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The Water Vapour Corrosion of Uranium and its Prevention

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Summary

The reaction between uranium and atmospheres containing water vapour in the presence of nitrogen and oxygen has been studied at 25 and 40°C. The steady production of hydrogen from uranium and moist nitrogen was suppressed by the presence of gaseous oxygen, which itself was slowly consumed. The ability of sulphide and arsenic coatings to suppress hydrogen production from uranium in moist nitrogen was also investigated.

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Recommended for issue by
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1. INTRODUCTION

During the prolonged storage of large uranium components in moist conditions at ambient temperatures, the metal is oxidised and hydrogen is formed. Oxygen is known to suppress the formation of hydrogen [1,2]. The present work was undertaken concurrently with other work at AWRE [3,] to evaluate the usefulness of oxygen as an inhibitor of the aqueous vapour corrosion of uranium, and if possible to provide information on the mechanism of corrosion. The need for direct practical application of the results determined to some extent the choice of conditions such as temperature, ratio of uranium surface to gas volume, and the presence of additional gases. Other requirements, for example the desirability of keeping oxygen pressures in practice below the lower explosion limits for hydrogen mixtures, were followed in planning the experiments.

2. EXPERIMENTAL

2.1 Reaction Vessel

The standard pyrex reaction vessel is shown in Figure 1. C_1 was the water reservoir. The bottom of the uranium container, C_2, was indented so that discs, when used, had point-contact support to ensure free access of gas to all surfaces. The tube joining C_1 and C_2 was designed for the limbs to be immersed in adjacent water-baths at different temperatures, to provide unsaturated pressures of water vapour over the uranium; this facility was not used in the present work. The spring-loaded three-way sampling stopcock T_1 had a special single bore straight-through key. The balljoints B_1 and B_2 mated with the ball sockets S_1 and S_2 on the chromatograph sampling system (Section 2.3 and Figure 2). The enclosed volume (250 - 400 ml) of each reaction vessel was measured by weighing the water required to fill it. The volumes (0.6 - 0.8 ml) of the sampling tapbores T_1 were measured in the same way, using mercury.

2.2 Uranium Preparation

Natural unadjusted uranium, conforming to weapons specification, was used either as 0.003 in - 0.007 in. rolled foil or as 0.25 in. discs cut from a 0.875 in. diameter cast bar. The surface area was derived from measurements with vernier callipers. The foil was prepared by pickling. Some discs were pickled and some were diamond polished. Finished pieces were handled with platinum tipped tongs, and used as soon as possible, usually a few minutes, after preparation.

2.2.1 Pickling

The uranium sample was immersed in 50% nitric acid for 1 - 2 min, washed with water, dried by rinsing with acetone and n-heptane, and weighed.

At the end of an experiment, the oxidised sample was pickled for 1 min, during which time all the oxide dissolved, and was dried and weighed. The sample was repickled for 1 min and weighed again. The difference between the weights of the pickled sample before and after the experiment, minus the weight change during repickling (the pickling correction), was taken to be the weight of metal consumed during the experiment.

2.2.2 Diamond Polishing

The whole surface of the uranium disc was polished on a horizontal wheel through various grades of emery and then with 4 μ diamond paste. The mirror-finished disc was washed with heptane and dried.

2.3 Gas Chromatograph

The gases in the reaction vessel were analysed for hydrogen, oxygen and nitrogen in a Perkin-Elmer model 116 Vapour Fraktometer equipped with a 4 metre molecular sieve column at 74°C and a thermistor-katharometer detector printing out on an integrating recorder. The carrier gas was usually argon, to make the instrument as sensitive as possible to hydrogen. For the detailed study of oxygen consumption, during inhibition experiments, helium was used to obtain a greater oxygen sensitivity, at the expense of a greatly reduced hydrogen sensitivity. It was not feasible to monitor both hydrogen and oxygen with high sensitivity by using argon and helium successively on gas samples from the same reaction vessel, because traces of carrier gas occasionally entered the reaction vessels via their sampling taps. Since, with helium carrier, argon had the same retention time as oxygen, and with argon carrier, helium had almost the same retention time as hydrogen, alternating the carrier gases involved an appreciable risk of invalidating the results.

The sample injection system is shown in Figure 2. Tubing between S_2 and the column was mainly capillary, with no abrupt changes in bore. T_3 and T_4 were tee-bore stopcocks. Carrier gas normally passed continuously through the $MglO_4$ tube D_1 and the chromatograph pressure controls and into the column via T_3, T_5 and T_4. The reaction vessel to be sampled was attached to the ball sockets S_1 and S_2. With T_1 in line with S_1 and S_2, the branch T_3 - T_1 - T_4 was evacuated through T_6. T_1 was then turned to open its bore to the reaction vessel and, with T_6 closed, T_3 and T_4 were turned to fill the tubing between T_3 and T_1, and T_4 and T_1, with carrier gas while the flow was maintained through T_5. Then T_5 was closed at the same time as T_1 was returned to its original position to bring an aliquot of the reaction vessel atmosphere into the carrier gas stream. The narrow-bore $MglO_4$ tube D_2 removed water vapour which would otherwise de-activate the column.

