Pakistan J. Sci. Ind. Res., Vol. 13, Nos. 1–2, August 1970

FIXED-BED STUDIES OF THE CATALYTIC DECOMPOSITION OF OZONE

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(Received April 1, 1969; revised July 15, 1969)

Results are reported of the catalytic decomposition of ozone, using metal oxide catalysts, in a fixed-bed reactor. These results are then discussed in the light of other work on similar studies given in the literature.

Introduction

Catalytic decomposition of ozone, using metal oxides, has been extensively made use of by research workers [2,5,7,9,13] to study the reaction kinetics in aggregatively fluidised bed reactors. This reaction has certain unique characteristics making it suitable for such studies, namely, the strong absorption spectrum of ozone at a wavelength of 2537 A°, leading to easy and continuous measurements of ozone concentrations using spectrophotometric techniques, the wide choice of a catalyst, and the relative ease with which ozone can be generated from air or oxygen.

Since most studies of reaction kinetics in gas–solid fluidised bed reactors are carried out in parallel with fixed bed reactors, catalytic decomposition of ozone was studied in a fixed-bed reactor. The results of these studies are presented in this contribution along with their analysis, to ascertain the effect of various operating conditions on the rate of ozone decomposition.

Equipment

The fixed-bed reactor used was made of Pyrex glass and was about 1 in i.d. and 3 in long, having a sintered glass disc inside it to act as the catalyst support. The catalyst temperature was measured by a thermometer contained in a thin glass thermowell which extended from the top of the reactor to within a few millimeters of the sintered support. The reactor was contained in a liquid paraffin constant temperature bath, heated by a 250W immersion heater and provided with a mechanical stirrer to ensure a uniform temperature. A thermistor probe in a thin glass sheath was immersed in the oil bath and controlled the temperature to within half a degree over the range of 25°C to 140°C.

The inlet gas stream to the fixed bed was preheated in a helical glass coil in the thermostat which surrounded the reactor and was then made to flow downwards through the reactor. The gas flow to the reactor was controlled by a needle valve. A down flow of gas ensured a uniform gas distribution, avoiding any channelling or spouting. The gas flow rate was measured by a 'rotameter' flowmeter and the inlet and outlet gas pressures were measured by two diaphragm pressure gauges. Inlet and outlet gas sample lines were connected to the ozone measuring equipment. The gas inlet line to the reactor was a 3/16-in dia copper tubing, all other gas lines being 3/16-in dia polyethylene or translucent elastic P.V.C. The fixed-bed reactor is shown in Fig. 1.

Ozone was obtained from a small scale laboratory type ozone generator supplied by E.C.D. Ltd. (U.K.). Dry oxygen from a cylinder was used for ozone generation, the use of air being avoided for this purpose because of the possibilities of the formation of oxides of nitrogen which can poison the catalyst. The ozone was diluted to a maximum of about 300 ppm by mixing it with a stream of dry air, obtained from the laboratory high pressure line through a pressure regulator valve. The air was dried through a calcium chloride

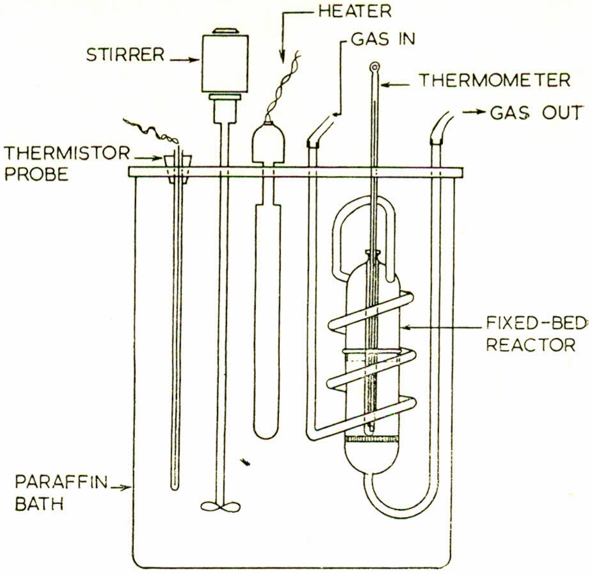

Fig. 1.—The fixed-bed apparatus.

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drier and passed through a glass wool filter to remove foreign particles.

The ozone analysis equipment consisted of a low pressure mercury resonance lamp having a peak emission wavelength of 2537A°, coincident with the absorption spectrum of ozone. The radiations from the UV lamp passed through a Pyrex glass analysis tube, 20 cm in length and 25 mm o.d. having end windows of 'Spectrosil' fused quartz attached to the ends of the tube by P.V.C. sockets and sealed with sweet rubber washers.

