non specific. Thus a degassified coke and water vapour in a TORCO system was not suitable for preferential deposition of copper on coke because the system generated gaseous hydrogen which reduced the cuprous chloride throughout the system. It was decided, therefore, that other sources of hydrogen for cuprous chloride reduction should be considered.

The O series of experiments were performed in order to discover the amounts of hydrogen that stably existed on a coke surface at reaction temperatures and whether this hydrogen ,once removed, could be replaced by reaction with water

vapour. On heating untreated coke from reaction temperatures of 750,800 and 850°C to 1000°C it was found that the ratio of hydrogen to carbon monoxide released varied from 4.5:1 to 2.8:1 . However when heating water-reacted degassified coke from the reaotion temperatures to 1000°C, the ratio of hydrogen to carbon monoxide produced varied from 1:4.2 to 1:4.6 . It was also found that the hydrogen inherently contained on an untreated coke surface was more plentiful than the hydrogen that could be generated on a coke surface at the same temperature.The ratio of hydrogen from untreated coke to hydrogen from the water vapour reaction varied from 28:1 at 700°C to 8:1 at 800°C.

Therefore,in order to nucleate copper growth on a coke surface,the P series of experiments were performed in which untreated coke,in a dry system, was reacted with a known partial pressure of cuprous chloride to discover if the inherently contained hydrogen on the coke could quantitatively reduce the cuprous chloride at the coke surface. The reaction was followed by monitoring the partial pressure of hydrogen chloride as well as periodic sampling of the exhaust gases for other reaction products. It was found that at each reaction temperature, the hydrogen contained on the coke surface was much greater in quantity than the O series of experiments had indicated. The O experiment at 750°C indicated that there was 5 ml per gram of hydrogen on the coke surface whereas the P experiment at the same temperature yielded 24 ml of hydrogen per gram.The bulk of this hydrogen reacted at a constant rate with cuprous chloride generating a constant partial pressure of hydrogen chloride. At 750°C, within experimental error, all the cuprous chloride was reduced to copper, however at the higher temperatures the reaction was less complete. A small amount of gaseous hydrogen together with large quantities of carbon monoxide were released in a non-steady state manner as the cuprous chloride reduction proceeded. Thus these experiments showed that the inherently-contained-hydrogen coke could reduce the chloride on the coke surface, but that the quantity and reactivity of this hydrogen rapidly decreased with increased reaction temperature.

The experiments and major results are summarised in the following table.

TABLE 2 TABULAR RÉSUMÉ OF EXPERIMENTS (for legend see page 34)

Exptl series	No. of run	Bed/weight in gms	T_1 °C	T_2 °C	H_2O %	Other addtns	Res.Time seconds	Comments and Results
A	A1 A2	ck/2.3 ck/1.6	various 1000	700 various	0.1,0.3 2	- CuCl	$\frac{3}{4}$ $\frac{1}{2}$	hydrogen and carbon monoxide main products CuCl frees adsorbed gases, water redn. incomplete
B	B1,2 B3,4	ck/2.3,gr/1.8 cl/2.4,ch/1.3	1000	various	1	-	$\frac{3}{4}$	steady state achieved but not thody equilibrium order of reactivity low gr,cl,ck,ch high
C	C1	ck/10.5	1000	various	1	-	17	higher reactivity at longer gas residence time
D	D1,2 D3,	ck/10.5,ch/5.9 gr/8.2	1000	750	1	-	various	all reactivities increase not only with temp but with gas residence time, CO_2 from coke exception
E	E1,2	ck/2.3,ck/10.5	1000	800	1	-	$\frac{3}{4}$,17	H_2 and CO adsorbed during initial reaction of H_2O
F	F1,2	ck/10.5	1000	800	1	0.1,1.0% Cu	17	copper powder little effect on initial reaction
G	G1,2	gr/8.2,ch/5.9	1000	800	1	-	22	H_2:CO adsorbed varies with carbon type
H	H1,2	ck/10.5	150	150 - 850	0,1	-	17	water vapour little effect on hydrogen produced
I	I1,2	ck/10.5	150	150 - 850	0,1	0.5% salt	17	salt has little effect on hydrogen produced
J	J1	ch/5.9	150	150 - 850	0	-	22	charcoal produces more hydrogen than coke gm/gm
K	K123,4	ck/10.5	150	150 - 850	0	-	17	sources of nitrogen from coke are chemical
L	L1	5 cm of salt	0	750	0	1.1% H_2	-	salt + H_2+ silica generates small HCl
M	M1,2	copper	0	various	0	chlorine	-	CuCl vessel designed,Cu + Cl_2 incomplete
N	N1	ck/10.5	1000	750	1	various CuCl	17	gaseous H_2 reduces CuCl, vp of CuCl measured
O	O1 O2 O3 O4 O5 O6	ck/10.5 ck/10.5 ck/10.5 ck/10.5 ck/10.5 ck/10.5	700 750 800 1000 1000 1000	700-750-1000 750-800-1000 800-850-1000 700-1000 750-1000 800-1000	0 0 0 1 1 1	- - - - - -	17 17 17 17 17 17	inherent H_2 on coke cannot be replaced by reactn with water vapour at same temp,hydrogen to carbon monoxide ratio from untreated coke high, ratio from degassed coke after reaction with water vap low,carbon monoxide sources on untreated coke much more stable than hydrogen sources wrt temp
P	P1 P2,3,4	ck/10.5 ck/10.5	0 0	750 750,800,850	1 0	various CuCl fixed CuCl	17 17	water vapour reacts with CuCl inherent H_2 reduces CuCl on coke surface

Legend of the tabular résumé

ok = coke, cl = coal, gr = graphite, ch = charcoal

T_1 is the temperature of any pre-treatment, T_2 is the temperature at which, or the temperature over which, gas analyses were performed.

(b) The apparatus

It was decided to contain the charge material in an externally heated reaction vessel, through which a purified helium carrier gas flowed.

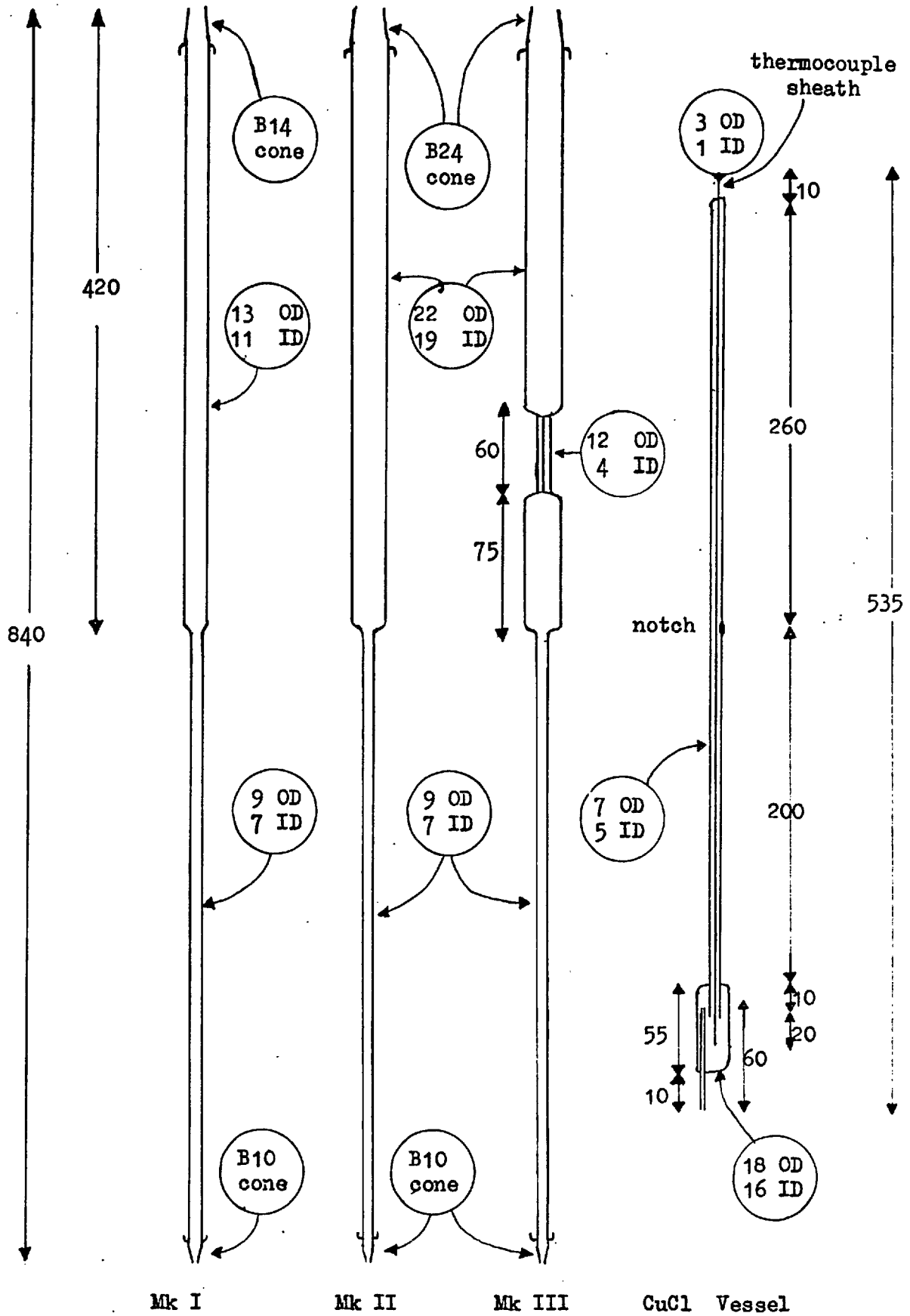
The reaction tubes used were of three types :- Mk I, Mk II and Mk III (see figure 3). Mk I was replaced by the wider bore Mk II because it was realised that the cuprous chloride ampule (see figure 3) would not fit inside a Mk I reaction tube. The Mk III was designed to prevent the back diffusion of hydrogen from the coke bed.

The helium was purified by passing it through a furnace containing copper oxide at 600°C to convert hydrogen and carbon monoxide to water vapour and carbon dioxide. The gas was then passed through 'sofnolite' to remove carbon dioxide and then through silica gel and magnesium perchloride to remove water vapour. Oxygen was removed by passing the helium through a furnace containing copper wool at 600°C, finally the gas was passed through molecular sieves to remove any traces of hydrocarbons. The gas train so constructed, produced one flow of purified helium for flushing purposes and another purified helium flow which could be passed through a water vapour saturator or could have various gases mixed into it. (see figure 4). The water saturator consisted of two dreschel bottles held in a water bath which was controlled by a heater/stirrer unit. Water from a refrigeration bath held at approximately 4°C was pumped through a copper coil held in the water bath. The water bath was controlled to 7°C ± 0.01°C and it was verified that the helium became saturated with water vapour at this temperature.

It was realised that if the product gases were slowly cooled, there could be a change in their equilibrium. It was decided to quench the gases as quickly as possible from the reaction temperature by extending the constant temperature zone below the charge. The furnace was specially designed and built by the fur-

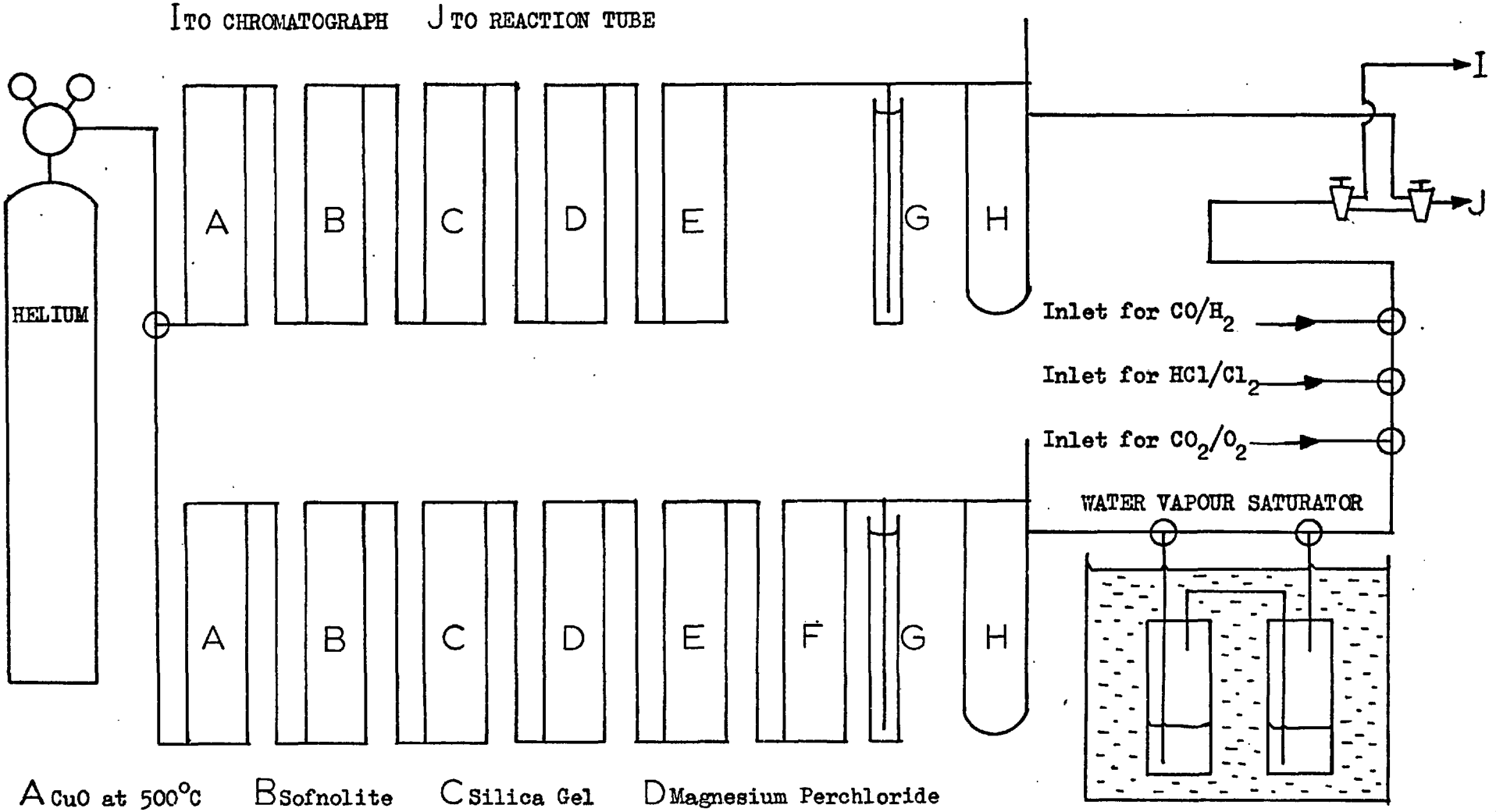
FIGURE 3. Reaction Tubes and the Copper Chloride Vessel

all measurements in millimetres



ALL TUBES AND CuCl VESSEL CONSTRUCTED FROM SILICA

FIGURE 4. THE HELIUM PURIFICATION TRAIN



A CuO at 500°C B Sofnolite C Silica Gel D Magnesium Perchloride

E Cu at 600°C F Mol. Sieve G Blow Off H Capillary Flowmeter

nace department of the 'Amalgams Co. Ltd.'to give a long constant temperature zone extending for as far as possible below the central constant temperature zone.(see fig. 5). The furnace was controlled by a Eurotherm SCR temperature controller which kept the set temperature to well within ± half a degree. The other furnaces were controlled by 'mini' Ethers which held the furnace temperature to a degree ± 1°C.

The exhaust gases from the reaction tube (see fig. 6) were passed through the sample injection valves of the chromatograph and were then either passed through the titrimeter cell or to extraction via a manometer and a blow off.(see fig. 7).

The automatic titrimeter consisted of a calomel and a glass electrode which measured the pH of the cell. A subsidiary unit operated the stirrer and the solenoid switches of the burette. The pH of the solution was preset by the main unit control and then when this value fell due to the dissolution of HCl, the burette would be allowed to run in NaOH solution to restore the set pH. A constant level device was built into the titrimeter cell in order to keep the volume of liquid constant. It was assumed that when either HCl or NaOH was added to the cell they were immediately dispersed by the stirrer and only constant pH liquid was lost to waste.

The chromatograph was a Pye Unicam series 104 model 34 consisting of an isothermal oven containing a katharometer detector. The oven temperature was controlled to ± 0.05°C by the hot air circulation system operated by column oven controller which was set to 100°C. The katharometer power supply also amplified the output and this signal was fed to a Kent Chromalog III integrator and to the Smith's Servoscribe flat bed pen recorder. The katharometer filaments were operated at 300 mA and to detect any drift a larger scale ammeter was built into the Pye circuit.

A three foot molecular sieve column was used which resolved the following gases :- hydrogen after 28 seconds from injection, oxygen after 39 seconds, nitrogen after 55 seconds, methane after 70 and carbon monoxide after 120 seconds. A three foot poropak S column resolved the following gases :- an air peak after 18 seconds, carbon dioxide after 31 seconds and water vapour after 155 seconds. The column carrier gas was helium which was passed thr-

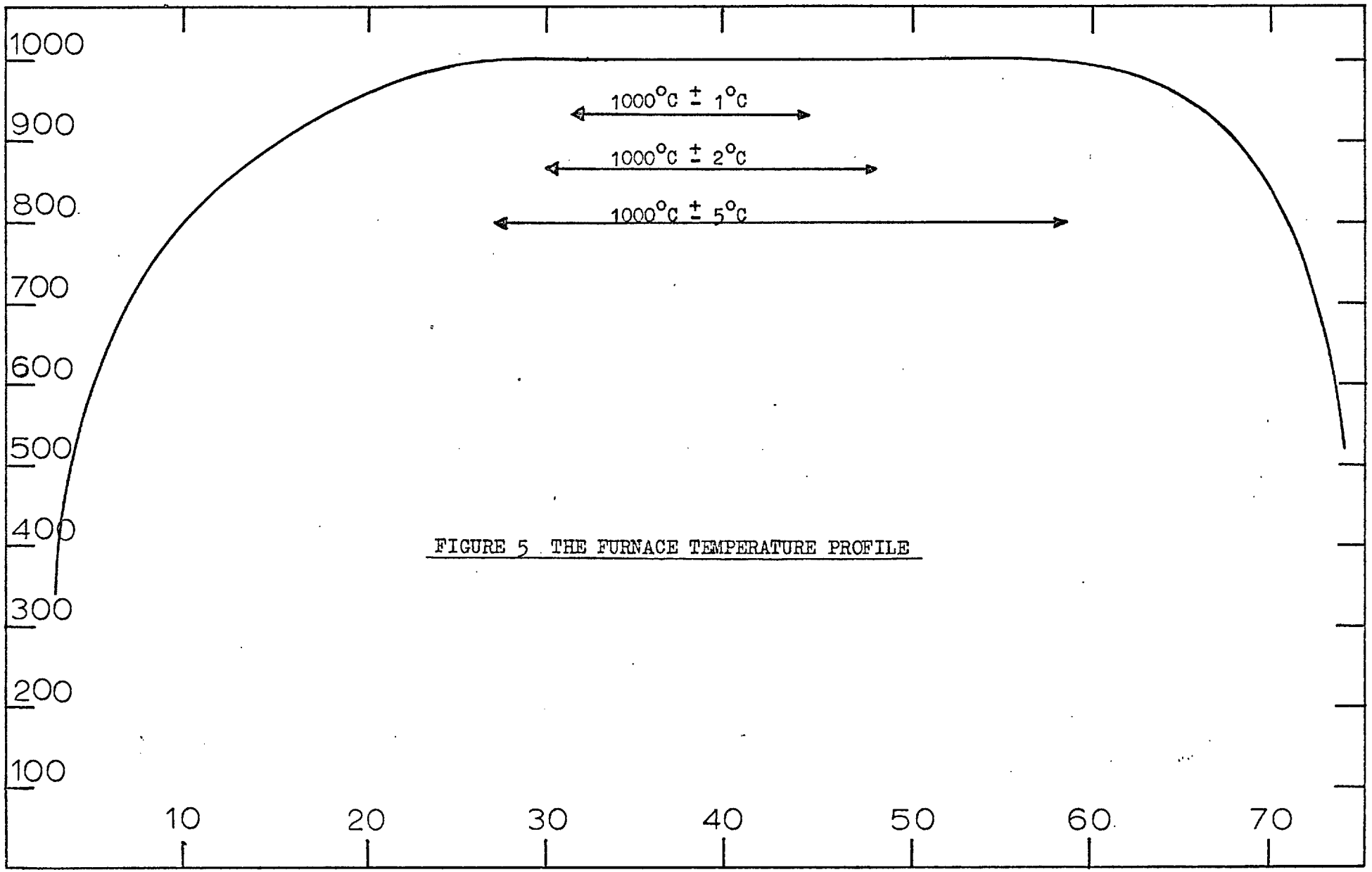


FIGURE 5 THE FURNACE TEMPERATURE PROFILE

FIGURE 6. THE FURNACE AND THE INLET AND OUTLET GAS MANIFOLDS

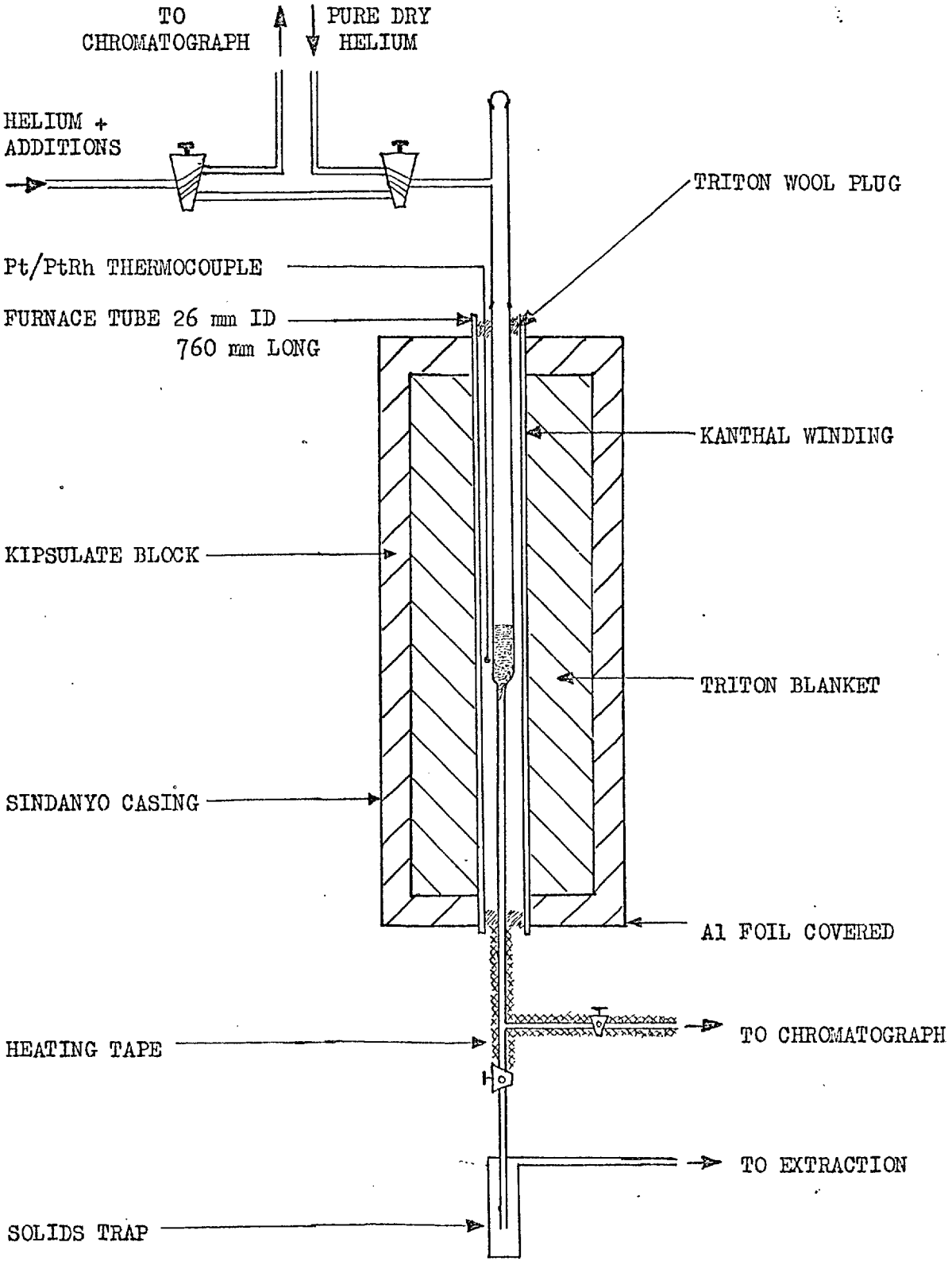


FIGURE 7 ARRANGEMENT OF CHROMATOGRAPH AND AUTOMATIC TITRIMETER

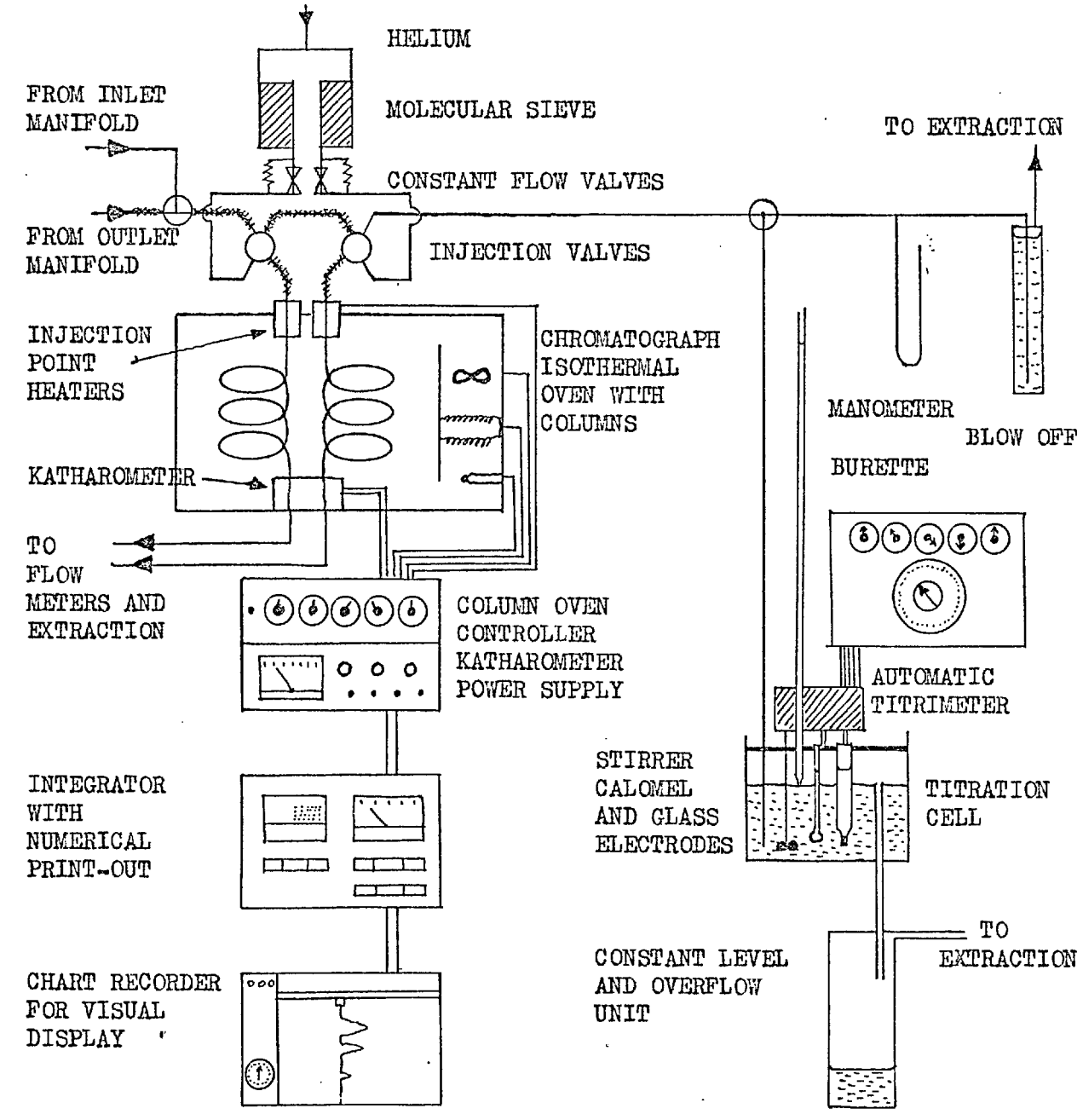
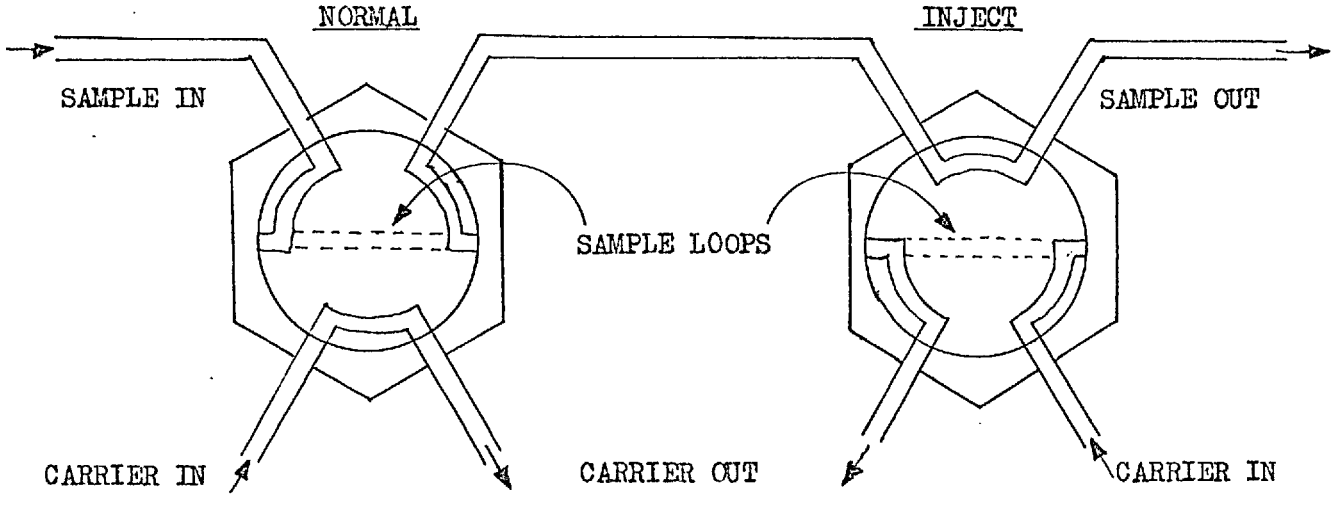


FIGURE 8 OPERATION OF THE SAMPLE INJECTION VALVES



ough molecular sieve 13X to remove moisture, carbon dioxide and hydrocarbons. The column carrier gas was controlled by special valves which maintained a constant mass flowrate of 50 ml/min through each column (see fig. 7). The sample injection valves (see fig. 8) were nominally 1 ml for the porpak column and $\frac{1}{2}$ ml for the molecular sieve 5A column. The volume of gas injected was thus constant for each column and the chromatograph was calibrated using these size sample loops.

The flowmeters were all of the capillary type and were calibrated with oxygen at 25°C. The manometers were filled with di-butyl phthalate and the blow-offs contained sulphuric acid.

The technical specifications of the equipment used appears in appendix A.

(c) Accuracies.

Using the above system for gas analysis when calibrated gave the following accuracies for gas concentration measurements :-

For CO, CO_2 and H_2O	above 5,000 ppm	error 1%	mean
	1,000 - 5,000 ppm	error 2%	"
	250 - 1,000 ppm	error 5%	"
	below 250 ppm	error 10%	"
For hydrogen	above 5,000 ppm	error 1%	"
	2,500 - 5,000 ppm	error 2%	"
	500 - 2,500 ppm	error 5%	"
	below 500 ppm	error 10%	"

Other accuracies for weighing and for HCl measurement will be discussed in the text.

(d) Materials used

graphite Hopkins and Williams synthetic graphite powder 99% +100 mesh

sugar charcoal ash about 0.1% -22 +160 mesh

coke Ord. Johannesburg coke -100 +200 mesh

coal Generator Nuss V +100 mesh

cuprous chloride Analar more than 97% CuCl

sodium chloride Analar more than 99.9% NaCl powder

copper electrolytically refined +200 mesh

helium after urification all exce t nitro en less than one art in 10^7

(e) Reactions studied.

A. Steam-coke reactions and the general effect of water vapour, temperature and cuprous chloride addition.

B. Steam-coke, coal, charcoal and graphite reactions and the effect of temperature on the steady state.

C. Steam-coke reactions and the effect of temperature at a longer gas residence time in the bed.

D. Steam-coke, charcoal and graphite reactions and the effect of residence time in the bed on the steady state.

E. Initial reaction of coke with water vapour at 800°C.

F. Initial reaction of coke plus 0.1 and 1.0% by weight of copper powder at 800°C with water vapour.

G. Initial reaction of charcoal and graphite with water vapour at 800°C.

H. Reaction of coke in a wet or dry helium gas flow when heated from 150-850°C.

I. Reaction of coke with salt additions in a wet or dry helium gas flow when heated from 150-850°C.

J. Reaction of charcoal when heated from 150-850°C in a dry helium gas flow.

K. Effect of pre-treatments on nitrogen evolution from coke when heated from 150-850°C.

L. Reaction of hydrogen with salt.

M. Methods of introducing known quantities of cuprous chloride vapour into a helium gas stream.

N. Effect of various cuprous chloride vapour pressures on the steam-coke reactions at 750°C.

O. Quantities of gases held on a coke surface in a dry helium gas flow and after reaction with water vapour.

P. Reduction of cuprous chloride by hydrogen adsorbed on a coke surface.

* * * * *

There now follows a detailed description of each experiment, including the reasons for the experiment, the experimental procedure followed and the results obtained; the experimental results are then discussed within their own context. This is repeated for each experiment, then, in chapter 4 , there is a general discussion of the results as a whole.

A. Steam-coke reactions and the general effect of temperature, initial water vapour concentration and of cuprous chloride addition.

The primary object of the A series of experiments was to determine the approximate quantities of gases involved in the various reactions so that the apparatus could be accurately calibrated. Thus the results obtained are only qualitative and the deductions made from them are relative. It was decided to heat the coke bed in steps to 1200°C in order to discover over what temperature range, the adsorbed gases on the coke surface, became unstable. The effect of an addition of cuprous chloride vapour was qualitatively followed by lowering an ampule of cuprous chloride into the reaction tube while the steam-coke reactions were in progress. The ampule consisted on a long, thin crucible, filled with cuprous chloride, and suspended on a platinum wire.

Experiment A1 A three centimetre bed of coke was held by a silica wool plug in the centre of a Mk I reaction tube and was heated in a flow of dry helium. The furnace temperature was set for short periods at 200, 400, 800, 1000 and 1100°C; it was then left overnight at 1100°C and subsequently raised to 1200°C for a brief period before being set at 700°C. Gas analyses were taken at each temperature. Water vapour at a concentration of 1260 ppm in helium was then passed through the bed at 700°C, the effluent gases were analysed and the water vapour concentration was then raised to 3200 ppm. After a while the temperature was raised to 800°C and the reaction was then terminated. In each run the empty tube linear velocity of the helium was 80 cm/min which gave a gas residence time in the bed of 0.75 seconds.

Results. At 200 and 400°C the concentrations of carbon dioxide and water vapour being initially evolved were large but decreased rapidly with time. At 400°C CH_4, C_2H_6 and other hydrocarbons were evolved. Hydrogen and carbon monoxide were first noticed in large quantities at 800°C but, after fifteen hours at 1100°C only carbon monoxide was being evolved and again at 1200°C only carbon monoxide was evolved. When water vapour was first introduced at 700°C , carbon monoxide and carbon dioxide were evolved in the ratio of approximately 2.7:1 (the equilibrium value is≈1:1) and when the water vapour concentration was increased the CO/CO_2 ratio began to decrease

and unreacted steam was detected for the first time. The unreacted steam concentration rose steadily with time to about 50% of the incoming steam concentration. When the temperature was raised to 800°C the CO/CO_2 ratio rose sharply and the unreacted steam concentration dropped rapidly and hydrogen in small quantities was detected for the first time some three hours after water vapour was first introduced into the system. The reaction vessel broke on removal from the furnace mainly because of serious devitrification of the silica where the coke had been in contact with it. Deposits of tars and oils had taken place at the cooler end of the reaction tube and off-white and brown powders were also deposited there.

Experiment A2 A two centimetre bed of coke was held in a Mk I reaction tube in a flow of dry helium at 1000°C until the exhaust gases only contained very small quantities of hydrogen and carbon monoxide (less than 100 ppm). The bed temperature was then lowered to 800°C and water vapour at a concentration of 20,000 ppm was passed through the coke bed at a empty tube linear velocity of 80 cm/min giving a residence time in the bed of about half a second. The temperature was changed to 700°C then to 750, 850 and then back to 800°C and the effluent gases were analysed for carbon monoxide, carbon dioxide and hydrogen.

At the end of this series of experiments an ampule containing cuprous chloride was lowered into the reaction tube until its temperature was at 750°C though the bed temperature was 800°C. (estimated CuCl temp° from fig.5)

Results. As the temperature of the bed was raised so the concentrations of the effluent gases increased. However it was noticed that at any one particular temperature the concentration of any particular species in the gaseous phase altered slowly with time. Thus the average gas concentration values of the first experiment at 800°C are different from the results obtained 300 hours later at the same temperature. The carbon monoxide values are similar however the concentrations of hydrogen and carbon dioxide have both slightly fallen.

The most interesting results however, occurred when gaseous cuprous chloride was introduced into the system. Large increases in the concentrations of

ever this was only a transitory effect and the concentrations of hydrogen and carbon dioxide quickly fell to their previous values. Carbon monoxide concentration however, only fell to twice its previous value. The highest concentration values reached corresponded to 5 times the previous value for carbon monoxide and carbon dioxide, and 10 times the previous value for hydrogen. The most striking effect however, occurred in the methane content of the effluent gases. During the period upto the introduction of cuprous chloride, methane was present at an approximate concentration of 100 ppm but immediately after the cuprous chloride addition this value increased by a factor of over 500 times but then it rapidly fell again to its previous value.

After the experiment it was found that 0.1 gms of cuprous chloride had been evapourated from the crucible and copper was observed to be deposited on the uppermost surface of the coke bed.

DISCUSSION

Experiment A1 The initial surges in the concentrations of water vapour and carbon dioxide when the bed was heated from 20°C to 200°C and again from 200°C to 400°C, suggest that these two gaseous species are not strongly adsorbed by coke and are thus easily driven off on heating. When the bed was heated from 400°C to 800°C and from 800°C to 1000°C very little water vapour or carbon dioxide was evolved, therefore this suggests that when heating coke from room temperature to 1000°C most of the water vapour and carbon dioxide contained by the coke, will be desorbed from the surface when the temperature of the bed has reached 400°C.

The hydrocarbons, which were first detected when the bed temperature was raised to 400°C but were principally evolved between 400°C and 800°C, consisted mainly of methane with some ethylene, ethane and acetylene. These were recognised from their relative elution times on the 'poropak' column. When the bed was heated from 800°C to 1000°C, of these, only methane was detected and so when a coke bed is heated to 1000°C the hydrocarbon products are mainly evolved in the temperature range 400°C to 800°C.

Carbon monoxide and hydrogen were first noticed when the bed temperature approached 800°C and the concentrations of each gas were high. Also as the bed temperature was raised from 800°C to 1000°C more hydrogen and carbon dioxide were detected.

Thus , this suggests that hydrogen and oxygen, held as CO, are more strongly adsorbed than are carbon dioxide and water vapour.

The initial higher-than-equilibrium value of the CO/CO_2 ratio at the lower water vapour pressure is thought to be due to the dominance of the primary reduction of water vapour by :-

$$C + H_2O = CO + H_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

over the secondary reduction of :-

$$CO + H_2O = CO_2 + H_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

As the water vapour concentration rose so the competition for water vapour between CO and C lessened and the CO/CO_2 ratio decreased from its higher-than-equilibrium value. Unreacted steam was now detected as a steady state was approached. Then, when the temperature rose in the system, this upset the balance of the primary and secondary reactions and the dominance of the primary was resumed and the CO/CO_2 ratio rose sharply as the unreacted water vapour concentration dropped.

The delayed appearance of hydrogen in the gas stream, three hours after reaction initiation, suggests that it is strongly adsorbed by the coke and only when the coke surface has achieved a certain saturation with hydrogen, does it appear as a gaseous product.

At 1100°C a steady concentration of carbon monoxide was observed in the effluent gas stream. This is thought to be a product of the reduction of silica by the coke since there was evidence of attack on the silica where it had been in contact with the coke.

For the partial reduction to silicon monoxide :-

$$C + SiO_2 = SiO_{(g)} + CO \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(16)$$

From the JANAF[62] tables it can be calculated that at 1100°C at equilibrium

$$P_{CO} = P_{SiO} = 1.5 \times 10^{-4} \text{ atmos.}$$

For the full reduction to silicon :-

$$2\,C + SiO_2 = Si + 2.CO \quad \ldots\ldots\ldots\ldots\ldots\ldots(17)$$

The calculated value of P_{CO} at equilibrium is 2.88×10^{-4} atmos.

For silicon carbide formation :-

$$3\,C + SiO_2 = SiC + 2.CO \quad \ldots\ldots\ldots\ldots\ldots\ldots(18)$$

The equlibrium value of P_{CO} was calculated as 3.74×10^{-3} atmos.

Thus any of the above reactions could be responsible for the production of carbon monoxide. However the presence of off-white to brown deposits above the tars, that is,at a higher temperature are thought to be the condensation products of silicon monoxide. Thus reaction (16) is thought to be the main producer of carbon monoxide at 1100°C.

Experiment A2 As would be expected , increasing the reaction temperature had the general effect of increasing the rate of the primary reduction of water vapour to give hydrogen and carbon monoxide. Since there was an excess of water vapour the rate of the secondary reduction was also increased, giving rise to an increase in the concentration of carbon dioxide in the effluent gas stream. However with increasing time the 'steady state' values of the product gases decreased slightly. This could be due to either the reaction of water vapour having the effect of 'healing' or 'sealing' the sites at which water vapour reacts, or to the fact that as water vapour reacts, the bed is gasified by the reaction and so the mass of coke decreases with time. Since the mass decreases the residence time of the water vapour in the bed also decreases and so the steady state generated at any one temperature may be a function of residence time .

The transient surge in the gas concentrations when cuprous chloride vapour was introduced into the system indicates that the initial deposition of copper on a coke surface by reduction of the chloride by hydrogen, has the effect of suddenly liberating some of the adsorbed gases. The continuous reduction of the chloride vapour has the effect of increasing the rate of the primary reduction of water vapour. Hence there is an increase in the concentration of carbon monoxide however any increase in the hydrogen conc-

entration is not noticed since this extra hydrogen is consumed in the cuprous chloride reduction to form hydrogen chloride. Since it was observed that the copper deposited mainly on itself, then it can be assumed that when it does so, this has the effect of increasing the water vapour reduction to such an extent that the extra hydrogen produced is equivalent to the rate of arrival of cuprous chloride. Thus the hydrogen concentration in the effluent gas stream remains unaltered at the pre-cuprous chloride level. The momentary large production of methane is thought to be due to the depositing copper displacing methane from the coke surface by weakening the surrounding C-C bonds. It is well known that a transition metal is capable of catalysing methane production from carbon and hydrogen. This method together with the gaseous reaction of carbon monoxide or dioxide with hydrogen, to give methane and water vapour over a nickel or cobalt catalyst at 400°C , are standard methods[161] for the preparation of methane. The gaseous reactions however, are temperature limiting since at 1200°C , methane in contact with carbon dioxide and water vapour produces hydrogen and carbon monoxide in the presence of a nickel catalyst. This is a standard method for the industrial preparation of 'endothermic gas' [162]. Thus a transition metal, by virtue of its unfilled 'd' sub-shell has some electronic effect on the bonding in a carbon matrix. Depositing copper could disrupt the surface bonding to produce methane by weakening the C-C bonds rather than the C-H bonds. The methane produced has to pass through the rest of the coke bed and so will decompose to hydrogen and carbon to a certain extent. Since the C-C bonds were weakened by the copper, carbon monoxide and possibly dioxide would be expected to be liberated and this was found to be so. However as copper was seen to deposit mainly on copper these gas liberation effects will only continue as long as the copper is depositing on coke, that is during the first few minutes of the reaction.

It was seen from the A series of experiments that coke must be degassed at 1000°C in order to achieve a steady system , with no gas evolution from the coke which would interfere with other effects that were under study.

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B. Steam-coke, coal, charcoal and graphite reactions and the effect of temperature on the steady state gas concentration values.

The aim of the B series of experiments was to obtain a quantitative and qualitative insight into the range of reactivity of four types of carbon and to study the effect of temperature on this reactivity. Also it was hoped to acquire knowledge of the secondary reduction of water vapour by carbon monoxide.

The A series of experiments had shown that degassing of coke at 1000°C was a neccessary prerequisite for there to be a minimal evolution of gaseous matter from the coke. Therefore this pre-treatment was a standard procedure for all the carbon types studied in this series of experiments. Ideally the carbon matter should be degassed at a much higher temperature, however the limitation of 1000°C was observed since, above this temperature, devitrification of the silica reaction vessel became a major problem.

It was decided that, for these experiments, a bed of constant volume should be employed and so all the reaction tubes were filled with carbon material to a depth of three centimetres. It was found that this volume of coke weighed 2.33 gms. To avoid errors due to packing, the bulk density of each material was measured by weighing a constant volume, and then, knowing that a three centimetre bed contains 2.85 cc of material, the weights required of each carbon type were calculated. The packing method then consisted of pouring the set weight of material into the reaction vessel and tapping the tube until the bed depth was three centimetres. The gas residence time was calculated for each bed; in each case it was approximately three-quarters of a second at 800°C.

Experiment B1 The bulk density of the coke was measured then a three centimetre deep bed of coke was preheated at 1000°C for 72 hours to rid the coke of the volatile content such as hydrocarbons, moisture and adsorbed gases. The temperature of the bed was then lowered to the initial starting temperature of 700°C and water vapour was then introduced into the gas stream to give a concentration of 9600 ppm i.e. approximately 1%. Readings

were taken until the values obtained for each gas concentration were constant over a 10 hour period ,the reaction was then assumed to have reached its steady state. The procedure was repeated for bed temperatures of 750, 800,850 and 900°C. The empty tube linear velocity in all these runs was approximately 80 cm/min giving a residence time in the bed of 0.75 seconds. Since these runs lasted over a period of several days, and coke was being constantly oxidised, it was to be expected that the bed depth decreased with time, and indeed when the reaction tube Mk I was removed from the furnace it was noticed that the bed depth had decreased from three to two cms.

Experiment B2 The method employed in this experiment was exactly the same as used in experiment B1 but the charge material for the reaction tube Mk I was graphite and the temperatures at which the steady state was studied were 700,800,850,900,950 and 1000°C.

Experiment B3 The same method was employed in this experiment as in B1 but sugar charcoal was used as the bed material and the steady state was studied at 600,650,700,750,800 and 850°C.