The instrument was calibrated frequently with tapbore samples of hydrogen, oxygen and nitrogen at known pressures. The graphs of peak height or peak area against quantity of gas were linear within a few per cent; the column sensitivity remained constant for long periods at the values shown in Table 1.

TABLE 1

Chromatograph Sensitivity

Carrier Gas	**Sample Gas**	**Lower Detection Limit mole × 10^{-8}**
A	H_2 O_2 N_2	1 20 35
He	H_2 O_2 N_2	40 2 3

2.4 Procedure

The prepared uranium sample was placed in C_2. For a reaction at 25°C, 10 ml of water was placed in C_1. For a reaction at 40°C, 10 ml of saturated potassium carbonate solution was used. (Vapour pressure at 40°C = S.V.P. of water at 25°C = 2.4 cmHg.) The joints were secured with picien wax and with T_2 connected to a vacuum system the water was degassed by repeated freezing and melting before the vessel was filled with the Appropriate gas mixture. T_2 was closed, a gas sample was analysed immediately, and the vessel was immersed in a thermostatically controlled water bath at 25 or 40°C ± 0.1°. When subsequent gas samples were taken for analysis the time of the reaction vessel's absence from the bath was kept as short as possible, consistent with the whole of the vessel having attained ambient temperature so that the gas samples were accurate aliquots. A cumulative correction was made for the small quantities of gas removed as chromatograph samples.

3. RESULTS - WATER VAPOUR CORROSION

3.1 Summary of Results

Samples of uranium metal were allowed to react under various conditions with water vapour at 2.4 cmHg, in the presence of a pressure of about 60 cmHg of nitrogen. Samples of the gaseous contents of the reaction vessels were analysed usually at daily intervals. The plot of hydrogen produced against time was in nearly all cases approximately linear throughout an experiment (100 - 1000 h).

Typical graphs are shown in Figure 3; numerical results are collected in Table 2 and illustrated in Figure 8.

TABLE 2

Uranium/Water Vapour Reaction. Rate of Hydrogen Formation at Various Temperatures and Surface Finishes

Experiment. No.	Uranium Sample No.	Uranium Temperature °C	Surface Finish	Rate mole ×10^{-8}/ cm^2/h
2	26	25	D	1.2
9	4	"	D	3.0
19	4	"	D	2.5
61	F1	"	P	10.1
62	F3	"	P	9.8
7	2	40	D	12.7
17	2	"	"	8.0
20	2	"	"	8.0
23	2	"	"	4.9
15	6	"	"	9.5
16	6	"	"	9.1
5	11	"	"	3.7
18	11	"	"	7.1
25	11	"	"	5.5
10	3	"	"	2.8
11	5	"	"	13.3
24	4	"	"	5.0
26	6	"	P	20.0
29	6	"	"	12.9
33	6	"	"	24.8
30	2	"	"	10.6
31	2	"	"	17.8
40	F1	"	"	15.5
41	F2	"	"	15.6
60	F2	"	"	23.6
65	F3	"	"	23.6

Summary

Conditions	Mean Rate, mole × 10^{-8}/cm^2/h	Standard Deviation	Deviation, %
25°C D	2.2	-	-
" P	10.0	-	-
40°C D	7.5	3.3	44
" P	18.3	5.1	28

D = Diamond polished.
P = Nitric acid pickled.

3.2 Reproducibility

Variations in the observed rates of hydrogen production under apparently identical conditions were much greater than could be expected from analytical errors. This indicates the presence of one or more hidden and uncontrolled variables. The first possibility, that of variations in the nature and products of the reaction, or in the loss of hydrogen by adsorption, was eliminated (at least for pickled specimens) by comparing when possible the quantities of hydrogen produced, uranium reacted, and oxide formed. Table 3 shows that the reaction was

$$U + 2H_2O \rightarrow UO_2 + 2H_2 .$$

In accordance with observations by other workers the spread in the H/U ratios is comparable with analytical errors. The O/U ratios are subject to further uncertainties because of spallation and further oxidation of the oxide.

TABLE 3

Uranium/Water Vapour Reaction. Stoichiometry

Experiment No	H_2 Rate, mole × 10^{-8}/cm^2/h	U Metal Used, g	Atom Ratio H/U	Oxide Formed, G	Atom Ratio O/U
31	17.8	0.0677	4.2	0.0761	1.9
33	24.8	0.1018	3.9		
40	15.5	0.2185	3.8		
41	15.6	0.1673	3.5		
60	23.6	0.9749	4.0	1.1211	2.2
61	10.1	0.4470	3.9	0.5124	2.2

Mean atom ratios: H/U - 3.9.
O/U - 2.1.