The radiations from the UV lamp fell onto a photocell after passing through the tube. A constant voltage from a Hanovia 'autoset mercury vapour meter' was supplied to the mercury lamp and the photocell signal was fed back to the Hanoviameter, which, after amplification, was directed to a Cambridge single point recorder to give a continuous trace.

The lamp and the photocell system, along with the glass analysis tube were contained in a thermostatically controlled aluminium box, painted black on the inside. A gas flow rate of about 3 ft^3/hr was maintained through the cell for all sample streams, a lower flow rate affecting the instrument sensitivity.[9]

The recorder chart deflection was calibrated in terms of ozone concentrations to facilitate a continuous analysis. This was done by first setting the recorder reading at zero with dry air. Ozone was then mixed with the air stream and the recorder deflection noted. The ozone concentration in this ozone–air mixture was determined iodimetrically by passing a known volume of the gas mixture through 50 ml 10% potassium iodide solution. The iodine liberated on the addition of 10 ml concentrated hydrochloric acid was titrated against standard sodium thiosulphate, using starch indicator. The calibration curve is shown in Fig. 2 and is compared with Beer's law in Fig. 3. The experimental setup is shown in Fig. 4.

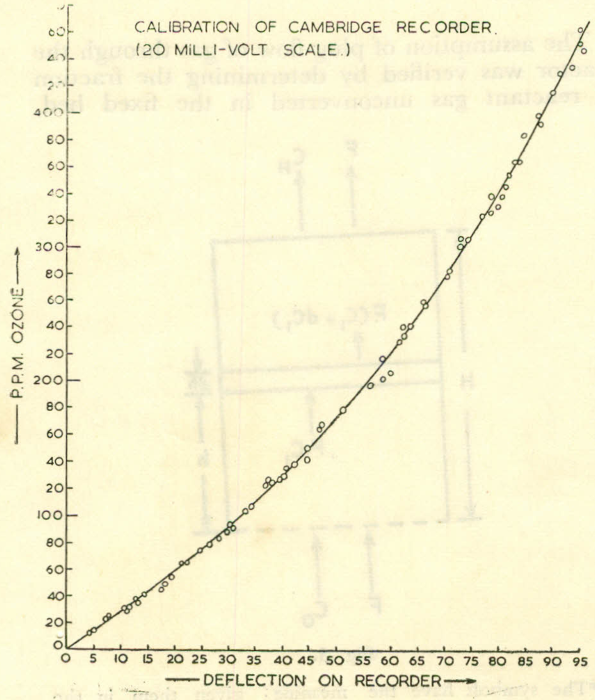

Fig. 2.

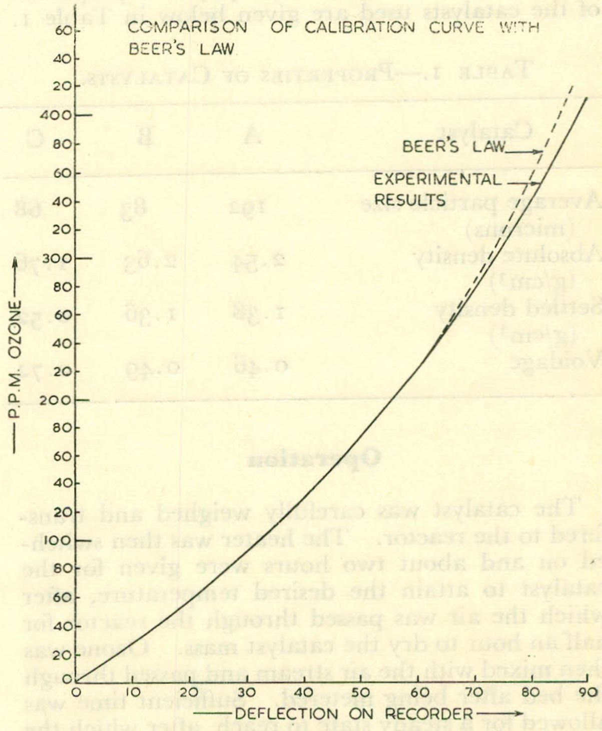

Fig. 3.