Experiment B4 The method employed was the same as in experiment B1 but with a bed of coal and the temperatures at which the steady state was studied were 750,800,900,1000 and 1100°C

Results As well as the concentrations of the exhaust gases, the mass balances at each temperature are given in tables 3 and 4 and were calculated as follows :-

$$\text{Oxygen balance} = \frac{\text{ppm CO} + 2\times\text{ppm } CO_2 + \text{ppm } H_2O_{out}}{\text{ppm } H_2O_{in}} \times 100\%$$

$$\text{Hydrogen balance} = \frac{\text{ppm } H_2 + \text{ppm } H_2O_{out}}{\text{ppm } H_2O_{in}} \times 100\%$$

Also the apparent activity of the carbon a_c was calculated as follows :-

for $$H_2O + C \longrightarrow CO + H_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

the equilibrium constant K_5 can be written :-

TABLE 3

EXHAUST GAS ANALYSES FOR EXPERIMENTS B1 AND B2

COKE bed residence time 0.75 seconds water vapour concentration 1%					
BED TEMPERATURE	700°C	750°C	800°C	850°C	900°C
HYDROGEN	10 ppm	425 ppm	1450 ppm	3150 ppm	3250 ppm
WATER VAPOUR	9457 "	9088 "	8294 "	6379 "	6392 "
CARBON MONOXIDE	86 "	217 "	1018 "	2405 "	2620 "
CARBON DIOXIDE	30 "	101 "	200 "	312 "	325 "
OXYGEN BALANCE	101	99	101	99.3	100.5
HYDROGEN BALANCE	99	99	101	99	101
a_c	5.4×10^{-8}	2.8×10^{-6}	2.3×10^{-5}	8.0×10^{-5}	4.8×10^{-5}
$K_{6\ obs} / K_{6\ calc}$	2.15×10^{-4}	1.67×10^{-2}	3.12×10^{-2}	7.00×10^{-2}	7.95×10^{-2}
$K_{6\ obs}$	3.5×10^{-4}	2.2×10^{-2}	3.4×10^{-2}	6.5×10^{-2}	6.3×10^{-2}
GRAPHITE bed residence time 0.75 seconds water vapour concentration 1%					
BED TEMPERATURE	800°C	850°C	900°C	950°C	1000°C
HYDROGEN	90 ppm	160 ppm	500 ppm	1750 ppm	6310 ppm
WATER VAPOUR	9500 "	9500 "	9268 "	7708 "	3306 "
CARBON MONOXIDE	28 "	82 "	220 "	1640 "	6344 "
CARBON DIOXIDE	7 "	25 "	52 "	55 "	125 "
OXYGEN BALANCE	99.9	100	99.9	95.5	103
HYDROGEN BALANCE	99.8	100.6	102	98.5	100
a_c	5.6×10^{-8}	9.3×10^{-8}	4.2×10^{-7}	7.6×10^{-6}	1.46×10^{-4}
$K_{6\ obs} / K_{6\ calc}$	1.65×10^{-3}	5.6×10^{-3}	1.6×10^{-2}	2.55×10^{-2}	6.18×10^{-2}
$K_{6\ obs}$	1.80×10^{-3}	5.3×10^{-3}	1.27×10^{-2}	1.76×10^{-2}	3.76×10^{-2}

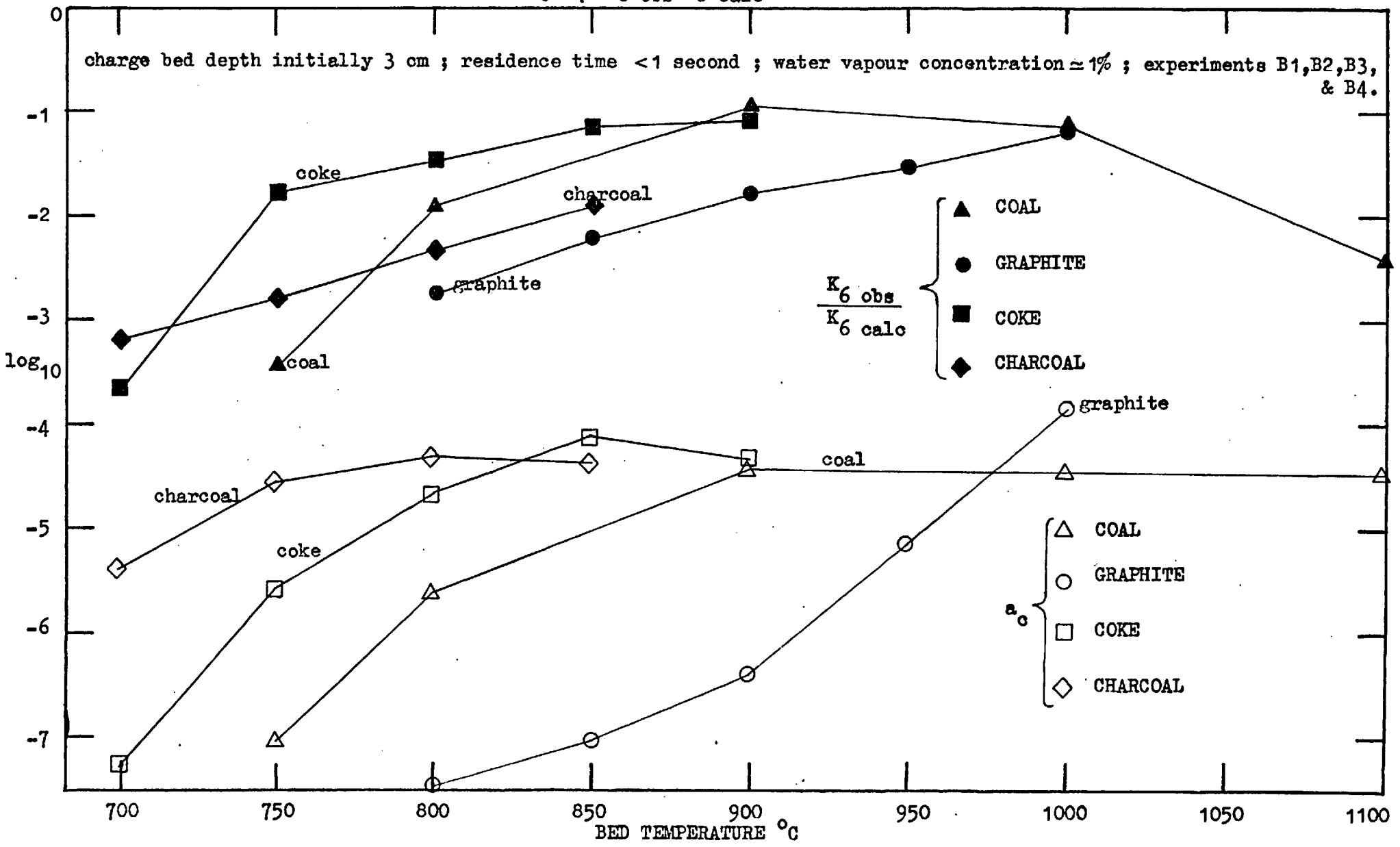
EXHAUST GAS ANALYSES FOR EXPERIMENTS B3 AND B4

TABLE 4

	CHARCOAL bed residence time 0.75 seconds water vapour concentration 1%					
BED TEMPERATURE	600°C	650°C	700°C	750°C	800°C	850°C
HYDROGEN	0 ppm	183 ppm	505 ppm	1014 ppm	1765 ppm	2228 ppm
WATER VAPOUR	9600 "	9487 "	8919 "	8790 "	7680 "	7296 "
CARBON MONOXIDE	44 "	147 "	445 "	897 "	1737 "	2183 "
CARBON DIOXIDE	0 "	3 "	8 "	16 "	37 "	82 "
OXYGEN BALANCE	100	100	98	101	99	100
HYDROGEN BALANCE	100	101	98	102	98	99
a_c		4.3×10^{-6}	1.6×10^{-5}	2.8×10^{-5}	5.2×10^{-5}	4.4×10^{-5}
$K_{6\ obs} / K_{6\ calc}$		2.0×10^{-4}	6.1×10^{-4}	1.5×10^{-3}	4.58×10^{-3}	1.2×10^{-2}
$K_{6\ obs}$		4.0×10^{-4}	1.0×10^{-3}	2.0×10^{-3}	5.0×10^{-3}	1.1×10^{-2}

	COAL bed residence time 0.75 seconds water vapour concentration 1%				
BED TEMPERATURE	750°C	800°C	900°C	1000°C	1100°C
HYDROGEN	100 ppm	480 ppm	3150 ppm	4100 ppm	4700 ppm
WATER VAPOUR	9500 "	9000 "	6500 "	5500 "	4500 "
CARBON MONOXIDE	40 "	350 "	2390 "	3800 "	5140 "
CARBON DIOXIDE	17 "	81 "	375 "	200 "	10 "
OXYGEN BALANCE	99	99	100	101	100
HYDROGEN BALANCE	100	99	100	100	96
a_c	10×10^{-8}	2.5×10^{-6}	4.2×10^{-5}	3.4×10^{-5}	3.4×10^{-5}
$K_{6\ obs} / K_{6\ calc}$	3.0×10^{-4}	1.1×10^{-2}	9.6×10^{-2}	6.4×10^{-2}	3.7×10^{-3}

FIGURE 9 PLOT OF a_c AND $K_{6\ obs}/K_{6\ calc}$ VERSUS BED TEMPERATURE.



$$K_5 = \frac{P_{CO} \times P_{H_2}}{a_c \times P_{H_2O}} = \exp\left(-\frac{\Delta G^\circ}{RT}\right) \quad \ldots\ldots(12)$$

$$\therefore \quad a_c = \frac{P_{CO} \times P_{H_2}}{K_5 \times P_{H_2O}} \quad \ldots\ldots(13)$$

by substituting ΔG° values from the JANAF[62] tables into (12) and then by substituting the value of K_5 so obtained as well as the observed concentration values into (13), the apparent activity of the carbon a_c can be calculated. From the water gas shift reaction :-

$$H_2O + CO \rightleftharpoons CO_2 + H_2 \quad \ldots\ldots(6)$$

$$K_{6\ \text{observed}} = \frac{P_{CO_2} \times P_{H_2}}{P_{CO} \times P_{H_2O}} \quad \ldots\ldots(14)$$

$$K_{6\ \text{calculated}} = \exp\left(-\frac{\Delta G^\circ}{RT}\right) \quad \ldots\ldots(15)$$

by substituting the observed concentration values into (14) a value for $K_{6\ obs.}$ can be obtained, also from the JANAF[62] table values of ΔG° for the reaction, from equation (15) a value of $K_{6\ calc.}$ can be obtained. By dividing these two values to obtain $K_{6\ obs}/K_{6\ calc}$ this gives an idea of the approach to equilibrium of the observed reactions by the closeness of this new function to unity. These values together with those of a_c are given in tables 3 and 4 for coal, graphite, charcoal and coke. They are also plotted in $\log_{10}$ form against the bed temperature in figure 9 .

It can be seen from figure 9 that in general a_c increases in value with increasing bed temperature and that overall at 800°C say, charcoal is more reactive than coke, which in turn is more reactive than coal which then is more reactive than graphite. However in terms of the water gas reaction in the coal and coke experiments, equilibrium was more closely approached than for either graphite or charcoal; and apart from coal at high temperatures, the approach to equilibrium is greater the higher the bed temperature. The surprising result of these experiments is the very low values of a_c.

DISCUSSION

The B series of experiments was an attempt to measure the effect of temperature on carbon reactivity towards water vapour.

From the mass balances in tables 3 and 4 it can be seen that the results are consistent with stoichiometric reduction of water vapour. The apparent inconsistency in the results is that the generally rising values of the apparent activity of carbon appear to level off and in some cases decrease at the higher temperatures. This is contrary to the expected increase in reactivity with increasing temperature. The only valid explanation for this discrepancy is that since in any one experiment, the mass of the bed is steadily decreasing with increasing time. Therefore, as the experiments were performed in order of rising temperature, the mass of the carbon bed was a minimum at the highest temperature. Thus it appears that carbon gasification at low residence times is a strong function of residence time. Also the approach to equilibrium in the secondary reduction of water vapour may be similarly affected so that the value of these experiments is limited.

The reactivity of the carbon type increases from graphite, through coal and coke to charcoal for the primary reduction of water vapour. This reactivity increases as a function of increasing temperature. The secondary reduction of water vapour however does not show the same sequence of reactivity and the behaviour of coke and coal more closely approaches equilibrium at any one temperature than does the behaviour of graphite or charcoal. This could be explained by the presence and possible catalytic nature of ash constituents in the coke and coal.

It would be expected that , if the secondary reduction were purely a vapour phase reaction , then all four plots would be similar. Since they are not it is suggested that this reaction takes place on and is affected by the carbon surface. This reaction is also a function of temperature and the approach to equilibrium appears to increase with increasing temperature. However, coal at higher temperatures shows a marked departure away

from equilibrium. This could be a significant temperature function or a possible result of the decreasing residence time at higher temperatures. It is noted from these experiments that the apparent activity of carbon a_c, is very low in the systems considered , 10^{-4} to 10^{-7} , and it appears to be a strong function of gas residence time in the bed when the gas residence time is of the order of one second.

Thus from these experiments, it was found that the steady state achieved in the system was far removed from true thermodynamic equilibrium; the thermodynamic equilibrium value of a_c should be unity.

Since the gas residence time appeared to have a considerable influence on the value of a_c it was decided that an experiment should be carried out at a much larger value of gas residence time. To increase the value of gas residence time, either the bed depth could be lengthened or the gas flow rate could be lowered. It was decided that to achieve a significant increase in the gas residence time, both methods should be used. Since this work is based on coke as the main carbon material, it was the charge material in the next experiment.

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C. Steam-coke reactions and the effect of temperature at a longer gas residence time in the bed.

Experiment C1 was performed at a substantially increased gas residence time, this was achieved by increasing the bed depth from three to thirteen centimetres and by reducing the gas flowrate. It was hoped to discover the effect of increasing the residence time, from less than a second to seventeen seconds, on the coke reactivity and on the approach to equilibrium of the secondary reaction.

Experiment C1 A deeper bed of 13½ centimetres of coke was heated at 1000°C in dry helium for about 50 hours in a Mk I reaction tube. The temperature was then lowered to 700°C and water vapour was introduced into the system at a concentration of 9600 ppm. Steady state concentration values of the effluent gases were obtained at temperatures of 700, 750, 800, 850 and 900°C. The gas residence time in the bed was calculated to be 17 seconds at 800°C. This increases, because of the temperature increase, to 18.7 at 900°C and falls to 15.5 at 700°C.

Results The concentration values are given in table 5 together with the oxygen and hydrogen balances as well as the values of a_c and $K_{6\ obs}/K_{6\ calc}$. The latter two values are plotted in $\log_{10}$ form in figure 10 together with the results of experiment B1 against bed temperature.

It can be seen from figure 10 that at a longer gas reidence time in the bed the values of a_c are higher at each temperature, but that the difference in these values decreases with increasing temperature. The behaviour of the $K_{6\ obs}/K_{6\ calc}$ plot for the longer gas residence time however is totally opposite to that of the low gas residence time plot. The approach to equilibrium in experiment C1 is initially high and then decreases at an increasing rate with increasing temperature. In experiment B1 at the lower residence time the approach to the water gas equilibrium is initially low but increases at a decreasing rate with increasing temperature.

TABLE 5 EXHAUST GAS ANALYSES FOR EXPERIMENT C1

COKE bed residence time 17 seconds at 800°C Water vapour concentration 1%					
BED TEMPERATURE	700°C	750°C	800°C	850°C	900°C
HYDROGEN	700 ppm	1945 ppm	3422 ppm	4300 ppm	4750 ppm
WATER VAPOUR	9000 "	7600 "	6300 "	4900 "	3800 "
CARBON MONOXIDE	350 "	733 "	2180 "	4520 "	5712 "
CARBON DIOXIDE	150 "	560 "	510 "	125 "	10 "
OXYGEN BALANCE	100	98	99	101	99
HYDROGEN BALANCE	100	99	101	96	90
a_c	10×10^{-8}	5×10^{-5}	1.6×10^{-4}	2.6×10^{-4}	2.9×10^{-4}
$K_{6\ obs}/K_{6\ calc}$	1.67×10^{-1}	1.46×10^{-1}	1.18×10^{-1}	2.6×10^{-2}	2.8×10^{-3}

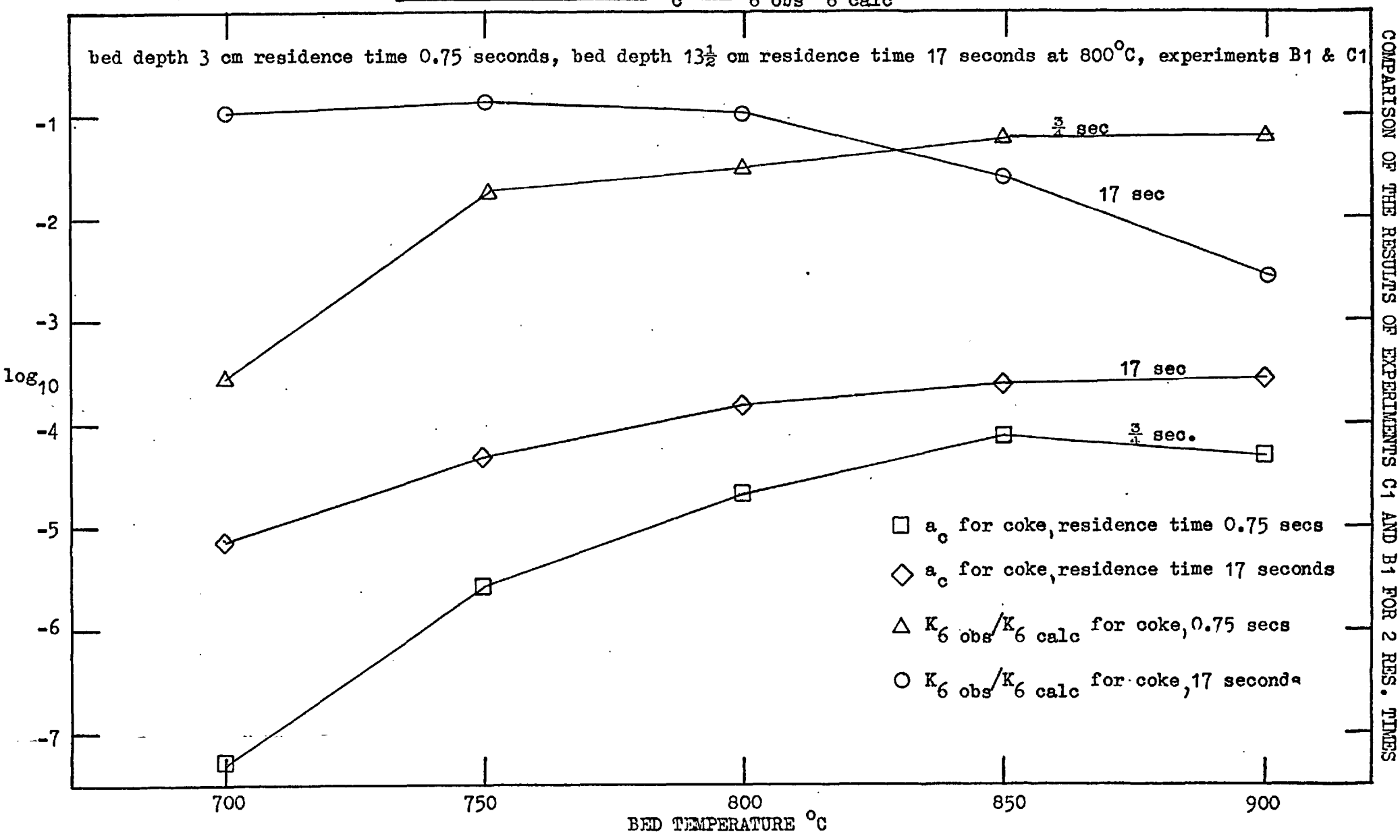
EXPERIMENT C1

TABLE 6 EXHAUST GAS ANALYSES FOR EXPERIMENT D1

COKE bed temperature 750°C water vapour concentration 1%						
GAS RESIDENCE TIME	0.75 secs	17 secs	34 secs	68 secs	137 secs	274 secs
HYDROGEN	425 ppm	1945 ppm	2388 ppm	2700 ppm	2907 ppm	3100 ppm
WATER VAPOUR	9080 "	7700 "	7200 "	6800 "	6500 "	6400 "
CARBON MONOXIDE	217 "	733 "	1036 "	1496 "	2233 "	2810 "
CARBON DIOXIDE	101 "	560 "	656 "	654 "	500 "	167 "
OXYGEN BALANCE	99	100	100	100	101	99
HYDROGEN BALANCE	99	99	99	99	98	98
a_c	2.8×10^{-6}	5.0×10^{-5}	1.0×10^{-4}	1.6×10^{-4}	2.8×10^{-4}	3.7×10^{-4}
$K_{6\ obs}/K_{6\ calc}$	1.67×10^{-2}	1.47×10^{-1}	1.6×10^{-1}	1.3×10^{-1}	7.7×10^{-2}	2.6×10^{-2}

EXPERIMENT D1

FIGURE 10 PLOT OF a_c AND $K_{6\ obs}/K_{6\ calc}$ VERSUS BED TEMPERATURE



DISCUSSION

The comparison of this experiment's results with those of the previous experiment (B1), show that both the apparent activity of carbon and the approach to equilibrium of the secondary reaction are strong funotions, not only of temperature, but also of gas residence time in the bed.

From table five it will be seen that the mass balances are again consistent with stoichiometric reduction of water vapour; however at the higher temperatures of 850°C and 900°C the hydrogen balances are low. This is thought to be due to methane production, since it is not included in the hydrogen mass balances. Thus it appears that at a longer gas residence time at higher temperatures, that either hydrogen is reacting with the coke or that methane is a product of a steam-coke reaction.

From figure 10 it can be seen that at a longer gas residence time, the apparent activity of carbon is at least a factor of 10 higher than at the lower gas residence time. The value of a_c increases with temperature but at a decreasing rate, therefore when water vapour remains longer in contact with a coke bed, its reduction is more complete.

The approach to equilibrium of the secondary reaction at a longer gas residence time is much closer at lower temperatures than it is at higher ones. Thus at a longer gas residence time in the coke bed the production of carbon dioxide decreases, whereas at the lower gas residence time it increases, with temperature.

It was now decided, that since gas residence time was a major parameter of the steam-carbon system, that all the carbon types under study should be reacted with water vapour at various gas residence times, but at one specific temperature.

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D. Steam-coke, charcoal and graphite reactions and the effect of gas residence time on carbon reactivity

This series of experiments were performed at one specific temperature, 750°C, but the gas residence time in the bed was varied by changing the helium flow-rate. It was hoped to confirm the previous series' deduction, that at low gas residence times, the reactivity of carbon is a sensitive function of gas residence time.

Experiment D1 10.5 gms of coke were packed into a Mk I reaction tube to give a bed depth of 13.5 cms. The bed was held at 1000°C in a stream of dry helium for about 50 hours. The temperature was then lowered to 750°C and water vapour was introduced into the helium gas stream to give a concentration of 1%. Readings were taken of the effluent gas until a steady state was achieved; then the helium flow rate was lowered to give an increased gas residence time. Again readings were taken until a steady state was reached. This procedure was repeated for several values of gas residence time from $\frac{3}{4}$ of a second to 274 seconds.

Experiment D2 5.9 gms of charcoal were packed into a Mk I reaction tube and then was treated in a similar manner to that of D1. The range of gas residence studied in this case was from 0.8 seconds to 352 seconds.

Experiment D3 8.2 gms of graphite were packed into a Mk I reaction tube and, as in D1 and D2, this gave a bed depth of 13.5 cms. The method employed was exactly the same as in D1.

Results Table 6 (p.58) contains the gas analyses from the coke experiment, D1. Table 7 contains the gas analyses for the charcoal and graphite experiments, D2 and D3. The oxygen and hydrogen mass balances, together with the values of a_c and $K_{6\ obs}/K_{6\ calc}$, are also given in these tables. The steady state gas concentration values, at each value of gas residence time, are plotted in figure 11; the $\log_{10}$ values of a_c and $K_{6\ obs}/K_{6\ calc}$ are plotted against gas residence time in figure 12.

It can be seen from figure 11 that, with increasing gas residence time in the bed, all gas concentrations in the effluent gas stream, except the carbon

TABLE 7 EFFLUENT GAS ANALYSES FOR EXPERIMENTS D2 AND D3 vs RES. TIME

GRAPHITE bed temperature 750°C water vapour concentration 1%

GAS RESIDENCE TIME	0.8 secs	22 secs	44 secs	88 secs	176 secs	352 secs
HYDROGEN	28 ppm	626 ppm	871 ppm	1180 ppm	1650 ppm	2100 ppm
WATER VAPOUR	9600 "	9000 "	8700 "	8500 "	8000 "	7300 "
CARBON MONOXIDE	14 "	217 "	264 "	340 "	600 "	1099 "
CARBON DIOXIDE	7 "	209 "	287 "	374 "	471 "	600 "
OXYGEN BALANCE	100	100	100	100	99	100
HYDROGEN BALANCE	100	100	99	101	100	98
a_c	1.1×10^{-8}	4.18×10^{-6}	7.31×10^{-6}	1.31×10^{-5}	3.43×10^{-5}	8.76×10^{-5}
$K_{6\ obs}/K_{6\ calc}$	1.11×10^{-3}	5.09×10^{-2}	8.27×10^{-2}	1.16×10^{-1}	1.23×10^{-1}	1.19×10^{-1}

CHARCOAL bed temperature 750°C water vapour concentration 1%

GAS RESIDENCE TIME	0.8 secs	22 secs	44 secs	88 secs	176 secs	352 secs
HYDROGEN	1014 ppm	2512 ppm	3002 ppm	3356 ppm	3589 ppm	3788 ppm
WATER VAPOUR	8700 "	6800 "	6300 "	5900 "	5500 "	4800 "
CARBON MONOXIDE	897 "	2446 "	2782 "	3121 "	3574 "	4266 "
CARBON DIOXIDE	16 "	193 "	224 "	297 "	297 "	316 "
OXYGEN BALANCE	100	100	99	100	100	101
HYDROGEN BALANCE	101	97	97	96	95	89
a_c	2.90×10^{-5}	2.5×10^{-4}	3.67×10^{-4}	4.92×10^{-4}	6.46×10^{-4}	9.33×10^{-4}
$K_{6\ obs}/K_{6\ calc}$	1.58×10^{-3}	2.21×10^{-2}	2.91×10^{-2}	4.01×10^{-2}	4.22×10^{-2}	4.41×10^{-2}

FIGURE 11 GAS CONCENTRATION VERSUS RESIDENCE TIME EXPERIMENTS D1, D2 & D3

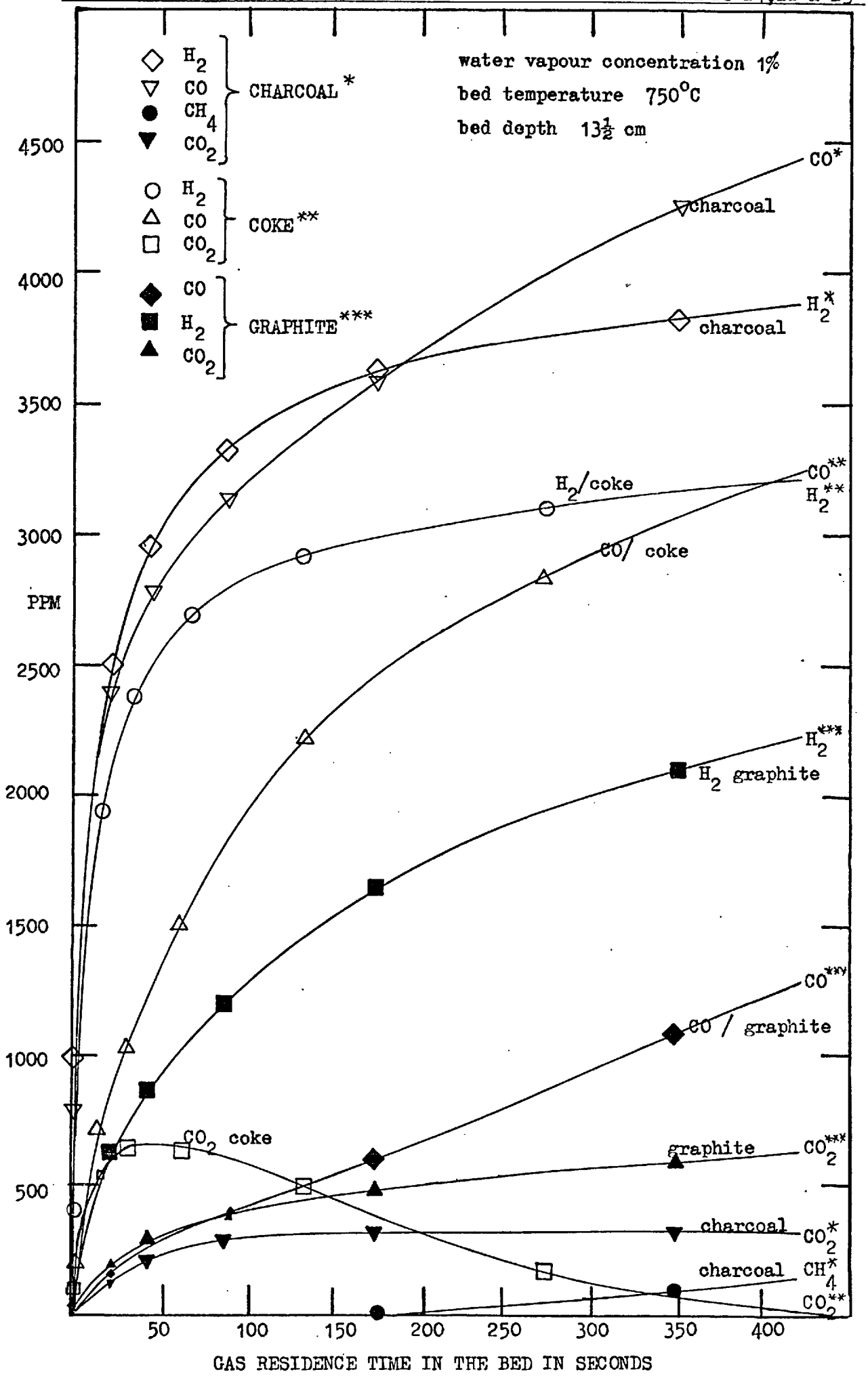


FIGURE 12 a_c AND $K_{6\ obs}/K_{6\ calc}$ VERSUS RESIDENCE TIME FOR EXPERIMENTS D1, D2 AND D3

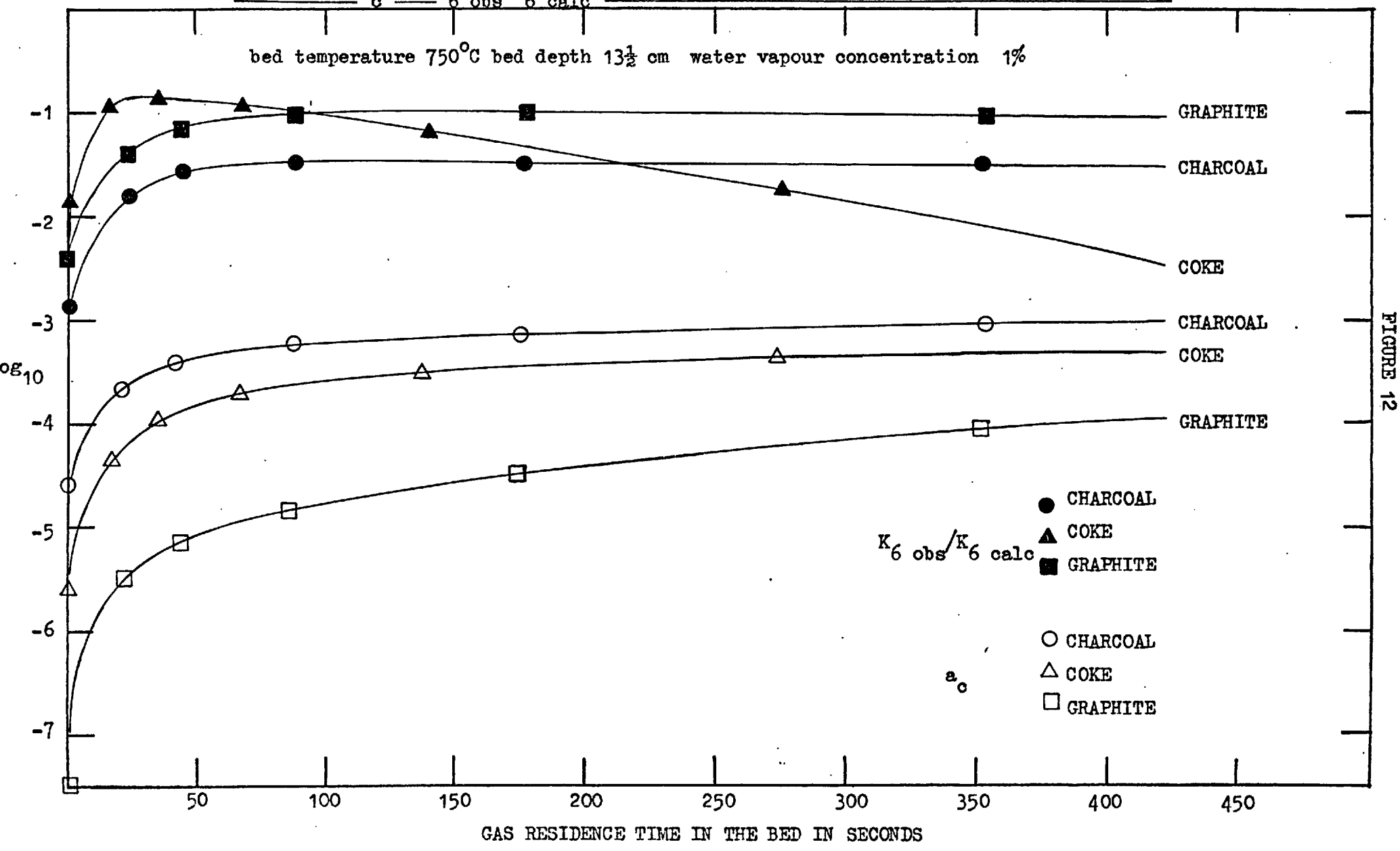


FIGURE 12

dioxide values for coke, increase. It will be noticed also that the methane concentration, while being minimal in most experiments, begins to make a significant appearance at longer gas residence times in the charcoal experiment. While differing in absolute value, the plots of hydrogen concentration, for coke and charcoal, appear similar in shape, as do the carbon monoxide concentration plots for the same materials.

From figure 12, it will be noticed that the above effects are emphasized in the similarity of the a_c plots, for coke and charcoal. Another similarity in shape is noticed for the K_6 ratio plots of graphite and charcoal. The coke plot, however, shows the effect of the decreasing values of carbon dioxide concentration with an increase in residence time, and so the K_6 ratio plot decreases with increasing residence time. The a_c plot for graphite shows the greater effect that gas residence has on the apparent activity of carbon, while the same plots for charcoal and coke, after an initial steep increase in value, show little variance with residence time . Similarly the K_6 ratio plots for graphite and charcoal, after an initial steep rise, remain virtually constant with increasing gas residence time in the bed. However the coke plot, after an initial rise to a maximum, decreases almost linearly with an increase in gas residence time.

DISCUSSION.

From the mass balances in tables 6 (p.58) and 7 (p.62), it is apparent that each result is consistent with the stoichiometric reduction of water vapour, however for charcoal, at high gas residence times, one of the reduction products was methane which does not appear in the mass balance equation, and so these balances are low at high gas residence times.

From figure 12, it is seen that the behaviour of the K_6 ratio plots, of graphite and charcoal, are virtually identical except that the values of K_{6obs}/K_{6calc} for graphite in $\log_{10}$ form, are consistently 0.5 above those for charcoal. Also , after the 100 second gas residence time, the two plots remain constant with increasing gas residence time. The constant value for graphite is 10^{-1} and for charcoal, it is $10^{-1.5}$.

The a_c plot for charcoal is consistently $\log_{10}$ 0.25 higher than that of coke and both plots seem to be exponentially approaching limits of 10^{-3} for charcoal and $10^{-3.25}$ for coke. The graphite plot of a_c, while differing in shape, also appears to be approaching an exponential limit of $10^{-3.5}$.

Thus from these experiments, as would be expected, as the residence time was increased to almost static conditions, so the values of a_c and the K_6 ratios also subtended towards definite limits. The only exception to this generalisation, is the K_6 ratio plot for coke which, with increasing gas residence time, decreased at a steady rate.

The difference in reactivity between coke, charcoal and graphite is thought to be due to the nature of the carbon surface. A detailed analysis of the steam-carbon reaction and the kinetics of that reaction, is made later in this work (see p. 172) and it is shown that the surface oxide $C'o$, is more stable on a carbon surface than is adsorbed carbon monoxide, (CO). Also, during the reaction with water vapour, both $C'o$ and hydrogen are adsorbed on the carbon surface, however it is extremely unlikely that water vapour exists, as such, on a carbon surface at the reaction temperatures of 700-850°C. It is also shown that the reaction mechanism is as follows :-

$$H_2 + C_f \longrightarrow (H_2O) \quad \ldots\ldots(19)$$

$$(H_2O) \longrightarrow Co + H_2 \quad \ldots\ldots(20)$$

$$Co \longrightarrow (CO) \quad \ldots\ldots(21)$$

$$(CO) \rightleftharpoons CO + n\,C_f \quad \ldots\ldots(23)$$

$$H_2 + C_f \rightleftharpoons (H_2) \quad \ldots\ldots(24)$$

$$CO + Co \rightleftharpoons (CO_2) \quad \ldots\ldots(25)$$

$$H_2O + Co \rightleftharpoons (CO_2) + H_2 \quad \ldots\ldots(26)$$

$$(CO_2) \rightleftharpoons CO_2 + n\,C_f \quad \ldots\ldots(27)$$

Where () indicates an adsorbed species, $C'o$ is the surface oxide, C_f is a free active site on the carbon surface, the value of n can be taken as unity. Also when the apparent activity of carbon is referred to, this should be more correctly named, the apparent activity of the free surface sites. Thus if the activity coefficient is assumed to be unity, then this is equal to

the number of active sites taking part in the water vapour reduction. So a_c can be read as a_{C_f} or $[C_f]$.

If carbon dioxide production was controlled by gaseous phase reactions then for the same degree of water vapour reduction for each carbon type, similar quantities of the product gases would be expected. From table 7 (p.62) , for charcoal, when the water vapour concentration has fallen to 8700 ppm, the concentrations of carbon monoxide and dioxide are 897 ppm and 16 ppm respectively;however for graphite at the same degree of water vapour reduction, the concentrations of carbon monoxide and dioxide are 264 ppm and 287 ppm. Similarly in the coke and charcoal experiments, when the water vapour concentration has fallen to 6800 ppm the concentrations of carbon monoxide and dioxide were 1496 ppm and 654 ppm for coke,and 2446 ppm and 193 ppm for charcoal. Therefore carbon dioxide production is a surface reaction and it is thought that its production is dependant on the concentration of Co on the surface as well as the concentrations of carbon monoxide and water vapour in the gas stream.

Catalysis of these reactions is a further consideration and, as coke contains ash constituents,it is expected that its reactions are more likely to be affected. One obvious effect,is the decline in the production of carbon dioxide at high residence times. It is thought that this is due to the positive catalysis of the reaction of carbon dioxide with carbon or, conversely, inhibitive catalysis of the reaction of carbon monoxide or water vapour with Co. Charcoal and graphite being virtually ash-free do not show the same effect.

Thus from this series of experiments it was found that Co and hydrogen can exist on carbon surfaces at reaction temperatures and it is proposed that,it is the quantity of these surface complexes together with the activity of the free surface sites,which decides the degree of reduction of water vapour. Also , in terms of activity of the free active sites, charcoal is more reactive than coke, which in turn is more reactive than graphite.

* * * * * * * *

E. Initial reactions of coke at 800°C with water vapour at values of gas residence time in the bed of $\frac{3}{4}$ and 17 seconds.

In the previous experimental series, it was found that Co and hydrogen exist on a carbon surface during its reaction with water vapour. It was now hoped to perform two experiments, with coke as a charge material, at two different gas residence times, in order to ascertain the actual quantity of these two species on the carbon surface. The coke beds were degassed at 1000°C to reduce the evolution of inherently contained gaseous species to a minimum, during the experiment.

The concentration of water vapour could not be included in the plots of the transient gas analyses, since it was discovered that water vapour adsorbs on the glass walls of the pipework leading from the furnace to the chromatograph injection valves. Heating tape was lagged around this piping but it failed to rectify the problem. Thus the concentration values obtained for water vapour are meaningless in all kinetic experiments and so , are only quoted in the steady state experiments' results.

In these experiments, the time taken for gas to pass from the gas inlet manifold to the injection valves, was measured by switching hydrogen into the gas stream at the manifold, and timing its appearance at the injection valves. Thus, it is assumed that when the flushing stream of helium is switched away, and the helium containing water vapour is switched into the system , the time taken for that water vapour or its reaction products to reach the injection valves , is the same as the time measured for hydrogen in an empty reaction tube but at the same temperature. Thus in experiment E2 when the helium flowrate at NTP was 8 ml/min and the bed depth was 13$\frac{1}{2}$ cms, the stop watch timing the experiment, was started 8 minutes after the water vapour was switched into the system at the manifold.

Experiment E1 2.33 gms of coke were held in a Mk I reaction tube at a temperature of 1000°C for about 50 hours in order to remove the volatile tars and other hydrocarbons. When only minute quantities of carbon monoxide (<10 ppm and hydrogen were being evolved from the bed, the temperature of the bed was lowered to 800°C and water vapour was introduced into the helium gas stream

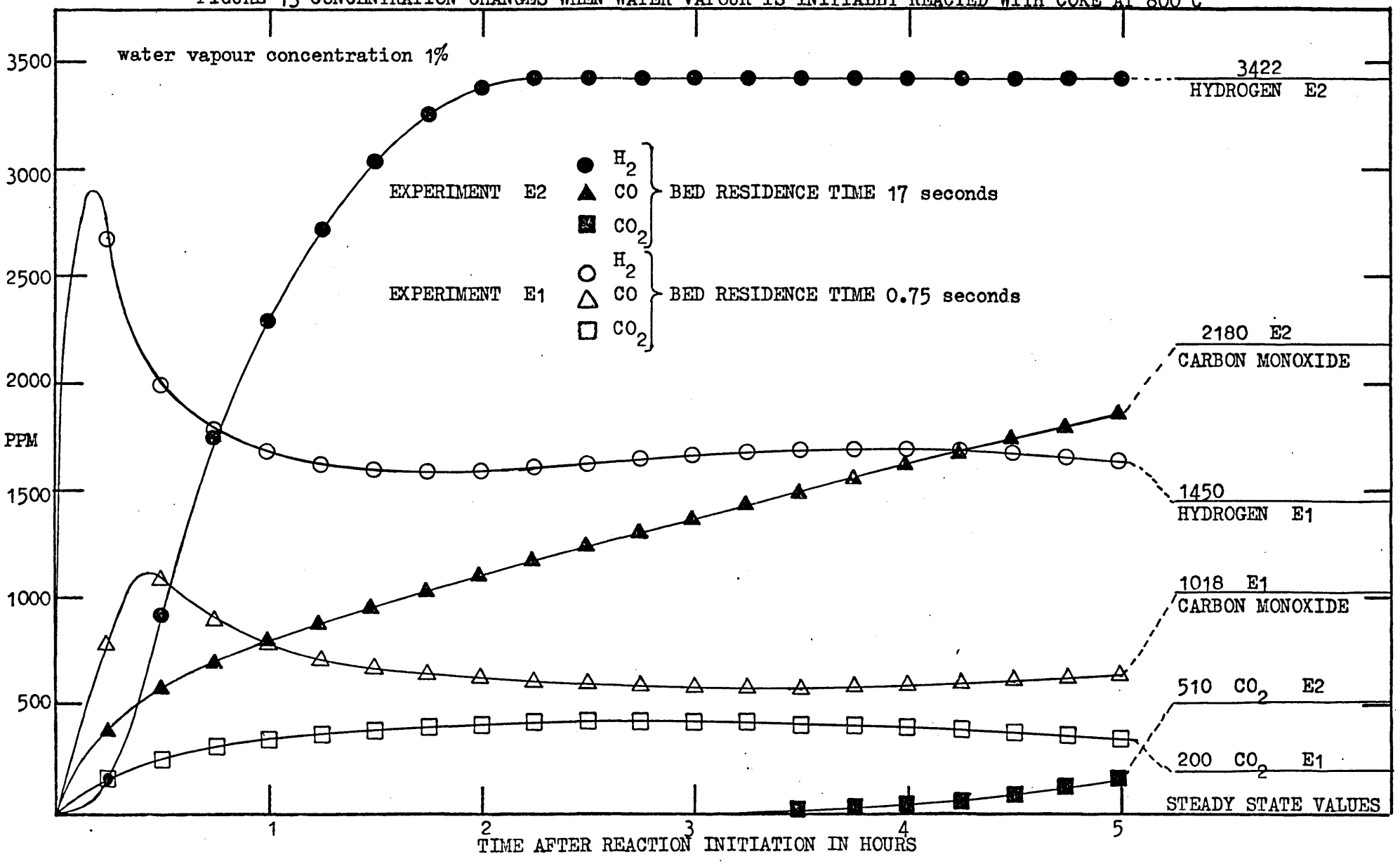
to give a concentration value of 1%. The concentration changes of the effluent gas stream were closely followed by sampling the exhaust gases every three minutes. The gas residence time in the bed was calculated to be $\frac{3}{4}$ secs.

Experiment E2 10.5 gms of coke were treated in a similar manner as in experiment E1, but the residence time was calculated to be 17 seconds.

Results In figure 13, the gas concentration values measured are plotted against time after the introduction of water vapour. For clarity the readings are plotted every fifteen minutes , whereas in fact, they were taken every three minutes. It can be seen that , at the lower gas residence time, the plots of carbon monoxide and hydrogen concentrations exhibit definite maxima in their shapes, then, having fallen away in value from their maxima, they still do not reach a steady state value, even five hours after the introduction of water vapour. In this same five hour period, the concentration of carbon dioxide in the gas stream slowly rose to almost 500 ppm, then slowly decreased in value. Thus in the period between two and five hours after the reaction initiation, the hydrogen plot rises and falls slighly; the carbon monoxide plot falls and rises slighly and the carbon dioxide plot increases in value slighly and then falls slowly with increasing time. From the concentration values at the five hour time point, hydrogen concentration fell 200ppm to its steady state value, carbon monoxide concentration rose 370 ppm to its steady state value and carbon dioxide concentration fell 175 ppm to its steady state value.

In complete contrast, no maxima were noticed in the results at the higher residence time, also the hydrogen concentration value reached its steady state value two hours after water vapour introduction. Also no carbon dioxide was detected in the first three hours of reaction. At the higher residence time the initial gas evolution was by no means as large as in the lower residence time experiment. After fifteen minutes of reaction hydrogen had only just appeared in the exhaust gases whereas in the lower residence time experiment the hydrogen concentration had reached its maximum and was falling. Similarly the carbon monoxide concentration in

FIGURE 13 CONCENTRATION CHANGES WHEN WATER VAPOUR IS INITIALLY REACTED WITH COKE AT 800°C



the exhaust gases was at 400 ppm in the higher residence time experiment , whereas in E1, after fifteen minutes of reaction, the carbon monoxide concentration was 850 ppm.

DISCUSSION

From figure 13 it can be seen in both instances,that there are subreactions involved because the instantaneous mass balances,for hydrogen and oxygen, do not suggest the same degree of water vapour reduction.

The differences in the concentration versus time plots for carbon monoxide and hydrogen at the two residence times are striking. In experiment E1, reactions 19 and 20 proceed rapidly giving rise to a large increase in the concentration of hydrogen in the gas stream. Reactions 21 and 23 also proceed but not as rapidly so that the rate of appearance of carbon monoxide in the gas stream is a less steep function of time than is hydrogen. Thus as equal amounts of hydrogen and carbon monoxide are generated, there must be an accumulation of $'Co'$ on the coke surface. Reaction 24 is now activated and hydrogen begins to adsorb onto the coke surface from the gaseous phase. The build up of $'Co'$ and (H_2) on the coke surface reduces the number of active sites at which water vapour can react so that the degree of reduction of water vapour decreases. The concentration of hydrogen in the gas stream is reduced by adsorption and by less being produced and so it falls to a reasonably steady value. The fall in concentration of carbon monoxide is due to the decrease in the degree of reduction of water vapour and so its rate of decrease is less steep than that of hydrogen. Carbon dioxide production is dependant on the concentration of $'Co'$ on the surface and as this steadily rises with time so the concentration of carbon dioxide in the gas stream also steadily rises. If carbon dioxide were a function of the gaseous concentration of carbon monoxide then it would be expected that their concentration plots would be similar in shape, but this is not so.

Thus after one hour of reaction the three concentration plots reach a reasonably steady state, however their values are still not those of the final steady state. There are slight but definite fluctuations in each

concentration plot and it is thought that this is due to the long delay in the setting up of steady state between the adsorbed and gaseous phases. Thus although hydrogen may have set up a steady state between itself, water vapour and carbon monoxide, carbon dioxide production from water vapour and C_o' is still on the increase and is producing hydrogen as a reaction product. This upsets the previous hydrogen steady state and so it has to readjust. This in turn upsets the steady state between C_o' and carbon monoxide and so it continues, all gas concentrations oscillating until the final steady state has been achieved. The surprising fact is that this process takes so long to achieve its steady state, this must be a function of the residence time since in experiment E2 the steady state has been achieved inside seven hours whereas in E1 this process takes at least twenty hours to come to the steady state.