It seems, then, that the same reaction was occurring at a rate which was variable from experiment to experiment, but invariant during any one experiment. An explanation might be found in the surface condition of the uranium.

3.3 Uranium Surface Preparation

Corrosion rates were faster on pickled surfaces than on diamond-polished surfaces at the same temperature. During the present work, only about 10^{-4} to 10^{-3} cm of uranium was corroded away during each experiment, so some surface characteristics could be expected to be preserved throughout each experiment.

The ratio of actual surface area to geometrical area is probably greater for pickled uranium than for polished uranium, but this difference in effective surface area might not account for such a large difference in reaction rates.

Polished specimens may react at a rate different from that of pickled specimens, owing to the presence of fractured crystals, oxide and the "skin" of strained metal, but the effect is not easy to predict. The greater surface energy of a polished, i.e., mechanically damaged, surface should cause it to react faster. This effect could have operated, undetected, during the very early stages of the reaction. If the rate of the subsequent steady, observed corrosion is considered to be controlled by diffusion processes in a compact oxide film [4] the results suggest that the coherent film supported by strain surfaces was thicker and/or less permeable than that on unstrained surfaces.

3.4 Temperature Effects

Corrosion rates were 1.8 times faster at 40°C than at 25°C on pickled surfaces. The ratio on polished surfaces was 3.4, which suggests that the activation energy of the rate-determining step on polished surfaces was greater than that on pickled surfaces. This temperature dependence agrees semiquantitatively with results obtained from measuring the growth of oxide films on uranium [5].

3.5 Uranium-Hydrogen Reaction

A diamond-polished disc of uranium was left in contact with 1.4 cm of hydrogen and 62 cm of nitrogen in anhydrous conditions at 40°C. No detectable changes occurred in 300 h. Since the detection limit was about 3 h freely corroding hydrogen production, the result confirms that the reaction between uranium and dry hydrogen at 40°C is many times slower than the reaction between uranium and water vapour. The reaction between uranium and molecular hydrogen can therefore be discounted in considering the overall rates and products of aqueous corrosion.

4. RESULTS - OXYGEN INHIBITION

4.1 Summary of Results

Uranium was corroded slowly by mixtures of water vapour (2.4 cm), nitrogen (~60 cm) and oxygen. Hydrogen was produced in negligibly small amounts; the oxygen was consumed approximately 40 times more slowly than hydrogen would have been generated by water vapour in the absence of oxygen; when the oxygen pressure had fallen below 0.5 mm, hydrogen began to appear at a fast, steady rate. The graph of a typical experiment is shown in Figure 4.

Recharging the system with oxygen immediately halted the production of hydrogen; artificially removing the oxygen resulted in renewed hydrogen production.

4.2 Suppression of Hydrogen Production

Virtually no hydrogen was formed from uranium and water vapour in the presence of oxygen. One experiment was designed to show up traces of hydrogen; 930 cm^2 of uranium foil at 40° was exposed to 2.4 cm of water vapour and 72 cm of oxygen in a volume of 300 ml. After 2000 h, when about 60 cm of oxygen remained, hydrogen was detectable in quantities too small for it to be clear whether the rate of formation was steady or intermittent. After 3600 h, 0.5 mm or 8×10^{-6} mole of hydrogen was present; this was 10^5 times smaller than the quantity which would have been formed in the same time under freely corroding conditions.

4.3 Rate of Oxygen Consumption

The rate of reaction of oxygen with uranium in the presence of water vapour varied within wide limits (see Table 4). The average rate of consumption of oxygen was approximately 40 times slower than the rate of formation of hydrogen from uranium and oxygen-free water vapour. In Experiments 48 - 50, the course of the oxygen reaction was followed, using helium carrier gas in the chromatograph.

The rate of consumption of oxygen was approximately constant during each run, except for an apparent increase in rates at low oxygen pressures (see Figure 4). This increase appeared to occur in only two out of the three runs; it may, therefore, be merely caused by errors in the measurement of low oxygen pressures.