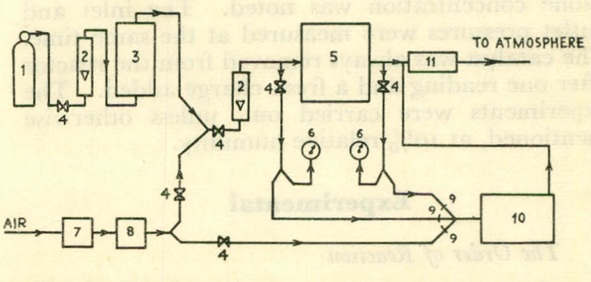

Fig. 4.—Experimental set-up. 1. Oxygen cylinder; 2. rotameters; 3. ozone generator; 4. flow regulator valves; 5. fixed bed assembly; 6. pressure guage; 7. air drier; 8. air filter; 9. two-way stop cock; 10. ozone analysis equipment; 11. furnace (400°C).

Catalyst

Three different sized particles were used, the two larger sizes being silica alumina sand and the third one being B.P. cracking catalyst. The catalysts were prepared by soaking the particles in 10% hot ferric nitrate for 12 hr. The supernatant solution was drained off, after making it alkaline by ammonia addition, and the particles were dried and roasted at 400°C till no smell of nitrogen dioxide or the presence of water vapour was apparent. These were then sieved to reject the lumps formed during the process. Treated thus, the catalysts contained about 0.5–1% by weight of iron oxide. The physical properties of the catalysts used are given below in Table 1.

TABLE 1.—PROPERTIES OF CATALYSTS.

Catalyst	A	B	C
Average particle size (microns)	192	83	68
Absolute density (g/cm³)	2.54	2.63	1.76
Settled density (g/cm³)	1.38	1.36	0.52
Voidage	0.46	0.49	0.72

Operation

The catalyst was carefully weighed and transfered to the reactor. The heater was then switched on and about two hours were given for the catalyst to attain the desired temperature, after which the air was passed through the reactor for half an hour to dry the catalyst mass. Ozone was then mixed with the air stream and passed through the bed after being metered. Sufficient time was allowed for a steady state to reach, after which the inlet ozone concentration was recorded. The cell was then flushed with dry air and the outlet ozone concentration was noted. The inlet and outlet pressures were measured at the same time. The catalyst was always removed from the reactor after one reading and a fresh charge added. The experiments were carried out, unless otherwise mentioned, at 10% relative humidity.

Experimental

1. *The Order of Reaction*

Assume that the ozone decomposition reaction is first order with respect to ozone concentration and that the gas is in plug flow through the reactor.

Then $r = K.\,P_I\,W$*

and since $P_I = P.C.$

$$\therefore \quad r = K.\,P.\,C.\,W$$

Taking a material balance over an infinitesimal height dh (Fig. 5) we get:

$$F.\,C_I = F(C_I + dC_I) + K.P.C_I.\,dW$$

$$\text{and } dW = \rho.\,A.dh$$

$$\therefore -F.dC_I = K.P.C_I.\,\rho.A.\,dh$$

$$\text{or } -\frac{dC_I}{C_I} = \frac{K.P.\rho.A.}{F}.\ dh$$

Integrating over the height of reactor, H, we get:

$$\ln\,(C_H/C_O) = -\frac{K.\,P.\,\rho.\,A.\,H.}{F} = -\frac{K.P.W}{F} \qquad (1)$$

Inlet ozone concentration to the fixed bed reactor was varied fivefold, using catalysts A and B, and keeping $P\ W/F$ ratio and the temperature constant. The results (Fig. 6) show that the plot of ln (C_H/C_O) against inlet feed concentrations of ozone is a straight line of zero slope for both catalysts A and B. The catalytic decomposition of ozone is, therefore, first order with respect to ozone concentration.

The assumption of plug flow of gas through the reactor was verified by determining the fraction of reactant gas unconverted in the fixed bed,

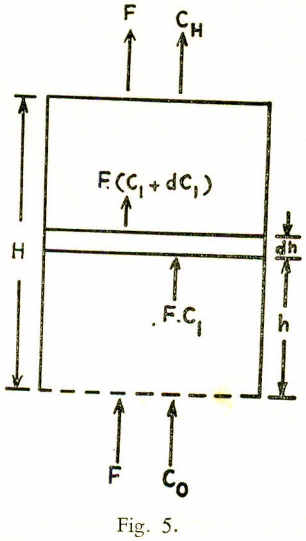

Fig. 5.

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*The symbols have the meanings given them in the Nomenclature.