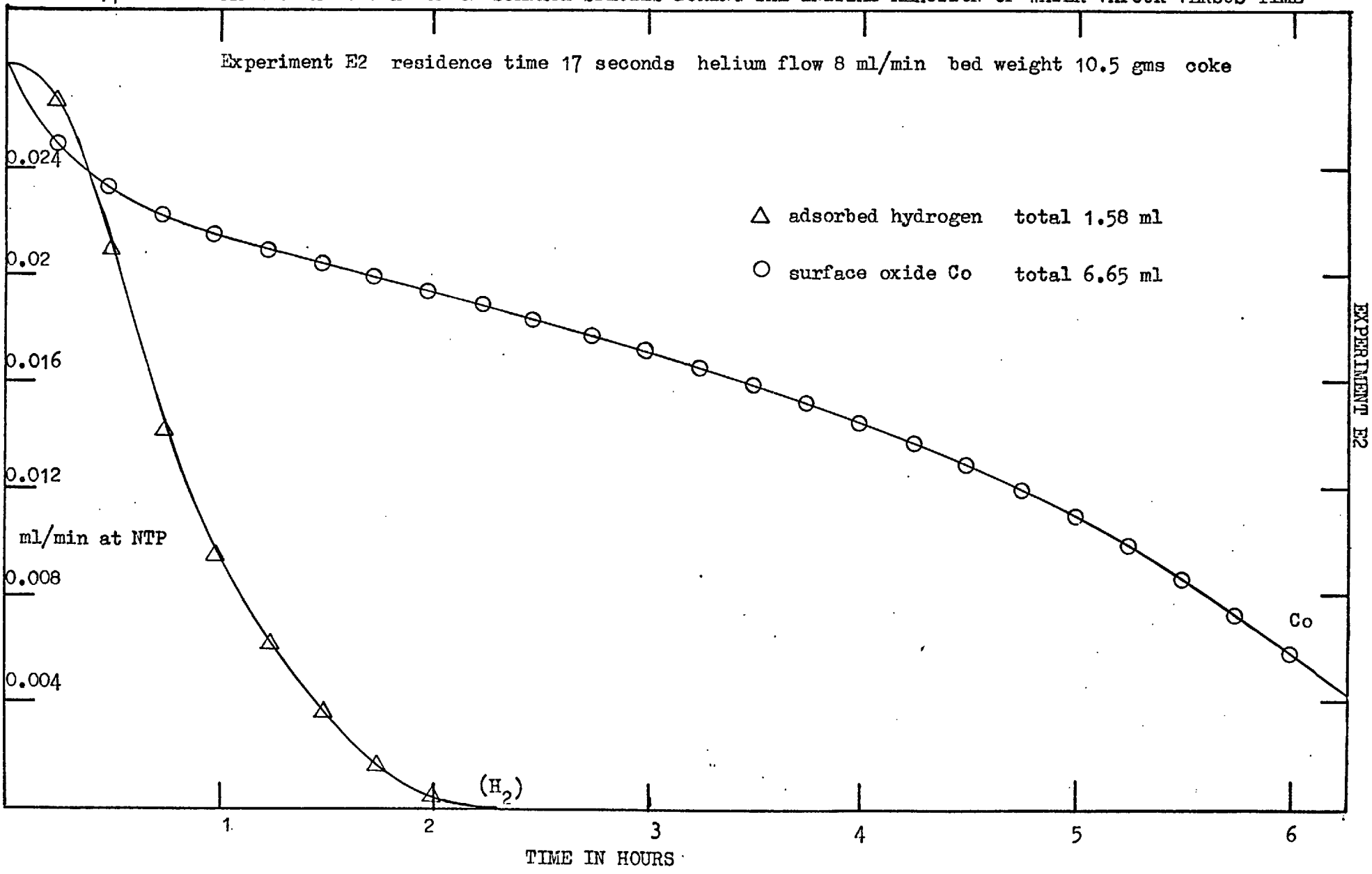
In experiment E2, the time spent by the product and reactant gases in the bed has increased by a factor of twenty-three. This has a significant effect on the sub-reactions involved. It is assumed that reactions 19 and 20 proceed rapidly, however reaction 24 is dominant and the rate of appearance of hydrogen in the gas stream is a strict function of the amount of adsorbed hydrogen on the coke surface. Therefore as the build up of (H_2) proceeds so the ooncentration of hydrogen in the gas stream steadily increases and after two hours the hydrogen systems have reached their steady state. The carbon monoxide behaviour reflects the ability of coke to adsorb more carbon monoxide as C_o' than it does hydrogen. Hydrogen and C_o' are being produced at the same rate but C_o' and adsorbed carbon monoxide are held on the surface. The rate of desorption of carbon monoxide is therefore smaller than that of hydrogen so its rate of appearance in the gas stream is a less steep function of time. Thus the amount of (H_2) needed at the steady state has been achieved within two hours however since much more C_o' is required for steady state conditions, so it takes much longer to achieve its neccessary concentration, six hours in fact.

The delay in carbon dioxide production is thought to be due again to a build up of sufficient Co on the coke surface before reaction with carbon monoxide or water vapour can take place. The plots on figure 13 are not representative of quantity since the ppm scale should be multiplied by the helium flowrate to give a scale of ml/min evolved. The NTP flowrate for E2 was 8 ml/min and for E1 it was 47 ml/min. Therefore the E1 plot, if multiplied by 5.9 would give a comparison of quantity with the E2 plot. Therefore according to the E2 results for carbon dioxide production, a sufficient concentration of Co on the coke surface has been achieved when the carbon monoxide gas concentration has reached about 1500 ppm. This assumes that the quantity of Co is directly related to the gaseous concentration of carbon monoxide. Therefore in the E1 experiment the C_o' concentration on the surface needed for carbon dioxide production has been achieved when the gas concentration has reached 1500/5.9 ppm = 254 ppm which, as can be seen from figure 13 is achieved within minutes. Thus carbon dioxide is produced almost immediately in experiment E1 whereas in E2 none appears for three hours.

In experiment E2, if it is assumed that water vapour reduction immediately achieves its steady state rate then the quantities of C_o' and (H_2) can be calculated by integrating a plot of rate of formation of these species versus time. The gaseous production rate when subtracted from the steady state rate will give this rate of accumulation of the adsorbed species. However it must be remembered that for the oxygen balance, the gaseous rate of carbon monoxide must be added to twice the gaseous rate of carbon dioxide production. From figure 14 it can be seen that the rate of accumulation of (H_2) is initially very high but this high rate rapidly decreases away to zero within two and a half hours. C_o' accumulation however is initially lower than for hydrogen, however after the twenty minute mark its rate of accumulation is higher and decreases at a slower rate than that of adsorbed hydrogen. Integration of these plots shows that 1.58 ml of hydrogen are adsorbed and 6.65 ml of C_o' are generated, both these species are stable at the reaction temperature of 800°C on the coke surface.

This same treatment cannot be applied to the E1 results since the initial

FIGURE 14 PLOT OF RATE OF ACCUMULATION OF SURFACE SPECIES DURING THE INITIAL REACTION OF WATER VAPOUR VERSUS TIME



rate of reduction of water vapour was much higher than the steady state rate. This may have been the case in experiment E2, but as the rate of appearance of the product gases never exceeded the steady state rate, it was possible to subtract them from the steady state rate. This is impossible for E1, however, in both cases, the amount of (CO) on the coke surface is much greater than the amount of (H_2).

From these experiments, it was found that both (CO) and adsorbed hydrogen are retained on the coke surface during the initial reaction with water vapour. Since , in a TORCO segregation chamber, the coke particles are covered with the deposited copper, it was decided to perform two experiments, in which copper powder was thoroughly mixed with the coke charge ; and the initial reaction of water vapour with this bed could then be studied to discover if the copper was responsible for any increase of adsorbed species on the coke surface.

The segregated copper from a TORCO plant is of such a particulate size and form, that its growth can only be attributed to copper deposition on copper. Thus, hydrogen must exist in quantity at the copper surface, in order to reduce the cuprous chloride vapour. The following experiments' aim was to discover if the amount of hydrogen, retained by the presence of copper in the coke bed, derived from the steam-coke reaction, could be responsible for possible cuprous chloride vapour reduction.

* * * * * * * * *

F. Initial reaction of coke plus 1.0 and 0.1 % by weight of copper powder at 800°C with water vapour at a gas residence time of 17 seconds.

The F series of experiments was performed to discover if the steam-coke reaction was catalysed, to produce more hydrogen, either in adsorbed or gaseous form, by the presence of physically admixed copper powder. Again, to reduce the amounts of inherently contained species in the coke, the beds were pre-heated to 1000°C.

Experiment F1 0.1% by weight of copper powder (electrolytic +200 mesh) was thoroughly mixed with coke and a 13½ cm deep bed of this mixture which weighed 10.517 ± 0.001 gms, was heated in a Mk I reaction tube at 1000°C for about 50 hours in a dry helium flow. The temperature of the bed was then lowered to 800°C and the flushing helium gas flow was switched out of the system and a flow of helium containing 1% of water vapour was switched into the system at the inlet manifold. The effluent gas was analysed every three minutes for three and a half hours. Readings were then taken periodically until a steady state had been achieved. The flowrate through the bed was such that the gas residence time in the bed was calculated to be 17 seconds.

Experiment F2 The procedure in this experiment was exactly the same as in F1 but 1.0% copper by weight was thoroughly mixed with the coke.

Results The concentration values obtained are plotted in figure 15 with the results of experiment E2 against time since reaction initiation. Again experimental points are only shown every fifteen minutes whereas they were taken every three minutes. From the integration of the hydrogen plots in figure 15 by multiplying the concentrations by the flowrate at NTP and plotting these results against time, the volume of hydrogen leaving the bed can be calculated and is plotted for the three reactions F1, F2 and E2 against time in figure 16. It can be seen that the presence of copper powder in a coke bed has the effect of delaying the appearance of hydrogen in the effluent gas stream. Also from figure 15 it will be noticed that

FIGURE 15 INITIAL REACTION OF COKE PLUS COPPER WITH WATER VAPOUR AT 800°C

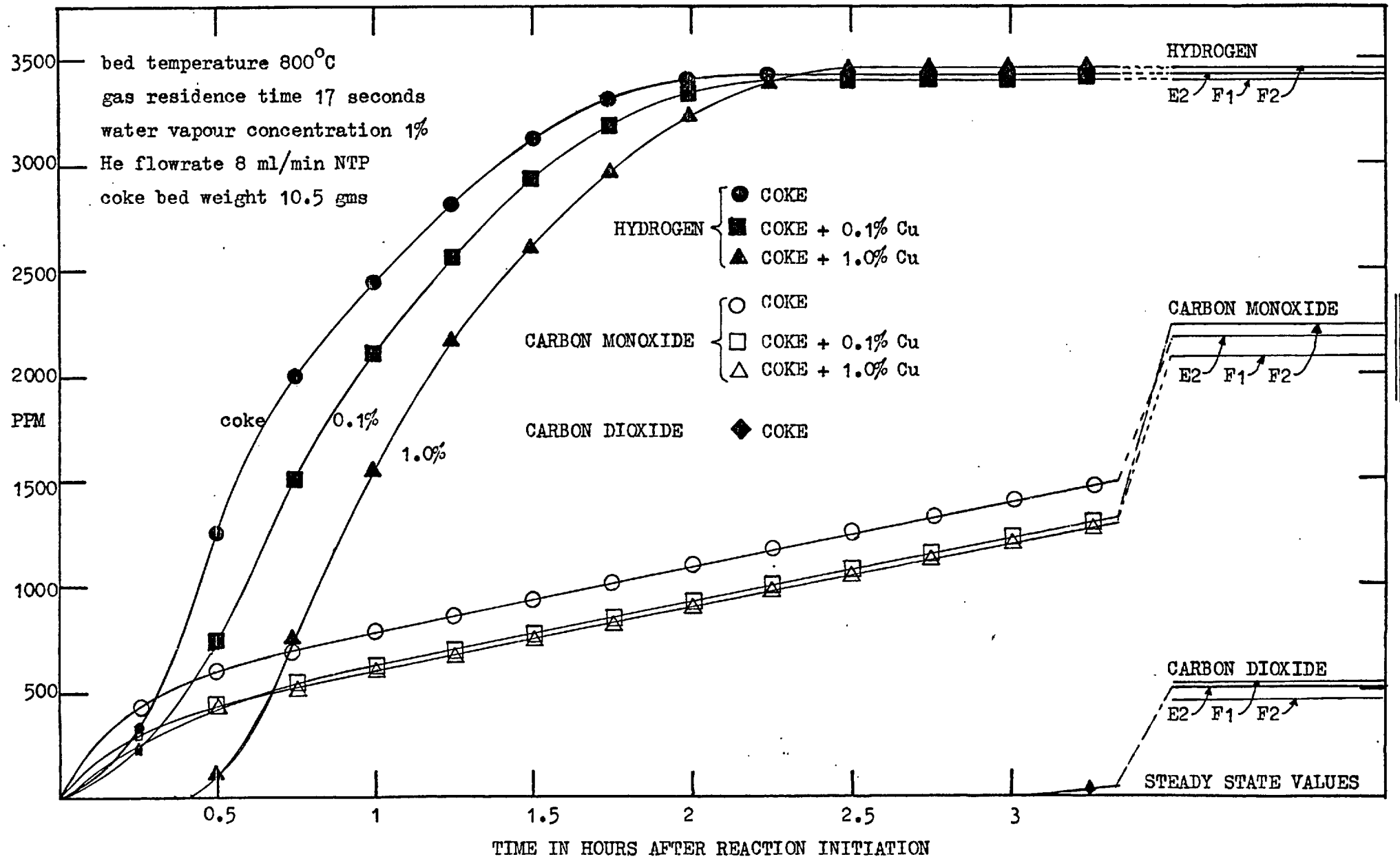
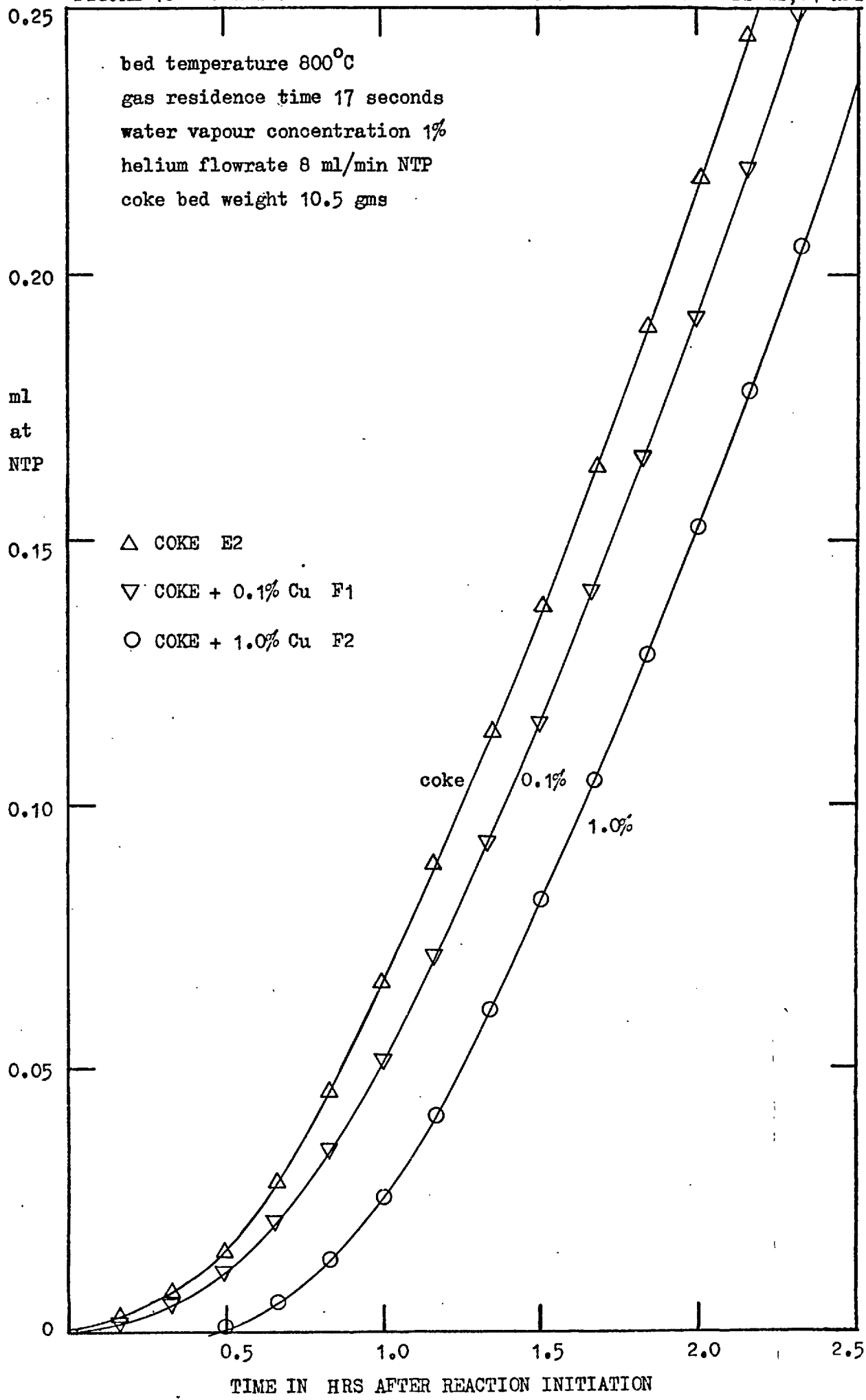


FIGURE 15

FIGURE 16 VOLUME OF EVOLVED HYDROGEN VERSUS TIME EXPERIMENTS E2,F1 &F2



irrespective of quantity, the presence of copper in the coke bed has the effect of reducing the initial amount of carbon monoxide produced but thereafter the rate of production of the gas is constant and equal to the rate of production of carbon monoxide in the experiment carried out in the absence of copper. Very little carbon dioxide was produced in the three and a half hours of initial reaction for the coke bed and it was not detected at all when copper was present. The steady state values of gas concentration remain largely unaltered when copper is present in the coke bed and any differences that arose in final concentration values could be due to slight variances in the packing of the beds which would give rise to small differences in the gas residence times in the beds. Thus it would appear from figure 15 that the presence of copper in a coke bed undergoing oxidation by water vapour, has the effect of delaying the production of hydrogen and carbon monoxide. The first effect, of hydrogen retention, is dependant on the quantity of copper present, the second effect , of carbon monoxide retention, is not dependant on the quantity of copper that is in the bed. The rate of evolution of hydrogen was constant and equal in all experiments after two hours and ten minutes of reaction. From figure 16, up to this point in time, experiment E2 produced 0.246 mls of hydrogen , correct to NTP; experiment F1 (+ 0.1% Cu) produced 0.229 mls of hydrogen; experiment F2 (+ 1.0% Cu) produced 0.178 mls of hydrogen.

By a similar method it was calculated that the presence of copper in both experiments F1 and F2,reduced the initial amount of carbon monoxide produced by 0.498 mls, hence carbon monoxide retention seems independant of the quantity of copper present. However, the retention of hydrogen is dependant on copper quantity ; in a coke bed of 10.5 gms , the presence of 0.1% copper is responsible for the retention of 0.017 mls of extra hydrogen on the coke, and 1.0% copper is responsible for the retention of 0.068 extra mls of hydrogen on the coke, which, on its own,retains 1.58 mls of hydrogen. (from figure 14 page 74). Both amounts of copper are responsible for the retention of 0.5 ml of extra carbon monoxide in addition to the 6.65 ml already ret-

ained by the coke in the absence of copper.

DISCUSSION

From the steady state results it can be seen that there was very little if any effect on the water vapour reduction. Any differences in concentration values could be due to slight differences in the flowrate which would have a considerable effect on a_{C_f} at this temperature and at this residence time.

The only significant effect is that, assuming that water vapour immediately achieves its steady state rate of reduction, the quantities of $'Co'$ and (H_2) on the coke surface are increased by the presence of copper powder. By following a similar procedure to that used in the previous discussion, it is found that 0.1% is responsible for 0.0167 ml more hydrogen and 1.0% copper is responsible for the retention of 0.0692 ml more (H_2). Thus the effect of copper on hydrogen adsorbtion is quantity dependant. The retention of carbon monoxide as the surface oxide (Co), appears to be independant of the amount of copper powder present, 0.5 ml of $'Co'$ in each case.

If the gases were adsorbed by the copper it would be expected that the ratio of hydrogen held by 0.1%copper to that held by 1.0% copper would be 1:10, in fact the measured ratio was 1:4.1 . Similarly the ratio of Co held by the two quantities of copper should be 1:10 and was measured at 1:1 . It could be argued that the contact between the coke and copper in each case varies according to mixing therefore the areas of contact are not in the ratio of 1:10 and so the quantities adsorbed could vary from the 1:10 ratio. However it is thought that this effect cannot explain such a large discrepancy.

It is supposed that the presence of copper particles physically in contact with a coke surface, can by electron interaction weaken the bonding between the matrix atoms and a surface carbon atom, thus generating an active site. The generation of these active sites, above a certain minimum concentration of copper, is independant of the copper concentration and the type of site generated shows a stronger adsorbtive tendency towards Co than to hydrogen.

Working on this supposition, then 0.1% copper adsorbs 0.0058 ml of hydrogen and generates 0.5109 ml of active sites of which the ratio of $C_o^{'}$ to (H_2) is 0.5/0.0109 = 1:4.6 ; 1% copper adsorbs 0.058 ml of hydrogen and generates the same number of actives sites 0.5109 ml of which the ratio of $C_o^{'}$ to (H_2) is also the same at 1:4.6 . Thus the quantities of hydrogen retained are 0.0058 + 0.0109 ml = 0.0167ml for 0.1% copper ; and 0.058 + 0.0109 = 0.0689 ml for 1.0% copper.

Thus copper on a coke surface not only adsorbs hydrogen itself but could be responsible for the generation of active sites . This active site generation does not upset the steady state reduction of water vapour since it initially increases the number of sites which contain adsorbed material and in no way generates new active sites which would be free to enhance water vapour reduction in the steady state. The above supposition tacitly assumes that a copper particle is capable of generating an active site, not neccessarily at the point of contact with the coke but, at some distance away from itself. From experiment E2 it was found that, assuming water vapour immediately achieves its steady state reduction rate, 8.27 ml of active sites are in existence at the reaction temperature, in this experimental series it has been found that 0.5109 ml of active sites are additionally generated. This corresponds to an increase of 6% totally attributable to the presence of copper in physical contact with the coke particles. The error estimated for the volume measurements is $\pm$ 2%, and for weighings is $\pm$ 0.5%.

Having ascertained the effect of copper on the initial adsorbtion of the reaction products from the steam-coke reaction , it was decided that for a comparison with other carbon types, two further experiments should be performed. These would duplicate the method of experiment E2, but the charge materials would be graphite and charcoal. It was hoped to discover any difference in quantity, and in the ratio, of the two adsorbed species, $C_o^{'}$ and (H_2) between all three types of carbon studied in this work.

* * * * * * * * * * *

G. Initial reaction of graphite and charcoal at 800°C with water vapour.

This series of experiments was carried out to discover if there were any similarities between the behaviour of charcoal and graphite, and that of coke during the initial reaction of water at 800°C.

Experiment G1 The method employed was similar to that in experiment E2 but graphite was used as the bed material, since its bulk density is less than coke the residence time of the gas in the bed has been increased to 22 seconds.

Experiment G2 Again the same method was employed as in experiment E2, however the charge material was charcoal and the gas residence time in the bed has been increased to 22 seconds.

Results. The concentration values obtained for G1 and G2 are plotted against time after reaction initiation in figure 17. It will be noticed that the behaviour of graphite closely resembles that of low residence time coke in experiment E1 (see figure 13) in as much as the concentration plots exhibit maxima after an initial rapid rise. However hydrogen and carbon monoxide achieve their steady state values of concentration much more quickly than in experiment E1. Carbon monoxide has reached its steady state in only 40 minutes and hydrogen takes $3\frac{1}{2}$ hours whereas in experiment E1 with coke these gases had not reached steady concentration values after 5 hours. Unlike experiment E1 no carbon dioxide could be detected during the initial $3\frac{1}{2}$ hours of reaction.

The charcoal behaviour however, slightly resembles that of longer residence time coke (experiment E2), only in as much that the general shape of the plots are similar. The major difference is that carbon monoxide initially rapidly evolves from the bed and has almost reached its peak value before hydrogen is first detected in the effluent gases. The rate of evolution of hydrogen is much slower than that of carbon monoxide in this experiment whereas in experiment E2 the reverse is true. Again no carbon dioxide was detected in the first $3\frac{1}{2}$ hours of the reaction.

FIGURE 17 CONCENTRATION CHANGES WHEN GRAPHITE AND CHARCOAL ARE INITIALLY REACTED WITH WATER VAPOUR AT 800°C

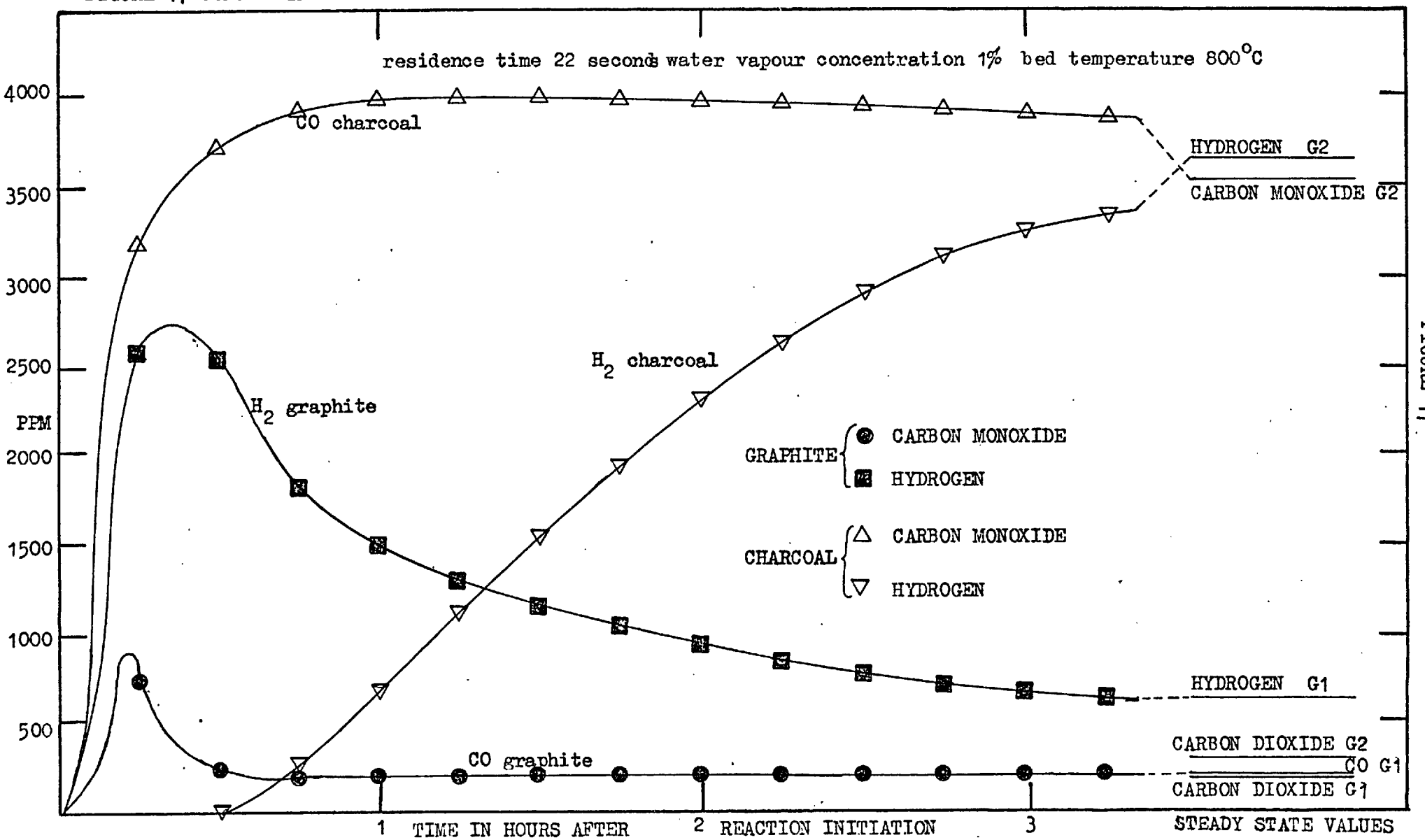


FIGURE 17

DISCUSSION

From figure 17 it can be seen immediately that charcoal adsorbs very little carbon monoxide, but its adsorbtion of hydrogen is large. Graphite, however, appears to adsorb carbon monoxide in preference to hydrogen, but the quantitie are much lower than in the charcoal experiment.

For graphite reactions 19 and 20 proceed rapidly with a corresponding increase in the gaseous concentration of hydrogen. Reactions 21 and 23 however are not as rapid but do continue such that the gaseous concentration of carbon monoxide rises gradually with time. Since carbon monoxide evolution is not at the same rate as that of hydrogen then there is a build up of $'Co'$ on the graphite surface. This poisons the reaction to such an extent that the rate of reduction of water vapour is substantially reduced. This is reflected in the gradual decrease in the concentration of hydrogen in the gas stream. Also the hydrogen adsorption reaction has now been activated and hydrogen begins to accumulate on the surface and reduces the gaseous concentration of hydrogen even further. It appears that the rate of decrease in the rate of water vapour reduction is the same as the rate of decrease in the rate of $'Co'$ accumulation, since the rate of carbon monoxide production is constant over this period ($\frac{1}{2}$ to the four hour mark).

Thus the initial reaction of water vapour with graphite is rapidly poisoned by the accumulation of $'Co'$ on the surface. At the reaction temperature the quantity of Co that is stable is very much greater than the quantity of (H_2). Therefore graphite behaviour is similar to that of low residence time coke. On coke at low residence times it is the high flowrate of the gases which delays the adsorbtion of hydrogen and for graphite it is the higher value of the energy of activation for adsorption.

Charcoal however shows the complete reverse. The initial rate of water vapour reduction is higher than the steady state rate but the $''Co''$ produced is very unstable on the charcoal surface and it immediately appears in the gas stream. Within an hour the reduction has reached a pseudo-steady state and the concentration of carbon monoxide is reasonably constant.

Hydrogen which is produced at the same rate as $'Co'$ does not appear in the

gas stream because the adsorbtion of hydrogen on a charcoal surface is considerable. Only after a half hour of reaction does hydrogen begin to appear in the gas stream. Thus after the half hour mark the rate of desorptio has now exceeded the rate of adsorption and does so increasingly until the tw hour mark where the difference between the two rates begins to diminish. In the steady state , of course, the rates are equal. Therefore the gaseous concentration of hydrogen increases at an increasing rate up to the two hour mark then increases at a decreasing rate thereafter until the steady state is reached. Hydrogen which has adsorbed onto the charcoal surface has reduced the number of sites at which water vapour can react and so during the hydrogen adsorbtion the concentration of carbon monoxide has decreased slightly.

Since the quantity of Co on the charcoal surface is so low there is no initia production of carbon dioxide and even in the steady state condition the Co concentration is so low that the production of carbon dioxide is minimal. The CO/CO_2 ratio is therefore quite high at 15:1 . Conversely on a graphite surface the build up of Co was quite considerable during the initial reaction and this is reflected in the CO/CO_2 ratio of 1:1 .

The volumes of Co and (H_2) retained on the two surfaces can be calculated if a reasonable assumption is made about the degree of water vapour reduction in each case. In experiment G2 for charcoal it is assumed that the initial amount of water vapour reduced was 4000 ppm and this decreased linearly with time over five hours to its steady state value of 3650 ppm. For graphite it is assumed that the initial amount started at 3000 ppm and continued at this rate to the half hour mark where it is assumed that adsorbtion of hydrogen is complete and so the concentration of the water vapour being reduced is identical the the hydrogen plot thereafter.

Figures 17a , 17b show the plots of accumulation rates of Co and (H_2) for charcoal and graphite respectively. The assumed degree of water reduction has also been plotted. The integration of the plots are given and were found to be 3.33 ml of (H_2) and 0.34 ml of Co for charcoal and 1.98 ml of Co

FIGURE 17a PLOT OF RATE OF ACCUMULATION OF SURFACE SPECIES DURING THE INITIAL REACTION OF WATER VAPOUR VERSUS TIME

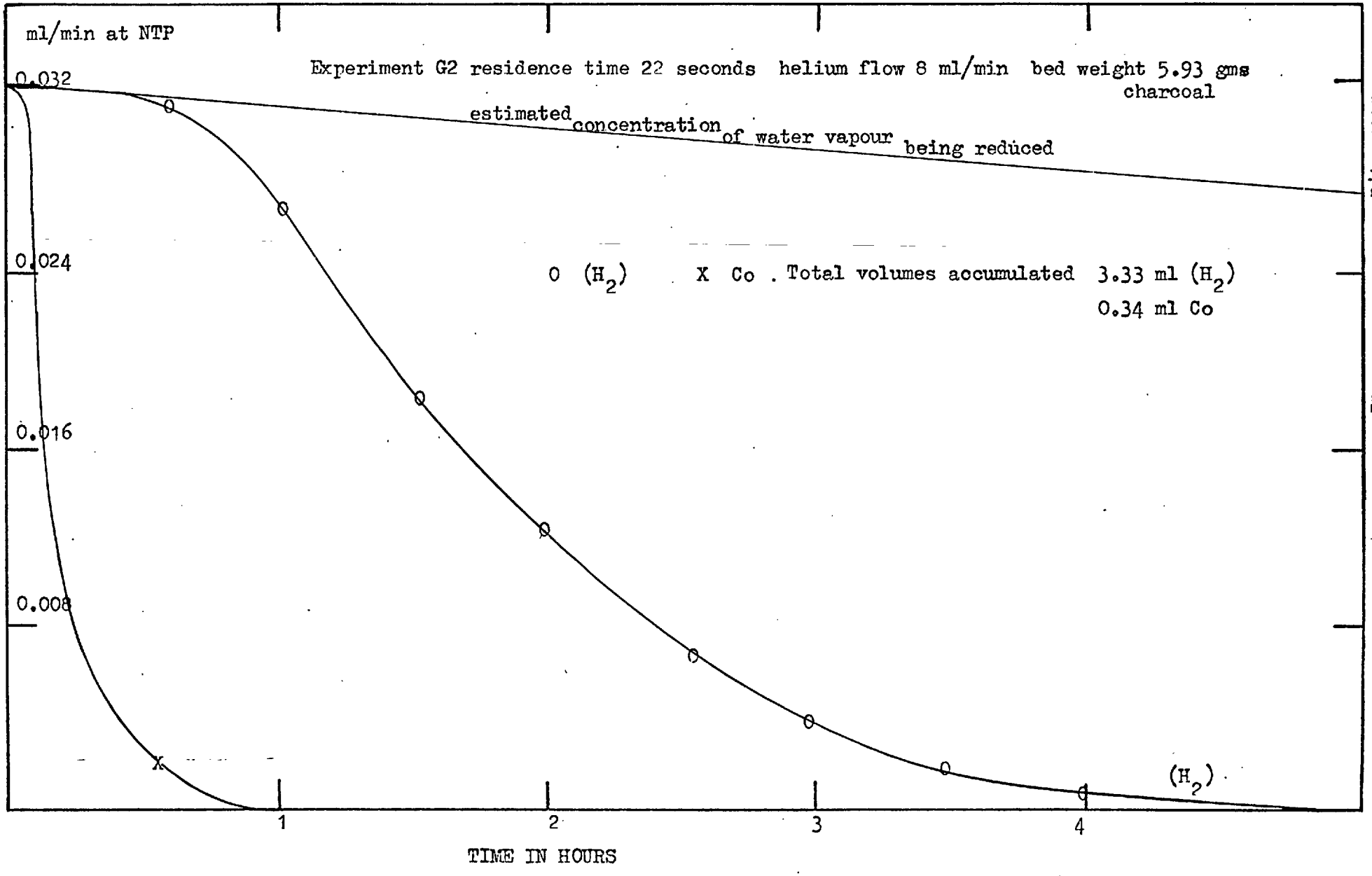


FIGURE 17a FOR EXPERIMENT G2

FIGURE 17b PLOT OF RATE OF ACCUMULATION OF SURFACE SPECIES DURING THE INITIAL REACTION OF WATER VAPOUR VERSUS TIME

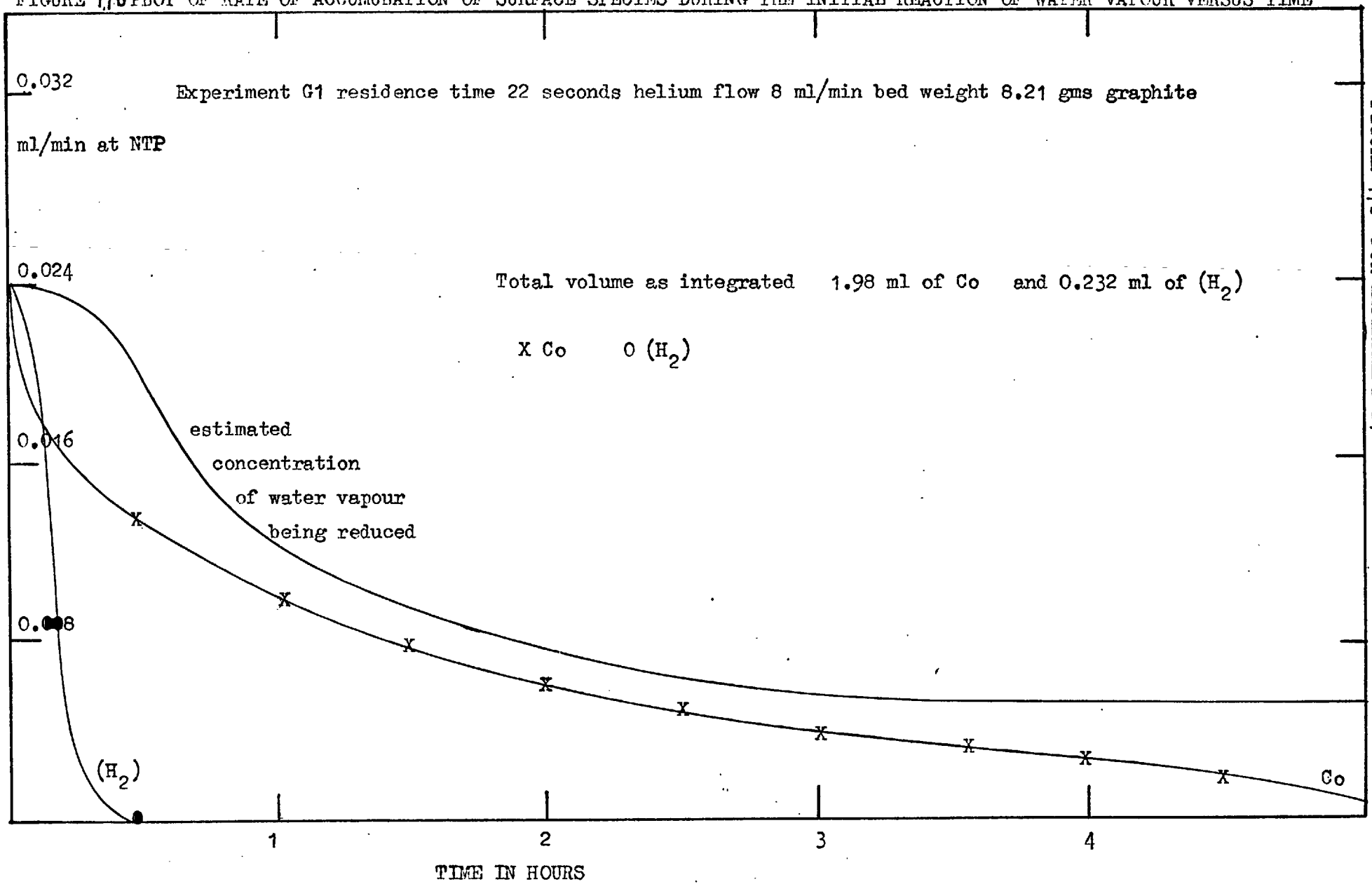


FIGURE 17b FOR EXPERIMENT G1

and 0.232 ml of (H_2) for graphite. For comparison with the E2 results it must be remembered that these beds were all of constant volume and the actual weights were 10.5,8.21 and 5.93 gms for coke, graphite and charcoal. Thus per gram of bed the ratios of Co to (H_2) were as follows :-

Coke $Co' : (H_2) = 0.6333 : 0.1505 = 4.21 : 1$ ml/ml at NTP

Charcoal $Co' : (H_2) = 0.05733 : 0.5621 = 0.102 : 1$ ml/ml at NTP

Graphite $Co' : (H_2) = 0.24117 : 0.0283 = 8.53 : 1$ ml/ml at NTP

Thus when water vapour reacts with these three types of carbon for every ml of Co' generated which exists on coke ,0.38 ml would stably exist on a graphite surface and 0.092 ml would be on a charcoal surface at 800°C. At this same temperature for every ml of hydrogen that will be stable on a coke surface 4.1ml would exist on a charcoal surface and 0.19 ml would be stable on a graphite surface.

Therefore from this series of experiments it was found that coke will hold more Co' than either graphite or charcoal , whereas charcoal will hold more hydrogen than either coke or graphite.

So far in this work, the steady state of the steam-carbon reactions has been studied, and found to be far removed from thermodynamic equilibrium. Also the initial reaction of water vapour, with three carbon types, has been studied, and the effect of copper particles, in a coke bed, has been studied with reference to the initial reaction with water vapour.

In a TORCO reactor, the charge materials only spend about fifteen minutes in the segrgation chamber, therefore the system will never have a chance to reach a steady state, let alone true thermodynamic equilibrium, with the water vapour in the system.

Also in a TORCO reactor, the carbonaceous material is not degassed at 1000°C . Therefore the reactions so far studied have no direct relevance to the actual workings of a commercial plant, even so, the results obtained from the early experiments will prove useful in the determination of a more suitable reducing agent for cuprous chloride.

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H. Reactions of coke in a wet or dry helium gas flow when the coke bed is heated from 150°C to 850°C

In a TORCO plant, ore together with coal, is fed into a fluidised bed, through which, air is blown. The coal burns in the air and heats the ore to a temperature of about 800°C. The hot ore and burnt coal, overflows into the segregation chamber where extra coal and salt are added. Although the flue gases are drawn off, some, inevitably, get into the segregation chamber; and it is found that these gases consist of about 1% oxygen and 1% water vapour, the rest being nitrogen plus carbon oxides.

If gaseous hydrogen is responsible for the reduction of the cuprous chloride vapour, then it would be advantageous to discover from what source this hydrogen is derived. Therefore, gaseous hydrogen was the main product analysed from the H and I series of experiments, which were designed to simulate the various conditions at the top of the segregation chamber; that is, coal and salt being rapidly heated to about 800°C. Experiment I2 reproduces these conditions; however, to separate the various effects of salt and water vapour on hydrogen production, experiments H1,H2 and I1 are needed. These four experiments cover all the combinations of coke in the absence, and in the presence of water vapour; and coke plus salt, in the absence and in the presence of water vapour, respectively.

The coal in a TORCO plant is pre-dried, and so all the coke beds were heated at 150°C to simulate the drying effect. As in the previous experiments, a constant weight of coke was used, 10.5 gms; however, the reaction tube used was now changed from a Mk I to a Mk II: 10.5 gms of coke in a Mk I tube, gave a bed depth of 13.5 cms, the same weight in a Mk II tube gave a bed depth of 5,5 cms. Thus a bed in a Mk II tube, was in a more even constant temperature zone. Also, as a coke bed is heated up to about 700°C, tars and oils are driven off, from the coke. In a narrow Mk I tube, these tars sometimes temporarily blocked the helium flow, but this did not happen in a wider Mk II tube. In the H and I series of experiments, measurements were to be taken as the bed was heated to 850°C, which required a constant flowrate.

Although the measured gas temperature,at the top of the segregation chamber, slightly varies around 750°C, the burning coal temperature could be higher than this, and so it was decided to heat the coke to a temperature of 850°C to simulate this possible extreme temperature condition.

A departure is made from the normal reporting style, in as much that the experimental procedures and results of the I series immediately follows those of the H series; then the combined results are discussed together. This is done, because the deductions made from each experiment are directly dependent on the results of the other three experiments, and so an isolated and separate discussion of each series would be pointless.

Experiment H1 10.5 gms of coke was preheated in a Mk II reaction tube for 18 hours in a dry helium flow, the temperature of the bed was then raised to 850°C by setting the furnace controller to 850,and the temperature was noted at each gas concentration reading, which took place every three minutes. The thermocouple was situated inside the furnace tube but outside the reaction tube,therefore the temperature of the bed was slightly lower than the measured temperature , during the heating process. This experiment was referred to as 'dry coke'.

Experiment H2. 10.5 gms of coke was preheated in a dry helium gas flow at 150°C for 18 hours, then water vapour was introduced into the system at a concentration of 1%. The temperature of the bed was then raised to 850°C and gas analyses were performed every three minutes. This experiment was known as 'wet coke'.

In both experiments, the helium flowrate was such that the gas residence time in the bed was 17 seconds at temperature.

Results. During the heating process, hydrocarbons (tars,oils etc.) other than methane were evolved from the coke. While some of the heavier hydrocarbons condensed in the cooler parts of the reaction tube, the rest were passed through the pipework and were subsequently injected into the chromatograph columns. Sampling by injection was performed every three minutes, during which time,the injected gases were being eluted from the columns. The elution times of the gaseous hydrocarbons was such that, during the

elution of gases from the fifth injection, two large 'rogue' peaks were detected. These peaks were probably due to the elution of hydrocarbons from the third and fourth injections. These 'rogue' peaks hindered the evaluation of the results of the sixth and seventh injections also. Similarly, one particular hydrocarbon, had such a long elution time, that after one hour, a peak started eluting , which took fully thirty minutes to elute completely, thus no results were possible during this period.

Figure 18 shows the concentration changes with temperature and time. Although readings were taken every three minutes, for clarity they are only plotted at fifteen minute intervals, and, for the reasons explained above, the results between the one hour and the one and a half hour mark, are estimated.

From figure 18 , it can be seen that the principal gaseous product, from heatin a coke bed from 150-850°C, was hydrogen, however, there were also significant quantities of methane and carbon monoxide evolved. A surprisingly large quantity of nitrogen was also evolved from the bed during the heating process. Figure 18, however, does not give a clear indication of the actual quantities of gas evolved, and so a different treatment of the results is required to give volume evolved versus time. Although the helium flowrate was 8 ml/min, the evolved gases increased this value and so the following equation was used to calculate actual flowrate :-

$$\frac{1{,}000{,}000}{1{,}000{,}000 - \Sigma ppm} \times 8 = \text{actual flowrate.} \quad ml/min$$

where Σppm is the sum, in ppm , of all the evolved gas concentrations , By multiplying each gas concentration by the actual flowrate, the individual gas flowrates can be calculated. By plotting these flowrates, versus time , for each gas, a graph is obtained which, upon integration, yields the total volume of each gas evolved. In fact , these graphs were integrated over ten minute intervals, and the running total of gas evolved was plotted against time in figure 19, for each measured gas.

Figure 19 contains the results for experiments H1 and H2, the dry and wet runs.

FIGURE 18 GAS CONCENTRATION CHANGES WHEN COKE IN 1% WATER VAPOUR IS HEATED FROM 150°C TO 850°C IN EXPERIMENT H2

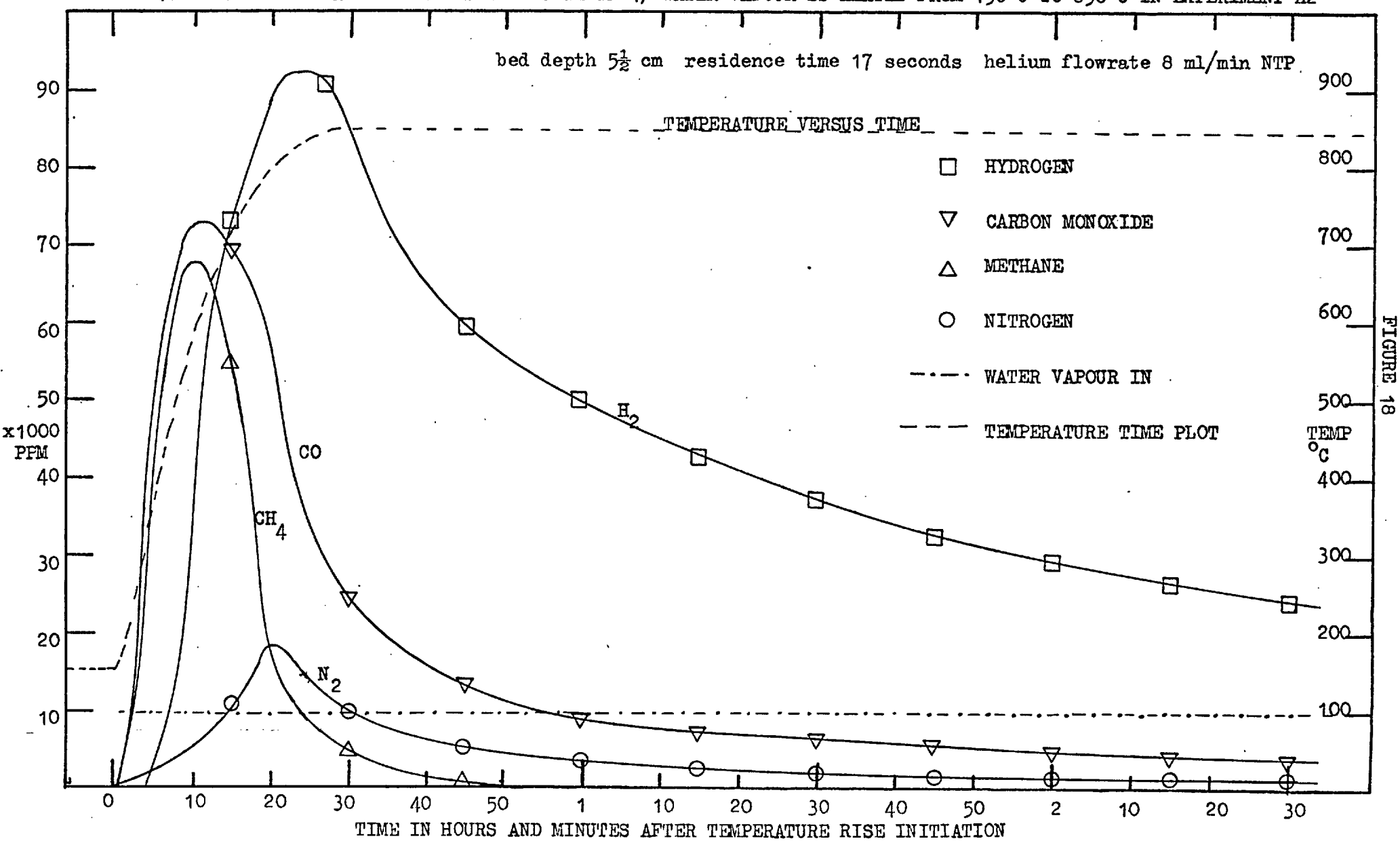


FIGURE 18

FIGURE 19 VOLUME OF GAS EVOLVED VERSUS TIME AFTER TEMPERATURE RISE

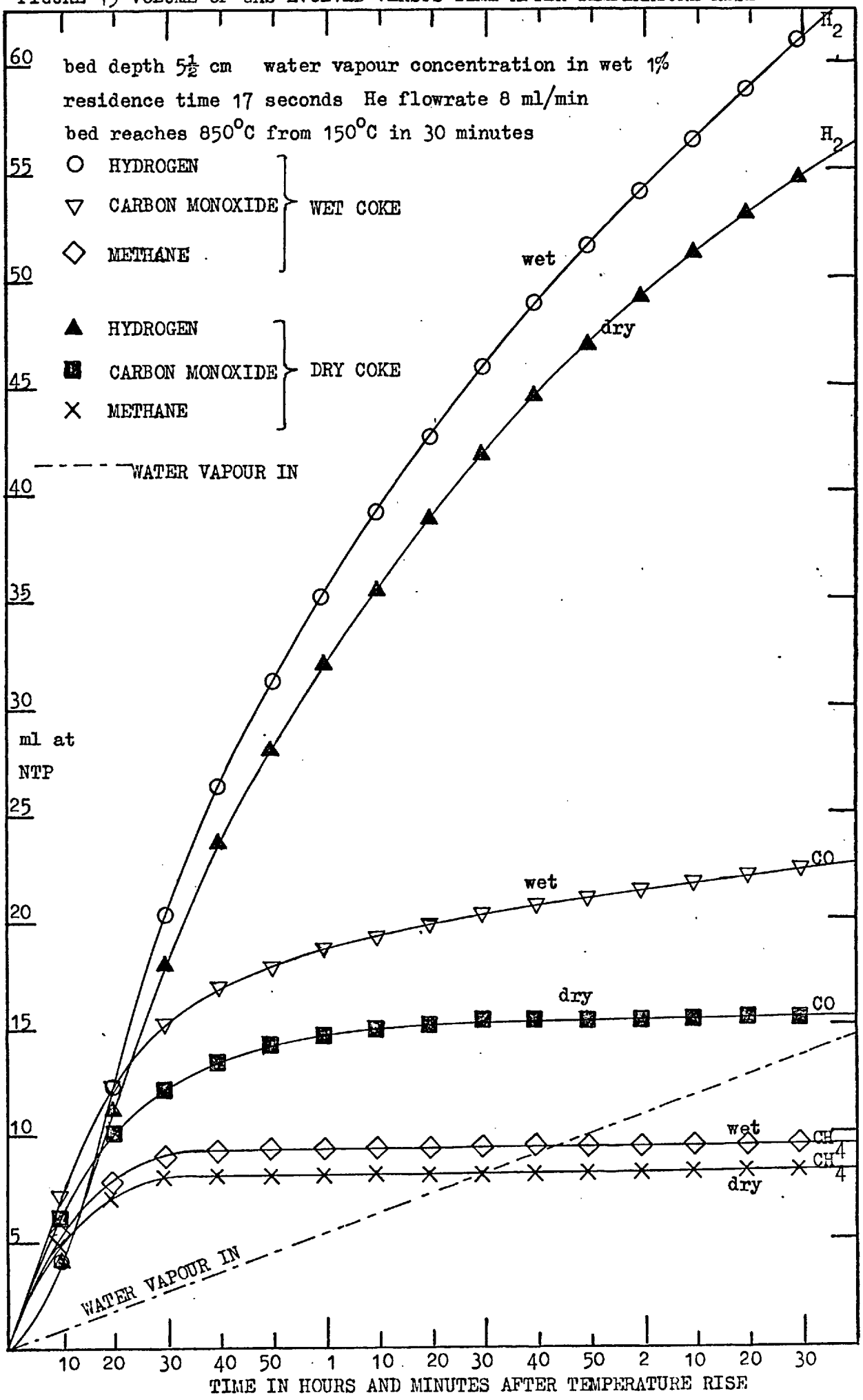


Figure 19 also shows the amount of water vapour passed through the coke bed in the wet coke experiment. It can be seen that as would be expected, more hydrogen and carbon monoxide are evolved in the presence of water vapour. However this extra amount of hydrogen is small compared to the amount released by the bed itself as it heats up. Since less carbon monoxide was released by the bed the extra amount of carbon monoxide produced by the water vapour reduction is a more significant effect. Methane production from the coke is also slightly enhanced in the water vapour experiment. Thus the presence of water vapour has increased the volume of hydrogen, methane and carbon monoxide by 7.00, 1.25 and 7.45 mls at NTP in two hours and forty minutes of reaction respectively. These increases when expressed as percentages of gas evolved in a dry experiment are 13% for hydrogen, 50% for carbon monoxide and 15% for methane. It can also be seenfrom figure 18 that methane production is virtually complete after forty minutes, but carbon monoxide and nitrogen production still remain significant, after the initial, high rate has diminished. Hydrogen however, after the initial large evolution, is still produced in quantity, but at a decreasing rate with time.

As was explained earlier, the discussion of the H series of experiments is combined with that of the I series of experiments and follows on page 97 . The experimental procedure and results of the I series follows immediately.

* * * * * * * *

I Reactions of coke plus 0.5% sodium chloride in a stream of wet or dry helium when heated from 150 to 850°C

Experiment I1 Coke and salt were thoroughly mixed together to give coke containing 0.5% salt by weight. This material was used as the charge in this experiment. The method of drying the bed, contained in a Mk II reaction tube at 150°C is described in H1. This bed was then heated to 850°C in a stream of dry helium at an NTP flowrate of 8 ml/min. This experiment is referred to as 'dry salt'.

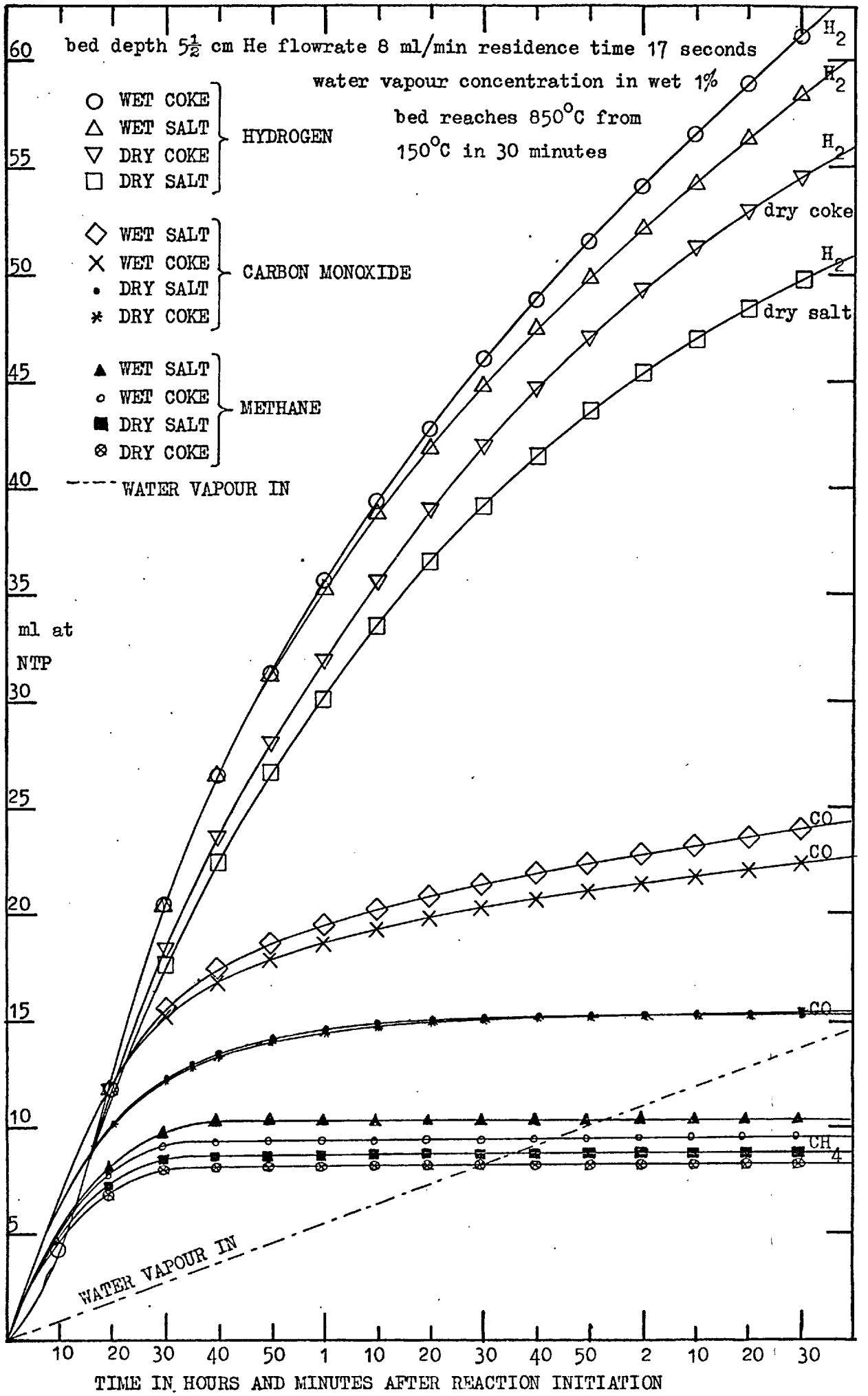
Experiment I2 The method employed in this experiment was identical to that used in experiment I1 except that instead of being heated from 150 to 850°C in a dry helium flow, the helium contained water vapour at a concentration of 1% in this experiment and so the run is known as 'wet salt'.

Results A similar procedure was carried out on the results obtained as in the above results section, thus figure 20 is a plot of volume of gas evolved from the bed against time after the initial temperature rise for both experiments I1 and I2 together with the results of H1 and H2.

It will be noticed that the presence of salt in a coke bed when the helium contains water vapour increases the amount of carbon monoxide produced over the amount produced in the absence of salt. Thus the salt is catalysing the reduction of water vapour or is catalysing the desorbtion of carbon monoxide from the coke surface. However in a dry system the amounts of carbon monoxide produced are almost identical in the presence or absence of salt. Therefore the action of the salt must be as a catalyst of steam reduction by coke. Thus it would be expected that in the 'wet salt' experiment the amount of hydrogen produced should be more than in the 'wet coke' experiment. However from figure 20 it can be seen that the volume of hydrogen is not greater than in the 'wet coke' run in fact, for the 'wet salt' run the volume of hydrogen produced is less than in the 'wet coke'.

By considering the 'dry coke' and the 'dry salt' experiments it will be seen that when salt is present in the system the amount of hydrogen is reduced. Thus after two hours and forty minutes of reaction the 'dry coke' run produced 55.75 ml of hydrogen at NTP whereas the 'dry salt' run produced 50.75 ml of hydrogen at NTP. Thus in this time period the salt has reduced the amount of hydrogen produced by 5 mls. Since salt catalyses

FIGURE 20 VOLUME OF GAS EVOLVED VERSUS TIME AFTER TEMPERATURE RISE



the reduction of water vapour and no carbon dioxide was evolved, the extra amount of carbon monoxide produced should be equal to the extra amount of hydrogen expected. Therefore instead of producing 2.25 extra mls of hydrogen 'wet salt' produces 2.60 mls less hydrogen, thus the presence of salt in a wet system reduces the amount of hydrogen produced by 4.85 mls.

Methane production appears to be enhanced by the presence of salt. In a dry system the amount of methane produced was 8.25 mls in the absence of salt and 8.75 mls in its presence. In a wet system, in the absence of salt 9.50 mls of methane are produced whereas in its presence 10.5 mls are produced. Thus the difference between wet and dry in the absence of salt is 1.25 mls of methane and in the presence of salt the difference is 1.75 mls. Therefore it appears that salt also catalyses the production of methane.

To summarise therefore, salt has no effect on carbon monoxide production from a coke bed in a dry system. In a wet system , it slightly catalyses the production of carbon monoxide. Salt reduces the amount of hydrogen produced, in both a wet, and in a dry system, by the same amount. Extra hydrogen is produced in a wet system, from the steam-coke reaction, and salt catalyses this reaction to a small extent. Both salt and water vapour increase the amount of methane produced from the coke, but their combined effect is greater than their summed individual effects.

DISCUSSION of the H and I series.

From figure 18 for the wet coke it can be seen that the oxygen on the coke surface is evolved mainly as carbon monoxide with little if any carbon dioxide. The temperature of maximum rate of production was about 600°C and as the temperature increased to 850°C less was produced. Its rate of production fell in an exponential manner gradually approaching the steady state rate of production from water vapour at this temperature.

The maximum rate of methane production was at 550°C and the rate rapidly fell as the temperature increased and after fifty minutes methane production had ceased. Nitrogen production had reached its maximum rate when the temperature was about 800°C and only hydrogen's maximum rate of production

coincided with the maximum temperature achieved, 850°C. Hydrogen constituted the greatest percentage of the evolved gases, the decrease in its concentration away from its maximum was very gradual and after two and a half hours its concentration was still far removed from its steady state value.

It is suggested that as carbon monoxide and methane are immediately produced as soon as the temperature begins to rise, these gases are derived from the desorption of adsorbed gas and their production is not due to thermal decomposition of any other species. Hydrogen production does not start until the bed temperature has reached 350°C, thus suggesting that the hydrogen produced in these experiments comes mainly from the cracking or thermal decomposition of hydrocarbons and very little is derived from adsorbed hydrogen.

Similarly it is proposed that the nitrogen evolved is derived mainly from a chemical source since its temperature of maximum production was much higher than that of either carbon monoxide or methane. Figure 18 shows that while methane production was complete after fifty minutes, nitrogen was still being evolved from the bed after two and a half hours, further suggesting that nitrogen comes mainly from the thermal decomposition of a nitrogen bearing compound. There is a small amount of adsorbed nitrogen since this evolves as soon as the bed is heated.

From figure 19 , compared to the dry coke run, the effect of water vapour on the bed is seen to increase all gas concentrations. According to the difference between the wet and dry carbon monoxide plots, the water vapour reduction is initiated as soon as the the bed temperature reaches 500°C and continues at an increasing rate as the temperature rises. At 850°C the rate stabilises at its steady state rate since the rate of production of carbon monoxide from the wet coke is virtually linear after the forty minute mark.

Methane at this temperature does not appear to be a steady state reaction product of water vapour reduction since the volume evolved does not increase with time after the bed has reached 850°C. However the presence of water

vapour in the coke while the temperature was being raised increased the amount of methane produced therefore it is assumed that this production was due to the reaction of water vapour with coke at the lower temperatures where methane is more stable.

Figure 20 shows all the combinations of 'wet','dry' and with salt. Salt appears to have no effect on the production of carbon monoxide in a dry system however in a wet system the presence of salt in the bed catalyses the steam coke reaction to produce more carbon monoxide.

Hydrogen production is affected both in the dry and wet systems by the presence of salt. After two and a half hours of reaction it reduces the amount of hydrogen produced by 5 ml. In a wet system it reduces the amount of hydrogen produced by 2.6 ml but 2.35 ml more hydrogen was expected from the catalysed water vapour reduction. Therefore whether in a dry or wet system , salt reduces the amount of hydrogen produced by approximately 5 ml after two and a half hours of reaction. It is thought that either salt slightly inhibits the cracking of hydrocarbons, producing methane instead of hydrogen, or that hydrogen reacts with salt in the presence of ash constituents to produce hydrogen chloride gas. This latter aspect will be dealt with in the discussion of experiment L.

Methane production is also a function of salt and water vapour, either improves methane production but their combined effect is greater than their summed individual effects. Therefore salt catalyses the production of methane from the steam coke reaction at temperatures below 850°C. From the JANAF[62] tables it is found that the free energy of formation of methane at 850°C from hydrogen and carbon is +7.25 kcal/mole. This means that $P_{CH_4}/P^2_{H_2}$ is approximately 0.04 at 850°C therefore the equilibrium partial pressures of methane at this temperature existing with 90,000 , 50,000 and 25,000 ppm of hydrogen are 314, 100 and 24 ppm. Thus from figure 18 these are the methane concentrations expected after twenty-five minutes, one hour and two hours of reaction. However in all the experiments the measured methane concentration was greater than these equilibrium values.

Thus methane is metastable at 850°C with respect to hydrogen.

In a dry system therefore 8.25 ml of methane are produced in two and a half hours from the desorption of adsorbed methane and from the incomplete cracking of hydrocarbons at temperatures below 850°C. When salt is added to the dry system it hinders the full cracking of hydrocarbons and produces 0.5 ml more methane with a corresponding reduction of 1ml of hydrogen.

In a wet system 8.25 ml are produced from the adsorbed state and from incomplete cracking, another 1.25 ml are produced from the reaction of water vapour with coke making 9.5 ml in all. When salt is present in the wet system the water reduction to methane is catalysed and produces 1.75 ml instead of 1.25 ml. Also the hydrocarbon cracking inhibition produces 0.5 ml making 10.5 ml in all.

Thus although salt inhibits the hydrocarbon cracking in each case, the 1 ml reduction in the amount of hydrogen produced does not account for all of the observed reduction in the hydrogen volumes, (5 ml).

Summarising therefore, water vapour in the system begins to react with coke at 500°C and in two and a half hours produces 7.00 ml of hydrogen, 7.45 ml. carbon monoxide and 1.25 ml of methane which increases the amounts of gases produced from the bed by :-

13% for hydrogen, 50% for carbon monoxide and 15% for methane.

The presence of salt in a coke bed catalyses the water vapour coke reaction by 34%, it also catalyses the minor steam coke reaction to produce methane by 40%, It slightly inhibits the full thermal cracking of hydrocarbons and produces methane with a corresponding reduction in hydrogen production and salt also reduces the quantity of hydrogen produced in a wet or dry system by their possible reaction to hydrogen chloride.

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J. Reaction of sugar charcoal when heated in a dry helium gas flow from 150°C to 850°C

Purely for the sake of comparison, charcoal was subjected to the same treatment described for coke in experiment H1. Since beds of constant volume are being studied, although the bed depth was the same, the weight of charcoal used in J1 was 5.9 gms.

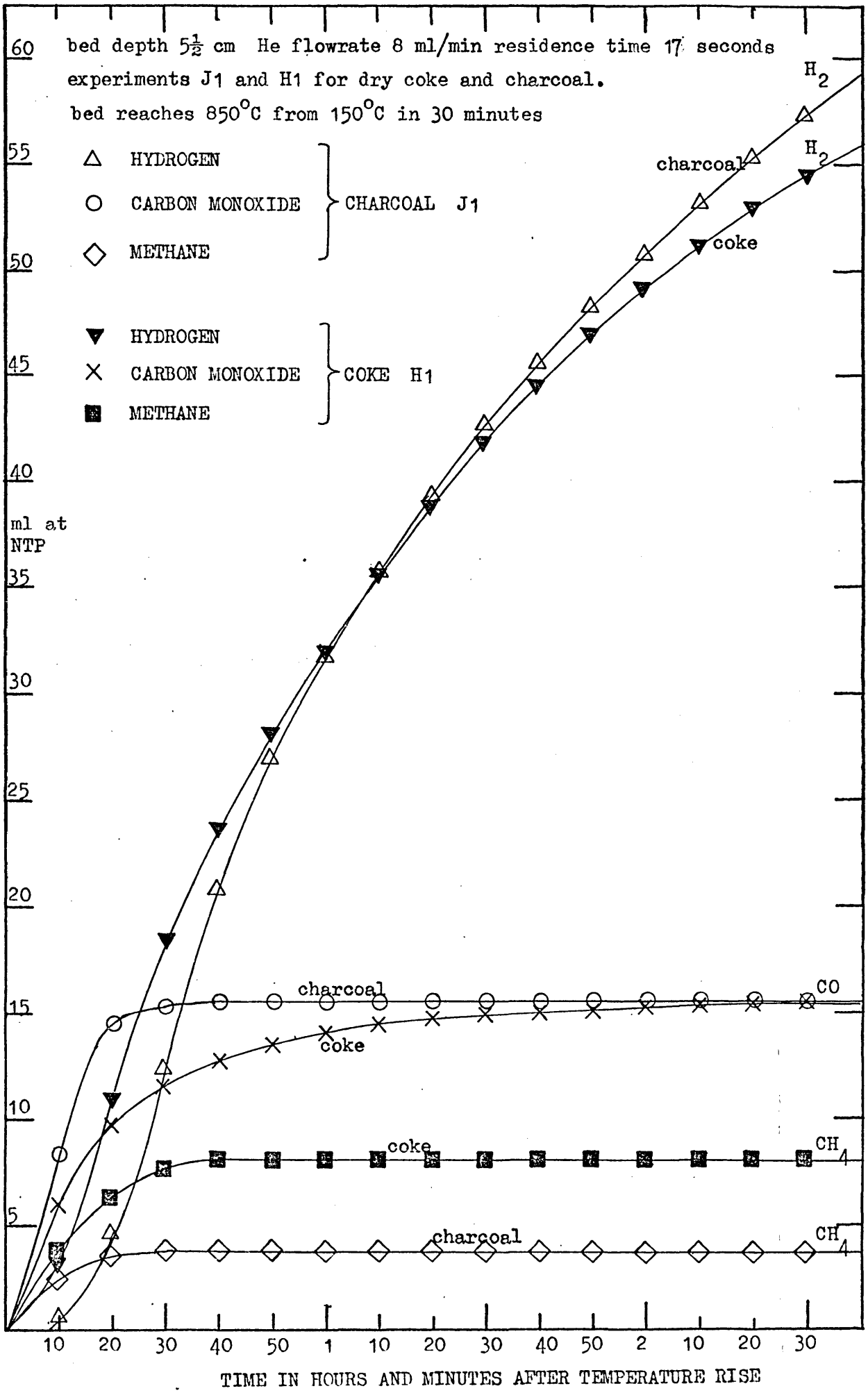
Experiment J1 A bed of sugar charcoal 5½ cms deep was held in a Mk II reaction tube at 150°C for 18 hours in a dry helium flow. The temperature of the bed was then raised to 850°C and the effluent gases were analysed.

Results The results of experiment J1 are plotted together with the results of H1 for dry coke in figure 21 as volume of gas evolved from the bed versus time after reaction initiation.

It can be seen that methane production is virtually halved in a charcoal bed compared to the coke experiment. Also the rate of evolution of carbon monoxide is very much greater in the charcoal run initially, than in the coke run. However the final volumes achieved were identical after two hours and forty minutes since the initial temperature rise. Thus charcoal produced 15.5 mls of carbon monoxide in this time period as did coke. Coke produced 8.25 mls of methane in the same time period but charcoal only produced 3.8 mls of methane.

The hydrogen, in the charcoal experiment, only appeared ten minutes after the temperature rise initiation, whereas in the coke experiment, the hydrogen appeared as soon as the temperature was raised . Thus although the hydrogen production in J1 suffered an early delay, its rate of production was greater than that in the coke experiment, so that after one hour and five minutes after the temperature rise, the volumes of gas produced in both experiments were the same. However the rate of evolution of hydrogen from the charcoal remained higher than that of coke, so that after two hours and forty minutes of reaction the charcoal has produced 58 mls of hydrogen whereas the coke produced 55.75 mls at NTP.

FIGURE 21 VOLUME OF GAS EVOLVED VERSUS TIME AFTER TEMPERATURE RISE



DISCUSSION

All experiments in a Mk II reaction tube always contain 10.5 gms of coke which gives a bed depth of five and a half centimetres. However in order to give the same residence time, the bed of charcoal only weighed 5.93 gms. Therefore figure 21 is only comparative as far as residence time and the effect on gas liberation. After two and a half hours of reaction the gases released per gram of sample were as follows :-

Coke 5.48 ml hydrogen, 1.48 ml of carbon monoxide and 0.79 ml of methane

Charcoal 10.0 ml of hydrogen, 2.6 ml of carbon monoxide and 0.64 ml methane.

In experiment J1 the production of methane and carbon monoxide was fully complete after thirty minutes of reaction i.e. as soon as the bed reached 850°C. Hydrogen was slow to evolve initially but after the twenty minute mark its production rapidly increased with time. No carbon dioxide or nitrogen was produced at all.

Sugar charcoal therefore contains weakly held 'oxygen' and some weakly held 'hydrogen', but also contains strongly held 'hydrogen'. It is thought that after sugar charcoal production is completed, the charcoal still contains semi-charred material. Sugar involves both C-H and C-O-H bonds and it is supposed that the C-O-H bonds on charring give rise to adsorbed carbon monoxide and methane. The C-H bonds however are much more stable and semi-charred material will contain plenty of these bonds. Thus by heating the semi-charred material the carbon monoxide and methane are readily desorbed while the thermal breakdown of the C-H bonds is a continual process at temperaure. Since the hydrocarbon bond breakdown takes place mainly at 850°C no methane will be produced since its free energy of decomposition is - 7.5 kcal/mole.

From this analysis it would be expected that the volume ratio of carbon monoxide to methane would be 4:1 since they are the sole products of the -O-H groups. In fact the ratio was measured at 4.06:1, suggesting that some of the methane produced at the higher temperaures has cracked to hydrogen. Comparing the rates of evolution of gas from the respective surfaces it is seen that methane production in both cases is completed as soon as the

bed reaches temperature. This is to be expected since the production of methane is very much dependent on the thermal stability of the gas and as the surfaces thus are relatively unimportant, the behaviour is similar in both cases.

The carbon monoxide behaviour however is less similar. The carbon monoxide produced from charcoal is thought to be derived mainly from adsorbed carbon monoxide (CO), since its production is solely a function of temperature and not of time at temperature. This cannot be the case with coke since carbon monoxide evolution continues at a steadily decreasing rate long after the bed has reached 850°C. It is thought that the carbon monoxide produced from coke is derived not only from adsorbed gas but also from the decomposition of the surface oxide 'Co', to (CO) which is the rate controlling step at 850°C since the desorbtion of carbon monoxide is rapid. Thus the plot before the thirty minute mark is that of the rate of desorbtion of adsorbed gas, and after the thirty minute mark the plot is of the rate of decomposition of 'Co' to (CO). Therefore of the carbon monoxide produced in the first two and a half hours, the main source is (CO). Carbon monoxide continues to be evolved from 'Co' breakdown for several days; after twenty-four hours its concentration in the gas stream was 340 ppm, after another day it was 250 ppm after another day it was 180 ppm and after a further twenty-four hour period it was 140 ppm. Therefore over this ninety six hour period another 2.20 ml per gm of coke has been evolved. Thus coke contains more 'oxygen' than charcoal but charcoal liberates all its 'oxygen' in thirty minutes as the bed is heated to 850°C. Coke takes a little under four days to liberate the same amount of carbon monoxide because its 'oxygen' consists mainly of 'Co' while that of charcoal is predominantly (CO).

Coke, unlike charcoal, contains adsorbed hydrogen which evolves during the initial heating. Both carbon types contain hydrocarbon bonds which progressively breakdown to hydrogen as the temperature and time at temperature increases. Charcoal contains the greater number of these hydrocarbons

per gram of sample, this is due to their respective production processes and geneses. (Coke from the ovens is cooled by water sprays, giving adsorbed hydrogen, forming on a rapidly cooling surface ; and the charring of sugar to give the charcoal, is far from being complete.)

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K. The effect of pre-treatment on nitrogen evolution from coke when heated from 150°C to 850°C in a dry helium flow

One of the more unusual results of the H and I experiments, was that each temperature rise in the coke , to 850°C, was accompanied by an evolution of nitrogen.

This series of experiments was designed to ascertain the nature of the source of this nitrogen. If it was found that a vacuum treatment , accompanied by purging with argon , reduced the nitrogen and gave rise to an evolution of argon, then it could be argued that the nitrogen source was physical in nature. However , if it was found that argon could not replace nitrogen, it could be argued that the nitrogen source was chemical . This could be confirmed,by lengthening the time,spent by the bed at 150°C . If, after a longer time at 150°C, the rate of evolution of nitrogen is lowered, then it could be argued that the source of nitrogen is mainly chemical.

All bed weights of coke were 10.5 gms.

Experiment K1 A $5\frac{1}{2}$ cm deep bed of coke was held in a Mk II reaction tube for 16 hours at 150°C.The temperature of the bed was then raised to 850°C and gas analyses were carried out every three minutes.

Experiment K2 The $5\frac{1}{2}$ cm coke bed while in position in the furnace in a Mk II reaction tube was subjected to a vacuum for two hours at 20°C. Then argon was bled into the system and was passed through the bed for fifteen minutes at the same temperature and then the argon was replaced by helium at a flowrate of 8 ml/min at NTP. The temperature of the bed was then raised to 150°C and held there for 16 hours. The bed temperature was then raised to 850°C and readings of the gas concentrations were taken every three minutes.

Experiment K3 This coke bed was subjected to a vacuum for 18 hours at 20°C and then argon was passed through the bed for 52 hours at the same temperature. Helium was then substituted for the argon and the bed temperature was raised to 150°C and held there for 18 hours prior to the temp-

erature rise to 850°C. Again readings of gas concentrations were taken every three minutes.

Experiment K4 Helium was passed through a coke bed held in a Mk II reaction tube for 64 hours at 150°C. The bed temperature was then raised to 850°C and gas analyses were performed every three minutes.

Results The running total of nitrogen evolved from the bed as it was heated to 850°C is plotted against time from the start of the temperature rise, in figure 22. The bed reached 850°C thirty minutes after the temperature rise was initiated and it can be seen that nitrogen evolution was far from being complete at this time. Indeed nitrogen in all the experiments continued to be evolved but at a decreasing rate for at least three and a half hours after this time. It will be noticed also that the pretreatment that has the greatest effect on the volume of nitrogen evolved was the one in which the coke bed was held at 150°C for 64 hours. The vacuum treatment seemed to have little effect. In experiments K2 and K3 as the temperature rose, small quantities of argon were detected in the gas stream. Thus it would appear that a small proportion of the nitrogen held on a coke surface can be replaced by argon if the coke is subjected to vacuum treatment. However the principal method of reducing the amount of nitrogen held in or on a coke bed is by heating the bed in a stream of dry helium for a long period of time. During this period, the helium either replaces nitrogen in an adsorbtive manner or serves to sweep any nitrogen produced from thermal decomposition of unstable nitrides, nitrates, cyanides, cyanates or other nitrogen containing organic substances, out of the bed.

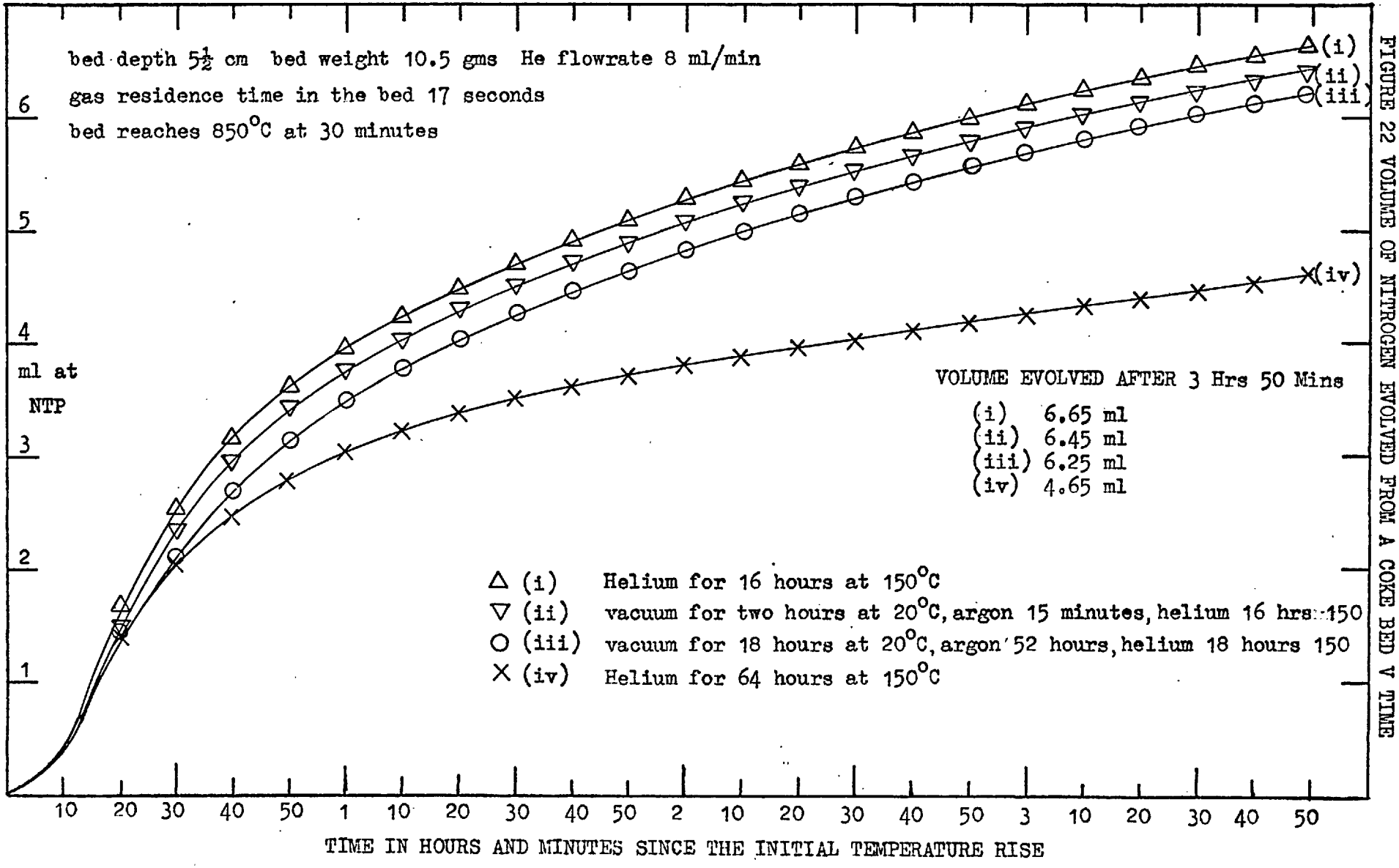


FIGURE 22 VOLUME OF NITROGEN EVOLVED FROM A COKE BED V TIME

DISCUSSION

The K series of experiments were performed to discover the nature of the nitrogen that evolved from a coke bed when subjected to a temperature rise. As can be seen from figure 22 the only treatment that had any significant effect on nitrogen production was when the bed was held at 150°C for sixty-four hours. The vacuum degassing at room temperature and argon flushing did reduce the volume of nitrogen evolved and did give rise to small quantities of argon being evolved when the bed was heated but these effects were minimal compared to the thermal treatment. It is thought that the nitrogen is mainly derived from organic nitrogen containing compounds in the coke which thermally decompose at temperature. The longer time spent at 150°C reduced the amount of these compounds and by a similar arguement as used in the evolution of carbon monoxide from Co and from (CO), it is thought that up to the thirty minute mark, the nitrogen evolved is derived from adsorbed gas and after the thirty minute mark the gas is derived from the thermal decomposition of the organic nitrogen bearing compounds. Thus after the thirty minute mark , the similarity of slopes of (i),(ii) and (iii) indicate that the organic nitrogen compounds were effected by the various pretreatments to the same degree and the difference in volumes emitted is due entirely to the quantities of adsorbed nitrogen removed by the pretreatments.However (iv) has a much altered slope compared to (i), (ii) and (iii) showing that the number of nitrogen bearing compounds has been reduced and as the least stable ones were decomposed first, the rate of release of the gas from the more stable ones is lower than the rate of release of the less stable ones as in (i),(ii) and (iii).

Thus coke contains a certain amount of adsorbed nitrogen, the concentration of which can be reduced by vacuum degassing and can be replaced to a small extent by argon. It also contains a greater percentage of 'chemical' nitrogen the concentration of which can be reduced,by heating at 150°C, by 30%. This 'chemical' nitrogen is thought to exist as cyanides,cyanates, iso-nitriles etc. .

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L. Reaction of hydrogen with salt.

In the I series of experiments,it was found that when salt was in the coke bed, its presence was responsible for a decrease in the amount of hydrogen produced from the coke. It was thought that salt was reacting , in some way , with the hydrogen, thereby reducing its concentration.
One possible reaction , is that the hydrogen reduces the sodium chloride to sodium. The free energy of activation of this process, is large and positive, therefore this reaction is unlikely to proceed, if the reaction product was liquid sodium at unit activity. However if the sodium activity was very much less than unity, then the process may proceed.
Experiment L1 A Mk II reaction tube containing a 5 cm deep bed of salt was heated at 750°C and a flow of dry helium containing 11,500 ppm of hydrogen was passed through the bed at this temperature for 24 hours. The exhaust gases were periodically analysed for hydrogen and the gases were passed through the automatic titrimeter cell.
Results. The chromatographic analysis of the effluent gases revealed that no hydrogen was reacting, However from the burette readings on the titrimeter it was calculated that 3.4×10^{-6} equivalents of hydrogen chloride had dissolved in the cell liquid. From the flowrate of the helium which was 7.1 ml/min it was calculated that the concentration of hydrogen in the gas stream leaving the bed should have been reduced by 3 ppm, which of course, is outside the limit of detection of the chromatograph. Thus the H_2/HCl ratio measured over a salt bed in the presence of silica was approximately 2000:1 at 750°C

DISCUSSION

This experiment was performed in order to determine if hydrogen reacted with salt in the presence of silica, since in the I series of experiments the presence of salt in the coke bed reduced the amount of hydrogen produced in both the wet and dry runs.

It was found from the experimental results that the H_2/HCl ratio over salt was approximately 2000:1 at 750°C. The experiment could not have been erformed at 800°C since sodium chloride melts at 801 °C

From the JANAF[62] tables for the reaction :-

$$H_2 + 2\,NaCl_s \rightleftharpoons 2\,Na_l + 2\,HCl_g$$

ΔG at 750°C is + 104.21 kcal/ 2 moles HCl

hence $K = a_{Na}^2 \times \frac{P_{HCl}^2}{P_{H_2}} = 0.541 \times 10^{-22}$ assuming $a_{NaCl_s} = 1$

thus $P_{HCl}^2 = 0.541 \times 10^{-22} \times P_{H_2} \times 1/\, a_{Na}^2$

in this experiment $P_{H_2} = 0.0115$ and $P_{HCl} = 0.0000077$ atmos.

then $a_{Na} = 1.08 \times 10^{-7}$

Therefore in this system the silica has apparently lowered the activity of liquid sodium by its immediate reaction to a sodium silicate. Indeed when the vessel was removed from the furnace there was definite evidence of attack on the silica vessel's walls where it had been in contact with the salt.

Considering the I series of experiments, in the first two and a half hours the average value of P_{H_2} was 0.046 and the volume of hydrogen was reduced by approximately 4 ml which gives an average concentration of 0.00167 atm. By calculation it can be shown that the activity of liquid sodium in this system was reduced to 0.74×10^{-8}, therefore the reduction in activity of liquid sodium, from being in contact with pure silica to that being in contact with the silicates of the ash constituents, was by a factor of 14.6 . This seems reasonable since silica and the silicates are quite stable. The free energy of formation of silica at 850°C is about - 165 kcal/mole whereas for Na_2SiO_3 it is - 58 kcal/mole and for the calcium silicates $CaSiO_3$, Ca_3SiO_5 and Ca_2SiO_4 their values of free energy of formation are in the range - 20 to - 30 kcal/mole ; the alumino silicate values are even smaller. (silicate free energies of formation are from the oxides.) Therefore the assumptions made in the I series of experiments have been vindicated in as much that hydrogen and liquid sodium chloride in contact with the silicates of coke ash will generate a small amount of hydrogen

M. Methods of introducing known quantities of cuprous chloride vapour into a helium gas flow

The M series of experiments and tests, were designed to produce a satisfactory method of introducing cuprous chloride vapour into the helium gas flow. This was necessary , in order to study the reduction of cuprous chloride on a coke bed.

Experiment M1 A plug of copper wool of approximate weight 15 gms was held in a Mk II reaction tube at a temperature of 800°C and chlorine was added to the pure dry helium flow to give a concentration of 1000 ppm. The effluent gases were passed over 0.88 ammonia which gives a sensitive reaction to the presence of chlorine by producing dense white fumes of ammonium chloride. This same procedure was repeated at a temperature of 850°C.

Results. Although it was discovered that cuprous chloride had been formed and condensed in the cooler end of the reaction tube, the reaction was incomplete and free chlorine was being detected at both temperatures. The cuprous chloride appeared as a white crystalline cubic solid which, on exposure to the atmosphere turned colour to light,pale green. It was assumed therefore that there was insufficient contact between the chlorine carried in the helium flow at 8 ml/min and the copper wool.

Experiment M2 A bed of fine copper powder was held in a Mk II reaction tube at 800°C in a flow of pure dry helium and then chlorine was introduced into the system to give a concentration of 1000 ppm. The copper bed was approximately 5 cm deep and the copper powder was +200 mesh to dust. The temperature of the bed was raised to 1000°C after a period of reaction at 800°C. The chlorine concentration was now raised to 20,000 ppm in the helium flow. It was calculated that the residence time of the gases in the bed was less than 10 seconds and was probably about 5 seconds. It was difficult to calculate this quantity, as the bulk density of the copper was difficult to measure, as it settled differently, according to the degree of agitation received.

Results. Free chlorine was detected in all these runs. Even at 1000°C and at a concentration of 1000 ppm, chlorine was not reacting quantitatively

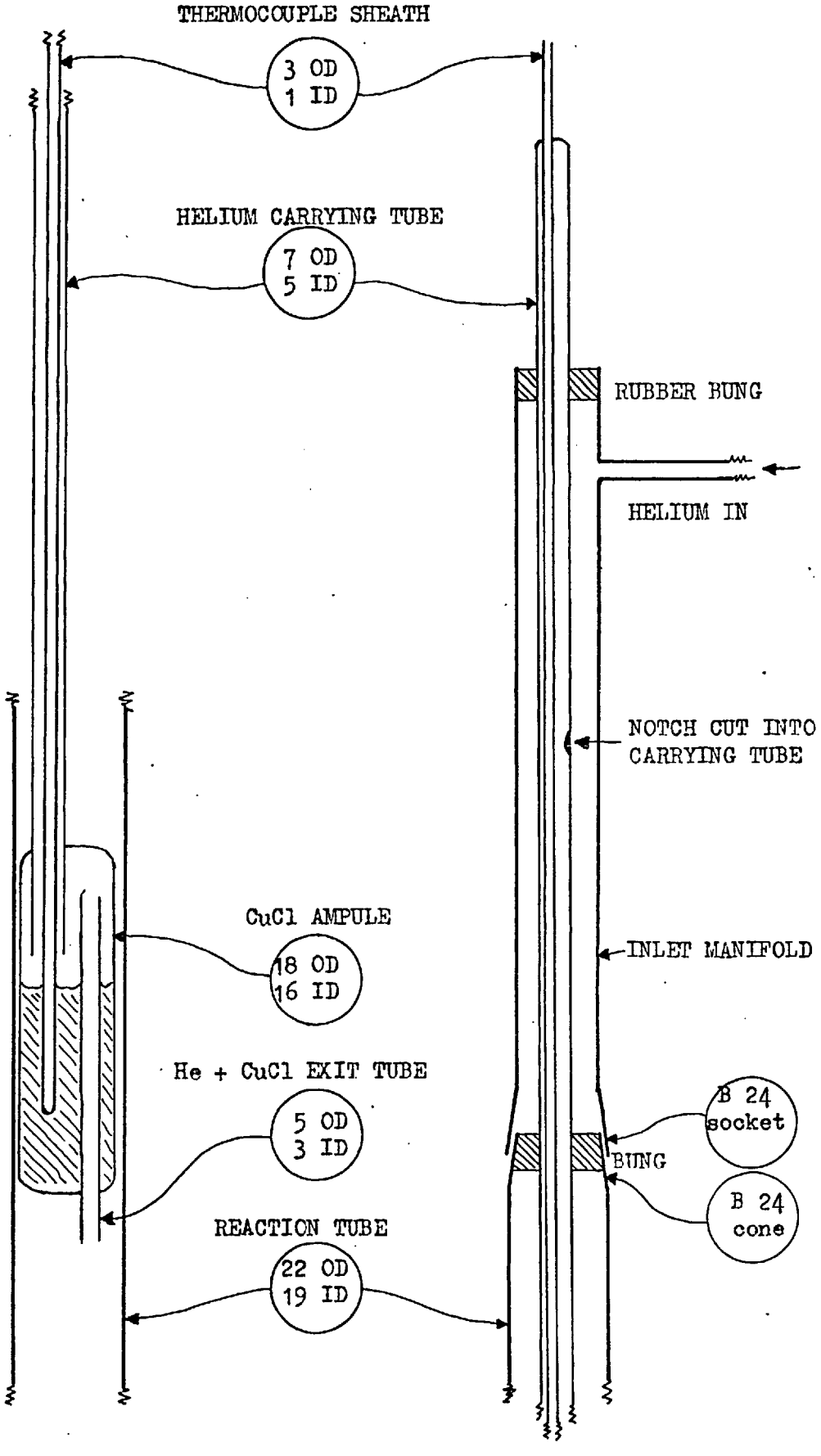
with the copper bed, and free chlorine was detected. Thus this method of introducing cuprous chloride vapour into the gas stream , was abandoned.

The Cuprous Chloride vessel. This piece of apparatus was designed such that the helium flow would pass over the surface of liquid cuprous chloride, become saturated with the vapour, and then , the helium containing the cuprous chloride vapour , would be passed towards the coke bed. The apparatus was built in silica and was named the cuprous chloride vessel.(see figure 3 page 35). The method of installation of this vessel into a Mk II tube, is shown in fig. 23. The sealing system designed allows the copper chloride vessel to be raised or lowered in the reaction tube thus the temperature of the cuprous chloride is variable up to the temperature of the bed. The temperature is measured by a mineral insulated thermocouple of overall diameter of 0.5 mm. This thermocouple was not constructed from the usual materials and had a kind of Ni/NiCr junction, therefore it was calibrated against a Pt/Pt-13%Rh thermocouple.

This vessel could only be used with either the Mk II reaction tube or a Mk III. The only problem encountered with this vessel was that due to the fact that since the entry tube into the copper chloride ampule was offset the holes bored in the bungs had to be offset and all three items had to be correctly aligned when the reaction tubes were being prepared. If they were not so aligned either the vessel could not be raised or lowered or, more frequently, the copper chloride vessel shattered as the manifold socket was finally mated with the reaction tube cone. The method of preparing a reaction tube was as follows; the copper chloride vessel,when charged with material, had the first rubber bung slid half way down it to below the gas inlet slit. The vessel was now slid into a reaction tube and the bung was firmly seated to be gas tight in the cone of the reaction tube. The vessel's free end was now pushed through the bung in the inlet manifold and this was now slid down to mate with the reaction tube;as was explained above, if the ampule offset was not aligned with both the bung offsets, it was at this point that the vessel broke. However, with increase in use, the breakages were fewer and fewer.

FIGURE 23 Cuprous Chloride Vessel.

all measurements in millimetres, made in silica



DISCUSSION

It was hoped, in this series of experiments , that chlorine could be passed over copper in a quantitative manner, to produce gaseous cuprous chloride.