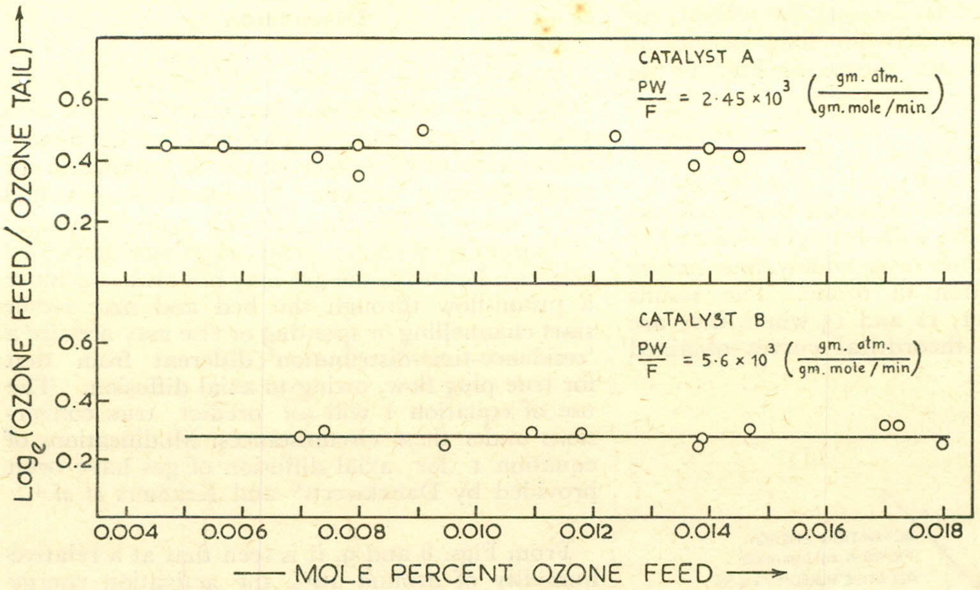

Fig. 6.—Order of reaction

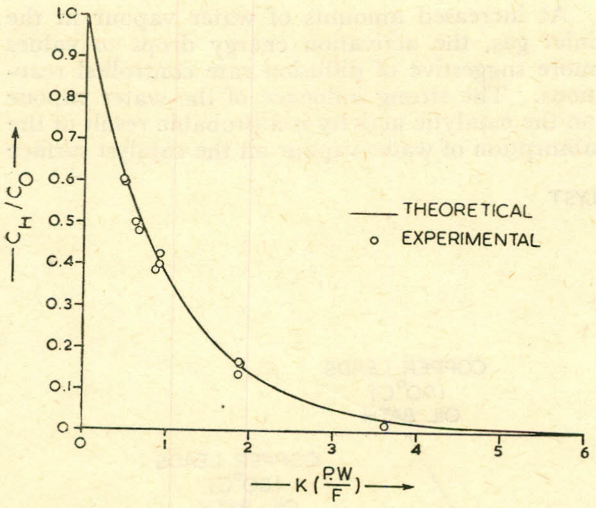

Fig. 7.

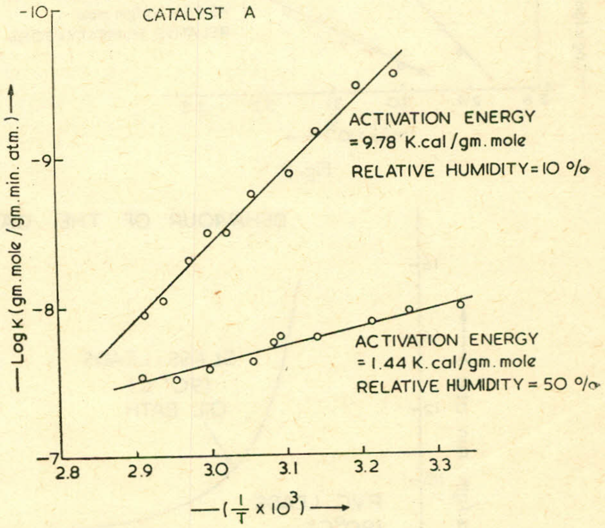

Fig. 8

(C_H/C_O), at various ratios of PW/F, keeping the temperature constant (Fig. 7). It is seen that the results agree with the predictions of equation 1, over a wide range of PW/F values.

2. *The Activation Energy*

According to Arrhenius equation, [8,10]

$$K = A_1 . \exp(-E/RT) \qquad (2)$$

The experimental results for catalysts A, B, obtained by varying the temperature are shown in Fig. 8 and Fig. 9 along with the values of activation energy, calculated from equation 2, for different humidity conditions of the inlet gas stream.