The free energy of formation of liquid cuprous chloride at 750°C is - 22 kcal /mole and at 1000°C it is - 20 kcal/mole thus at these temperatures the equilibrium partial pressure of chlorine is of the order of 10^{-9} atmos. Since the partial pressures of chlorine used in experiments M1 and M2 were 10^{-3} and 2×10^{-2} it would be expected that virtually all the chlorine would react with the copper. In fact, from the experimental results it was found that the reaction of copper and chlorine did not reach equilibrium since dense white fumes were noticed when the effluent gases were passed over 0.88 D ammonia. When 10^{-6} atmos. of chlorine were passed over ammonia only whispy white fumes were detected. Therefore this system was governed by the kinetics of the gas solid interaction.

The cuprous chloride vessel (see figure 23) was designed to give a controlled partial pressure of cuprous chloride at a known temperature. It was decided not to bubble helium through liquid cuprous chloride since it was felt that the liquid would splash . Therefore a stream of hydrogen was directed at the surface of the liquid cuprous chloride and the resulting gas mixture was then directed downwards again towards the coke bed, The main disadvantage of this system is that the temperature of the vapour is not known exactly. Ideally the thermocouple should be placed at the top of the exit tube inside the ampule. However this would have brought numerous construction difficultie Therefore it was decided to measure the temperature of the bulk of the liquid cuprous chloride and make a reasonable assumption about the temperature of the vapour. Since the helium gas flow is directed onto the surface of the liquid and there is a comparatively large mixing volume the reasonable assumption is made that the partial pressure of cuprous chloride so generated is the saturation partial pressure.

* * * * * * * * *

N. Effect of various cuprous chloride vapour pressures on the reactions of coke and water vapour at 750°C.

It was now decided to try and ascertain the nature of cuprous chloride reduction by gaseous hydrogen. To enable the reaction to be studied accurately, it was decided to use water vapour-generated-hydrogen, rather than the unsteady coke-generated-hydrogen, hence the bed was degassed at 1000°C.

Experiment N1 Following the above procedure a Mk II reaction tube was filled with coke to give a bed depth of 5.3 cm. The cuprous chloride vessel was filled to the tip of the gas inlet tube with analar material, placed in the reaction tube and the inlet manifold was then mated to the reaction tube as outlined above. The coke bed was then heated to 1000°C with the cuprous chloride vessel retracted to its full limit and dry helium was passed through the bed for about 50 hours. The temperature of the bed was then lowered to 750°C and helium containing 10,000 ppm of water vapour was passed through the bed. The steady state values of the effluent gas concentrations were noted as well as the temperature of the cuprous chloride. The vessel was now lowered 3 cm into the reaction tube and when a steady state was attained the gas concentration values were noted. The vessel was then lowered one centimetre further into the reaction tube and the steady state gas concentrations were noted together with the cuprous chloride temperature. This procedure of lowering the vessel a centimetre in an evening and taking readings of the effluent gas stream during the following day was repeated for ten consecutive days, the reaction was then terminated.

Results The steady state gas concentrations are given in table 8 together with $K_{6\ obs}/K_{6\ calc}$ and the oxygen balance values. It was assumed that the decrease in the hydrogen concentration with increase in cuprous chloride temperature was due to hydrogen chloride formation only. Thus since the oxygen balance figures are consistent with an increase in the reduction of water vapour, the value of the hydrogen concentration substituted in the a_c and K_6 equations was taken as the difference between the inlet and exit water vapour concentrations. From this value of theoretical hydrogen concentration was subtracted the actual values and the resulting values are referred to as 'lost' hydrogen. Thus table 8 contains 'lost' hydrogen as

TABLE 8 Experiment N1

CuCl TEMPERATURE °C	340	501	530	553	580	612
H_2 theoretical	3200 ppm	3200 ppm	3300 ppm	3400 ppm	3600 ppm	3800 ppm
H_2 actual	3188 "	3150 "	3152 "	3111 "	3072 "	3069 "
H_2 'lost'	12 "	50 "	148 "	289 "	528 "	731 "
water vapour	6400 "	6400 "	6300 "	6200 "	6000 "	5800 "
carbon monoxide	1747 "	2060 "	2134 "	2154 "	2232 "	2508 "
carbon dioxide	650 "	575 "	575 "	600 "	650 "	650 "
oxygen balance	99 %	99 %	100 %	100 %	100 %	100 %
a_c	2.41×10^{-4}	2.91×10^{-4}	3.09×10^{-4}	3.20×10^{-4}	3.60×10^{-4}	4.56×10^{-4}
$K_{6\ obs}/K_{6\ calc}$	0.141	0.106	0.107	0.113	0.129	0.129

CuCl TEMPERATURE °C	631	646	658	673	685	699
H_2 theoretical	4000 ppm	4400 ppm	4800 ppm	5300 ppm	5800 ppm	6500 ppm
H_2 actual	2792 "	2360 "	2017 "	1485 "	1123 "	650 "
H_2 'lost'	1208 "	2040 "	2783 "	3815 "	4677	5850 "
water vapour	5600 "	5200 "	4800 "	4300 "	3800 "	3100 "
carbon monoxide	2890 "	3502 "	4136 "	4798 "	5410 "	6251 "
carbon dioxide	525 "	420 "	350 "	260 "	225 "	125 "
oxygen balance	100 %	100 %	100 %	100 %	100 %	100 %
a_c	5.64×10^{-4}	8.01×10^{-4}	1.16×10^{-3}	1.64×10^{-3}	2.35×10^{-3}	3.63×10^{-3}
$K_{6\ Obs}/K_{6\ calc}$	0.0988	0.0754	0.0652	0.0509	0.0425	0.0318

well as the theoretical and the actual values.

The actual gas concentration values are plotted against the temperature of cuprous chloride in figure 24. 'Lost' hydrogen is also plotted against cuprous chloride temperature in figure 25. $K_{6\ obs}/K_{6\ calc}$ and a_c are plotted in $\log_{10}$ form against cuprous chloride temperature in figure 26. The reaction tube and the cuprous chloride vessel are shown as they were after the experiment in plates 1 and 2 respectively. The tip of the cuprous chloride vessel has been enlarged in plates 3 and 4 to show the nature of the deposit and the discolouration of the ampule.

It will be seen from figure 24 that there are three regions of developement, firstly the 340°C to 500°C area where the hydogen and water vapour plots change very little but since the carbon monoxide plot increases slightly the carbon dioxide values fall to keep the mass balance correct.

In the second region, water vapour reduction increases and consequently the concentrations of carbon monoxide and dioxide increase, however the actual concentration of hydrogen in the effluent gases falls over 500°C to 600°C.

The third region shows a rapid decrease in the hydrogen concentration with increase in the cuprous chloride temperature from 500°C to 700°C. Over this same temperature range the carbon dioxide concentration also diminishes as does the water vapour concentration. The carbon monoxide concentration however rapidly increases.

In figure 25 it can be seen that the 'lost' hydrogen concentration is a strong function of cuprous chloride temperature especially at the higher temperatures. Thus although from the water vapour and carbon monoxide plots of figure 24 it appears that the degree of reduction of water vapour increases markedly with cuprous chloride temperature, a corresponding increase in the concentration of hydrogen is not noticed in the effluent gases. In fact the reverse is observed and the actual concentration decreases with increasing cuprous chloride temperature thus giving rise to the rapid change of 'lost' hydrogen concentration with temperature.

The degree of reduction of water vapour , calculated as the apparent activity

FIGURE 24 CHANGES IN EFFLUENT GAS COMPOSITION WITH CuCl TEMPERATURE

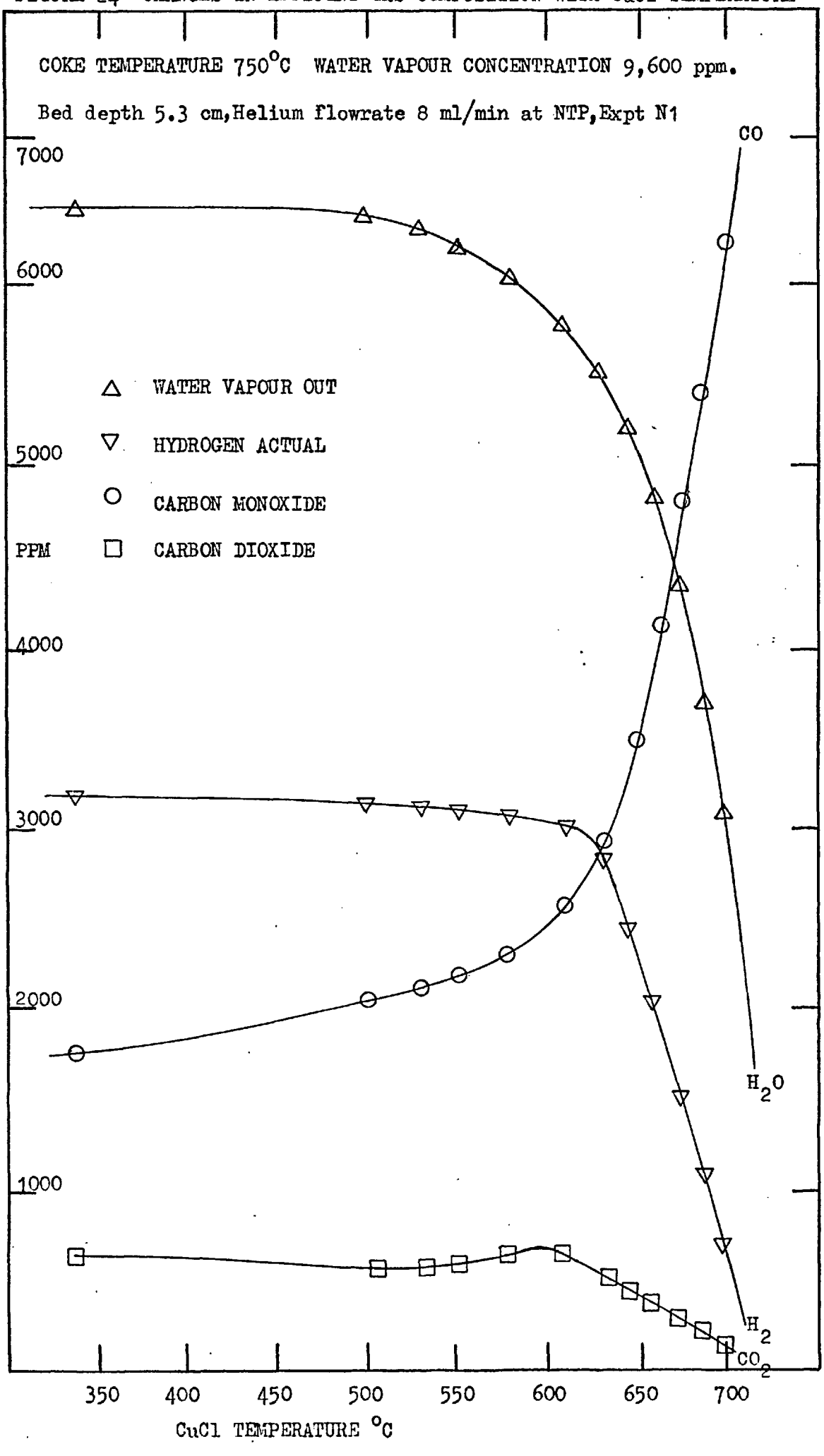


FIGURE 25 CHANGES IN 'LOST' HYDROGEN CONCENTRATION WITH CuCl TEMP°.

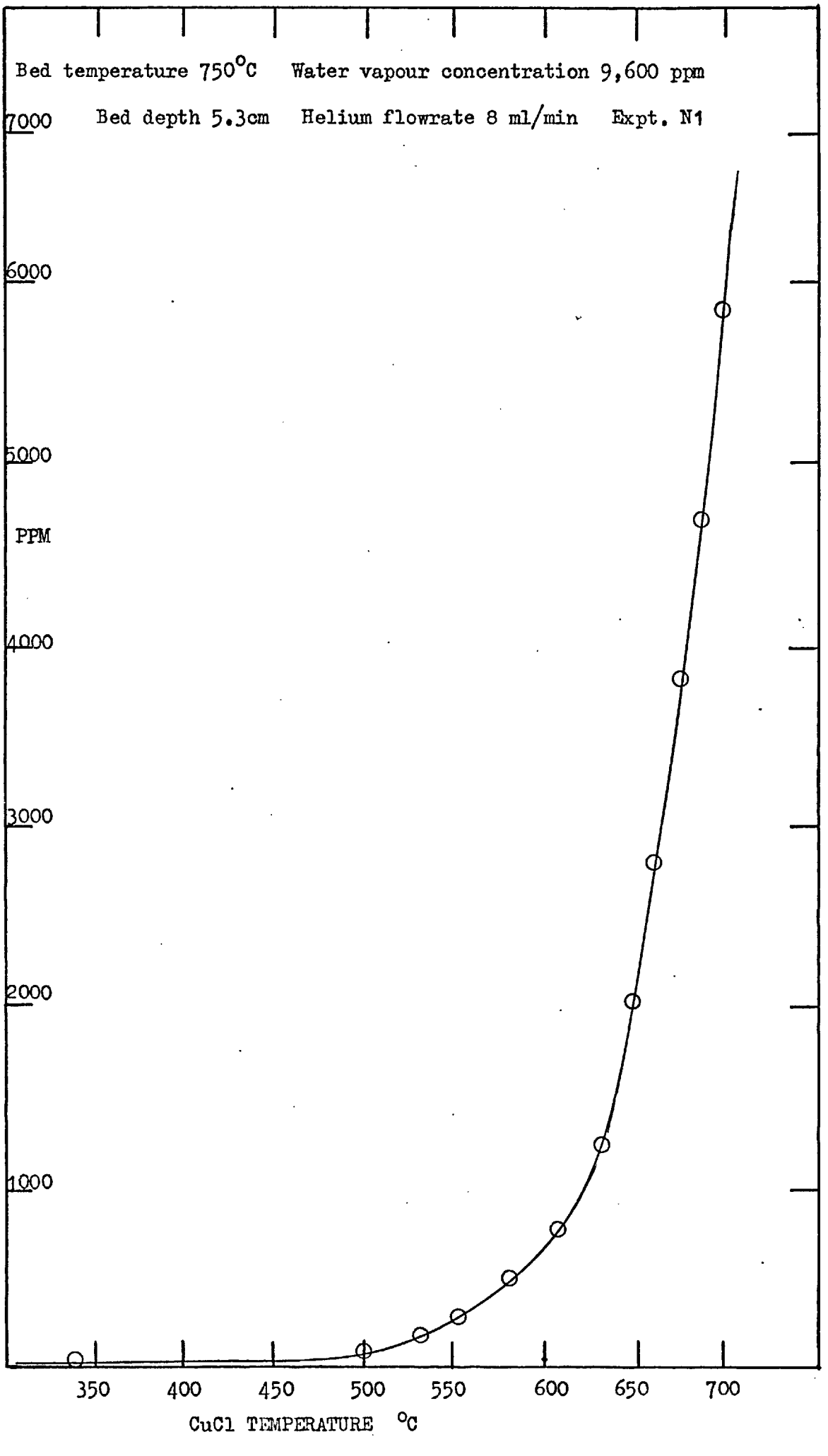


FIGURE 26 a_c AND K_6 PLOTS AGAINST CuCl TEMPERATURE FOR EXPERIMENT N1

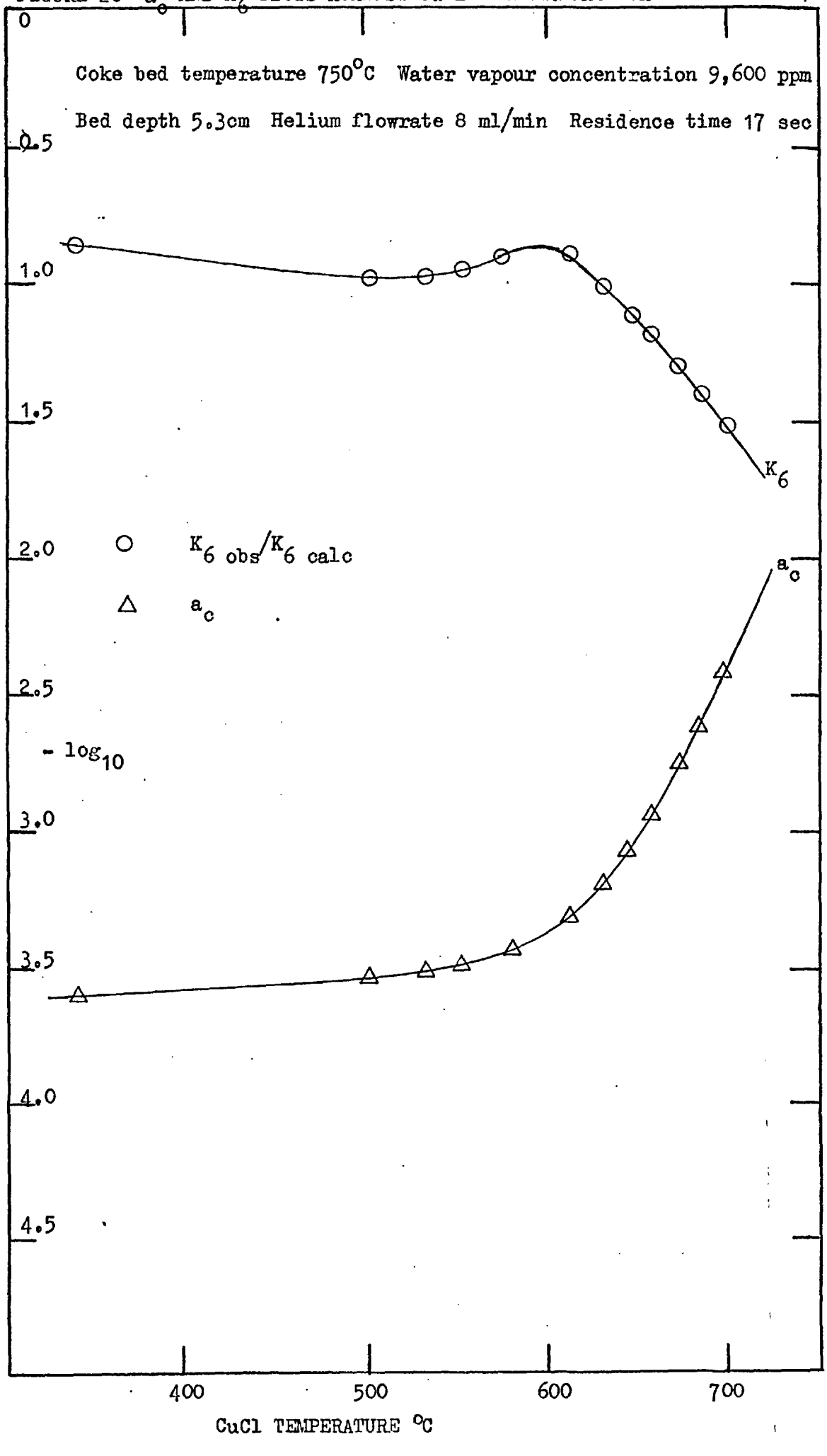




PLATE 1



PLATE 2



PLATE 3 ←1 cm→



PLATE 4 ←—— 1 cm ——→

of carbon rises rapidly as the copper chloride temperature increases from 500°C to 700°C and only confirms the first stage behaviour from 340°C to 500°C as being relatively constant. However the K_6 plots accentuate the three individual stages; in the first stage the plotted value gradually falls with increasing cuprous chloride temperature, but from 500°C to 600°C the plot experiences a minima and begins to rise in value again. However at 600°C there is a maxima and the plot diminishes in value at a steeper rate than in the first stage.

In plate 1 it can be seen that there was an extensive deposit of metallic copper which extended for twenty centimetres on the silica tube reaction vessel walls above the coke bed, and there was a two centimetre gap of clear silica between this deposit and a small amount of copper deposited on the silica wool plug on top of the coke bed. As far as could be seen, and by subsequent reaction of the coke with nitric acid, there was very little if any copper deposited on or in the coke bed. There was a deposit of condensed cuprous chloride at the top of the reaction tube formed by cuprous chloride vapour diffusing past the cuprous chloride ampule and by being forced back past the ampule every time the ampule was lowered. Plate 2 shows that there was copper deposited not only on the underneath of the CuCl ampule but also on the down tube above the ampule. This second deposit was thought to be due to hydrogen diffusing back past the ampule and reducing the chloride. As on the main reaction vessel, there was a deposit of cuprous chloride higher up the down tube.

Plate 3 shows that there was some reaction between the cuprous chloride and water vapour to produce some copper oxide inside the ampule. Plate 4 shows that the nature of the deposit on the ampule bottom was twofold. The main deposit was a continuous sheet but this was sporadically dotted with clusters of dendritic growths. The copper deposit on the reaction tube walls was all smooth, continuous, sheet-like foil which in places had become detached from the vessel's walls.

Below the coke bed there was a deposit of solid cuprous chloride, which can be just distinguished in plate 1, about four centimetres above the bottom cone joint. In air, both this deposit and the one above the ampule in the reaction vessel, are oxidised from white to a green colour.

DISCUSSION.

From the A series of experiments , it was found that the deposited copper only existed on the coke surface, and so it came as a surprise, in this series of experiments, to find that copper deposition had taken place on every surface in the system, except that of the coke. The major difference between this series and the A series, is that the helium flowrate was very much lower in this series, and the gas residence time , compared to the A series, has increased by a factor of 24. Thus, although this series resembled a static TORCO system more closely, the non-static A series gave a much better type of copper deposition, i.e. on the coke.
The major finding from this series therefore, is that, in reducing cuprous chloride , gaseous hydrogen leads to the non-specific deposition of copper. In regard to a TORCO process, this is unsatisfactory.

The N experiments were the first real attempt at depositing copper on coke but as can be seen from plate 1 no copper did deposit on the coke.
It is thought that since the linear velocity of the helium in the gap between the cuprous chloride vessel and the coke bed was 0.2 cm/sec at 750°C, the system can be regarded as almost static, therefore diffusion becomes a major influence on the reactions. Since, generally gaseous diffusion rates are inversely proportional to the square root of their molecular weights, so hydrogen can diffuse some 12 times as fast as cuprous chloride trimer vapour. Thus it is supposed that hydrogen diffuses away from the coke bed and reduces the trimer on the silica vessel's walls. This means that the hydrogen concentration in the coke bed is lowered from its steady state value. In a system without cuprous chloride vapour, hydrogen diffuses out of the coke bed but also diffuses back in and so keeps the

partial pressure of hydrogen leaving the bed constant, however when cuprous chloride is reacting with the hydrogen that has diffused out of the bed the concentration of hydrogen re-entering the bed falls and so the concentration of hydrogen in the bed, and subsequently the effluent gas stream, falls below the steady state value. To try and reinstate the steady state more water vapour reacts and as the temperature of the cuprous chloride is raised so its vapour pressure increases and so more hydrogen is consumed and so more water vapour reacts and the concentration of carbon monoxide reflects this increase by itself increasing.

Since no copper is deposited in the bed it is thought that the concentration of active sites involved in water vapour reduction remains constant and the extra water vapour reacting does so at the sites vacated by the desorbing hydrogen. Consider water vapour reacting to give hydrogen and carbon monoxide only, which then set up a steady state condition between the adsorbed and gaseous states. Now if hydrogen is removed from the gas phase by reaction with cuprous chloride then the adsorbtion /desorption steady state is upset. More hydrogen is desorbed to try and restore the gaseous concentration so generating free active sites. Water vapour reacts with these sites producing more hydrogen and carbon monoxide and surface oxide C_o'. Because the poisoning effect of adsorbed hydrogen is reduced so the coke surface appears to be more active (viz. the increase in a_c), but the same number of active sites are involved. The apparent activity of carbon increases because it was assumed that the equilibrium constant was unaffected by the presence of cuprous chloride vapour and, the value of P_{H_2} substituted into the equations was the theoretical value calculated from mass balances i.e. the value of P_{H_2} if none was reacting with cuprous chloride. Thus as a whole, the carbon is more reactive, however if just the bed is considered and the value of P_{H_2} substituted is the actual value leaving the bed, i.e. in a steady state with the coke surface and instead of a_c the concentration of active sites $[C_f]$ is substituted, which, by the above reasoning should be constant, then:-

$$K = \frac{P_{H_2 \text{actual}} \times P_{CO}}{[C_f] \times P_{H_2O \text{ out}}}$$

and so $K \times [C_f] = \frac{P_{H_2 \text{ actual}} \times P_{H_2 \text{ theoretical}}}{P_{H_2O \text{ out}}}$

assuming that $P_{CO \text{ actual}} = P_{H_2 \text{ theoretical}}$ i.e. no carbon dioxide is formed

The values of $K \times [C_f]$ obtained from the experimental results are 1.6, 1.65, 1.6, 1.7, 1.8, 2.0, 1.9, 1.9, 1.8, 1.7, 1.6 all x 10^{-3} over the cuprous chloride temperature range of 340 to 699°C . Since these values roughly rise and fall according to the carbon dioxide production which was assumed to be zero, it can be said that the value of $K \times [C_f]$ is not significantly altered during the increasing reaction of water vapour.

Therefore, as was proposed earlier, the number of active sites involved in water vapour reduction remains largely unaltered and the increase in water vapour reduction is due to the releasing of active sites for reaction , which were previously occupied by hydrogen. Hydrogen is effectively removed from the bed by one way diffusion to meet cuprous chloride which it reduces on the nearest surface which happens to be the silica vessel walls and the cuprous chloride ampule.

Carbon dioxide production initially decreases slightly up to about 500°C this is not really significant since the fall is minimal. It is thought that this slight decline is a function of the small decline in the water vapour concentration up to this point. After 500°C the reduction of cuprous chloride becomes significant and the water vapour concentration begins to fall dramatically. The carbon dioxide concentration however, rises as the concentration of Co and carbon monoxide both rise with the increasing reduction of water vapour. This confirms earlier assumptions that carbon dioxide is formed by the reaction of Co. . After the

temperature of cuprous chloride reaches 600°C the concentration of carbon dioxide falls and as the concentration of water vapour approaches zero so does that of carbon dioxide. Thus carbon dioxide production appears to be a function of water vapour. Previously it was thought that carbon dioxide formation was a function of 'Co' in as much that the concentration of 'Co' on the carbon surface has to achieve a certain level before the dioxide appears in the gas stream. This still holds true. However the reaction of 'Co' to the dioxide cannot be considered to be totally dependent on the gaseous concentration of carbon monoxide. It can be said however, that above a critical concentration of water vapour , 'Co' and the monoxide may react to produce the dioxide ; this occurs between cuprous chloride temperatures of 500 and 600°C. Above 600°C the critical concentration of water vapour has been achieved and now the dioxide production becomes a strict function of the water vapour concentration. So as the gaseous concentration of water vapour approaches zero so the rate of production of carbon dioxide also tends towards zero. This same effect was noticed to a lesser degree in the residence time experiments. As the water vapour reduction increased with increase in residence time so the concentration of carbon dioxide decreased. This action was peculiar to coke only and was attributed to the inhibitive catalysis by the ash constituents, of the 'Co' and water vapour reaction. Thus it is possible that carbon dioxide is produced partly by the reaction of Co and carbon monoxide :-

$$Co + CO \rightleftharpoons (CO_2) \rightleftharpoons CO_2 + C_f \quad \text{.....(25) \& (27)}$$

This reaction is strongly retarded by some of the ash constituents in coke in which case the secondary reaction of Co to CO_2 predominates :-

$$Co + H_2O \rightleftharpoons (CO_2) + H_2 \rightleftharpoons CO_2 + C_f + H_2 \quad \text{.....(26) \& (27)}$$

The retardation of reactions 25 and 27 by ash constituents appears to be inhibited by the presence of water vapour, above a critical concentration, in the coke bed, or, more likely, that carbon dioxide is produced solely by the reaction of 'Co' and water vapour.

Since the 'lost' hydrogen has been presumed to reduce the cuprous chloride then :-

$$\frac{n}{2} H_2 + (CuCl)_n \longrightarrow n\ Cu + n\ HCl \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

therefore 1 mole of 'lost' H_2 = 1 mole $(CuCl)_2$ = 2/3 mole $(CuCl)_3$ etc.

The temperature of the cuprous chloride as measured is the temperature of the liquid and so the results of this experiment have been lowered by two readings which is equivalent to taking the temperature of the vapour above the liquid surface rather than the temperature two centimetres below this point in the liquid. Thus the results for the liquid temperature of 699°C are taken to be the results for a vapour temperature of 673°C. This procedure implicitly implies that the vapour generated above the liquid does not condense as it moves up to the top of the exit tube in the ampule. This procedure had to be adopted since the CuCl ampule is lowered into a steep temperature gradient inside the reaction tube and so there may be a temperature difference of 100°C across the ampule. It is the temperature of the vapour that is really required and rather withdraw the thermocouple back by two centimetres where it might be subject to a cooling effect of incoming helium it was left at the bottom of the sheath measuring the liquid temperatures which are now transposed by two readings to give a more accurate value of the vapour temperature. Since no condensed cuprous chloride was noticed in the top of the ampule it was decided that the vapour went into the super-saturated state before it emerged out of the exit tube and so did not condense. This is why it was decided to standardise the position of temperature measurement of the vapour at just above the initial liquid surface.

If the lost hydrogen results are plotted as $\log_{10} P$ versus $1/T$ (see fig 26a) this gives a Van't Hoff plot which is equivalent to the vapour pressure of $(CuCl)_2$ over liquid cuprous chloride. The results were subjected to a linear regression analysis and the following equation was derived :-

$$\text{Log}_{10}\ P_{H_2}\ (\text{atmos}) = -5{,}539 \times 1/T + 3.597 \quad \text{corr.coeff } .99886$$

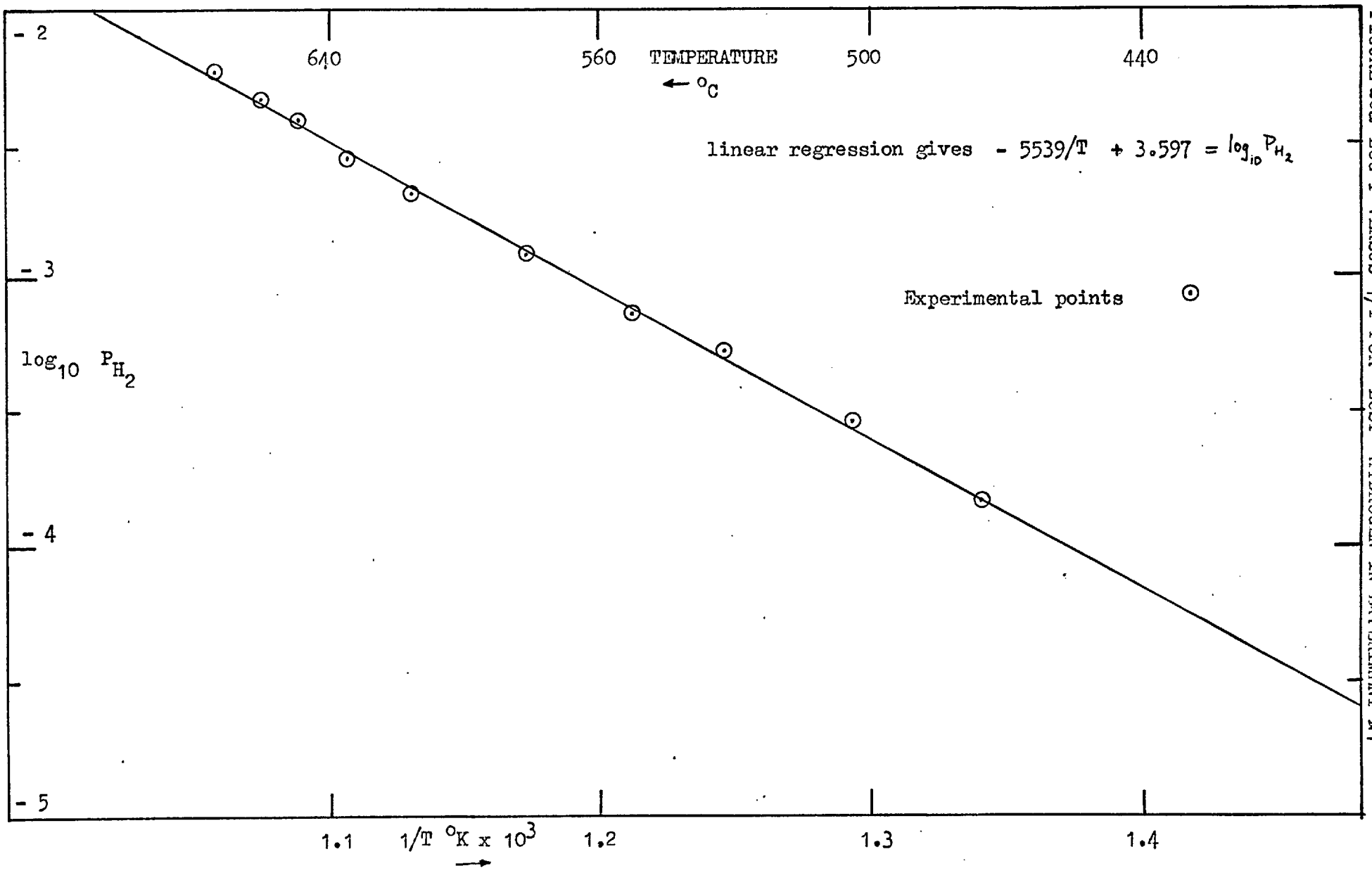


FIGURE 26a LOG P VERSUS 1/T FOR 'LOST' HYDROGEN IN EXPERIMENT N1

To convert this to a trimer equation the lost hydrogen results must be multiplied by 2/3 or -0.1761 must be added to the above equation and converting to P in mm Hg :-

$$\log_{10} P_{(CuCl)_3} = -5,540 \times 1/T + 6.3 \pm 0.1 \text{ (graphical error)}$$

Therefore for $(CuCl)_3$ over the temperature range 700°K to 1000°K this gives ΔH_v as 25 kcal /mole trimer. It is estimated that including the temperature uncertainty and the concentration errors this figure is accurate to ± 8 %.

Therefore ΔH°_{v} = 25 kcal/mole trimer ± 2 kcal.

The JANAF[62] tables which use the same results to compute their figures as were used in the introduction to give a $\log_{10} P_{(CuCl)_3}$ value, give :-

$\Delta H^{\circ}_{s_{298}}$ = 37.2 ± 0.2 kcal/mole trimer and ΔH°_{m} = 7.3 kcal/mole trimer at 700°K

therefore $\Delta H^{\circ}_{v_{700}}$ = 29.9 ± 0.2 kcal/mole trimer.(assuming ΔH°_{s} is constant)

Therefore the agreement with previous work appears reasonable and the vapour pressure of cuprous chloride trimer can be followed by the lost hydrogen method. This is confirmed by considering the log P equation for the trimer which was generated from the previous work of six authors on the vapour pressure of cuprous chloride trimer.[83,84,85,89,90,92] viz.

$$\log_{10} P_{(CuCl)_3} \text{ mm Hg} = -5276/T + 6.354 \pm 0.25 \quad \ldots\ldots\ldots(30)$$

There were two distinct types of growth of copper; on the silica reaction vessel walls and to some extent on the CuCl vessel, there was a uniform flat crystal growth which built up into a smooth sheet. The other type was dendritic and was only detected on the underneath of the CuCl vessel. It is thought that the nature of the deposits is a function of the ratio of hydrogen to cuprous chloride but as the gas mixing is complicated by diffusion , thermal segregation and natural convection, no rigorous attempt will be made to explain the different deposits.

An experiment was carried out whereby silica wool was held in a dry flow of helium and hydrogen . The hydrogen was then removed from the gas stream and just helium flowed through the wool. After five hours the effluent gas stream was analysed for hydrogen, none was present. The bed of silica

was now heated to 1100°C and the effluent gas stream was analysed for hydrogen but none was evolved. Thus silica does not adsorb hydrogen in great quantities at 750°C , the temperature at which this experiment was carried out. Thus it cannot be the preferential adsorbtion of hydrogen on silica that is responsible for the copper depositing on silica. Thus it is thought that hydrogen reduces the cuprous chloride on the nearest available surface which in this experiment happened to be the reaction vessel walls. Cuprous chloride vapour never reached the coke bed since hydrogen was diffusing out of the bed faster than cuprous chloride was moving towards the bed. It is tentatively suggested that the flow pattern is as follows ; hydrogen moves up the middle of the reaction tube towards the CuCl vessel where it mixes with the vapour and together they pass down the outside of the reaction tube. Thus P_{H_2} is high in the vicinity of the CuCl vessel and low on the walls of the tube.

As reduction of cuprous chloride by gaseous hydrogen is not desirable for a TORCO system, since it leads to non-specific deposition, then an alternative source of hydrogen is required.

It was found in the E series, that water vapour can generate adsorbed hydrogen on a coke surface; also in the A series , it was found that coke contains inherent hydrogen, which can be driven off by heating to high temperatures. These two sources of hydrogen are studied in the following experimental series. It was decided to measure the amount of hydrogen that is evolved when coke is heated to 1000°C from the reaction temperature. It is realised that heating to only 1000°C is a poor method of releasing the hydrogen contained on the coke, but this limitation is placed by the silica ware in the system, ideally the coke should be heated to 2000°C.

From the following series , it was hoped to determine how much hydrogen stably exists on a coke surface , at temperature, and whether water vapour can generate similar amounts,as adsorbed hydrogen.

* * * * * * *

O. Quantities of gases held on a coke surface in a dry helium flow, before and after reaction with water vapour

The object of the O series of experiments, was to determine the volume of hydrogen and carbon monoxide contained on a coke surface, at various temperatures, by heating to 1000°C. It was hoped that it would be possible to measure the quantity of hydrogen and Co, contained on a coke surface, during reaction with water vapour, by heating to 1000°C.

Experiment O1 part I 10.5 gms of coke was placed in a Mk II reaction tube and was heated to 700°C in a flow of dry helium. The helium flowrate was 16 ml/min at NTP and after a period of four days at 700°C the concentrations of hydrogen and carbon monoxide were minimal (20 ppm). The temperature of the bed was then raised to 750°C and the effluent gas stream was analysed for CO, CO_2, CH_4 and H_2. Readings were taken for seven hours and on the following day it was found that the gas concentrations had virtually returned to their previous values.

Part II The bed was then heated to 1000°C and the effluent gas stream was again analysed. The helium flowrate was still kept at 16 ml /min.

Experiment O2 parts I and II. In this experiment the procedure followed was exactly the same as in experiment O1 except that the bed was initially heated to 750°C, then subsequently to 800°C and finally to 1000°C.

Experiment O3 parts I and II Again the same procedure was followed as in experiment O1 but the bed was initially heated to 800°C then to 850°C and finally to 1000°C.

Results O1,O2 and O3 part I In figures 27,28 and 29, the concentration changes of hydrogen and carbon monoxide are plotted against time. These were the only two gases evolved during the whole of the experiment. The carbon monoxide concentration values had returned to their previous values by the following day so these plots were easily integrated to give a volume. However hydrogen was still being evolved after a whole day of reaction but its concentration was low (70 ppm).Therefore for the sake of simplicity and uniformity the volume of hydrogen produced after the 25 hour mark was not taken into account and the plot was merely integrated up to this point.

FIGURE 27 CONCENTRATION versus TIME for EXPERIMENT 01

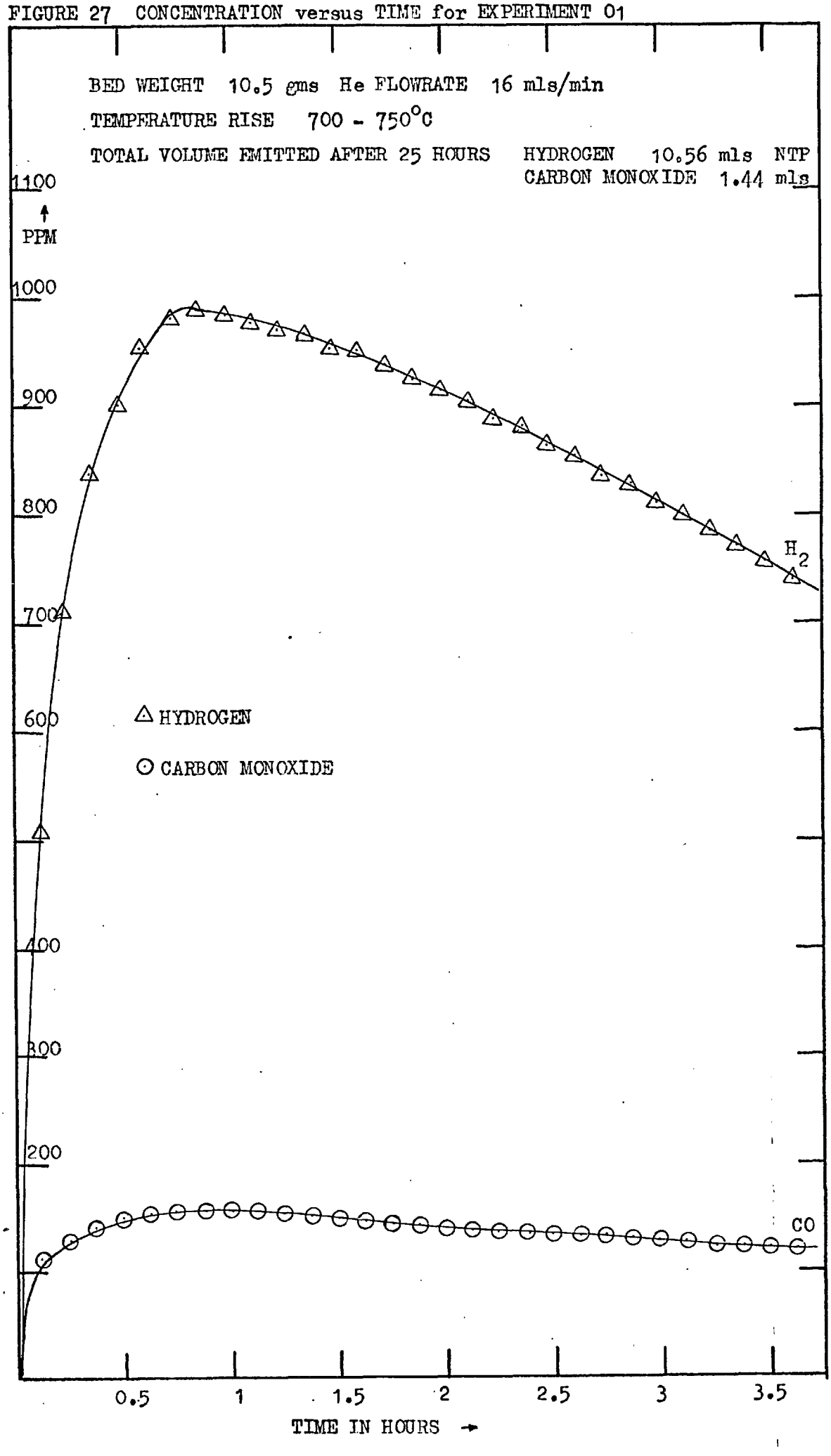


FIGURE 28 CONCENTRATION versus TIME for EXPERIMENT 02

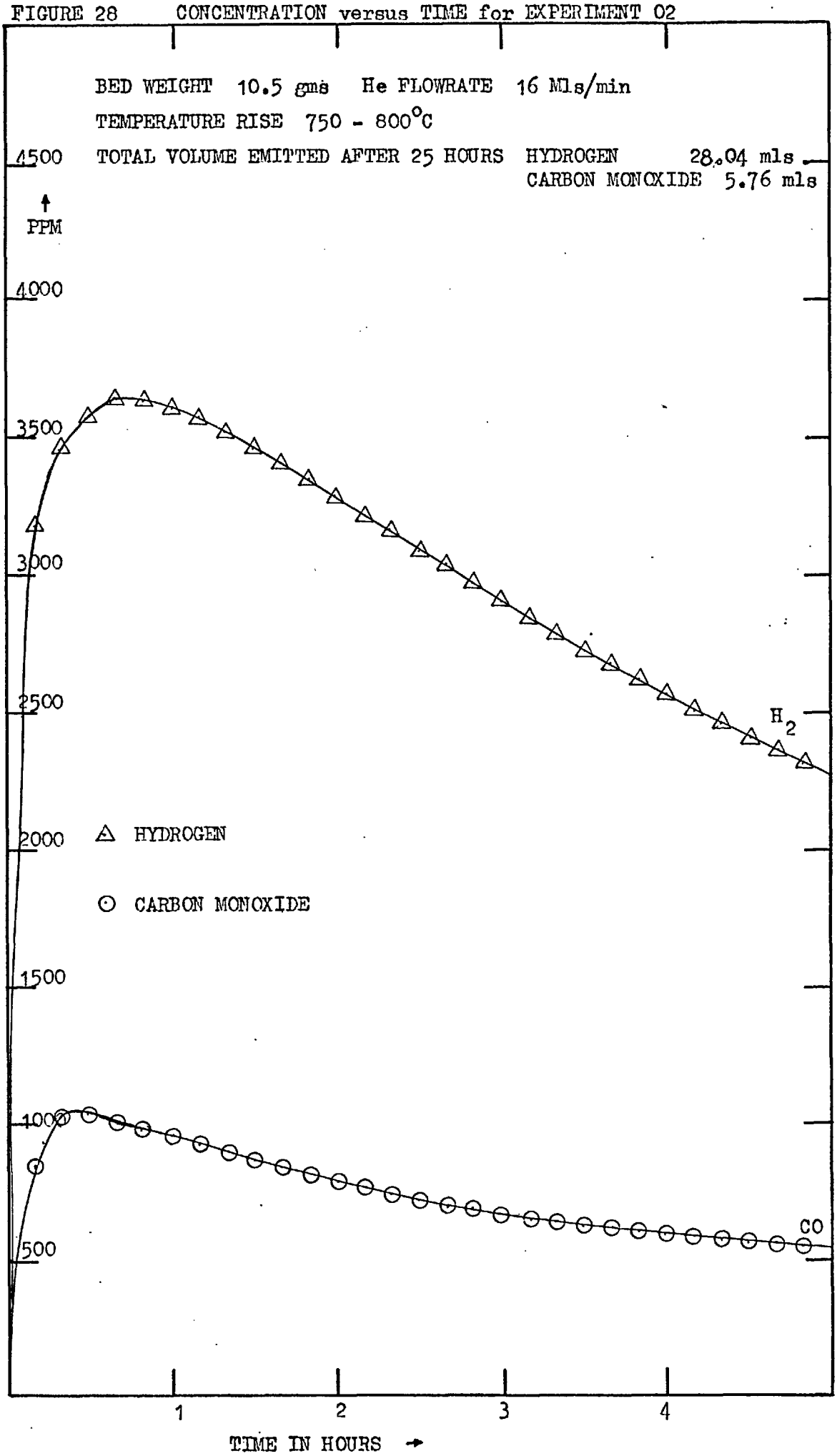
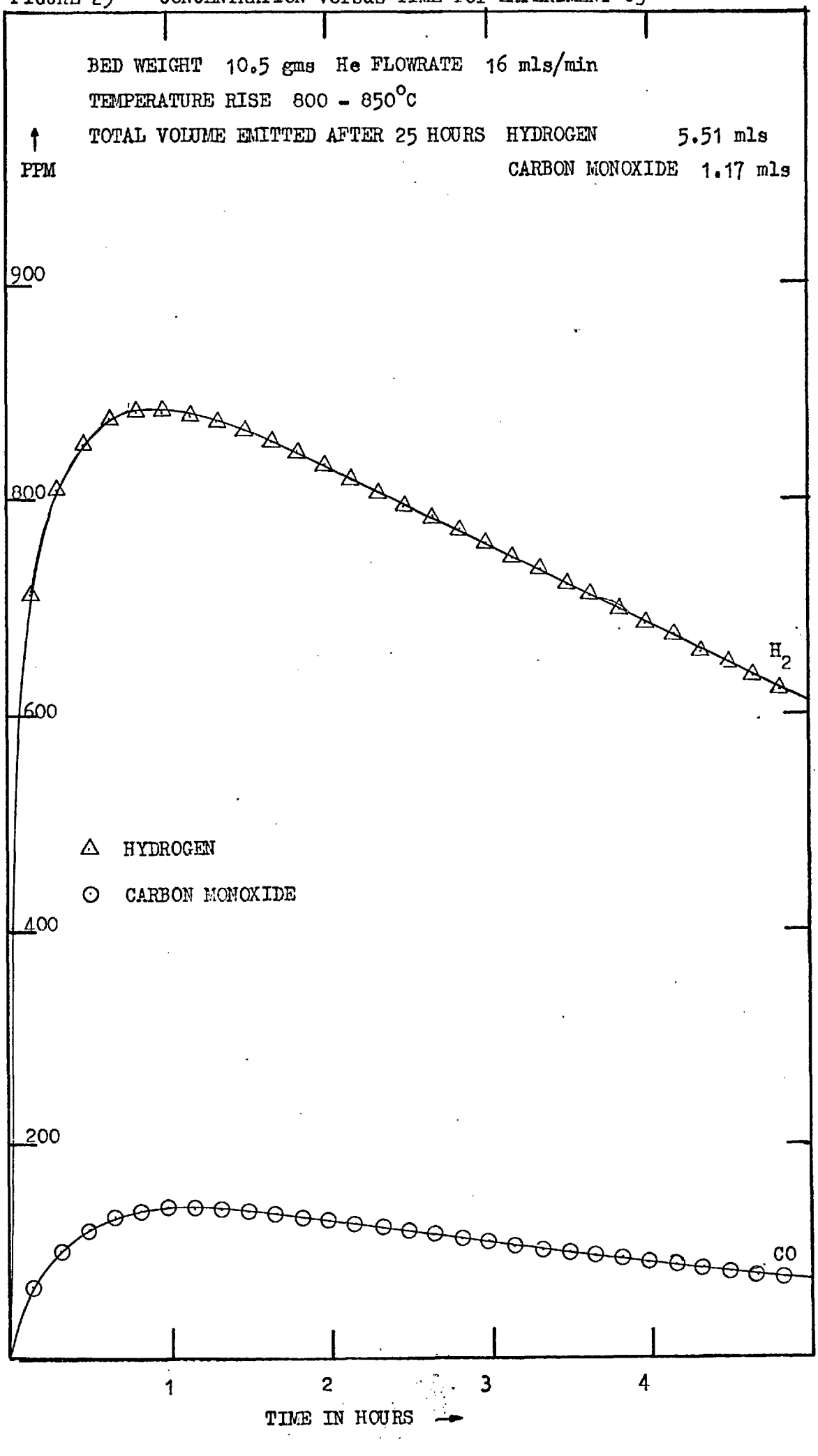


FIGURE 29 CONCENTRATION versus TIME for EXPERIMENT 03



Thus for a 50°C temperature rise from 700°C,750°C and 800°C the values quoted in figures 27,28 and 29 are taken to represent the total volumes of hydrogen and carbon monoxide displaced by this temperature rise. The error in these figures was estimated to be ± 2% for carbon monoxide and ± 5% for hydrogen.