3. *Behaviour of the Catalyst*

When the catalyst activity was noted for long periods of time under varying conditions of operation, it was found that the activity showed a continuous decrease when the gas inlet tube was made either of PVC or glass. Using a copper inlet tube, the activity decreased over an initial period of 2–3 hr and then became constant. When an electric oven was used for heating the reactor, the activity remained constant for long periods of time. These results are shown in Fig. 10 for catalyst A.

4. *The Kinetic Data*

The kinetic data for the catalytic decomposition of ozone were obtained with catalysts A,B and C by varying the *P W/F* ratio widely and noting the unreacted fraction of ozone. The results are shown in Figs. 11, 12 and 13 where they are compared with the theordtical curves obtained using equation 1.

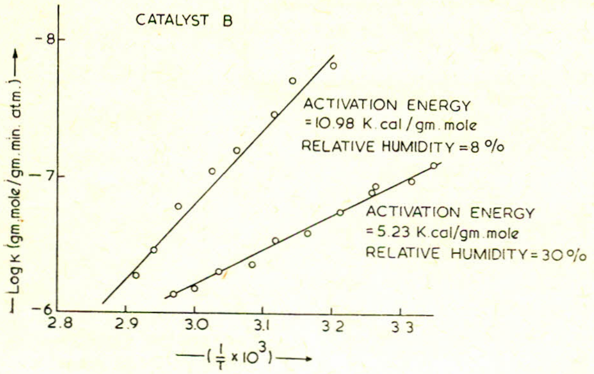

Fig. 9.

Discussion

Figures 6 and 7 prove that the catalytic decomposition of ozone is a first order reaction with respect to ozone concentration and that the assum-assumption of plug flow of gas is reasonable for small diameter reactors. Similar conclusions had been made earlier by Schwab and Hartmann [11,12] and Frye *et al.*[2]. With large size fixed-bed reactors, however, the gas may not always achieve a piston-flow through the bed and may either start channelling or spouting or else may acquire a 'residence-time-distribution' different from that for true plug flow, owing to axial diffusion. The use of equation 1 will *not* predict true conversions under these circumstances. Modifications of equation 1 for axial diffusion of gas have been provided by Danckwerts[1] and Kramers *et al.*[4]

From Figs. 8 and 9, it is seen that at a relative humidity of around 10% the activation energy has a value corresponding to surface rate controlled reactions.

At increased amounts of water vapour in the inlet gas, the activation energy drops to values more suggestive of diffusion rate controlled reactions. The strong influence of the water vapour on the catalytic activity is a probable result of the absorption of water vapour on the catalyst surface

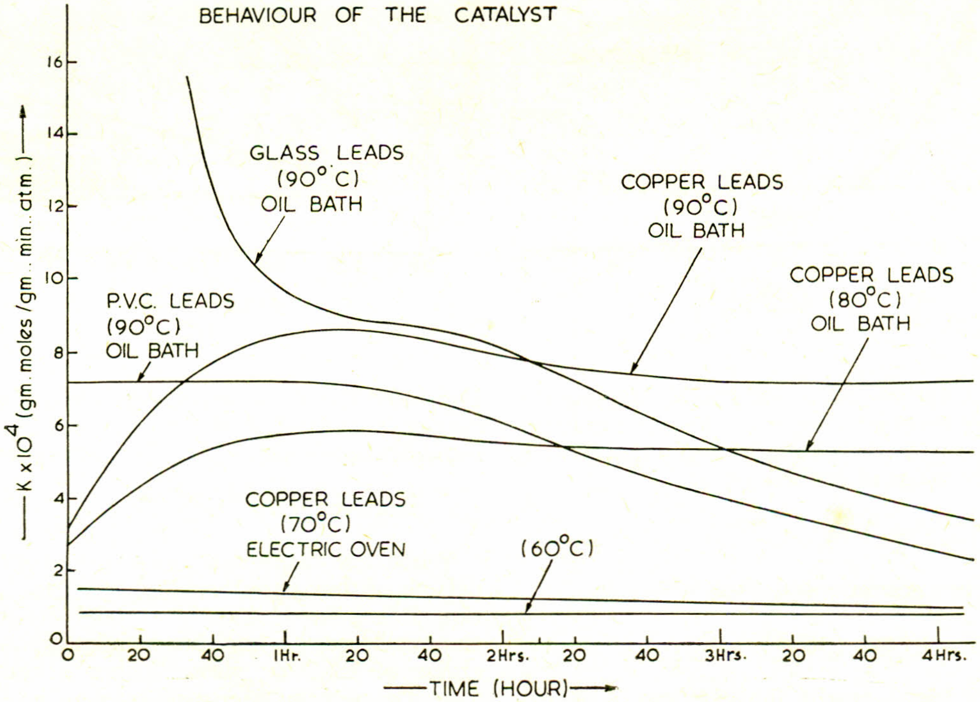

Fig. 10.

which inhibits the effectiveness of contact between ozone and catalyst surface. Since, ozone now has to diffuse through the water layer surrounding the catalyst particles, the reaction becomes diffusion rate controlled. Other authors[7,9] have reported that the catalytic activity can be regenerated by heating the catalyst to above 100°C for long periods of time.