For hydrogen evolution it can be seen that there was a rapid rise in its concentration upto the one hour mark and after this point, where a maximum was attained, the plot gradually decayed with time. Similarly for carbon monoxide evolution there was a rapid initial rise in its concentration which then fell away with increasing time.

No methane or carbon dioxide was detected at all during all these experiments.

01,02 and 03 parts II The results were initially plotted as concentration versus time and as it was apparent that gas evolution was virtually complete after five hours, the plots were each integrated upto this point and the volumes emitted are plotted against time in figures 30, 31 and 32. It can be seen from these plots that carbon monoxide evolution is completed after about ninety minutes. Similarly methane production had ceased after one hour. Hydrogen was still being produced even after two days at 1000°C however its concentration was only 120 ppm.

As the bulk of the hydrogen was evolved during the first five hours at 1000°C the figure for total volume evolved has been taken as the five hour figure. The volume ratio of hydrogen to methane rises over the three experiments from 110:1 through 147:1 to 437:1 for 01,02 and 03. The hydrogen to carbon monoxide volume ratio falls from 4.35:1 to 3.46:1 to 2.54:1 for 01,02 to 03. A comparison of the results for both parts of the experiments can be made by taking the results of the 750°C to 1000°C experiment and comparing them with the sum of the 750°C to 800°C and the 800°C to 1000°C experiments and with the sum of the 750°C to 800°C and the 800°C to 850°C and the 850°C to 1000°C experimental results. These calculations together with the % differences are shown in table 9.

FIGURE 30 VOLUME EMITTED versus TIME for EXPERIMENT 01

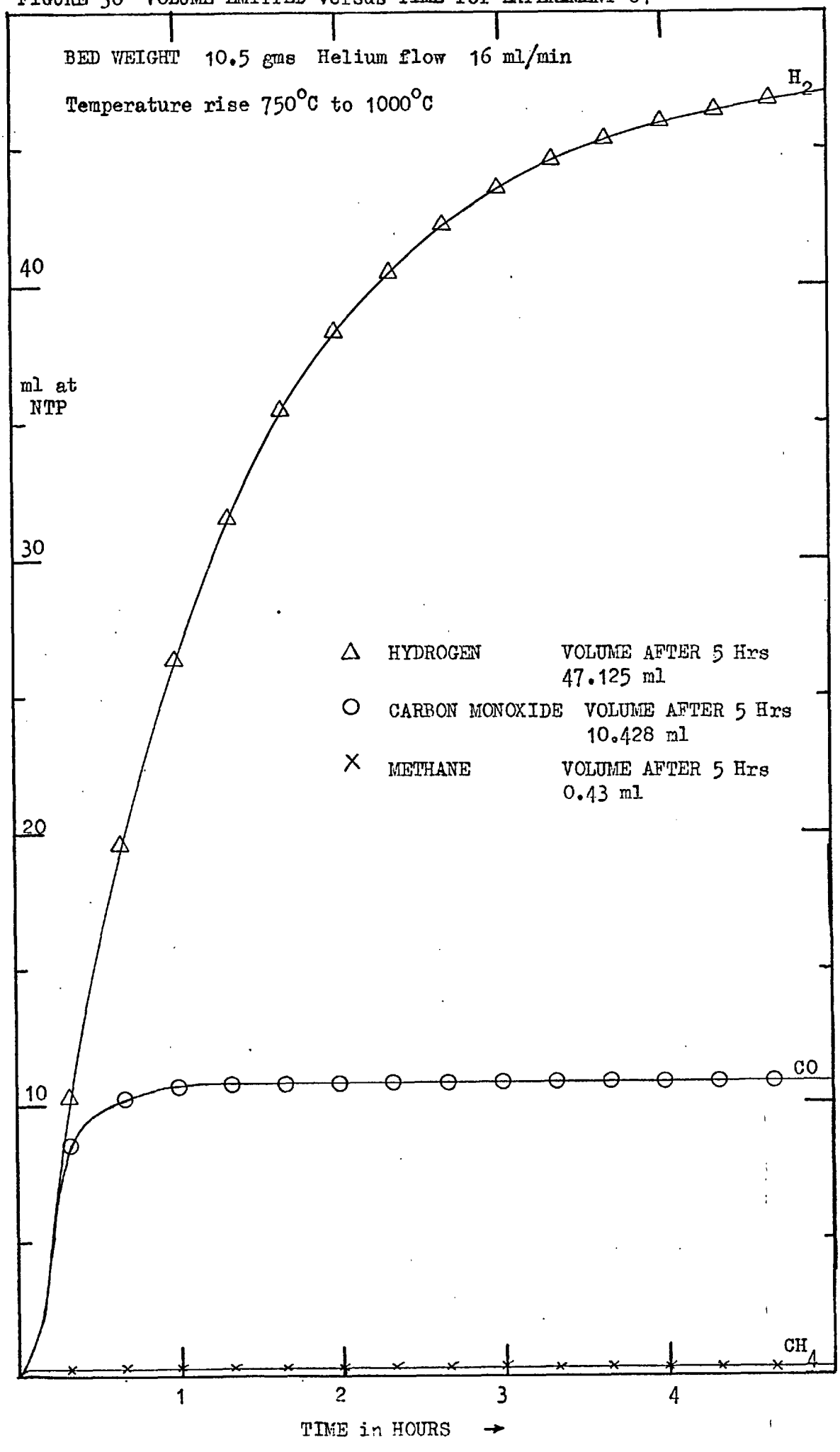


FIGURE 31 VOLUME EMITTED versus TIME for EXPERIMENT 02

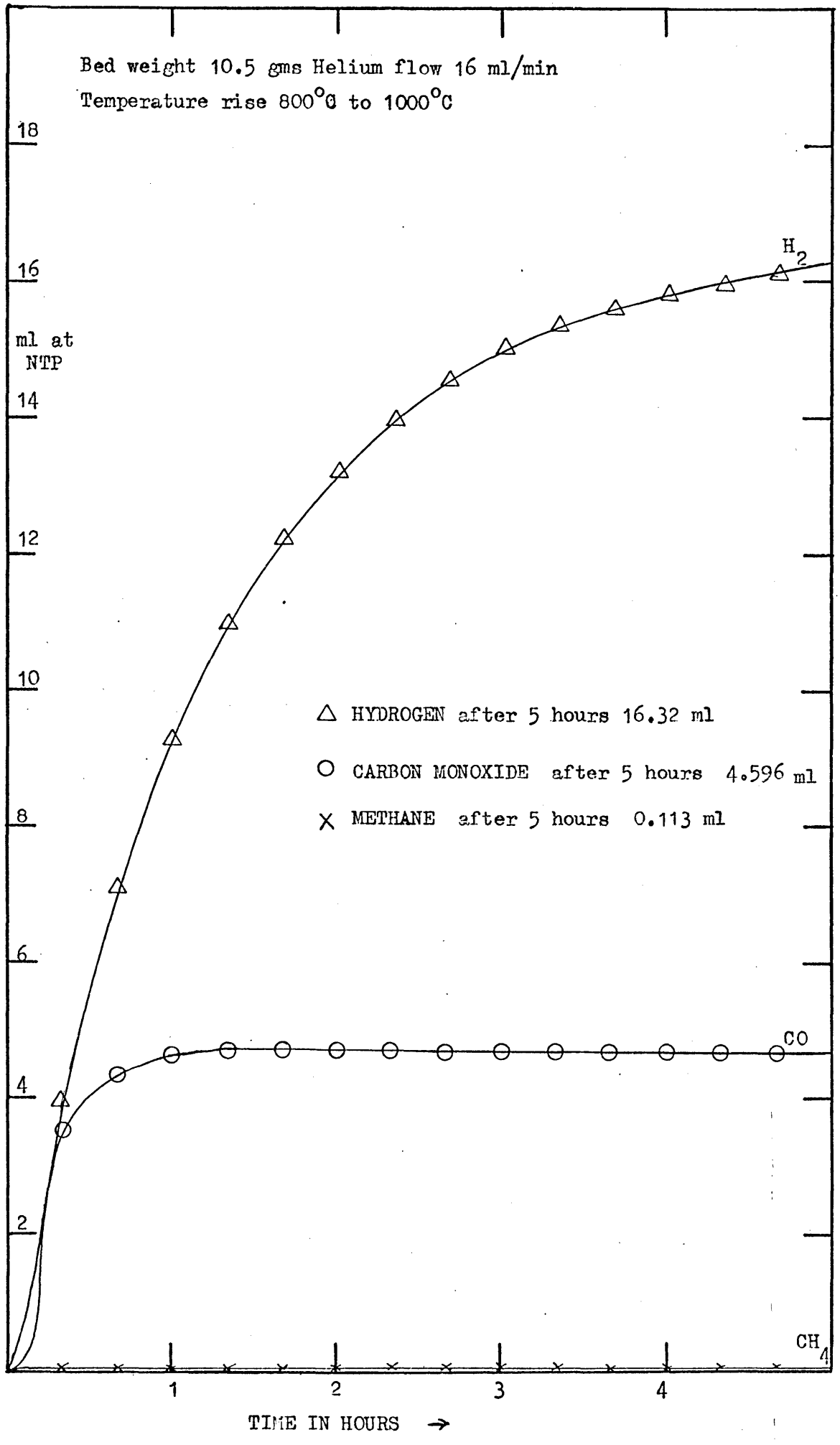
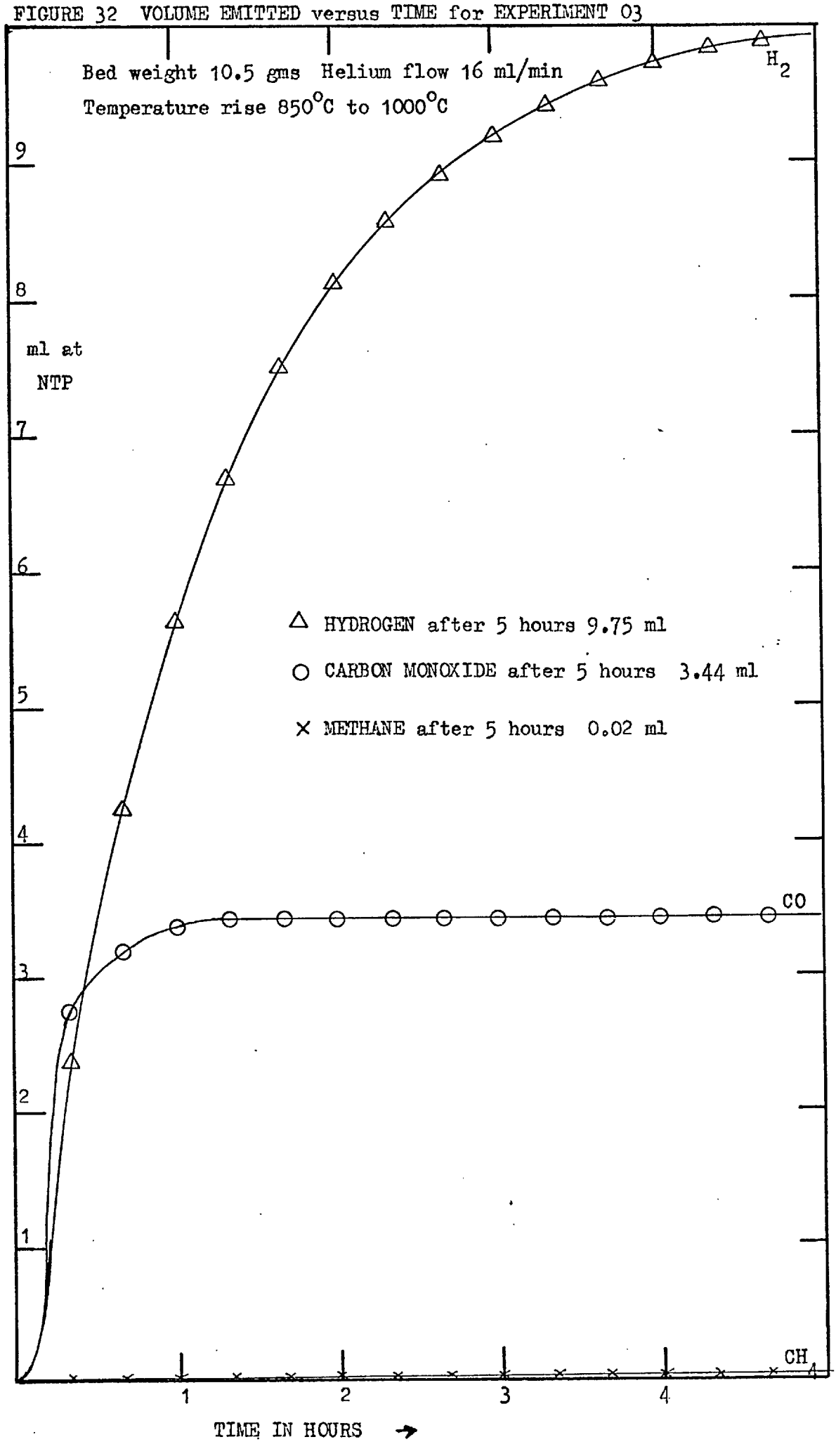


FIGURE 32 VOLUME EMITTED versus TIME for EXPERIMENT 03



Temperature rise °C	H_2 ml at NTP	CO ml at NTP
750 - 1000	47.13	10.43
750 - 800 - 1000	44.36 (-6%)	10.36 (-2%)
750 - 800 - 850 - 1000	42.30 (-10%)	10.37 (-2%)

TABLE 9

The error calculated from the experimental results and on graphical integration was ± 2% for carbon monoxide and ± 5% for hydrogen. Thus it can be said that the summation results for carbon monoxide agree within experimental error however, the hydrogen results'deviations are outside the error range. This would be expected since a major source of error, not considered in the error summations, was introduced when it was assumed that hydrogen production was completed,in five hours for the second part results and in twenty-five hours for the first part results.

Experiment 04 A 10.5 gm bed of coke was heated to 1000°C in a dry helium flow of 16 ml/min at NTP. After four days at 1000°C the effluent gases consisted of hydrogen (20 ppm) and carbon monoxide (50 ppm). The temperature of the bed was then lowered to 700°C and the dry helium flow was replaced by a flow of helium containing 1% water vapour also at a flowrate of 16 ml/min. The system was allowed to come to a steady state over a period of twenty four hours then the flow of water vapour containing helium was replaced by the initial dry helium flow. This dry helium was passed through the coke bed for another twenty four hours by which time there was no detectable amounts of hydrogen or carbon monoxide in the effluent gas stream. The bed temperature was then raised to 1000°C and the exhaust gas stream contents were analysed.

Experiment 05 The procedure followed was exactly the same as in experiment 04 but the temperature at which water vapour was allowed to react was 750°C.

Experiment 06 Again a similar procedure was followed as in experiment 04 but 800°C was the temperature at which water vapour was allowed to react with the coke bed.

Results. The plots of volume emitted against time are shown in figures 33,34 and 35 for experiments 04,05 and 06. Since the major concentration changes occurred within the first two and a half hours of reaction, the concentration versus time plots were only integrated upto this time.
In all three experiments neither methane nor carbon dioxide was detected. The most noticeable result was that, contrary to experiments 01,02 and 03, more carbon monoxide was evolved, on heating to 1000°C, than was hydrogen, after reaction with water vapour at a lower temperature. However, similar to experiments 01,02 and 03, the ratio of carbon monoxide to hydrogen rises as the temperature rises from 4.186:1 to 4.381:1 to 4.57:1 for experiments 04,05 and 06. The volumes of hydrogen and carbon monoxide evolved do not decrease with increasing temperature of reaction, as in the previous runs, but rise and then fall. (see table 10).

TABLE 10

	700°C (04)	750°C (05)	800°C(06)
Carbon monoxide	8.85 ml	12.12 ml	10.74 ml
Hydrogen	2.11 "	2.77 "	2.35 "
CO/H_2	4.19	4.38	4.57

The plots of volume of gas evolved versus time are similar in nature to the previous plots for experiments 01,02 and 03 in as much as carbon monoxide evolution is virtually complete within the first hour at 1000°C and there is very little evolved after this time, compared to the volume evolved during the first hour. Hydrogen evolution is much more gradual, its production is more continuous and steady, although the rate of evolution decreases with time.
This suggests that the sources of hydrogen are metastable, and as such, the release of hydrogen gas is mainly a function of time held at the degassing temperature. However , the source of carbon monoxide, is more stable , since its release is strictly a function of the temperature rise, to which the coke has been subjected.

FIGURE 33 VOLUME EMITTED versus TIME for EXPERIMENT 04

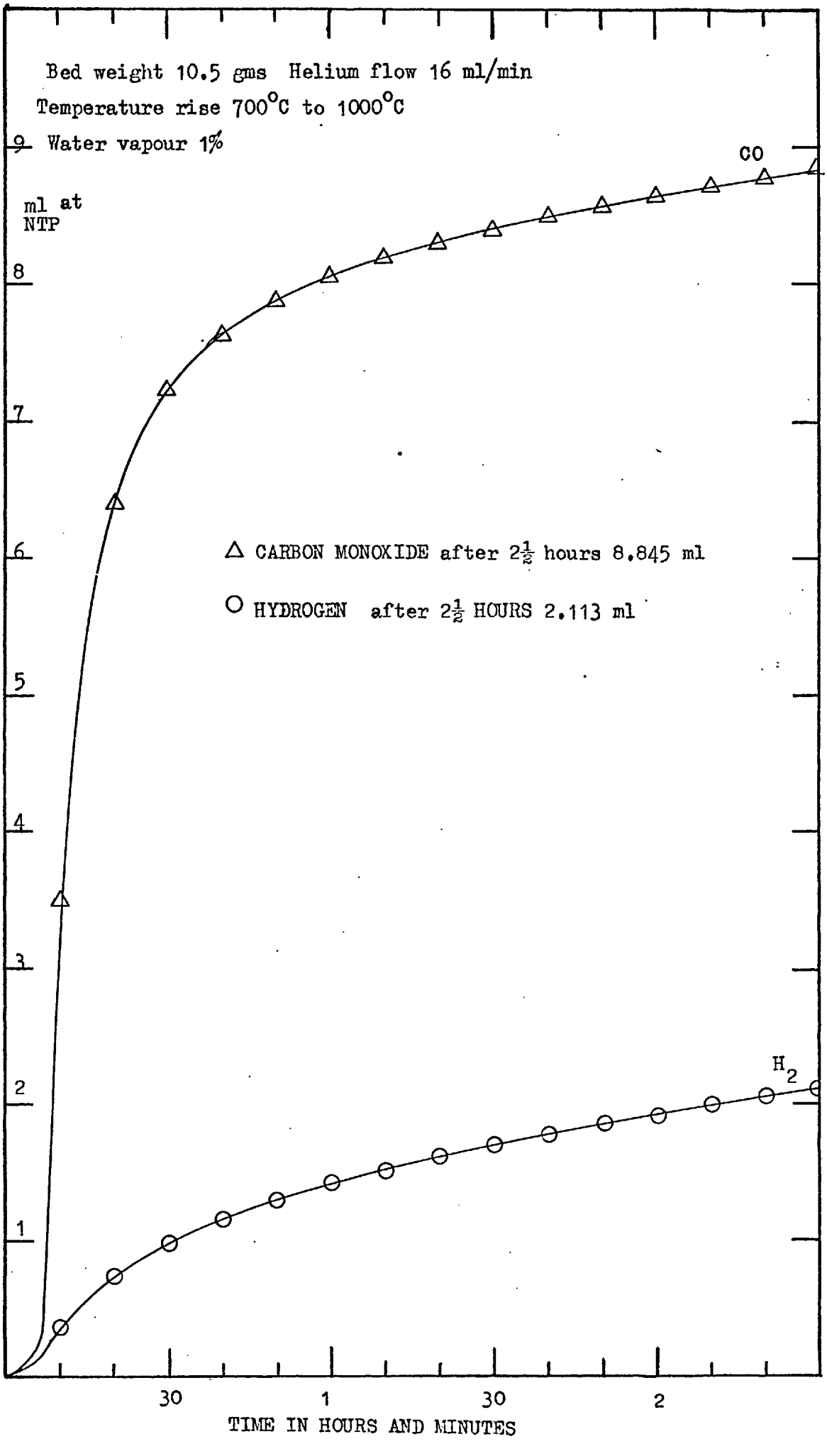


FIGURE 34 VOLUME EMITTED versus TIME for EXPERIMENT 05

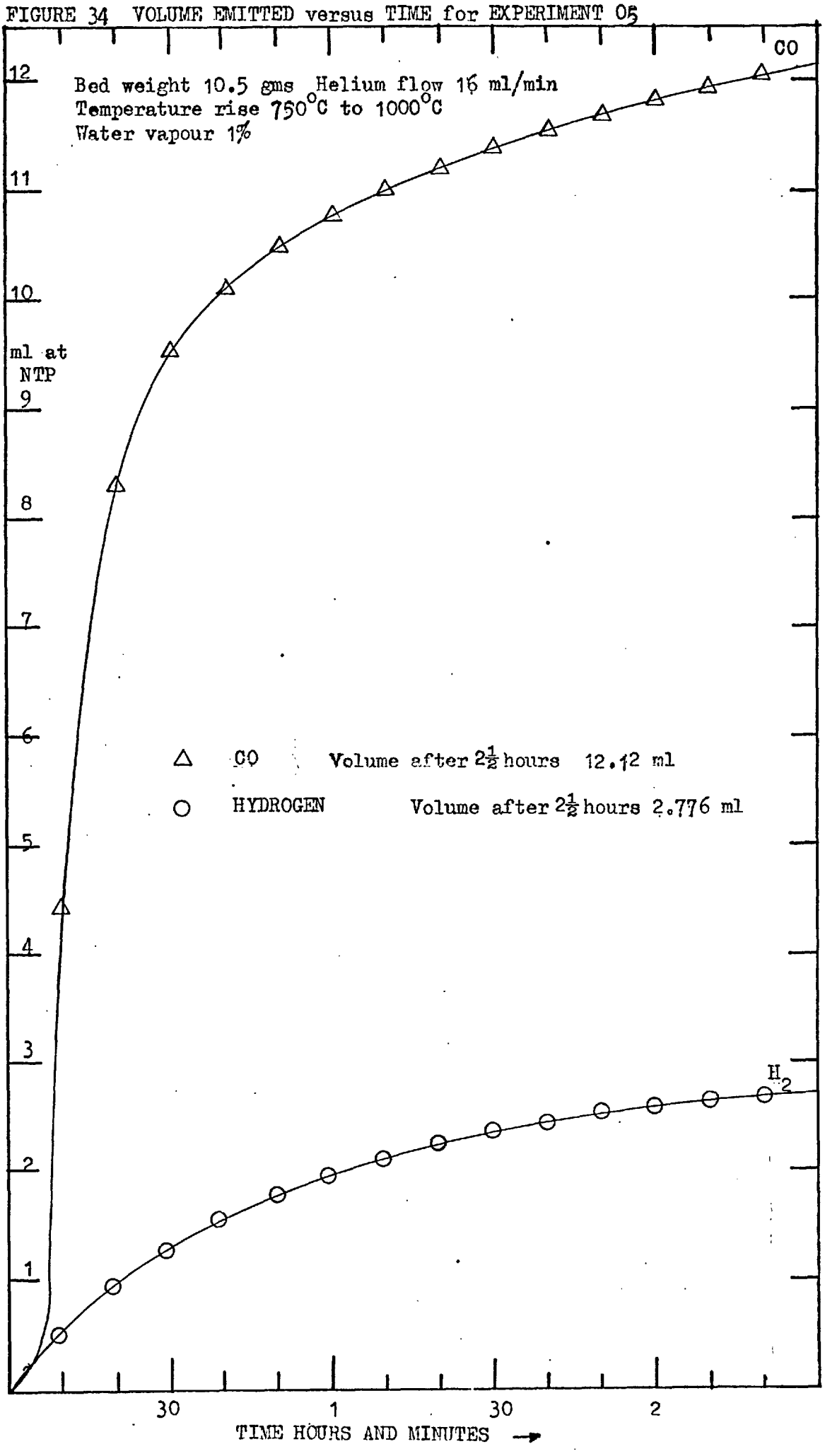
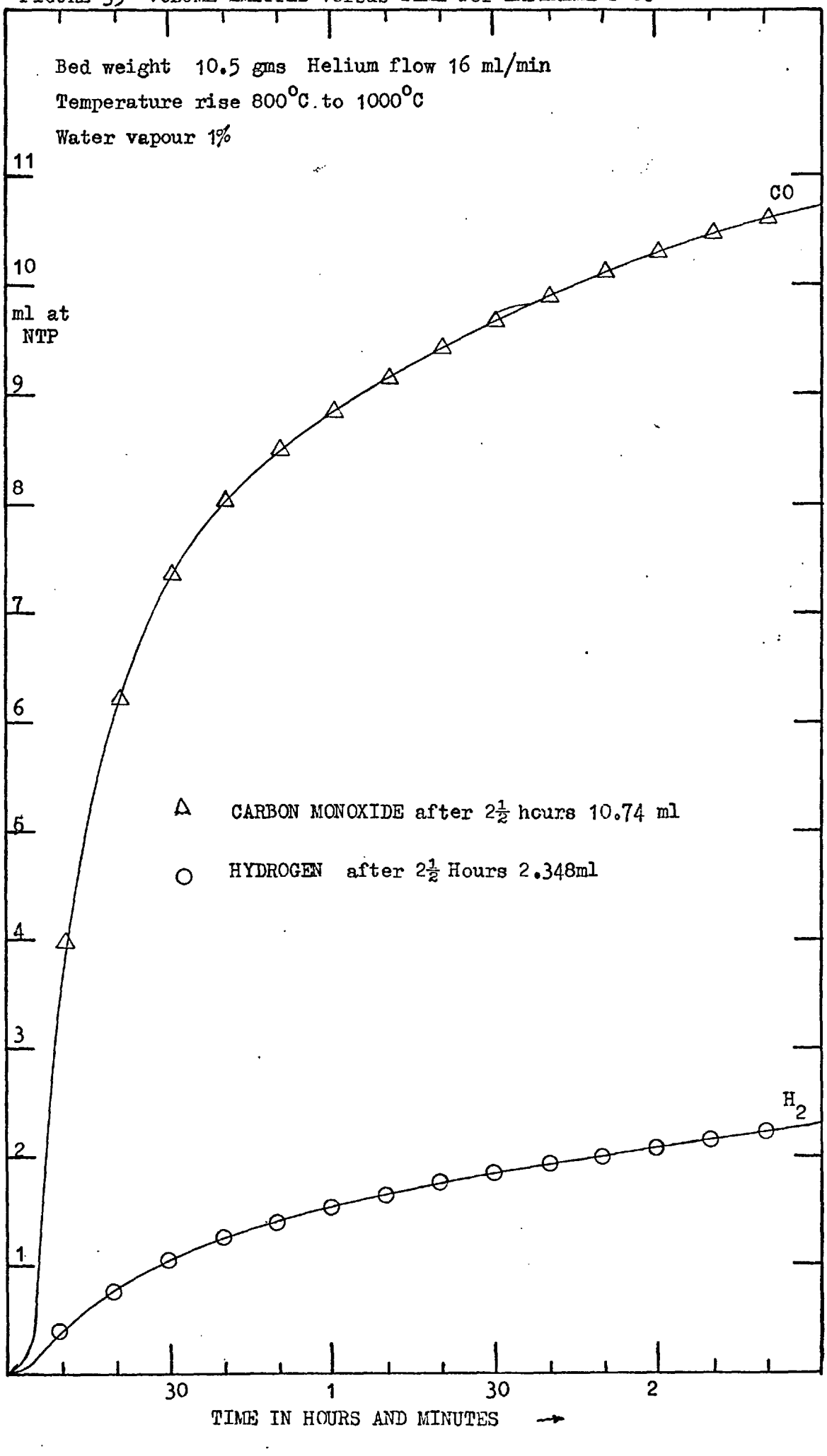


FIGURE 35 VOLUME EMITTED versus TIME for EXPERIMENT 06



DISCUSSION

Although these experiments were designed to detect the amounts of hydrogen and carbon monoxide,that are contained on a coke surface before and after reaction with water vapour, it is obvious from the experimental results, that heating to 1000°C was not a suitable method of releasing the contained gases. It must be realised that the quantities of gases measured,specifically refer to the amounts of gases that are unstable at 1000°C, and that the total quantities of gases that are contained on a coke surface,at the reaction temperatures, may very well be much greater in volume.

Even so, the results of this series of experiments are still important. Generally it was found that the sources of carbon monoxide are much more stable with temperature, than are the sources of hydrogen. Also, the ratio of evolved hydrogen to evolved carbon monoxide, from an untreated coke, is of the order of four to one. This ratio, from the water-vapour-treated-coke, is reversed and so the ratio of hydrogen to carbon monoxide is now one to four Also, untreated coke releases at least eight times as much hydrogen, as does water vapour-treated-coke.

Thus, as regards the better source of hydrogen on a coke surface, untreated coke is far more suitable than coke which has been degassed at 1000°C, and then reacted with water vapour.

From experiments 01,02 and 03 it was seen that the volumes of hydrogen and carbon monoxide which were driven off by heating to 1000°C, decreased with an increase in the annealing temperature. Also with increasing temperature the sources of carbon monoxide became relatively more stable than the sources of hydrogen since the ratio of hydrogen evolved to that of carbon monoxide decreased with increasing temperature. Methane production, whether by reaction of hydrogen with coke or by the decomposition of hydrocarbon groupings on the coke surface, decreased substantially with increasing temperature From table 9 it will be seen that as the volume of carbon monoxide emitted by step heating to 1000°C is the same, within experimental error, as the

volume emitted by continuous heating to 1000°C, this suggests that the volume of carbon monoxide evolved is principally a function of the temperature range over which the sample was heated and not a function of time held at a certain temperature. From figures 30,31 and 32 it will be seen that carbon monoxide production is very soon complete at 1000°C, irrespective of starting temperature.Also in the 50°C rise experiments, carbon monoxide production was complete long before that of hydrogen. Thus it is suggested that above 700°C the retention of 'oxygen' on a coke surface is semi-quantised, that is , after a certain temperature rise a fixed quantity of carbon monoxide will be principally evolved and the subsequent rate of production of carbon monoxide at temperature is definite but very small. Earlier it was proved that the surface oxide 'Co' was more stable on a coke surface than adsorbed carbon monoxide, therefore it is proposed that the monoxide produced in these experiments is the product of the thermal decomposition of 'Co' to adsorbed carbon monoxide which is then desorbed.

These quantised units of 'Co' do not all exhibit the same degree of thermal stability nor are there equal numbers in each unit of the same degree of thermal stability. For any temperature rise some monoxide is produced but the quantity generated by a 50°C rise depends on the initial temperature. Thus there are more quantised units liberated on heating from 750 to 800°C than there are when heating from 700 to 750°C or from 800°C to 850°C. When heating from 700°C to 1000°C , of the total volume liberated by the full temperature rise, 14% is produced in the first 50°C, 56% in the second, 11% in the third and the remaining 20% is produced in the last three 50°C temperature rises.

The question of hydrogen evolution is completely different.From earlier experiments it was found that adsorbed hydrogen was much more unstable on a coke surface than was 'Co' at these temperatures.These experiments show that more hydrogen is evolved on heating annealed coke from its annealing temperature to 1000°C than is carbon monoxide. Therefore to conform with previous thinking, the hydrogen contained on coke at these temperatures

cannot be derived purely from adsorbed hydrogen. Thus it is suggested that hydrogen is present as hydrocarbons which are metastable at these temperatures. Hydrogen production is due to 1, the rapid thermal decay of the least stable of these hydrocarbons 2, the desorption of any adsorbed hydrogen plus 3, the slow decay of the more stable hydrocarbons at temperature. Therefore as the hydrogen volume produced by any set temperature rise is subject to the time spent at the final temperature , integration of the concentration versus time plots is a major source of error in the calculation of the total volume. These plots should be integrated to infinit rather than the twenty-five hour and five hour marks as was done in experiments 01,02 and 03 parts one and two.

One further point should be noted in respect of these metastable hydrocarbons and this is that each particular hydrocarbon changes from metastable to totally unstable over a very small temperature range. Thus one particular hydrocarbon or hydrocarbons , which are responsible for about half the hydrogen produced when coke is heated from 700°C to 1000°C,become unstable somewhere between 750°C and 800°C. Thus there are several types of hydrocarbon on the coke surface, in various proportions, and each one has a different temperature at which it becomes unstable and cracks to hydrogen and in some cases at the lower temperatures, to methane.

It is not suggested that the volumes of gas evolved on heating to 1000°C are the total volumes of gas contained by the coke. It is quite conceivable that there are species of C_o' and hydrocarbon which are perfectly stable at 1000°C.

In experiments 04,05 and 06 it is assumed that during the steady state reduction of water vapour, the coke surface contains the steady state quantities of (C_o') and (H_2) and when the water vapour is removed from the system, some (C_o') and (H_2) are desorbed but there remains on the coke surface a stable concentration of these two species which may be indicative of the steady state quantities.It is also assumed that when the coke was

heated at 1000°C for four days, all the Co and hydrocarbons which were unstable at that temperature have been desorbed.

The results confirm the earlier findings that adsorbed hydrogen is much less stable than C_o and as the temperature increases the difference in respective stabilities increases since the ratio of volumes of carbon monoxide to hydrogen increases with temperature. The actual volumes evolved rise and fall from experiment 04 through 05 to 06. This is because not only are the quantities of carbon monoxide and hydrogen evolved on heating indicative of the quantities stable during the steady state, and hence should increase with increasing reaction temperature, but also they are indicative of the quantities that are desorbed when the water vapour is removed from the gas stream or conversely,the quantities that are stable at each temperature. Thus at 800°C more active sites are taking part in the water vapour reduction than are taking part at 700°C hence the steady state concentrations of C_o and (H_2) are higher at the higher temperature. However at the higher temperature, in the absence of water vapour, C_o and (H_2) are less stable on the coke surface than they are at the lower temperature. Therefore a plot of carbon monoxide and hydrogen evolved on heating the dried bed to 1000°C versus temperature, is a combination of the plot of the amount of C_o and (H_2) generated on the coke surface at the reaction temperature from water vapour and the plot of the amounts of hydrogen and Co that are stable in a helium flow at each temperature. Figure 35a shows this more clearly and so below about 750°C,generation is the controlling factor and above about 750°C,stability is the predominant consideration. By drawing up a table of the volumes of gases liberated by heating to 1000°C after the two pretreatments,(1, degassing at the required temperature and 2, degassing at 1000°C, reaction with water at the required temperature;) see table 11, it can be seen that above 750°C there is more C_o generated by water vapour that is stable at temperature than the inherent C_o on the untreated coke. This suggests that the nature of C_o generated by water vapour is different to that already existing on coke. Since it has been

FIGURE 35a VOLUMES OF HYDROGEN AND CARBON MONOXIDE FROM H_2O ON COKE

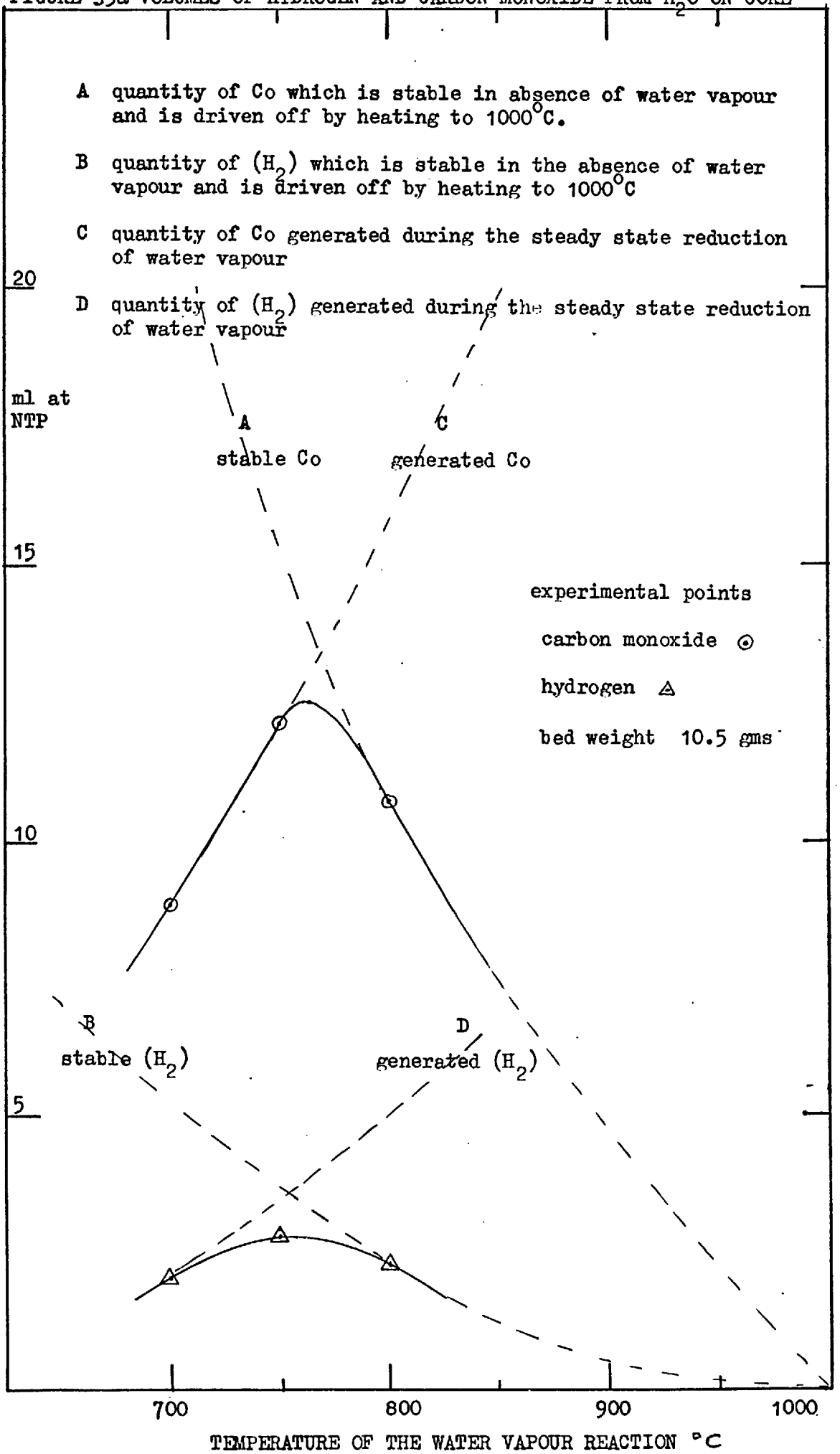


TABLE 11

ml of gas evolved when heating 10.5 gms of:-	to a temperature of 1000°C from :-	H_2	CO	CH_4
untreated coke	700°C	56.7	11.9	0.9
degassed coke after reaction with H_2O at temperature then dried at same temperature	700°C	2.11	8.85	0
untreated coke	750°C	47.1	10.4	0.4
degassed coke after reaction with H_2O at temperature then dried at same temperature	750°C	2.77	12.1	0
untreated coke	800°C	16.3	4.60	0.1
degassed coke after reaction with H_2O at temperature then dried at same temperature	800°C	2.35	10.7	0

stated earlier that Co stability is quantised then it follows that at 750°C and above, the Co generated by water vapour contains more Co types which are stable at temperature, than are inherently contained in untreated coke. However below 750°C , water vapour does not generate as much Co stable at temperature, as there is in untreated coke.

The hydrogen evolved when heating treated coke to 1000°C can only be derived from adsorbed hydrogen, however on the untreated coke there are metastable hydrocarbons which are responsible for the bulk of hydrogen contained on untreated coke. Even at 800°C, there is seven times more stable hydrogen as hydrocarbons on the untreated coke, than can be generated by reaction with water vapour at the same temperature.

Methane production must come from the incomplete cracking of these unstable hydrocarbons on heating since the water vapour experiments did not generate any methane at all. Therefore methane adsorbed on a coke surface at temperatures of 700°C and above is unstable and it is only contained on coke at these temperatures in a hydrocarbon form bonded to the coke surface.

Thus for purposes of cuprous chloride reduction by hydrogen the untreated coke is by far, more suitable than coke being reacted with water vapour because the former contains much more hydrogen.

P. Reduction of cuprous chloride vapour on a coke surface by hydrogen

It was shown in the previous experiment that, although water vapour did generate adsorbed hydrogen on a coke surface, the amount was small compared to that already,inherently contained on the coke surface. Thus,untreated coke was a better source of surface hydrogen,which was available for cuprous chloride reduction.

The aim of the P series of experiments,was to study the nature of cuprous chloride reduction by the inherently contained hydrogen, on a coke surface. In the N series of experiments , it was found that back diffusion of hydrogen was responsible for the non specific reduction of cuprous chloride vapour. The MkIII reaction tube was specially designed to counteract this back-diffusion. Just above the coke bed, there was a constriction in the reaction tube. When the helium and cuprous chloride passed through this restriction, it was hoped that the increased linear flowrate, would prevent hydrogen from diffusing back towards the cuprous chloride vessel.

A preliminary experiment was performed, duplicating the experimental procedure of experiment N1, but a Mk III reaction tube was used instead of the Mk II. Back diffusion of hydrogen was prevented, but the water vapour in the system was found to have reacted with the liquid cuprous chloride.

The remaining experiments in this series were , therefore,performed in totally dry systems. There was no degassing of the bed,and it was hoped that the hydrogen chloride,generated from the cuprous chloride reduction, would give a better indication of the amount of stable hydrogen, that existed on a coke surface at the reaction temperatures.

It was also decided to employ one specific vapour pressure of cuprous chloride and it was hoped that this would be quantitatively reduced by the surface hydrogen at each temperature of the bed.

Eperiment P1 A 10.5 gm bed of coke was held in a Mk III reaction tube at 1000°C for five days until the concentrations of hydrogen and carbon monoxide were minimal (less than 20 ppm). The temperature of the bed was

then lowered to 750°C and water vapour was introduced into the gas stream to give a concentration of approximately 1% in the helium flow of 16 ml/min A previously prepared ampule of cuprous chloride was now lowered into the reaction tube at a rate of a centimetre a day. Readings of the effluent gas stream were taken and these product gases were also passed through the cell of the automatic titrimeter for hydrogen chloride analysis. After five days and five centimetres the ampule was lowered another five centimetres into the reaction vessel and the product gases were analysed.

Results Experiment P1 was an attempt to duplicate experiment N1, but, by using a Mk III reaction vessel and by doubling the helium flowrate, it was hoped that the back diffusion of hydrogen and its subsequent reaction with cuprous chloride on the CuCl vessel and reaction vessel walls would be stopped.

The initial results at the lower temperatures of cuprous chloride, compared favourably with those of N1, but at the four and five centimetre marks, the initial raising of the cuprous chloride temperature was accompanied by a surge in the concentrations of hydrogen and carbon monoxide and these concentrations diminished with time and did not reach a steady state as in experiment N1. The hydrogen concentration usually reached zero but the concentrations of carbon monoxide and carbon dioxide gradually decreased with time at a steady cuprous chloride temperature. Similarly the concentration of hydrogen chloride also gradually decreased with time. When the CuCl vessel was lowered by a further five centimetres, again there was a surge in the concentrations of all gases this time i.e. H_2,CH_4,CO,CO_2 and HCl. Hydrogen again decreased to zero fairly rapidly (in an hour) and the concentrations of all the other gases gradually diminished with increasing time. Table 12 shows the instantanious gas concentrations in the effluent gas stream during the day after the full five centimetre lowering.

Table 12 also shows the value of 'lost' hydrogen as calculated from figure 25 for experiment N1, at this temperature (656°C) of cuprous chloride. It was

assumed from the quantitative reduction of water vapour that :-

$$\text{ppm 'lost' } H_2 = \text{ppm CO} + \text{ppm } CO_2 \times 2$$

Water vapour cannot be included in this table since its concentration was continually changing and for reasons explained earlier, a changing water vapour concentration cannot be accurately followed, however it was of the order of 6,000 ppm.

TABLE 12 (concs. in ppm)

GAS CONCENTRATIONS VERSUS TIME AFTER THE 5CM LOWERING (in hours)

TIME	HCl	CO	CO_2	lost H_2	HCL-2x. lost H_2	lost H_2 from Expt N1
24.5	7914	843	621	2085	3744	2500
25.5	7640	787	614	2015	3610	"
27.0	7570	736	609	1954	3662	"
28.0	7435	707	591	1888	3659	"
28.5	7165	595	572	1740	3685	"

When the reaction vessel and the CuCl vessel were removed from the furnace it was found that copper had deposited on the upper surface of the coke bed as a sort of 'crust', and on further examination it was found that there was very little if any copper deposited in the bulk of the coke. There was an extensive deposit of copper on the silica vessel walls above the coke bed but below the restriction. However there was no deposit below the CuCl vessel and the restriction. Therefore it was assumed that there had been no back diffusion of hydrogen up the narrow part of the Mk III reaction vessel. The CuCl vessel contained large amounts of black and red deposits of copper oxides, much more than was found in the N1 experiment. There was a deposit of a white solid below the coke bed but above the tar deposits i.e at a higher temperature. This was found to be cuprous chloride and on exposure to air it turned to green. It was the build up of this deposit which so increased the pneumatic resistance of the system that the reaction had to be terminated.

It was thought that water vapour was reacting in this experiment with the

liquid cuprous chloride to give copper oxides, this reaction must also have occurred in experiment N1 but not to the same large extent. Also it was apparent that copper was mainly depositing on previously deposited copper. Thus it was decided to repeat the experiment but in a totally dry system and with no degassing of the coke bed at 1000°C.

Experiment P2 A 10.5 gm coke bed was held in a Mk III reaction tube at 750°C for four days in a dry helium flowrate of 16 ml/min. After this time when the concentrations of hydrogen and carbon monoxide were minimal a previously prepared CuCl vessel was lowered nine centimetres into the reaction vessel when its temperature was 646°C. At this temperature of liquid cuprous chloride the 'lost' hydrogen concentration was 1980 ppm according to experiment N1, which in turn is equivalent to a concentration of cuprous chloride vapour (trimer) of 1320 ppm. (from figure 25 page 120)
The concentration changes in the effluent gas stream of the product gases CO, CO_2, H_2, CH_4 and HCl were followed for a period of several days until all had returned to virtually zero (less than 20 ppm).

Experiment P3 The procedure was followed as outlined in P2 except that the bed temperature was set at 800°C and the cuprous chloride vessel was lowered into the reaction tube until its temperature was 646°C.i.e. the same CuCl temperature as in P2 but the CuCl vessel did not have to be lowered into the reaction tube as far as was done in P2,

Experiment P4 A similar procedure was followed as in experiment P3 except that the bed temperature was 850°C but the cuprous chloride temperature was still kept at 646°C.

Results For experiments P2,P3 and P4 the concentrations in the exhaust gas stream are plotted against time for the first seven hours of reaction in figures 36,37 and 38 respectively.

There was an initial delay in the appearance of hydrogen chloride and it is thought that this was due to a certain amount of adsorbtion of that gas on the glass and steel pipework leading to the titrimeter cell. Thereafter it was found that the concentration plot of hydrogen chloride was constant to

FIGURE 36 PLOT OF CONCENTRATION VERSUS TIME FOR EXPERIMENT P2

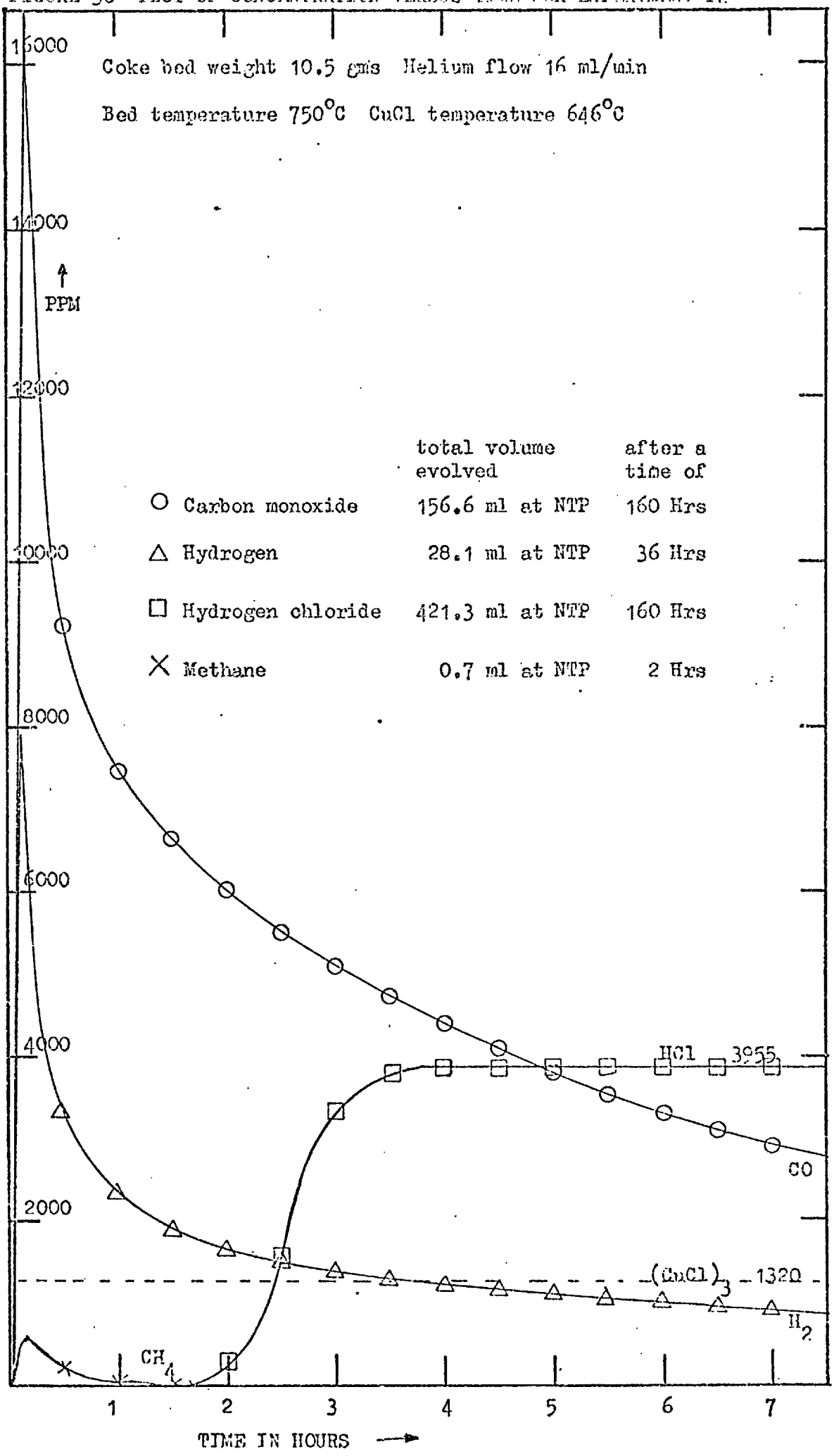


FIGURE 37 PLOT OF CONCENTRATION VERSUS TIME FOR EXPERIMENT P3

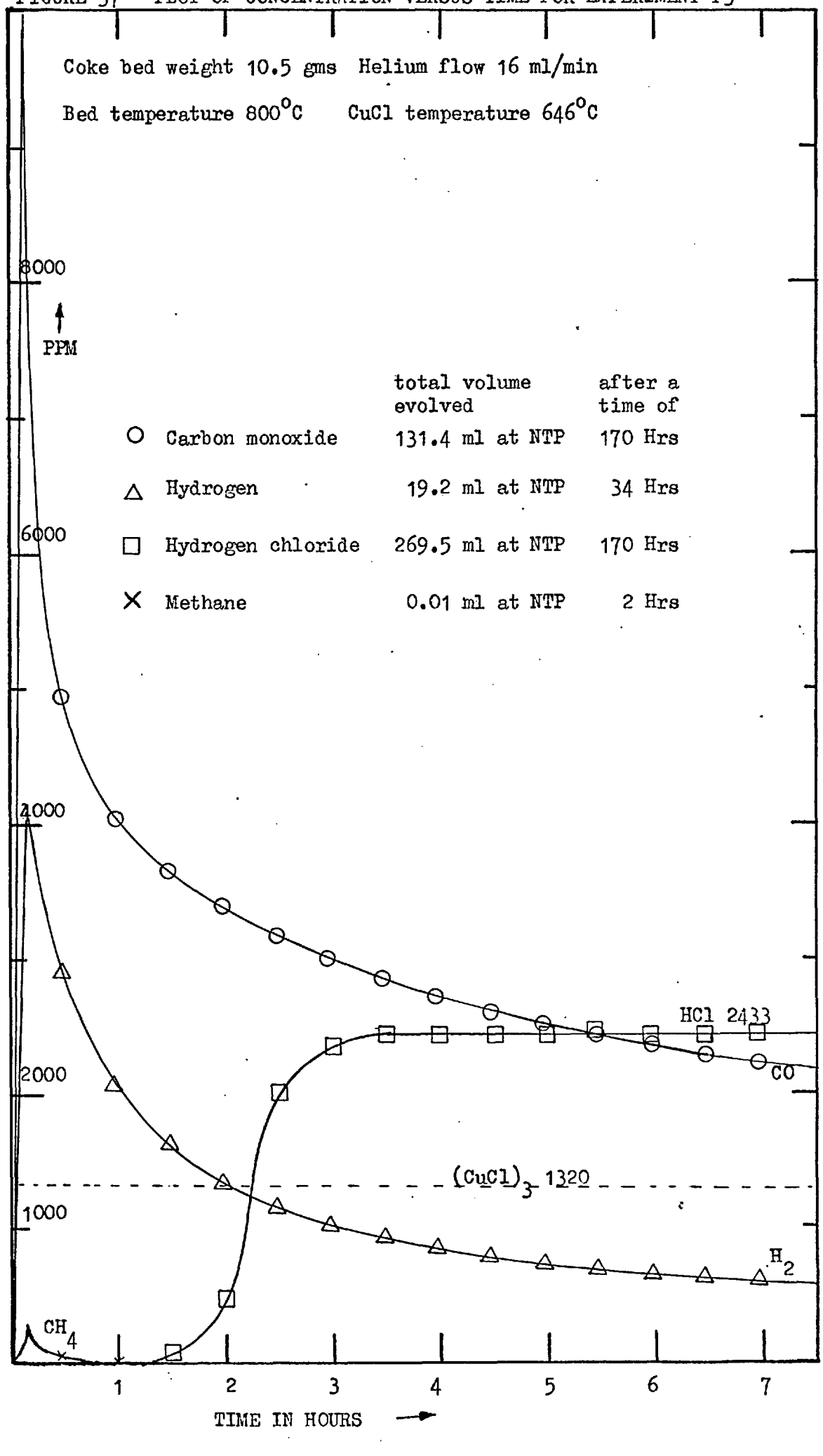
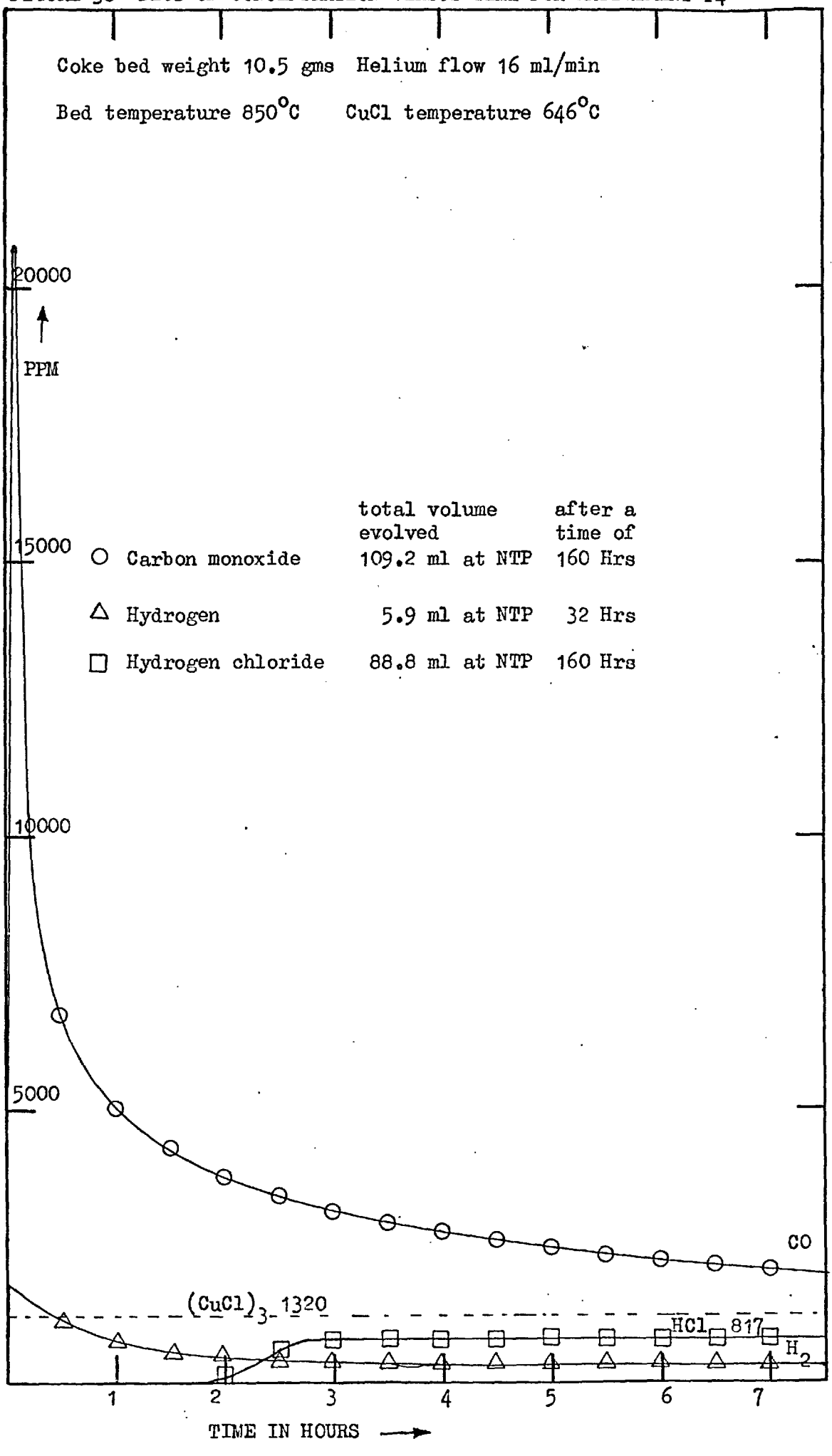


FIGURE 38 PLOT OF CONCENTRATION VERSUS TIME FOR EXPERIMENT P4



± 2% for five days in each experiment then it gradually fell over a period of two days to zero. The gaseous hydrogen concentration plots were initially high but they all fell away to zero during the second day of reaction. Methane production, if any, was usually complete within two hours. The carbon monoxide concentrations were initially very high indeed in each experiment, then they decreased exponentially to zero over the same period of time as it took the hydrogen chloride concentration to reach zero. Each plot was completely integrated and the volumes quoted on figures 36, 37 and 38 are the total volumes of each gas evolved together with the time taken for its concentration to reach zero. The results are summarised in table 12.

TABLE 13

Temp. °C	HCl ml	HCl ppm	H_2 ml	CO ml	CH_4 ml	total H_2 ml	$(CuCl)_3$ ppm
750	421.3	3955	28.1	156.6	0.7	238.9	1320
800	269.5	2433	19.2	131.4	0.01	154.0	"
850	88.8	817	5.9	109.2	0	50.3	"

It can be seen that in going from 750°C to 850°C, the amount of carbon monoxide released is reduced by 30% but the amount of hydrogen released has decreased by 80%. This again suggests that 'oxygen' on a coke surface is more stable at higher temperatures than is 'hydrogen'. It is suggested that the carbon monoxide liberated is derived from the surface oxide Co, and that the hydrogen, as hydrogen chloride and hydrogen gas, is derived from the residual volatile matter that is metastable at each temperature. A surprising result is that the cuprous chloride is not quantitatively reduced at each temperature, if it were the partial pressure of hydrogen chloride evolved would be 3960 ppm. At 750°C, within experimental error, this is so. However at 800°C the value of P_{HCl} falls to 2433 ppm and at 850°C it is further reduced to 817 ppm. This suggests that the activity or the equivalent partial pressure of hydrogen on the coke surface decreases with increasing temperature.

In all experiments, no carbon dioxide was detected.

The weight of the coke bed in experiment P2 was initially 10.5003 gms. The weight of the coke bed plus the deposited copper after the experiment was 11.5026 gms, the weights of carbon monoxide and hydrogen lost from the coke were 0.1957 and 0.0213 gms. The observed weight of copper in the coke bed is therefore 11.5026 - 10.5003 + 0.0213 + 0.1957 = 1.2193 gms. The weight of copper calculated as being derived from the reduction of cuprous chloride to hydrogen chloride is $\frac{421.3}{22,400} \times 63.54 = 1.1951$ gms.

The difference between the two results expressed as a percentage error of the observed weight of copper is -2%. This error could come from the integration of the concentration plots for HCl, H_2 and CO.

Similar errors were observed for experiments P3 and P4, $-\frac{0.0153}{0.7644} \times 100 = -2\%$ and $+\frac{0.0050}{0.2519} \times 100 = +2\%$. respectively.

The copper was deposited throughout the bed in each case. The copper deposit was nodular and very small. These nodules were difficult to see with the naked eye but under the microscope it appeared as if each coke particle was partially covered with small flat spheroids of copper. At a magnification of x500, the particle diameters were estimated to be :-

0.0004 cm actual size.

In the bulk of the coke there was no evidence of any filament type of growth. On the top of the coke bed there was a small 'crust' of copper deposited on copper. There was no copper deposited on any of the silica vessels' walls. In all cases there was a deposit of cuprous chloride below the coke bed, also there was a deposit above the cuprous chloride vessel where the vapour had diffused back past the ampule. There was no evidence of any oxides having been formed in the cuprous chloride vessel. Also there was no reduction of cuprous chloride vapour on the walls of the silica reaction vessel, either above the coke bed or below it. There was a deposit of cuprous chloride, below the coke beds in experiments P2, P3 and P4, where unreduced cuprous chloride had condensed.

DISCUSSION

The object of the P1 experiment was to repeat experiment N1 but, by using a Mk III reaction tube and by doubling the flowrate , it was hoped to prevent back diffusion of hydrogen.

It was found after the experiment that the deposition of copper took three forms, 1, a deposit of copper on the coke, 2, a deposition on the silica vessel walls and on the silica wool plug on top of the coke and 3, a deposition of copper on copper (both on the coke and silica deposits). The latter form was the most predominant.

It is thought that at very low partial pressures of cuprous chloride, the vapour was reduced by the hydrogen that had diffused into the gap above the coke bed but below the restriction. The deposit was smooth sheet-like on the reaction tube walls but was of a dendritic nature on the silica wool. As the vapour pressure increased the cuprous chloride was not completely reduced in the gap above the coke and so reached the coke bed where it was reduced. Where the copper had been reduced on the coke surface by hydrogen there was a crust of copper deposited on copper, this deposit was of a platelet and dendritic type.

Each temperature rise of the liquid cuprous chloride was accompanied by a shortlived surge of carbon monoxide and hydrogen gas. It is suggested that this is due to the reduction of copper on the coke surface by the adsorbed hydrogen and this copper in replacing the hydrogen disrupts the C-C bonding surrounding this site sufficiently to dislodge any nearby adsorbed gases. When there is enough copper on the coke surface to reduce the incoming cuprous chloride by its own adsorbed hydrogen then copper deposition on coke ceases and copper deposits on copper. The hydrogen necessary for this reduction is produced on the coke by water vapour reduction and it then migrates down the chemical potential of hydrogen to the copper surface. The dislodging of the adsorbed gases now ceases and the lost hydrogen as calculated from $[CO + 2.CO_2 - \text{actual } H_2]$ becomes equivalent to the hydrogen chloride and hence to cuprous chloride. When copper deposits on coke it

replaces hydrogen that has already been formed and no increase in the rate of water vapour reduction should be detected and so the rate should remain at the pre- CuCl temperature increase level. (This could not be detected since the surge of desorbed gases obscured this) However when copper deposits on copper the hydrogen required is derived from an increase in the rate of water vapour reduction and at a steady vapour pressure of cuprous chloride the water vapour reduction rate should increase to supply the necessary hydrogen and then should achieve a new steady state rate.

In the later stages of this experiment a steady state rate of water vapour reduction was not achieved and the product gas concentrations all fell with time. It is suggested that at a steady temperature of cuprous chloride the vapour pressure of the vapour decreased with time, thus requiring less hydrogen and so the water vapour reduction decreased. The vapour pressure of cuprous chloride decreased because water vapour was reacting with the liquid and gaseous chloride producing the oxide. This reduces the activity of the liquid cuprous chloride and hence its vapour pressure reduces as the concentration of oxide increases. It is presumed that this reaction is strongly retarded by hydrogen since in experiment N1 the oxide formation in the CuCl vessel was minimal.

The calculated vapour pressure of cuprous chloride trimer at this temperature of the liquid from the lost hydrogen plot in figure 25 is 1666 ppm, the ppm of hydrogen chloride expected from the total reduction of this cuprous chloride is 5000 ppm. The ppm actually measured for this experiment was higher than this value so it was a reasonable assumption that cuprous chloride was reacting in another way, producing the extra hydrogen chloride. It is assumed that water vapour reacts with both the liquid and gaseous cuprous chloride depositing cuprous oxide on the liquid surface and on the vessel walls. It is the dissolution of the oxide in the liquid that is responsible for the reduction in its activity. Thus cuprous chloride vapour in equilibrium with the liquid containing oxide, and hydrogen chloride leave the CuCl vessel and pass down to the coke bed. From the JANAF[62]

tables for the reaction :-

$$2(CuCl)_3 + 3\,H_2O \rightleftharpoons 3\,Cu_2O + 6\,HCl$$

the equilibrium partial pressure of hydrogen chloride generated at 656°C is approximately 600 ppm, and for the reaction with liquid cuprous chloride the value is slightly less at 400 ppm. However the measured value (P_{HCl} - 2 lost H_2) is approximately 3700 ppm. Therefore this analysis is in error by a factor of six. The considered sources of error, experimental readings and JANAF accuracy cannot account for such a large discrepancy. It was considered that above liquid cuprous chloride at this temperature that the vapour phase was the trimer. From experiment N1 it was found that assuming the trimer to be present, the experimental results were in good agreement with previous work. Thus it must be accepted that in a helium gas flow the trimer is the stable species of cuprous chloride vapour. However if cuprous oxide dissolved in the liquid cuprous chloride, then the activity of cuprous oxide relative to pure cuprous oxide,would decrease dramatically. Thus the above equation would lie more to the right than it would do according to cuprous oxide activity being equal to unity. Thus the partial pressure of hydrogen chloride would increase and the partial pressure of water vapour in equilibrium with the new system would decrease. Therefore the partial pressure of water vapour reaching the coke bed would decrease with time as more reacts with the liquid cuprous chloride. Since the partial pressure of water vapour reaching the coke decreases with time then the availability of hydrogen decreases and so 'lost' hydrogen may decrease. Also since the activity of liquid cuprous chloride is decreasing so the vapour pressure decreases and so less hydrogen is required to reduce it, this also lowers the 'lost' hydrogen. The falling concentration values of the product gases were not observed in experiment N1 and the only difference between the two experiments was that in N1 hydrogen diffused upto and into the CuCl vessel since there were small copper deposits in the CuCl ampule. Thus it is assumed that the presence of hydrogen strongly retards the reduction of water vapour by

the liquid cuprous chloride.

The total mass balance for hydrogen, including hydrogen chloride and the water vapour concentrations in and out of the system is consistent with all the hydrogen chloride being derived from water vapour and none being formed from hydrogen remaining on the coke surface after the degassing at 1000°C.

As the vapour pressure of cuprous chloride reaching the coke falls with time so the degree of water vapour reduction also decreases. However the ratio of carbon monoxide to dioxide is not constant as rate of reduction decreases, so it is presumed that as copper deposits on copper on coke this alters the surface nature in a way such that the formation of carbon dioxide is preferred to the formation of monoxide from water vapour.

The disadvantages of experiment P1 were that the presence of water vapour disrupted the equilibrium concentration of cuprous chloride vapour and, more important, the gaseous hydrogen generated from the water vapour reduced the chloride on any solid surface present, not necessarily on the coke or the copper on the coke. Thus the partial pressure of hydrogen was too high and so there was no selective deposition of copper on the coke.

Experiments P2, P3 and P4 were therefore performed in the absence of water vapour and, in order to study the copper deposition from the hydrogen inherently contained in the coke, there was no degassing of the bed at 1000°C prior to the introduction of the CuCl vessel.

From the results it will be seen that the cuprous chloride vapour was not quantitatively reduced at each temperature. Since hydrogen exists on the coke surface as an extension of that surface its chemical affinity will be defined as an apparent activity a_H. For the reaction :-

$$3\,H + (CuCl)_3 \rightleftharpoons 3\,HCl + 3\,Cu \quad \text{.....(28)}$$

then:-

$$K_{28} = \frac{P^3_{HCl}}{P_{(CuCl)_3} \times a^3_H} \qquad \text{assuming } a_{Cu} = 1 \quad \text{.....(29)}$$

From the JANAF[62] tables it is calculated that at the temperatures of 750°C

800°C and 850°C the values of $\log_{10}K$ are + 2.5599, + 2.5099 and + 2.4558 respectively. By substituting the measured values of the partial pressures of hydrogen chloride and cuprous chloride trimer, it can be calculated that the values of the apparent activities of hydrogen on the coke surface at the three temperatures are 0.04451, 0.004438 and 0.00123 respectively. Conversely, when the apparent activity of hydrogen equals unity, then the equilibrium concentration of cuprous chloride in the effluent gas stream would be 1×10^{-4}ppm. (a_H is relative to gaseous monatomic hydrogen)

Of the total hydrogen contained on the coke surface, at the three temperature of 750, 800 and 850°C, 88.2%, 87.5% and 88.3% react to give hydrogen chloride, the rest is evolved as gaseous hydrogen. The hydrogen which reacts to hydrogen chloride by cuprous chloride reduction does so at a steady rate for five days, the hydrogen which evolves as gas does so at a decreasing rate over a period of two days. Carbon monoxide production extends over the same period as that of hydrogen chloride but its rate of production gradually falls with time. Therefore the reduction of cuprous chloride vapour is a steady state effect while the generation of the two gaseous species is a non steady state effect.

It is proposed that as cuprous chloride is reduced at the coke surface it electronically disturbs the π bonding within the immediate carbon matrix. This has the effect of weakening any other surface bonding on the surrounding coke and so any adsorbed hydrogen or 'Co' which were previously quite stable now become unstable and are desorbed to give gaseous hydrogen and carbon monoxide.

It has been found that at temperature, adsorbed hydrogen is much less stable than 'Co' on a coke surface and so the perturbation of the π bonding will have a greater effect on hydrogen than it will on 'Co'. Of these two species hydrogen is also the less temperature stable and so as the temperature increases, relatively more hydrogen than 'Co' is evolved. Therefore of the volumes of gas stable at 750°C, 79% of the hydrogen and only 30% of the carbon monoxide become unstable and are desorbed when the temperature is

raised by 100°C to 850°C and held there for four days.

It is proposed that on a coke surface at each temperature there are two major types of hydrogen. The ratio of the quantities of each type is constant with temperature since 88 ± ½% of the total hydrogen at each temperature is released as hydrogen chloride.

Type I consists of a C-H bond or groups of C-H bonds which are quite stable and are only disrupted to produce type II and subsequently hydrogen gas, by a temperature rise. The decay of these hydrocarbon bonds to hydrogen at a higher temperature is exponential with time.

Type II consists of $C\text{-}H_2$ or of two closely associated C-H bonds with a low activation energy of rupture, which with the slightest disruption will form hydrogen gas. Type II can be regarded as an adsorbed hydrogen type.

When heating coke from a temperature of 750°C to 1000°C , the adsorbed hydrogen type II is rapidly evolved over a period of a few hours, but the partial breakdown of the type I hydrogen to type II and hydrogen is a slow continual process which takes many hours at a decreasing rate. Type I breakdown generates a new type II which is stable at the higher temperature and hydrogen which is evolved as gas. The activation energy of formation of hydrogen from type I is much higher than it is for type II.

As copper deposits on a coke surface , type II hydrogen is dislodged as the π bonding is disrupted and if it does react with cuprous chloride it does so in the gaseous phase, to deposit copper on copper. Cuprous chloride vapour reacts with type I hydrogen on the coke surface and it deposits on the coke by replacement of the type I hydrogen, thus the copper is chemically bound to the coke surface.

As copper continues to deposit on the coke the degree of perturbation of the π bonding throughout the coke bed, necessary to dislodge all the type II hydrogen, is achieved within two days. However as the copper deposition only weakens the type I bonding, copper will continue to deposit on the coke as long as there is type I hydrogen left to reduce the chloride.

For the three experiments less type II hydrogen is evolved in the two days

but less copper was deposited (as measured by HCl production), as the temperature of reaction increased. The amount of π perturbation necessary to dislodge 1 ml of type II hydrogen, as measured by (ml HCl in two days / ml of gaseous hydrogen produced) was 2.33, 2.07 and 2.13 for temperatures of 750,800 and 850°C. Thus 2.2 $\pm$ 0.13 ml of hydrogen chloride must be generated in order to liberate 1 ml of type II hydrogen. The error involved is $\pm$ 6% which, considering experimental and integration errors is quite comparable to the expected error.

Thus the ratio of type I to type II hydrogen is constant with temperature and the degree of perturbation of the π bonds necessary to release a unit of type II hydrogen is also independant of temperature. Figure 39 shows these effects in diagramatic form. At 750°C, there are 210 mls of type I hydrogen which will all react with cuprous chloride to produce hydrogen chloride, in doing so it will weaken the bonding of type II hydrogen so much that it will become unstable and will be desorbed. As the rate of reaction of type I is steady and constant, the activation energy of rupture for all types of type I hydrogen is constant. On the seventh day there was a gradual,not sharp,fall in the hydrogen chloride concentration to zero and so there may be a small percentage of type I hydrogen which has a higher activation energy of rupture than the constant value. The release of type II hydrogen was not steady nor was it linear with time, therefore there are several kinds of type II hydrogen on the coke surface each having a different energy of rupture. However as the degree of perturbation required to dislodge a unit of type II hydrogen is independant of temperature and is constant , then the activation energy of rupture of the most stable kind of type II hydrogen is also constant with temperature. At 800°C , the type II stable at 750°C is all released as gas as the bed is heated to 800°C. Of the 210 ml of type I stable at 750°C , only 135 ml has remained stable at 800°C. The remaining 75 ml has decomposed into 19 ml of a type II stable at 800°C and 56 ml have been released as gas when the bed was held at 800°C for four days. Thus the temperature rise can be

FIGURE 39 PLOT OF ACTIVATION ENERGY OF RUPTURE VERSUS VOLUME OF HYDROGEN TYPES I AND II FOR EXPERIMENTS P2,P3 AND P4.

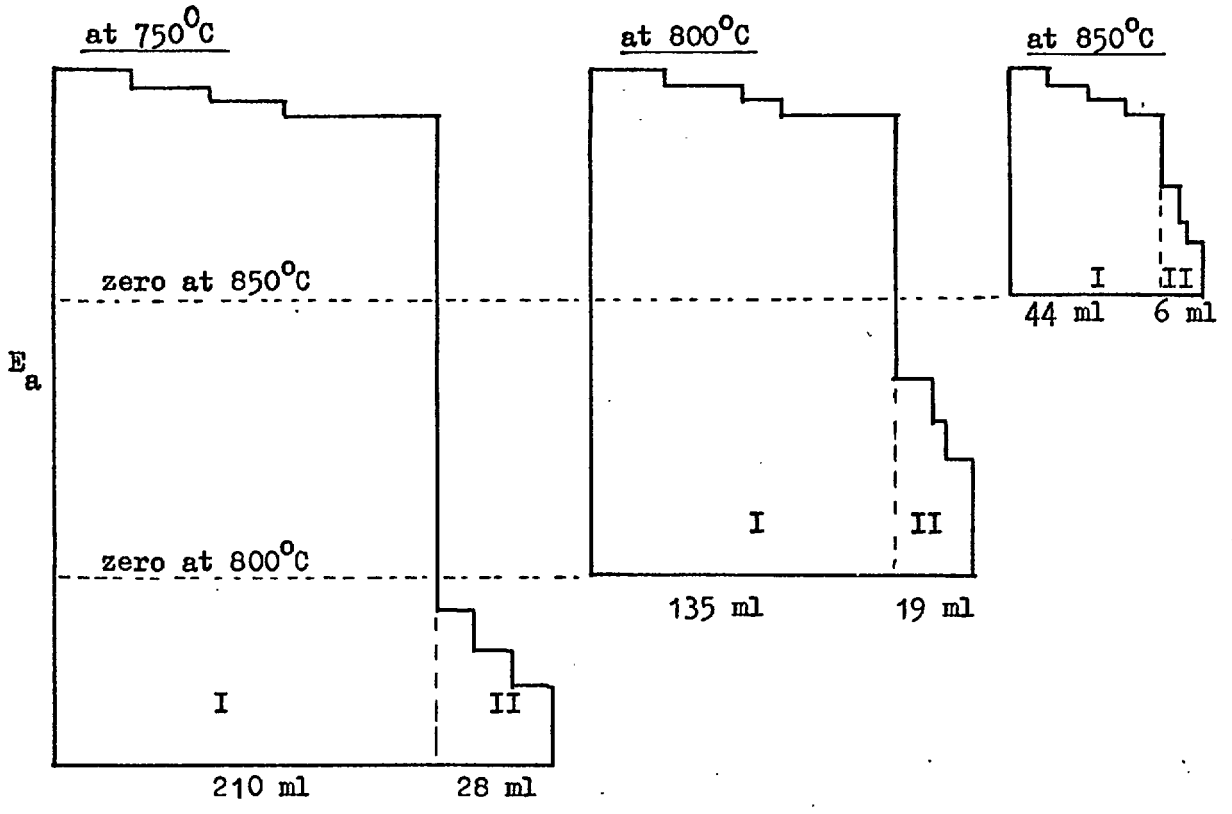
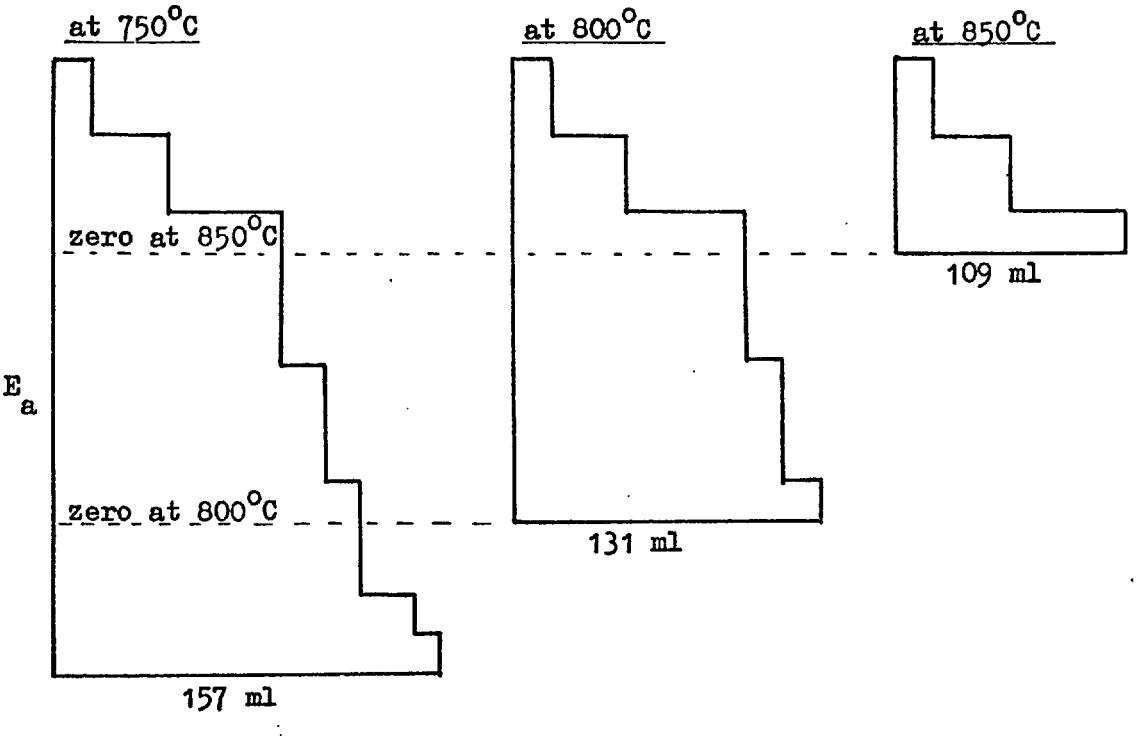


FIGURE 40 PLOT OF ACTIVATION ENERGY OF RUPTURE OF Co VERSUS VOLUME OF CARBON MONOXIDE FOR EXPERIMENTS P2,P3 AND P4.



considered as an overall reduction in the activation energies of rupture. Similarly, of the 135 ml of type I stable at 800°C when heated to 850°C only 44 ml remain stable and the rest has decomposed into 6 ml of a type II hydrogen stable at 850°C and 85 ml were evolved as gas while the bed was held at 850°C.

The Co on the surface is also affected by cuprous chloride reduction. The activation energy of carbon monoxide formation from Co is thought to lie between that of type I and type II hydrogen, thus while the type II C-H bonds are broken by π perturbation and type I bonds are weakened, the bonding of the Co is progressively weakened and then broken. During the initial copper deposition all the weakly bonded Co is liberated as carbon monoxide in a surge. As the degree of π perturbation increases with increasing deposition of copper with time, so the Co breakdown is a function of time and hence of the strength of the bonding of the Co. The weakly held Co is liberated first and as the carbon monoxide evolution continues the strength of the Co bonds to be broken increases. Thus the amount of copper required to liberate 1 ml of carbon monoxide increases with increasing Co bond strengh and so the concentration of carbon monoxide in the gas stream is a decreasing function of time since the rate of copper deposition is a linear function of time.

Since it was thought that there are several types of surface oxide of differing bond energies, it would be expected that the carbon monoxide production would decrease in a step-like manner as each supply of constant bond energy Co was exhausted. No definite steps were noticed in the carbon monoxide output but the concentration during any one day was usually constant to within the calibration error. However the following days 'constant' level was always lower than that of the preceeding day. This suggests that there might have been a step-like form of carbon monoxide production but it cannot be definitely proved.

From figures 36,37 and 38 it will be seen that the peak value of the carbon monoxide plots were 17,000 , 10,000 , and 21,000 ppm respectively. Also the concentration value after seven and a half hours reaction was in each

2750, 2250 and 2000 ppm respectively. Thus although the total volume of carbon monoxide evolved decreased with increasing reaction temperature this effect was not observed during the first seven and a half hours of reaction since at 850°C more carbon monoxide was liberated in this time than was liberated at 800°C during the same time period. Thus the stability of the Co bonds at each temperature differs for each temperature.

The temperature stability of the $\overset{\prime}{C}o$ types can be more easily considered by determining how much perturbation of the π bonding was necessary to generate 1 ml of carbon monoxide. The degree of perturbation is equivalent to the amount of copper deposited which in turn is equivalent to the volume of hydrogen chloride liberated. Thus the average degree of perturbation required to liberate 1 ml of carbon monoxide at 750°C was 2.69 ml of hydrogen chloride, at 800°C it was 2.05 ml and at 850°C it was 0.81 ml. Although heating the bed from each of these temperatures by 50°C has liberated 16% from 750°C and 17% from 800°C of the total amount of Co present, the degree of weakening of the $\overset{\prime}{C}o$ bonds has increased by 24% and by 60% respectively. Considering this in another way, when heating coke from 750°C to 800°C the bond energies of all types of $\overset{\prime}{C}o$ are weakened by 24% of their previous levels ; 16% of all bond types are so weakened that they become unstable and are desorbed as carbon monoxide. Figure 40 shows this in diagramatic form. When heating from 750°C to 800°C the zero on the activation energy scale is effectively moved up and the $\overset{\prime}{C}o$ types with activation energies below the zero are all desorbed as carbon monoxide. A similar thing happens on heating to 850°C, some of the $\overset{\prime}{C}o$ is weakened so much that it is desorbed and all the rest of the $\overset{\prime}{C}o$ types are weakened. When copper deposits this has the effect of progressively disrupting the $\overset{\prime}{C}o$ bonds in order of their strength.

Methane production is minimal and is probably due to the incomplete breakdown of some of the type I hydrogen .

Summarising, copper replaces type I hydrogen as it deposits, in doing so it liberates type II hydrogen and carbon monoxide from the $\overset{\prime}{C}o$ held on the

coke surface. The activity of the type I hydrogen reduces with increase in temperature therefore the higher the temperature the less the degree of reduction of cuprous chloride. Also as the temperature of the coke is raised so the amount of type I hydrogen is drastically reduced. Thus on two counts is it desirable to reduce cuprous chloride on coke at the lowest temperature possible.

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CHAPTER 4

OVERALL DISCUSSION OF RESULTS

This general discussion of the results of this work, is divided into ten sections. Each section collates the relevant deductions made from each individual discussion. An attempt is made, in each section, to relate the results obtained, to the work of previous workers. The last section , specifically relates this work to the TORCO process, and makes certain suggestions as to the improved operation of this process.

The first section contains a detailed analysis of the steam-carbon reaction mechanism, and attempts to derive a reaction rate equation from the suggested mechanism. The equation obtained for the reaction rate,was used with the results of the D series of experiments in order to make some conclusions about the species in existance on a coke surface,at temperatures of about 750°C.

(1) The kinetics and mechanism of the steam-carbon reaction.

The difference in reactivity between coke,charcoal and graphite is thought to be due to the nature of the carbon surface. From earlier experiments it was found that both hydrogen and carbon monoxide can exist on a coke surface at temperatures up to 1100°C . Therefore these adsorbed gases on the coke surface must decrease the area of the coke surface available to attack by water vapour. It is thought that a major difference between the carbon types is the quantity,nature and type of carbon monoxide and hydrogen that is adsorbed by the different carbons.during reaction with water vapour.

The following proposal for the reaction mechanism is based on Ergun's Unified Theory[132,134] but includes the possible adsorption of the reactant and product phases.

Consider water vapour to be initially adsorbed on the carbon surface by a physical bond between the oxygen atom inthe water molecule and a surface carbon atom which is a free active site C_f.(equation 19). This bond now

changes to a chemical bond weakening the O-H bonds and so the hydrogen atoms combine to give gaseous hydrogen. The surface oxide 'Co', so formed can alter its structure by strengthening the C-O bond to a double bond and it can then be said to be adsorbed carbon monoxide (CO). This can be desorbed. Hydrogen can set up a steady state on the coke surface by an adsorbtion-desorbtion method.

Carbon dioxide production is due to gaseous carbon monoxide or water vapour reacting with the surface oxide 'Co' to give adsorbed carbon dioxide (CO_2). This can now be desorbed and a steady state is set up between the adsorbed and desorbed molecules. The reactions are written :-

$$H_2O + C_f \rightleftharpoons (H_2O) \quad \ldots\ldots\ldots\ldots\ldots\ldots (19)$$

$$(H_2O) \longrightarrow Co + H_2 \quad \ldots\ldots\ldots (20)$$

$$Co \longrightarrow (CO) \quad \ldots\ldots\ldots\ldots\ldots\ldots (21)$$

$$(CO) \rightleftharpoons CO + nC_f \quad \ldots\ldots\ldots\ldots (23)$$

$$H_2 + C_f \rightleftharpoons (H_2) \quad \ldots\ldots\ldots\ldots\ldots\ldots (24)$$

$$CO + Co \rightleftharpoons (CO_2) \quad \ldots\ldots\ldots\ldots\ldots\ldots (25)$$

$$H_2O + Co \rightleftharpoons (CO_2) + H_2 \quad \ldots\ldots\ldots (26)$$

$$(CO_2) \rightleftharpoons CO_2 + nC_f \quad \ldots\ldots\ldots (27)$$

Where () indicates an adsorbed species and the values of n in equations 23 and 27 are unity. Statistically n can have any value between 0 and 2 but if its value was less than unity the reaction rate would decrease with time since active sites are being consumed in the reactions but are not being generated at the same rate. If the value of n was greater than unity, active sites would be generated at a faster rate than the rate at which they would be consumed, therefore the reaction rate would increase with time. Since the steady state is being considered n is therefore taken as unity. Considering the primary reduction of water vapour, the above reactions can be written as :-

$$H_2O + C_f \underset{k'_1}{\overset{k_1}{\rightleftharpoons}} (H_2O) \xrightarrow{i} Co + H_2$$

$$Co \xrightarrow{j} (CO) \qquad + \; C_f$$

$$(CO) \underset{k_2}{\overset{k'_2}{\rightleftharpoons}} CO \qquad (H_2) \underset{k_3}{\overset{k'_3}{\rightleftharpoons}} C_f$$

To avoid over-complication it is assumed that (1) all generated free surface sites are of a similar nature to the existing free sites, (2) the carbon monoxide adsorbed from the gas phase is exactly the same as the adsorbed carbon monoxide generated by the decay of $'Co'$, (3) the fractions of the surface occupied by (H_2O), $'Co'$, (CO) and (H_2) are σ, σ', σ'' and σ'''; then in the steady state the rates of appearance of all the surface complexes are equal to their rates of disappearance. If P_1', P_2' and P_3' are the partial pressures of water vapour, carbon monoxide and hydrogen then :-

for water vapour,

$$k_1P_1'(1 - \Sigma\sigma) = k_1'\sigma + i\sigma = \sigma(k_1' + i)$$

for carbon monoxide,

$$k_2P_2'(1 - \Sigma\sigma) = k_2'\sigma'' - j\sigma' = \sigma'(k_2'\frac{\sigma''}{\sigma'} - j) = \sigma''(k_2' - j\frac{\sigma'}{\sigma''})$$

for hydrogen,

$$k_3P_3'(1 - \Sigma\sigma) = k_3'\sigma''' + i\sigma = \sigma'''(k_3' - i\frac{\sigma}{\sigma'''})$$

summing,

$$\left[\frac{k_1P_1'}{(k_1' + i)} + \frac{k_2P_2'(1 + \frac{\sigma'}{\sigma''})}{(k_2' - j\frac{\sigma'}{\sigma''})} + \frac{k_3P_3'}{(k_3' + i\frac{\sigma}{\sigma'''})}\right][1 + \Sigma\sigma] = \sigma + \sigma' + \sigma'' + \sigma'''$$

let $k_1^o = k_1/(k_1' + i)$, $k_2^o = k_2(1 + \frac{\sigma'}{\sigma''})/(k_2' - j\frac{\sigma'}{\sigma''})$, $k_3^o = k_3/(k_3' + i\frac{\sigma}{\sigma'''})$

then, $$1 - \Sigma\sigma = \frac{1}{1 + k_1^oP_1' + k_2^oP_2' + k_3^oP_3'}$$

since the formation of carbon dioxide is not being considered, then if P^o is the original partial pressure of water vapour :-

$$P_2' = P_3' = P^o - P_1'$$

then the free surface is equal to $1 - \Sigma\sigma = \dfrac{1}{1 + k_1'P_1' + (k_2^o + k_3^o)(P^o - P_1')}$

Then the rate of reaction is given by the product of the free surface area and the specific reaction rate per unit free surface which is proportional to the partial pressure of the reacting water vapour :-

$$-\frac{dP_1'}{dt} = k(1 - \Sigma\sigma)P_1' = \frac{kP_1'}{1 + k_1^oP_1' + (k_2^o + k_3^o)(P^o - P_1')}$$

by separating the variables :-

$$\int_0^T kt = -\int_{P^o}^{P_1} \left[\frac{1}{P_1'} + k_1^o + (k_2^o + k_3^o)\left(\frac{P^o}{P_1'} - 1\right)\right] . dP_1'$$

and integrating between time 0 and the residence time T, and the initial and final partial pressures of water vapour P^o and P_1 then :-

$$kT = \left[1 + P^o(k_2^o + k_3^o)\right] \ln \frac{P^o}{P_1} + \left\{k_1^o - (k_2^o + k_3^o)\right\}(P^o - P_1)$$

$$\text{or } \frac{\{P^o - P_1\}}{T} = \left\{\frac{k}{k_1^o - (k_2^o + k_3^o)}\right\} - \frac{1}{T} \ln \frac{P^o}{P_1}\left\{\frac{1 + P^o(k_2^o + k_3^o)}{k_1^o - (k_2^o + k_3^o)}\right\}$$

therefore by calculating $(P^o - P_1)/T$ and $1/T . \ln P^o/P_1$ from the experimental D results and subjecting them to a linear regression analysis, the slope and intercept will give $-\left\{\frac{1 + P^o(k_2^o + k_3^o)}{k_1^o - (k_2^o + k_3^o)}\right\}$ and $\frac{k}{\{k_1^o - (k_2^o + k_3^o)\}}$ respectively

TABLE 14

	slope	intercept	correlation coefficient
charcoal	0.009195	-0.0004765	0.999956
coke	0.009267	-0.0003263	0.999907
graphite	0.009802	-0.0000697	0.999712

Table 14 shows the results obtained and since all intercepts are negative and as k must be positive, since the reaction does take place, then $k_1^o - (k_2^o + k_3^o)$ must also be negative. Therefore $(k_2^o + k_3^o) > k_1^o$ and by considering the minimum value case, then $(k_2^o + k_3^o)$ must be positive and so k_1^o can be either positive or negative.

for charcoal :- $\left\{\frac{1 + P^o(k_2^o + k_3^o)}{k_1^o - (k_2^o + k_3^o)}\right\} = -0.009195$

from which $k_2^o + k_3^o = -\frac{\{0.009195\ k_1^o + 1\}}{0.000405}$ must be positive.

therefore $(-22.7\ k_1^o - 2469)$ must be positive, and so k_1^o must be negative and its numerical value must be greater than 109 .

By dividing the intercept by the slope and multiplying up :-

$$k = 0.0518 + 0.000497\,(k_2^o + k_3^o)$$

therefore k must be positive and its numerical value must be greater than 0,0518.

By a similar procedure the following table 15 can be drawn up.

TABLE 15

	k_1^o negative	$(k_2^o + k_3^o)$	k
charcoal	>109	>0	>0.0518
coke	>108	>0	>0.0352
graphite	<102	>0	>0.00711

from the equations for k_2 and k_3 it is found that $k_2^o = k_3^o \frac{P_3}{P_2}\left\{\frac{\sigma'' + \sigma'}{\sigma'''}\right\}$

therefore both k_2^o and k_3^o are positive.

Thus by a comparative analysis it is found that as k_1^o is negative for coke and charcoal, the existance of adsorbed water molecules on their surfaces is highly unlikely. However for graphite the value of k_1^o must be more positive than - 102 so that a positive value is possible and adsorbed water molecules are more likely to exist on a graphite surface than either a coke or charcoal one. Since k_2^o and k_3^o are both positive then carbon monoxide and hydrogen can both exist as adsorbed species on any of the surfaces.

Finally if k_2^o is positive then $k_2'\sigma'' > i\sigma'$ therefore the rate of removal of (CO) which is equvalent to $k_2'\sigma''$ is greater than the rate of formation of (CO) which is equvalent to $i\sigma'$. Therefore an oxygen atom on a carbon surface is more stable as C_O' than it is as (CO).

Since there were several unknowns only a comparative analysis has been possible and from this analysis it has been found that (H_2) and C_O' can exist on coke, charcoal and a graphite surface but only on the latter is adsorbed water vapour a possibility. The relative quantities of C_O' and (H_2) are unknown.