Frye *et al.*,[2] using mill scale catalyst, concluded that the catalytic decomposition of ozone is reciprocal third order with respect to water vapour. Strict humidity control is, therefore, necessary to have reproducible results.

The values of activation energy as given in Figs. 8 and 9 for 10% relative humidity are of the same order of magnitude as reported by other workers [2,5,6,11,12] for surface rate controlled systems.

The catalyst behaviour depicted by Fig. 10 is peculiar and has been noted earlier by Lancaster[5] who made use of a PVC gas inlet tube. Supposedly, PVC tube picks up moisture during the initial drying period which is then released during subsequent operation.[14] Using a copper inlet tube, the catalytic activity becomes constant after the initial period needed to reach the steady state conditions.

It is also reported [11,12] that, using metal oxide catalysts, a hysteresis effect exists with change in temperature and the catalytic activity obtained when the temperature is increased is not reproduced at the corresponding temperature, when the temperature is decreased. This may again be an effect of not allowing the catalyst surface sufficient time to attain equilibrium.

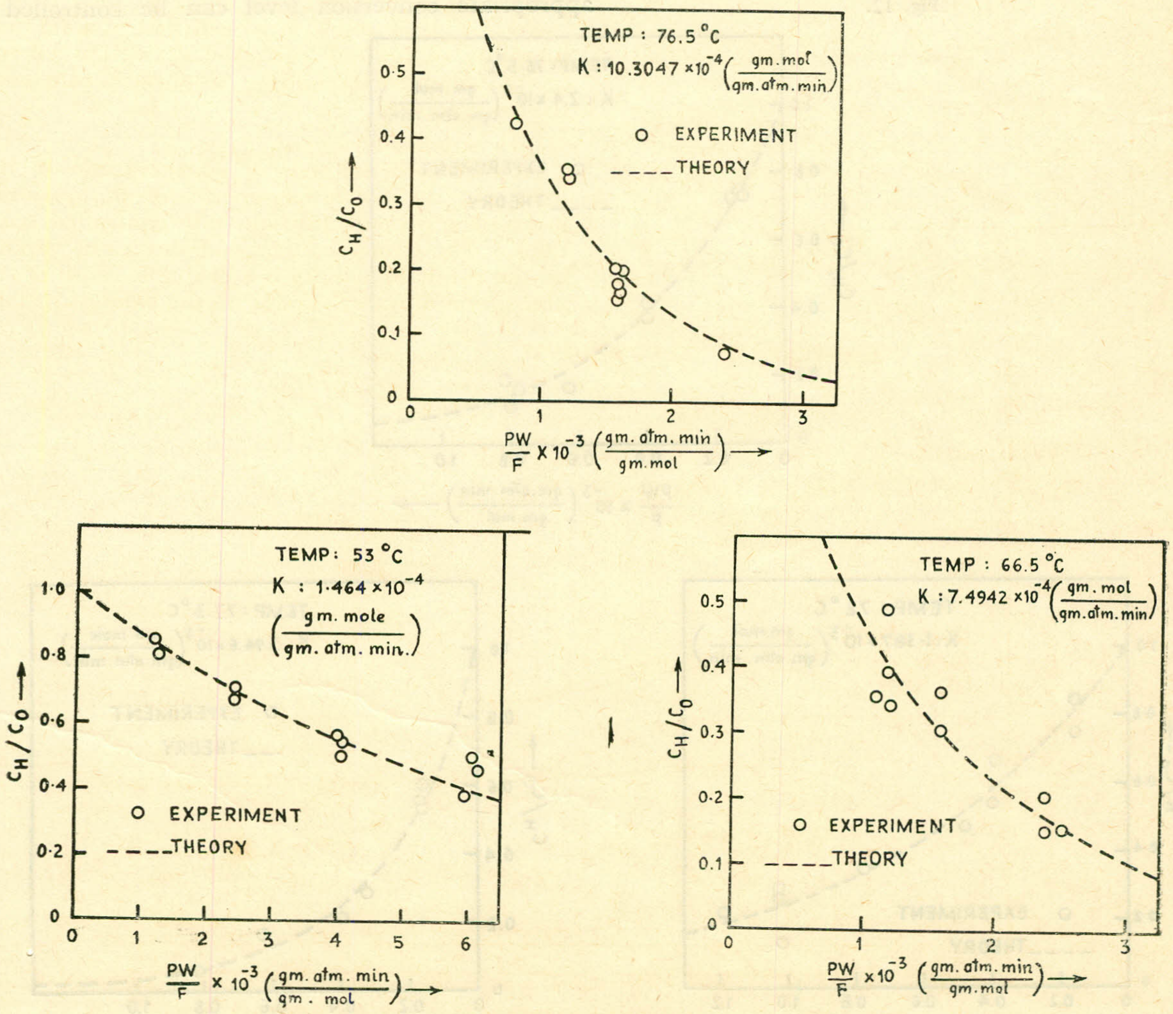

Fig. 11.—Kinetic data (Catalyst A.)

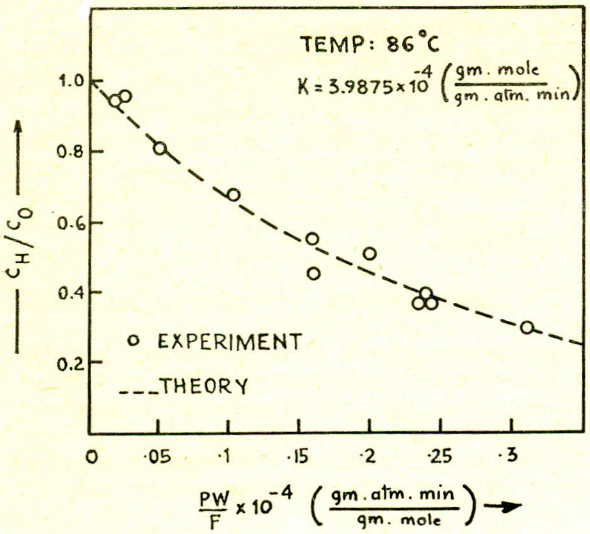

Fig. 12.

It is, therefore, necessary to allow sufficient time to make sure that a steady state is reached, before taking any readings. The kinetics data in Figs. 11, 12 and 13 show that conditions of plug flow of gas are sustainable for different gas flow rates and catalyst inventories and the rate of reaction is accurately predicted by equation 1, under these conditions. The effect of catalyst enrichment is seen from Figs. 11a, 13a and 13b, where the reaction rate constant has widely different values for nearly the same temperature. The rate of ozone decomposition is dependant upon the amount of iron oxide deposited on the 'carrier' particles, and since the catalysts used for the experimental runs of Figs. 11a, 13a and 13b had different degrees of enrichments, the overall rate of reaction and the reaction velocity constant are affected.

The degree of catalyst enrichment to get an appropriate conversion level can be controlled