(2) Gas evolution on heating carbons

In experiment A it was found that the major part of the carbon dioxide contained by coke is evolved when the temperature reaches 400°C and has virtually ceased at 800°C. This confirms the work of Emmett[103] who found that, of the amount of carbon dioxide liberated by heating a steam activated coal to 1200°C, 82% of the carbon dioxide evolves before the bed reaches 900°C. Similarly he found that 23% of the hydrogen and only 10% of the carbon monoxide is liberated by heating to 900°C. This is in fair agreement with the results obtained in experiment A.

In experiments H and J when coke or charcoal was heated to 850°C in a dry helium gas flow, no carbon dioxide or water vapour was detected at all when the beds were heated from 150°C to 850°C. This means that either all the water vapour and carbon dioxide have been evolved at 150°C or that they completely react as the bed is heated. Emmett[103] could only produce large quantities of carbon dioxide (20% of total gas) when the charcoal was first extracted with HF. Normally for steam activated coconut charcoal and for steam activated coal, of the total volatiles, he only found 0.7% carbon dioxide and 2.2% water vapour and 1.1% carbon dioxide and 2.1% water vapour respectively.

Hydrogen evolution after two and a half hours at 850°C is by no means complet in both experiments H and J, however charcoal produces nearly 100% more in the same time period, gram for gram, as does coke. Charcoal also produces 70% more carbon monoxide than coke in the same time period per gram of sample but by taking a time period of four days at 850°C, the position is reversed and coke produces 40% more carbon monoxide than charcoal. This is because the carbon monoxide production from charcoal is complete as soon as the bed reaches temperature however the production from coke is a function of the time held at temperature.

Methane production in each case is complete as soon as the bed reaches temperature and coke produces 23% more than charcoal per gram of sample.

Konchesky and Stewart[102] found that in their flash heating experiments of coal and water vapour in a coil, 70% of the volatile matter evolves within 0.6 seconds at 850°C and of this volatile matter, 57% is hydrogen, 17% is carbon monoxide, 19% is carbon dioxide, 4.4% is methane and the rest is unsaturated hydrocarbons. The different method of heating in experiments H and J meant that gas evolution was much slower and thermal cracking was far more complete. In the first two and a half hours in experiment H, of the gases volatilised, 70% was hydrogen, 19% was carbon monoxide and 10% was methane, there being no water vapour or carbon dioxide evolved and no hydrocarbons were measured. For charcoal the figures are 75% hydrogen, 20% carbon monoxide and 5% methane.

In experiment K it was found that nitrogen was produced from coke as it was heated from 150°C to 850°C and that it was mainly derived from chemical sources and constituted about 7% of the total gas evolution after two and a half hours at 850°C.

It is surmised that methane production is a by-product of hydrocarbon cracking below 850°C and is also due to the desorbtion of methane. No stable methane is produced at 850°C, since at this temperature the free energy of decomposition to hydrogen is - 7.5 kcal/mole CH_4.

Carbon monoxide produced from charcoal is derived mainly from adsorbed gas bu the production from coke is partially due to the adsorbed gas but mainly it is the product of the thermal decay of the surface oxide Co.

Hydrogen is derived from the thermal cracking of hydrocarbon groups on the carbon surface. The quantity and stability of these hydrocarbon groupings varies with carbon type. Coke contains more hydrocarbons which are unstable at lower temperatures than does charcoal but overall charcoal contains more hydrocarbon groups which produce hydrogen on heating to 850°C than does coke per gram of sample.

(3) Species contained on a carbon surface at high temperatures.

(a) Water vapour From experiment D it was found that of coke, charcoal and

graphite only on the latter was there a possibility that water vapour could exist at a temperature of 750°C. Both charcoal and coke produced result which showed that once water vapour came into contact with the carbon surface it reacted and could not be desorbed.In all heating to 1000°C experiments from reaction temperatures of 700-850°C (experiments E and O) no water vapour was detected at all. When either coke or charcoal was heated from 150°C to 850°C again no water vapour was detected as having been evolved. Thus it seems unlikely that above 150°C and definitely above 700°C, water vapour molecules do not exist as such on a coke or charcoal surface. For graphite, however, this possibility cannot be ruled out on the evidence of these experiments.

Strickland Constable[163,164], Long and Sykes[116,125-127], Binford and Eyring[165], Blyholder and Eyring[129], Johnstone et al[123] all accept that water vapour reacts to form a surface oxide and gaseous hydrogen. Stickland Constable[163,164] proposes the adsorbtion of water vapour in molecular form, largely because of the reversible adsorbtion of water vapour on charcoal below 700°C, Long and Sykes[116] and Eyring and co-workers[129] proposed the predissociation of steam to hydrogen and oxygen which are then adsorbed separately onto different sites. Johnstone[128] proposed that water vapour exists as OH and H radicals which are contained on neighbouring sites on the carbon surface. Long and Sykes[116] do not stipulate that the adsorbtion of the hydroxyl and hydrogen groups has to take place on adjacent sites. Montet and Myers[136] proposed that water vapour reaction with graphite was by dissociative adsorption.

Therefore this work agrees with most workers as regards the non-existance of water vapour molecules on charcoal and coke surfaces at temperatures above 700°C. The possibility of water vapour molecules existing on graphite is proposed and together with McKee's findings that water vapour in small[166] quantities retards graphite oxidation by oxygen, and Montet and Myers [135] findings that the apparent activation energy of the reaction of graphite and water vapour increases with decreasing water vapour concentration, suggest that water vapour may exist on a graphite surface as discrete molecules

at 750°C.

(b) Carbon dioxide. In all heating experiments from 150°C to 850°C and from reaction temperatures to 1000°C, no carbon dioxide was detected as having been evolved. Also when water vapour was reacted with coke in experiment E2 no carbon dioxide was evolved until there had been a sufficient build up of Co on the coke surface. In experiments G1 and G2 when water vapour was reacted with graphite and charcoal, again no carbon dioxide was evolved until there had been a sufficient build up of Co on the carbon surface. Therefore this work suggests that carbon dioxide does not exist in molecular form on a carbon surface above 700°C . Ergun[167] proposed a direct gas/solid interaction between carbon dioxide and carbon with the formation of the surface oxide and release of carbon monoxide. Langmuir[168] first discovered that when carbon dioxide reacts with a clean carbon surface there is no increase in pressure in the system, i.e. one molecule of carbon dioxide converts to one molecule of carbon monoxide and the remaining oxygen atom is retained by the carbon surface.

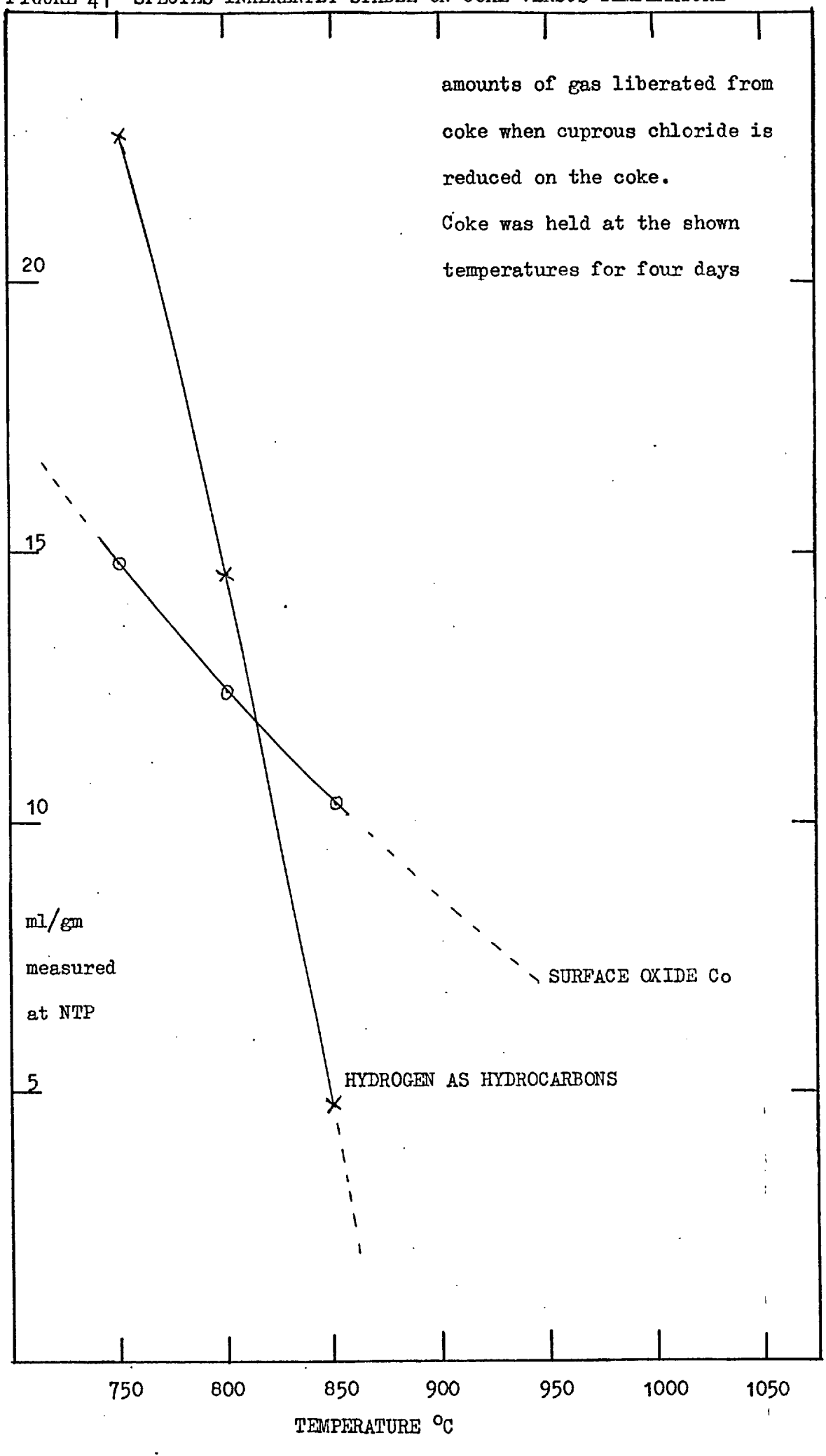
(c) Carbon monoxide and the surface oxide C_o' Experiments E and G show that oxygen is held by a carbon surface during the initial reaction with water vapour. Oxygen could be retained as adsorbed carbon monoxide (CO) or as a surface oxide C_o'. Experiment D's results suggest that of these two species, for coke, charcoal and graphite, C_o' is the more stable at 750°C. On heating coke or charcoal from 150°C to 850°C there is a large burst of carbon monoxide gas as the temperature rises, however at temperature, the carbon monoxide production from charcoal ceases while the production from coke gradually decreases with time over a period of four days. It is suggested that adsorbed carbon monoxide constitutes a major part of the carbon monoxide evolution on heating to 850°C and Co is responsible for its evolution at 850°C. In experiment G it was calculated that the amount of stable C_o' generated by the reaction of water vapour, assuming that the initial reaction rate was equal to the steady state rate, was 0.63 ml/gm on coke,

0.057 ml/gm on charcoal and 0.256 ml/gm on graphite at 750°C. Thus gram for gram coke will hold eleven times as much 'Co' as charcoal and two and a half times as much as graphite.

The inherent 'Co' on a coke surface that is released as carbon monoxide on heating to 1000°C from various temperatures, can be replaced to a certain extent, by reacting water vapour with the degassed coke at the initial reaction temperature. Thus from experiment O on heating from 700,750 and 800° to 1000°C, 1.13 ml/gm, 1 ml/gm and 0.44 ml/gm of carbon monoxide are evolved from untreated coke. After reaction with water vapour at the same temperature degassed coke gave 0.84 ml/gm, 1.15 ml/gm and 1.02 ml/gm on subsequent heating to 1000°C. However it was noted that the carbon monoxide which was evolved on heating to 1000°C is not the total quantity of carbon monoxide held on the coke surface as 'Co'. In experiment P it was found that cuprous chloride reduction on a coke surface releases 'Co' as carbon monoxide and at the temperatures of 750,800 and 850°C then 14.9 ml/gm, 12.5 ml/gm and 10.4 ml/gm of carbon monoxide were evolved. Thus of the Co contained on a coke surface at the most, only 7% is released by heating to 1000°C. Also from experiment P, the difference between the amounts of Co stable after four days at 750°C and 800°C was 2.4 ml/gm, in experiment O after twenty five hours from heating coke from 750°C to 800°C only 0.55 ml/gm was evolved. Thus the nature of 'Co' stability is complex.

There was slight evidence in experiment P that Co is liberated in steps by copper deposition on a coke surface, however the number of steps was indeterminate. Thus it is proposed that there are several types of carbon surface oxide each exhibiting different degrees of thermal stability. It can be seen from the results of experiment O that the types of 'Co' generated by water vapour at high temperatures on a coke surface differ in thermal stability from the 'Co' types inherently contained in coke, since when both samples are heated to 1000°C the rates of evolution of carbon monoxide are not similar nor are the quantities evolved equal. Figure 41 shows the amounts of 'Co' that are stable at each temperature calculated from experiment P. It can be seen that if the plot is extrapolated to 1000°C there should still be a

FIGURE 41 SPECIES INHERENTLY STABLE ON COKE VERSUS TEMPERATURE



significant quantity of 'Co' stable at this temperature. It was once thought that Co was equivalent to adsorbed carbon monoxide however both forms exhibit different types of adsorbtion spectra[169-171] and when carbon dioxide is reacted with graphite, by tracer analysis[172,173] it has been found that there is exchange of oxygen between carbon dioxide and monoxide and negligible transfer of carbon from the solid to the gas phase. Thus a surface oxide does exist, clearly distinct from adsorbed carbon monoxide and Mentser and Ergun[140] postulated that the C-O bond in Co is 2/3 of a double bond.

Ergun[134] states that the surface oxide 'Co' is formed by the reaction of water vapour and carbon and it is exactly the same as the surface oxide formed by the reaction of carbon dioxide and carbon. Strickland Constable[174] postulated that the similarity of the reactions of nitrous oxide, carbon dioxide, water vapour and oxygen with a carbon filament was due to the natur and characteristics of the carbon surface i.e. the product was always 'Co'. Walker and co-workers[118,119] conclude that chemisorption of oxygen to 'Co' occurs on five different types of active site to give five different types of 'Co'.

This work concludes that the surface oxide does exist as distinct from adsorbed carbon monoxide and that water vapour can generate stable Co on a coke surface at reaction temperatures but that this 'Co' is different from that inherently contained by coke. Also it has been proposed that some of the 'Co' inherently contained by coke is quite stable at temperatures above 1000°C. It has been shown that, gram for gram, for every ml of 'Co' generated on a charcoal surface by water vapour, 5 ml are generated on graphite and 11 ml are generated on a coke surface.

(d) Hydrogen and methane. Hydrogen is inherently contained in coke and sugar charcoal but not on graphite. When these three carbon types are reacted with water vapour, then gram for gram, for every ml of stable adsorbed hydrogen generated on a graphite surface, there is generated 5 ml on coke and 19 ml on charcoal. For coke at 750°C, assuming water vapour immediately assumes its steady state rate of reduction, then 0.15 ml/gm of stable hydrogen is

adsorbed by the coke surface. On heating from 750°C to 1000°C coke, which has been reacted with water vapour after pretreatment at 1000°C, 0.26 ml/gm of hydrogen are evolved; on heating to 1000°C from 750°C coke which has had no pretreatment then 4.99 ml/gm are evolved and on reducing cuprous chloride on untreated coke at 750°C, 22.75 ml/gm are evolved as hydrogen and hydrogen chloride. Thus of the quantity of hydrogen stable at 750°C on a coke surface only 20% is evolved on initial heating to 1000°C. Also of the hydrogen that is evolved on heating untreated coke to 1000°C from 750°C only 6% can be replaced by reacting the coke with water vapour at the same temperature. Also from these results it is obvious that water vapour reacts with coke at a much higher rate initially than the steady state rate. Since water vapour generates adsorbed hydrogen then the hydrogen inherently contained by the coke cannot possibly exist in the adsorbed state since by heating both types to 1000°C from 750°C twenty times as much hydrogen evolves from untreated coke as does from the known stable adsorbed hydrogen on the water treated coke. It follows therefore that the inherent hydrogen exists as hydrocarbons. It is the thermal breakdown of these hydrocarbons to hydrogen and in some cases methane, that generates the detected hydrogen. In experiment P it was postulated that there are two main types of hydrocarbon groupings on a coke surface, type II, which can be regarded as a form of adsorbed hydrogen such that on heating or on disturbance of the carbon matrix bonding by copper deposition, it will be desorbed as gaseous hydrogen. Type I is much more stable and decomposes very slowly when subjected to a temperature rise. It is type I that reacts with cuprous chloride vapour on the coke surface and its activity was calculated to be 0.044 at 750°C. The volume ratio of type I to type II was constant over the temperature range 750-850°C at 15:1. When type I begins to decompose when subjected to a temperature rise , it does so by initial breakdown to type II which then is evolved.

The stability of total hydrogen with temperature is shown in figure 41 , it is obvious that no hydrogen is stable on a coke surface at 1000°C, however

the rate of decay of the hydrocarbons at this temperature is so slow that it would take several days for the hydrogen to be completely evolved. The difference between the hydrocarbons contained on coke at 750°C and 800°C according to experiment P is 8.1 ml/gm, of which 2.67 ml/gm are type II and 5.43 ml/gm are of type I. When untreated coke was heated from 750°C to 800°C in experiment O, after twenty five hours 2.68 ml/gm of hydrogen had evolved, i.e. all of the type II and some of the type I that had started to decompose at 800°C. The difference in volume between the coke heated to 1000°C from 750°C and from 800°C was 2.95 ml/gm, i.e. all the type II and substantially more of the type I which has evolved during the pretreatment at 800°C.

Workers[112,113] have found that the activation energy of chemisorption of hydrogen on graphite varies according to the coverage of the surface by hydrogen. Walker[122] et al found four different types of adsorbtive site for hydrogen. Puri and co-workers[123,124] found that hydrogen from charcoal is driven off in steps on heating from 30 to 1200°C again suggesting that there are several types of adsorbtive site. Emmett[103] has shown that when coal is heated from 900°C to 1000°C 35.6 ml/gm of hydrogen are evolved. In this work it was found that 23 ml/gm of hydrogen still stably exist on a coke surface at 750°C.

Methane production in these experiments was minimal at reaction temperatures and only charcoal in experiment D produced significant quantities on reaction with water vapour. On heating unreacted coke to 1000°C the volume ratio of methane to hydrogen evolved was less than 1:100. The free energy of formation of methane at 750°C is + 8.00 kcal/mole CH_4 . Thus it can be said that methane molecules do not exist as such on a coke surface but, the hydrocarbons that do exist can, in certain circumstances, thermally decay to give methane. When cuprous chloride is reduced at a low rate on a coke surface as in experiment P the π bonding disruption is sufficient to promote the gradual and complete decay of type II hydrocarbons to gaseous hydrogen. However when the rate of cuprous chloride reduction is sudden and extremely

rapid as in experiment A2, the π bonding disruption is so massive and sudden that the hydrogen , forced off the surface, drags with it carbon atom that are loosely held by the carbon matrix, i.e. the type II hydrocarbons are dislodged as the lowest hydrocarbon grouping , methane.

(4) The steam-carbon reactions

In all experiments it was found that gaseous hydrogen and carbon monoxide were the principal products of the reaction of water vapour and carbon. It was found in experiment D that adsorbed water vapour molecules are not likely to exist on coke or charcoal surfaces. Thus it is proposed that the principal reaction is a gas/solid reaction producing a surface oxide and gaseous hydrogen. The rates of adsorption of hydrogen and of decay of C_o' and the subsequent desorption of carbon monoxide vary according to the carbon type and with the gas residence time. In the steady state it was calculated that on a graphite surface the ratio of C_o' to hydrogen generated from water vapour was 8.5:1, on charcoal it was 0.1:1 and on coke it was 4.2:1.

The number of active sites $[C_f]$ involved in the reaction increases with temperature and with gas residence time, and in general at any one temperature there are 5 times more active sites per gm involved in the water vapour reaction on charcoal than on coke and some 42 times as many as on graphite.

It was found that in the systems considered, the reaction was slow in achieving a steady state and that the steady state attained was far removed from thermodynamic equilibrium. It was also found that adsorbed hydrogen severely limited the degree of reduction of water vapour and when this adsorbed hydrogen was removed as in experiment N1, by the cuprous chloride reduction by hydrogen above the coke bed, although the number of active sites involved remained virtually the same, the sites vacated by hydrogen were open to attack by water vapour and so the apparent activity of the carbon increased dramatically (by a factor of 100 from a liquid cuprous

chloride temperature of 400°C to 700°C).

In experiments H and I as the temperature increased from 150°C to 850°C water vapour started to react with the coke at about 500°C and the reaction products were hydrogen, carbon monoxide and methane, however at 850°C, methane production ceased. In two and a half hours the water vapour reaction had increased the amounts produced by 13% for hydrogen, 50% for carbon monoxide and for methane by 15% over the amounts of gas produced from the coke in a dry system.

An equation for the rate of water vapour reaction in the steady state was derived as :-

$$- dP_{H_2O}/dt = k P_{H_2O}/(1 + k_2^o P_{CO} + k_3^o P_{H_2} + k_1^o P_{H_2O})$$

which on the simplification that $P_{CO} = P_{H_2}$ is equivalent to the rate equation developed by Gadsby et al[125]. Upon integration this gives :-

$$(P^o - P)/\tau = X - Z.\ 1/\tau \ln P^o/P \qquad Cf\ \ y = c - mx$$

where P^o and P are the initial and final partial pressures of water vapour and τ is the residence time in the bed and,

$$X = k/[k_1^o - (k_2^o + k_3^o)]$$

$$Z = [1 + P^o(k_2^o + k_3^o)] / [k_1^o - (k_2^o + k_3^o)] \qquad \text{(see p 115)}$$

when the experimental values of τ and P were used in the above equations and the results subjected to a linear regression analysis it was found that Z and X were constant and thus the derived equation was adequate in assessing the results obtained.

It was found in experiments E and G that carbon dioxide production was initiated when there was a sufficient build up of the surface oxide C_o' on the carbon surface. From experiment N1 it was found that the production of carbon dioxide was strongly dependant on the partial pressure of water vapour in the system, and as the latter fell with increased cuprous chloride temperature so the concentration of carbon dioxide also fell. This occured even though there was a high concentration of C_o' on the coke surface and the concentration of carbon monoxide in the gas stream was high. Thus it

appears that the principal source of carbon dioxide in a steam-carbon system is from water vapour and the surface oxide $C_o^{(\ )}$ and not from $C_o^{(\ )}$ and carbon monoxide. Therefore it would be expected that the amount of carbon dioxide produced from coke, charcoal and graphite would be in the same proportion to the amount of $C_o^{(\ )}$ held on their surfaces. It was found that, gram for gram, for every ml of $C_o^{(\ )}$ on charcoal at 750°C there was 4.5 ml on graphite and 11 ml on coke. Thus considering the approach of the K_6 ratios, for carbon dioxide production in experiment D, to unity as a function of the amount of carbon dioxide produced, then from figure 12 (p 64) it can be seen that at low residence times at 750°C, that the order of ability to produce carbon dioxide is from coke, then graphite and finally from charcoal. However at long residence times this correlation between amounts of Co and carbon dioxide produced is not true since the K_6 ratio for coke decreases with residence time. Also from figure 10 (p 59), it can be seen that, unlike charcoal and graphite, for coke as the temperature increases from 700°C to 900°C for a residence time of seventeen seconds, the K_6 ratios fall but, the converse happens at residence times of less than a second and the K_6 ratios increase with temperature. Thus carbon dioxide production from coke is not only governed by the partial pressure of water vapour but also is strongly influenced by the catalytic impurities in the ash. It is well known that the reaction of carbon dioxide and water vapour with coke to produce carbon monoxide is catalysed by a number of compounds[127,130,156,157,158] and it is proposed that these catalytic effects are only able to exert their influence to keep the partial pressure of carbon dioxide minimal, at long gas residence times in the bed; and so, at shorter gas residence times the amount of carbon dioxide produced is a truer reflection of the reaction between $C_o^{(\ )}$ and water vapour.

Thus this work agrees basically with Ergun[134], that the initial reaction is of water vapour reacting with solid carbon to form a surface oxide and gaseous hydrogen. However Ergun's work suggests that the principal source of carbon dioxide is from $C_o^{(\ )}$ and carbon monoxide and in experiment N1 this was found not to be so, and it was water vapour that was reacting with $C_o^{(\ )}$.

This work suggests that the rate controlling step of the steam-carbon reaction is the transfer of carbon from the solid to the gas phase i.e. the release of Co as carbon monoxide: and that this rate was largely determined by the concentration of the adsorbed reactants on the carbon surface, this is in agreement with a number of workers .(116,175,176)

(5) Catalysis of the steam-carbon reactions.

In experiments H and I, the presence of 0.5% salt by weight in two and a half hours increased the reaction products from the water vapour reduction by 34% of hydrogen and carbon monoxide, it also increased the amount of methane produced from the reaction of water vapour with coke by 40%, during the same period. In experiment A2 it was shown that when copper deposits on copper the rate of reduction of water vapour increases to supply the cuprous chloride with sufficient hydrogen. In experiment N1 this was again found. The catalytic action was explained by the setting up of a potential gradient of hydrogen between the coke bed and the region of copper deposition. As the need for hydrogen increased as the partial pressure of cuprous chloride increased, so the potential gradient steepened to provide sufficient hydrogen for complete reduction. Thus the rate of water vapour reduction increased and the amount of hydrogen that was stable in the adsorbed form on the coke surface decreased, freeing more active sites for attack by water vapour.

Copper in physical contact with coke was found to be a poor catalyst of the steam-carbon reaction in experiment F, whereas chemical contact between copper and coke, as afforded in experiments P2,P3 and P4 as well as A2, showed that the deposition of copper on coke was accompanied by release of adsorbed gases carbon monoxide, hydrogen and methane as well as the release of the surface oxide to carbon monoxide. This was explained from the π bonding perturbation by the unfilled 'd' bands of copper metal after Long and Sykes(125,152) and Rakswarski(153).

It was also found that in experiment F copper was responsible for the retention of hydrogen on a coke surface by adsorption and by creation

of active sites containing adsorbed hydrogen.

(6) The vapour pressure of cuprous chloride

In experiment N1 it was found that the partial pressure of cuprous chloride could be followed by indirectly measuring the partial pressure of hydrogen chloride, this being assumed to be the sole gaseous product of cuprous chloride reduction. This was verified in experiment P by direct measurement of the hydrogen chloride partial pressure, thus by assuming the trimer to be the sole vapour species, from the 'lost' hydrogen results of experiment N1 it was found that:-

$$\log_{10} P_{(CuCl)_3} \text{ mm Hg} = -5540/T^{\circ}K + 6.3 \pm 0.1$$

as compared with the directly measured partial pressure of cuprous chloride from a number of workers as being :-

$$\log_{10} P_{(CuCl)_3} \text{ mm Hg} = -5276/T^{\circ}K + 6.354 \pm 0.25 \quad \ldots\ldots (30)$$

Thus measuring the partial pressure of cuprous chloride by the indirect 'lost' hydrogen method in experiment N1 was a reasonable experimental procedure for the determination of the vapour pressure of cuprous chloride. Also as the experimental results, calculated on the trimer, agree well with the measured vapour pressure, then the trimer is assumed to be the dominant vapour species in the temperature range studied, 500-700°C. This work shows that ΔH_v° for the formation of the trimer from three moles of liquid monomer was 25 ± 2 kcal/mole trimer. The JANAF[62] figure is 29.9 ± 0.2 kcal/mole trimer, but this figure was calculated on the assumption that ΔH_s° was constant with temperature, which of course it is not. Guido's[177] mass spectrometric work , which is more recent than JANAF gives $\Delta H_{s\ 640^{\circ}K}^{\circ}$ as 33.7 ± 0.8 kcal/mole trimer. Thus as $\Delta H_{v\ 700^{\circ}K}^{\circ}$ is 7.3 kcal/mole then a more accurate value of $\Delta H_{v\ 700^{\circ}K}^{\circ}$ is 26.4 ± 1 kcal/mole trimer . This gives a closer agreement with the measured value of ΔH_v° from this work of 25 ± 2 kcal/mole trimer over the temperature range 800-1000°K.

(7) Cuprous chloride reduction by hydrogen

In experiment N1, cuprous chloride vapour was reduced by gaseous hydrogen

to copper and hydrogen chloride on the surface of the silica reaction tube. Very little copper was deposited on the coke bed itself while some copper was deposited on the silica wool plug on top of the coke bed. It was found that silica does not adsorb hydrogen to a measurable extent at these temperatures and so the deposition could not be due to there being a greater hydrogen potential on a silica surface than on the coke. This effect was explained by the diffusion of hydrogen out of the coke bed being greater than the linear velocity of the cuprous chloride vapour towards the bed. In experiments with the Mk III reaction tube which restricted back diffusion of hydrogen, no copper was deposited between the cuprous chloride vessel and the restriction but copper was deposited on the coke as well as on the silica reaction tube walls above the coke. Therefore it is concluded that in a system containing gaseous hydrogen, as generated by water vapour and coke, there is no preferential deposition of copper on coke.

In experiments with water vapour present there was a certain amount of copper deposition on copper. This is assumed to take place by hydrogen migrating to the surface of the deposited copper enabling more cuprous chloride to be reduced there. The extent of the copper on copper growth was severely limited and only a few dendritic growths were noticed on the underneath of the CuCl vessel. On the copper crust in experiment P1, the copper on copper growth was mainly plates and filaments. In all experiments with water vapour, no cuprous chloride was observed to pass through the system without being completely reduced. Only in experiments P1 and N1 when water vapour was removed from the system was a plug of condensed cuprou chloride noticed below the coke bed. When water vapour was absent from the system as in experiments P2,P3 and P4, the reduction of cuprous chloride was incomplete. This was explained by the hydrogen on the coke surface having an activity of less than unity. At 750°C it was calculated that this apparent activity of hydrogen was 0.04, even so 99% of the cuprous chloride was reduced. However at 850°C only 20% of the cuprous chloride vapour was reduced as it passed through the bed. Hydrogen generated by the action of copper depositing on the coke did not subsequently reduce further

amounts of cuprous chloride since the partial pressure of hydrogen chloride measured was always constant irrespective of the partial pressure of the gaseous hydrogen.

In experiment A2 when a high partial pressure of cuprous chloride was suddenly introduced into the coke bed , the initial deposition was of copper on coke. However after not more than five minutes, the method of deposition changed to that of copper on copper and as the flowrate of helium was high there was no back diffusion of hydrogen out of the bed to reduce cuprous chloride on the silica vessel walls. Thus the result was a porous plug of copper which had grown up into the space above the coke bed and was not friable at all and consisted of a single mass. Therefore this growth was by migration of hydrogen to the copper surface from the coke bed down a chemical potential.

Hadjiat[81] found that when employing hydrogen from the reaction of charcoal and water vapour, to reduce cuprous chloride vapour on the charcoal surface, that deposition of copper was more complete at 700°C than at 900°C even though at 900°C more hydrogen was produced from the steam reaction. He tentatively suggested that this effect might be due to the nature of the inherent hydrogen on the charcoal. In a completely dry system he found that cuprous chloride reduction was not as complete as it was in a wet system. However when water vapour was present in the system in reasonable quantities (10^{-4} atmos.) he discovered that copper would deposit on the silica walls next to the plug of charcoal as well as on the charcoal.

In his nucleation work with cuprous chloride and hydrogen he found no difference in the nature or rate of deposition of copper from cuprous chloride and gaseous hydrogen on several substrates including :- copper powder, graphite, charcoal or silica.

Thus from this work cuprous chloride will deposit copper from the reaction with gaseous hydrogen on any convenient surface. Copper will only deposit on a carbonaceous material when there is hydrogen on that surface either in the adsorbed state or as a hydrocarbon grouping.

(8) Reaction of cuprous chloride and water vapour

It was found that to a large extent in experiment P1 and to a much smaller extent in experiment N1, that water vapour reduces cuprous chloride to cuprous oxide and hydrogen chloride. The partial pressure of hydrogen chloride so generated was much higher than the thermodynamic partial pressure. This was explained by the dissolution of cuprous oxide in cuprous chloride which lowered its activity and hence the reaction proceeded more towards completion. Hadjiat[81] also found this effect but the partial pressure of hydrogen chloride measured was lower than the thermodynamic value. However in his experiment the cuprous oxide formed was not in contact with cuprous chloride.

(9) Nature of copper deposition

When copper is deposited, from cuprous chloride vapour by hydrogen 'held' on a coke surface i.e. not gaseous, on that surface, then the deposit is of platelike form. When gaseous hydrogen is the reducing agent the deposit takes two forms, (a) dendritic and (b) fine crystals. In experiment N1 both types of deposit were found. Fine crystals built up into a sheet on the reaction tube walls and dendrites on the underneath of the CuCl vessel. It is proposed that since the cuprous chloride vapour is jetted out from below the bottom of the CuCl vessel, the vapour therefore must travel down and be reduced on the reaction tube walls by the hydrogen diffusing out of the coke bed. If any cuprous chloride is caught in a back flow of hydrogen and helium towards the CuCl vessel, its partial pressure will be extremely low. Therefore it is suggested that dendritic growth, as on the underneath of the CuCl vessel, only occurs when $P_{H_2} > P_{(CuCl)_3}$, and the fine crystals are the predominant growth form when $P_{H_2} < P_{(CuCl)_3}$ as on the reaction tube walls.

Hadjiat[81] came to the same conclusions in his experiments of entrainment deposition of copper on substrates from cuprous chloride vapour and hydrogen He also noticed platelet and filament growth when copper was deposited on charcoal.

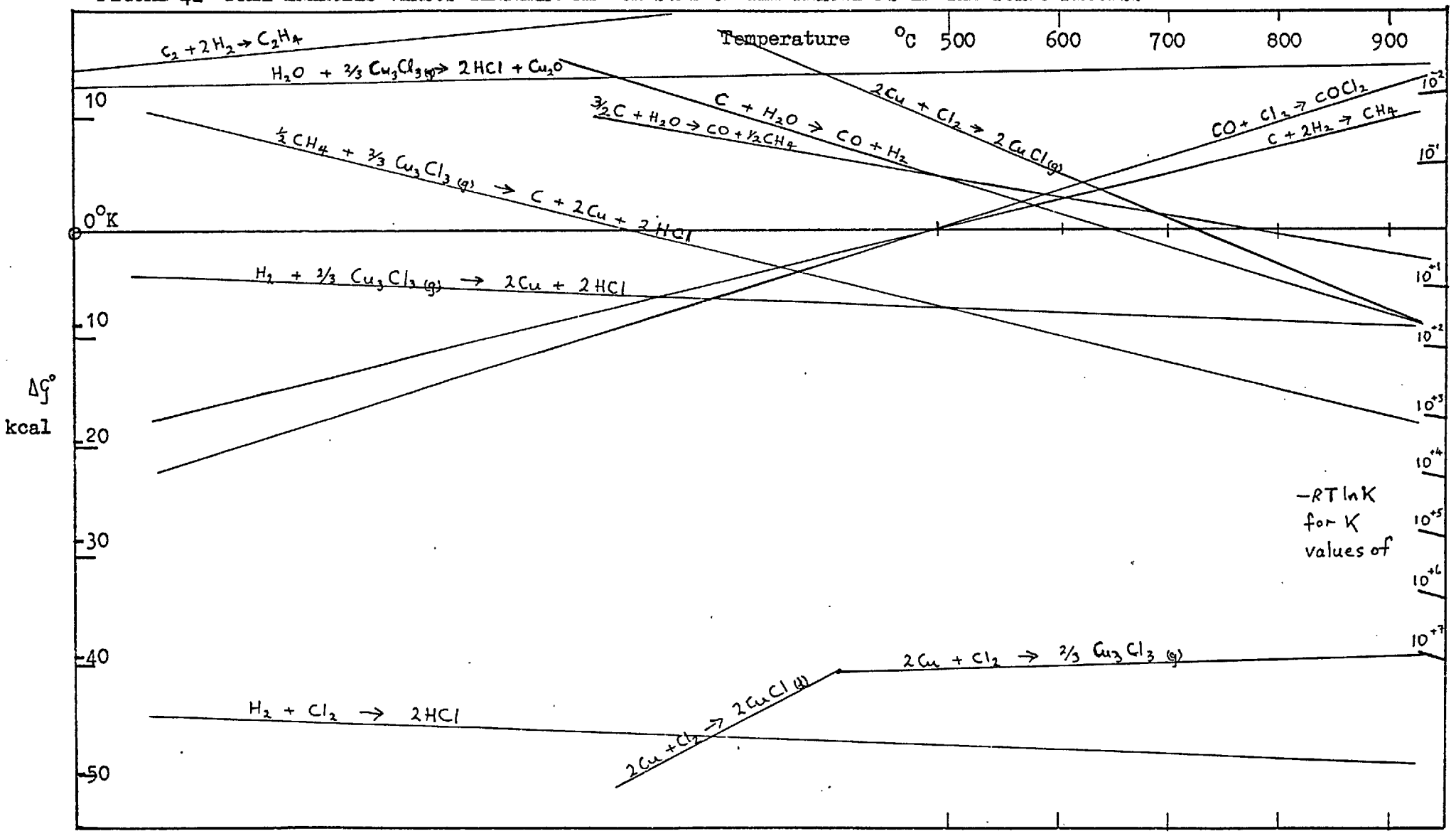
In experiment A2 and to some extent in experiments P2,P3 and P4, when copper deposited on copper by hydrogen migration from the coke, the nature of the growth was filiform. Also the copper on copper growth is upwards i.e. towards the cuprous chloride source and away from the hydrogen source. Thus copper growth is from its tip into a region of high partial pressure of cuprous chloride vapour rather than from its base into a region of high partial pressure of hydrogen. The nature of the deposit was fine crystals and filaments confirming that this type of growth is predominant in a region where $P_{H_2} < P_{(CuCl)_3}$. Hadjiat also noticed these effects. Thus when cuprous chloride is reduced by gaseous hydrogen on any substrate when $P_{H_2} < P_{(CuCl)_3}$ then fine crystals and filaments predominate whereas when the reverse is true , a dendritic type of growth is observed. When cuprous chloride is reduced by the hydrocarbon hydrogen on the coke surface the growth is of a platelike nature.

(10) Applications to the TORCO process.

Figure 42 shows a free energy diagram of some of the reactions involved in the TORCO process, both proved and speculated, together with the reaction studied in this work. It can be seen that, as was shown in experiments N and P, the trimer is more stable than the monomer in the gas phase below 1000°C. The most efficient reducing agent for cuprous chloride is seen to be hydrogen although if methane did exist in a metastable state it would be the more efficient reducing agent above 500°C. This is obvious since methane is unstable with respect to hydrogen and carbon above 500°C. Thus any short chain metastable hydrocarbon would be a better reducing agent at reaction temperatures than hydrogen, this is why cuprous chloride will be reduced most effectively on a coke surface containing metastable hydrocarbons i.e. type I hydrogen.

From the equilibrium constant K scale on figure 42 it can be seen that its value for cuprous chloride reduction by hydrogen is $50 = P^2_{HCl}/P_{H_2} \times P^{2/3}_{(CuCl)_3}$ however for reduction of the trimer by methane at the same temperature of 750°C its value is $750 = P^2_{HCl}/ P^{\frac{1}{2}}_{CH_4} \times P^{2/3}_{(CuCl)_3}$.

FIGURE 42 FREE ENERGIES VERSUS TEMPERATURE FOR SOME OF THE REACTIONS IN THE TORCO PROCESS



From the K equations it will be seen that the trimer reduction is dependent on the total pressure of the system to the 1/3 power. If the total pressure of the system were reduced this would favour reduction of the trimer.
The presence of salt in the system catalytically increases the amounts of hydrogen and more importantly methane, from the water vapour coke reaction, as the temperature of the system is raised to 850°C.
Thus cokes and coals of high volatile content would make better segregation agents, since they contain more surface hydrocarbons and subsequently generate more hydrogen on heating and contain more metastable hydrocarbons at reaction temperatures. However with too high a volatile content the large partial pressure of gaseous hydrogen produced would reduce cuprous chloride anywhere in the system and not necessarily on the coke and the deposit would be fine and crystalline, whereas with low partial pressures of hydroge dendritic and agglomerated copper on copper deposition is favoured. So if copper recovery was plotted against volatile content it would be expected that recovery would rise initially with increasing volatile content. However at very high volatile contents the recovery would be poor since hydrogen is reducing the cuprous chloride to fine crystals all over the system. This was found to be so.(78)
If a coal of high volatile content were coked at a low temperature (750°C) and used as a segregation agent instead of coal, then it would be expected that copper recovery would be much improved since some of the excess hydrogen would have been removed in coking but there would be sufficient metastable hydrocarbons on the coke surface to initiate copper deposition on that surface and a sufficient partial pressure of hydrogen to ensure copper deposition on copper. Segregation tests have been made with a high temperature coke but as would be expected recoveries were poor.(178) Also when using coal in a water vapour containing system, from this work, it would be expected that there would be three types of deposit: Copper on coal by hydrocarbons., copper on copper by hydrogen migration and low partia pressure of hydrogen and copper on gangue from high partial pressures of hydrogen. This is found to be so in practice(178).

It was also found that copper deposition on coke will lead to the evolution of carbon monoxide in largerquantities than are generated from the steam-coke reaction. It has been found that carbon monoxide in a segregation system is beneficial for the pre-reduction of the copper ore to cuprous oxide.(41)

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CHAPTER 5

This chapter contains the conclusion and some proposals for future work.

CONCLUSION

The most efficient method of reducing cuprous chloride trimer to copper is by gaseous hydrogen and according to the thermodynamics and kinetic considerations, this process will proceed faster and to a greater degree of completion, the higher the temperature of reaction. However when cuprous chloride trimer is reduced by gaseous hydrogen , copper will deposit on any convenient substrate, there is no preferential deposition on carbonaceous materials when reduction is solely by gaseous hydrogen. The most effective method of depositing copper on a carbonaceous material is by hydrogen contained on that material surface. In coke and charcoal this hydrogen exists as metastable hydrocarbon groupings on the surface and the quantity and apparent activity of these hydrocarbons increase with a decrease in the maximum temperature to which the material has been subjected.

Although reactions with water vapour will create adsorbed hydrogen on a degassed coke or charcoal surface, the quantity replaced on the surface is small compared to that inherently contained by either carbonaceous material (1/100). However of the two , charcoal can adsorb four times as much hydrogen, gram for gram, than can coke.

Any beneficial effect that water vapour has in generating adsorbed hydrogen is offset by the the fact that gaseous hydrogen is also generated, thus leading to non specific copper deposition.

If the partial pressure of gaseous hydrogen is lower than that of the cuprou chloride vapour, then dendritic growth is favoured, if the reverse is true then crystal and filament growth is more predominant.

Copper can deposit on the copper deposited on the coke if the partial pressure of hydrogen is low and the nature of this growth is platelike and filiform.

The effect of water vapour in the system has a negligible effect on hydrogen production, compared to the amount produced by the thermal treatment of coke

However it does increase the amount of methane in the system by 15% by its reaction with coke at temperatures below 850°C.

Thus from this work it is suggested that a coal coked at temperatures not exceeding 800°C would be a better segregation agent than coal for copper reduction.

As regards the steam-carbon reaction it was found that the surface oxide Co is stable on the coke surface at temperatures up to 1000°C. The amount of hydrogen 'held' on coke as hydrocarbons decreases rapidly with temperature and as such, only adsorbed hydrogen contained on the surface during reaction with water vapour would be the sole source of hydrogen for cuprous chloride reduction on the surface. It was found that a charcoal can adsorb four times as much hydrogen at reaction temperatures and this would be a better segregation agent at temperatures higher than 850°C.

The mechanism accepted for water vapour reaction with carbon is :-

$$H_2O + C_f \longrightarrow Co + H_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(8)$$

$$H_2 + C_f \rightleftharpoons (H_2) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(24)$$

$$Co \longrightarrow CO + C_f \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(9)$$

$$Co + H_2O \rightleftharpoons CO_2 + H_2 + C_f \quad \ldots\ldots\ldots\ldots(26) \text{ and } (27)$$

There was little evidence to support the theory that Co and carbon monoxide react to form carbon dioxide. It was proposed that when copper replaces hydrogen on the coke surface, this disrupts the π bonding within the carbon matrix and releases adsorbed gases and activates the breakdown of Co to carbon monoxide and of the hydrocarbon groupings to hydrogen. This can be regarded as catalysis of the steam-carbon reaction since the vacation of active sites by the adsorbed gases frees the active sites for further attack by water vapour.

The cuprous chloride trimer was indirectly found to be the most prominant species in the vapour phase over the temperature range 500-700°C and its vapour pressure was calculated to be :-

$$\log_{10} P_{(CuCl)_3} \text{ mm Hg} = -5{,}540/T^{\circ}K + 6.3 \pm 0.1$$

and H_v° over the same temperature range was found to be 25 ± 2 kcal/mole.

PROPOSALS FOR FUTURE WORK.

From this work it has been shown that up to temperatures of 800°C , a low temperature coked coal was the best segregation agent , however at temperatures above this, the hydrocarbons metastably existing on the coke surface rapidly decline in quantity. Therefore it is suggested that a charcoal be used at temperatures higher than 850°C for segregation since sugar charcoal can adsorb four times as much hydrogen from the reaction with water vapour than can coke. This would apply to nickel segregation which is carried out at 950°C. Thus further experiments with different types of charcoal at higher temperatures than employed for cuprous chloride reduction would be beneficial in determining the best segregation agent for nickel chloride and other refractory metal chlorides.

For far more accurate kinetic measurements of the reduction of chloride vapour by carbonaceous materials, a fluidised bed could be employed with the chloride vapour passing through the bed at different flowrates.

The chromatograph could be improved by fitting sample injection valves of the push-pull type situated inside the column oven. This would give much better reproducibility on injection, especially of water vapour detection which tended to be a function of the time the valves were left in the inject position.The sensitivity of the chromatograph to hydrogen was poor since helium was used as a carrier gas, and to change to argon would have been too involved for rapid sampling of other gases as well as hydrogen, thus an on-line continuous hydrogen meter would be preferable. Although the Pye chromatograph was run at its maximum sensitivity (burning out three katharometers in the process) for two years continuously, it performed extremely well and background noise was much lower than expected. Even so a more sophisticated machine (e.g. Hewlett-Packard) with automatic injection would give a much greater constancy in use for repeatable injection.

Only one vapour pressure of water vapour was used in these experiments since this was the value of the water vapour partial pressure found in TORCO segregation chambers. If future work was carried out at a much lower partial pressure it might prove capable of reducing the amount of copper deposition on the silica while still generating sufficient gaseous hydrogen within the coke to reduce gaseous cuprous chloride on the copper already deposited on the coke.

The Mk III reaction tube and CuCl vessel could be well used for nickel chloride experiments at 950°C and also for mixtures of chlorides. i.e. nickel-iron.

The 'lost' hydrogen method proved so effective in determining the partial pressure of cuprous chloride, it is suggested that this method may be used to determine the vapour pressures of chlorides which are difficult to determine conventionally.

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APPENDIX

GAS CHROMATOGRAPH Pye Unicam Series 104 chromatograph Model 34

katharometer max. temperature 350°C.

carrier gas 15 ml/min to 200 ml/min

detection volume 0.3 ml per port

sensitivity 1000 mv per mg of toluene

noise and stability in 5 hours does not exceed ± 0.02m

katharometer power supply

bridge current 500 mA bridge voltage 30 V max

stability varied by less than ± 0.02% of bridge current

for either 10% variation in voltage supply or temperat

variation of 1°C.

column oven controller

range of control 0 - 500°C in fixed steps of 50°C and

incremental control 0 - 50°C

setting reproducability ± 0.25° Stability ± 0.1°C

INTEGRATOR KENT CHROMALOG III

mode of operation manual or remote or automatic, slope controlled.

slope linearity better than 0.1%

repeatability typically ± ½ μv, ± 0.1% of area ± 1 cnt

dynamic range 10^4 to 10^6 dependent on peak size and duration

maximum count rate 40,000 counts per sec. om either rg

range 0 to 1000 mv or 0 to 100 mv

printer six digit can print three peaks per sec.

count capacity infinite reset in blocks of 900,000

temperature stability typically 1 μv per 1°C

auto zero output in excess of 0.5% of range

drift rate less than 10 ppm of range per hour

slope sensitivities variable between 0.75 to 288 ppm/se

sampling rate 8,2 or $\frac{1}{2}$ samples per second

recorder and computor outputs

AUTOMATIC TITRIMETER EIL TITRIMETER MODEL 24

ranges 3 to 11 pH subdivided into 0.1 pH

-800 to + 400 mv subdivided into 10 mv

end point anticipation variable 0 to 300 mv

stability 0.1 pH

titration accuracy 0.05 ml in 50 ml

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