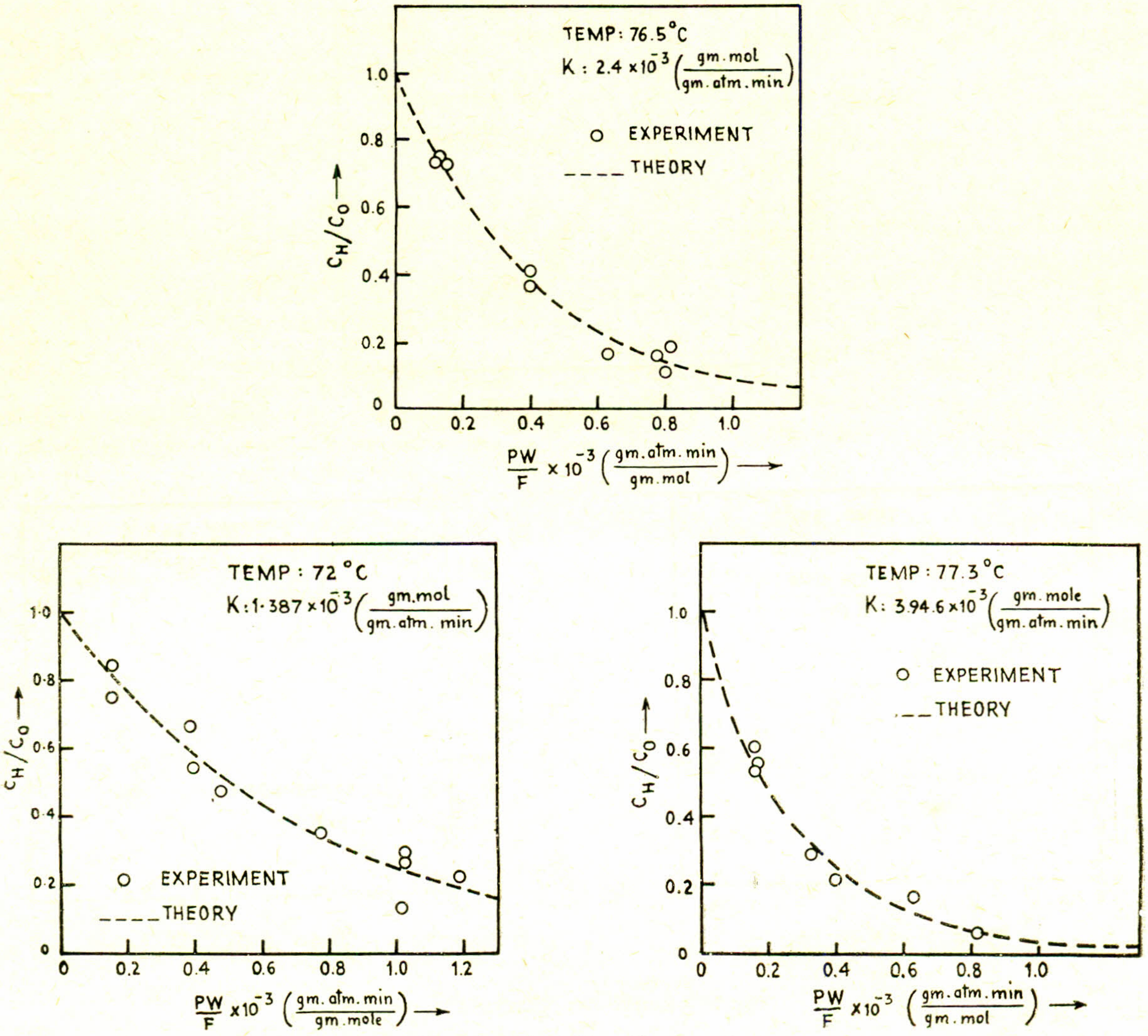

Fig. 13.—Kinetic data (Catalyst C)

either by further soaking the treated particles in ferric nitrate solution (to increase the activity) or by mixing the treated mass of catalyst with fresh, untreated particles.

Although, there is no catalytic activity of metals towards the decomposition of ozone, it has a strong tendency to decompose on contact with most metal oxides at high temperatures. The use of metals like iron, copper and nickel should especially be avoided as constructional materials for studying the reaction, as these metals will readily form oxides due to the oxidizing nature of ozone. Frye *et al.*[2] have reported that the walls of their stainless steel equipment became catalytically active after some time and were responsible for a fair degree of ozone being converted at them.

Also, homogeneous decomposition of ozone starts above a temperature of 100°C and the maximum operating temperature for studying hetrogeneous systems, using ozone, should not exceed 100°C.

Conclusions

Catalytic decomposition of ozone can be conveniently used, in systems like aggregatively fluidised bed reactors, where it is desired to use a reaction of known kinetics in order to study other variables, provided that the following are kept in view:

(1) Sufficient time should be allowed to attain the steady state, before taking any readings and strict humidity control should be maintained for all experimental runs.

(2) Metallic constructional parts should be avoided and the temperature should be kept below 100°C for hetrogenous decomposition studies.

Acknowledgements.—The author feels indebted to his supervisor, Professor P.H. Calderbank, D.Sc., for his help and guidance during the course of these studies. Thanks are also due to the Trustees of Saigol Foundation, 6 Egerton Road, Lahore, for providing the financial assistance to carry out these studies.

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Nomenclature

A= area of x-section of bed (cm^2)
A_1= frequency factor constant
C= mole fraction of reactant gas (mole/mole)
C_H= outlet gas concentration (mole fraction)
C_O= inlet gas concentration (mole fraction)
E= activation energy (K cal/gm mole)
F= total molar gas flow rate (moles/min)
H= bed height (cm)
K= reaction velocity constant (mole/min/g/atm.)
P= total pressure (atm)
P_1= partial pressure of ozone in the reactant stream (atm)
r= rate of reaction (moles/min)
R= gas constant/mole
T= Temperature (°K)
W= weight of the catalyst (g)
ρ= density of solids (g/cm^3)