TABLE 4

Oxygen Inhibition
Rate of Oxygen Consumption under Various Conditions

Experiment, No.	Temperature, °C	Surface Finish	U Surface Area, cm^2	Initial O_2 Pressure, cmHg	Inhibition Time, h	Rate, mole × 10^{-8}/cm^2/h
28	40	D	12.1	0.3	850	0.49) Mean : 0.42
35	"	"	12.0	0.7	2750	0.34)
32	40	P	12.1	0.1	300	0.39)
37	"	P	12.1	0.1	370	0.37)
38	"	"	12.1	0.3	540	0.69)
44	"	"	114	1.0	370	0.39) Mean : 0.46
45	"	"	120	0.5	90	0.76)
47	"	"	120	1.5	600	0.35)
48	"	"	930			0.27)
49	25	P	930			0.21) Mean : 0.18
50	"	"	947			0.15)

D : diamond polished
P : pickled

4.4 Renewal of Hydrogen Production

When the oxygen pressure had fallen below about 0.5 mm, or if the oxygen/nitrogen atmosphere was pumped away after a time and replaced by nitrogen, hydrogen was produced at a steady rate not significantly different from the rates observed on uranium which had not been treated with oxygen (see Figure 4 and Table 5). The inhibiting effect of oxygen was caused by its presence in the gas phase; the oxide film was not permanently protective. However, it appeared, from extrapolation of the graphs of hydrogen produced against time in experiments in which the oxygen was pumped away (see Figure 5), that the onset of hydrogen production occurred up to 50 h after the oxygen had been removed. Since in these experiments the time of re-exposure of the uranium to water vapour could not be specified exactly, and some oxygen could have remained dissolved in the water, it is not certain whether the observed delay in fact represents the slow breakdown of a semi-permanent oxide film produced by the oxygen. Further experiments are in progress to study the reaction more closely during the first few hours after the removal of oxygen.

TABLE 5

Renewal of Hydrogen Production from Uranium/Water Vapour after a Period of Oxygen Inhibition

Run	Temperature, °C	Surface Finish	Rate, mole × $10^{-8}/cm^2/h$	
34	40	D	20.5)	Mean : 17.6
35	40	D	23.0)	
39	40	D	9.4)	
37	40	P	21.3)	Mean : 22.8
38	40	P	28.5)	
42	40	P	25.0)	
43	40	P	23.0)	
44	40	P	32.1)	
45	40	P	24.5)	
47	40	P	21.2)	
48	40	P	6.7)	
49	25	P	5.9)	Mean : 6.4
50	25	P	6.8)	

D : Diamond polished
P : Pickled

4.5 Renewal of Inhibition

When oxygen was added to a vessel in which uranium had been corroding freely in water vapour/nitrogen, whether the accumulated hydrogen was removed or not, hydrogen production immediately ceased. The oxygen was consumed at a variable rate different from the rate of consumption on clean uranium (see Figure 6). The initial rapid consumption of oxygen must be ascribed to the further oxidation of the UO_2 previously formed by aqueous corrosion [6, 7]. The quantity of oxygen used up in this initial, rapid stage was approximately the amount required to convert the oxide present (calculated from the hydrogen produced during its formation) from UO_2 to $UO_{2.2}$.

5. RESULTS - EFFECT OF COATINGS

5.1 Sulphide Coatings

Pickled uranium foil was heated at 700°C for 2 h in hydrogen sulphide at a few cm pressure. The grey sulphide coating was unaffected by normal handling, but was easily scratched by metal tools.

A sample of sulphide coated foil at 40°C was exposed to 2.4 cm water vapour and about 40 cm nitrogen. No hydrogen was detected for 700 h. Then hydrogen was produced at an accelerating rate (see Figure 7), while visible corrosion patches spread over the surface. After 2000 h only a small proportion of the surface was visibly corroded and the rate of hydrogen production (0.5×10^{-8} mole/cm$_2$/h) was still considerably slower than the observed range ($10.6 - 24.8 \times 10^{-8}$ mole/cm^2/h) of freely corroding rates. A further sample of sulphided foil was scratched several times with a scriber before it was exposed to moist nitrogen. Hydrogen production began sooner than from the unscratched foil (see Figure 7); the visible corrosion areas spread from the scratches.

The observations suggest that the uranium was protected mechanically by the sulphide coating, through which aqueous corrosion eventually occurred, slowly at first then more freely as the coating broke down.

A sample of pickled uranium foil, exposed at 40°C to 2.4 cm water vapour and 50 cm hydrogen sulphide, produced hydrogen steadily at 1.9×10^{-8} mole /cm^2/h; this was considerably slower than the free corrosion rates, perhaps because of a surface poisoning effect. It was clear, however, that the observed effect of sulphide coatings was not caused by the presence of free hydrogen sulphide.

5.2 Arsenic Coatings

Pickled uranium rods, 6.3 cm long and 1 cm in diameter, were kept at 500°C by radio frequency heating for several hours in an atmosphere of argon containing a few p.p.m. of arsine. The arsenic-coated rods, scratched and unscratched, were exposed to moist nitrogen under conditions similar to the sulphide coated foils (Section 5.1). The pattern of corrosion was similar, but the onset of hydrogen production was earlier than on the sulphide coated samples (see Figure 7). The effect of arsenic coating in reducing corrosion was apparently similar to, but less efficient than, sulphiding.

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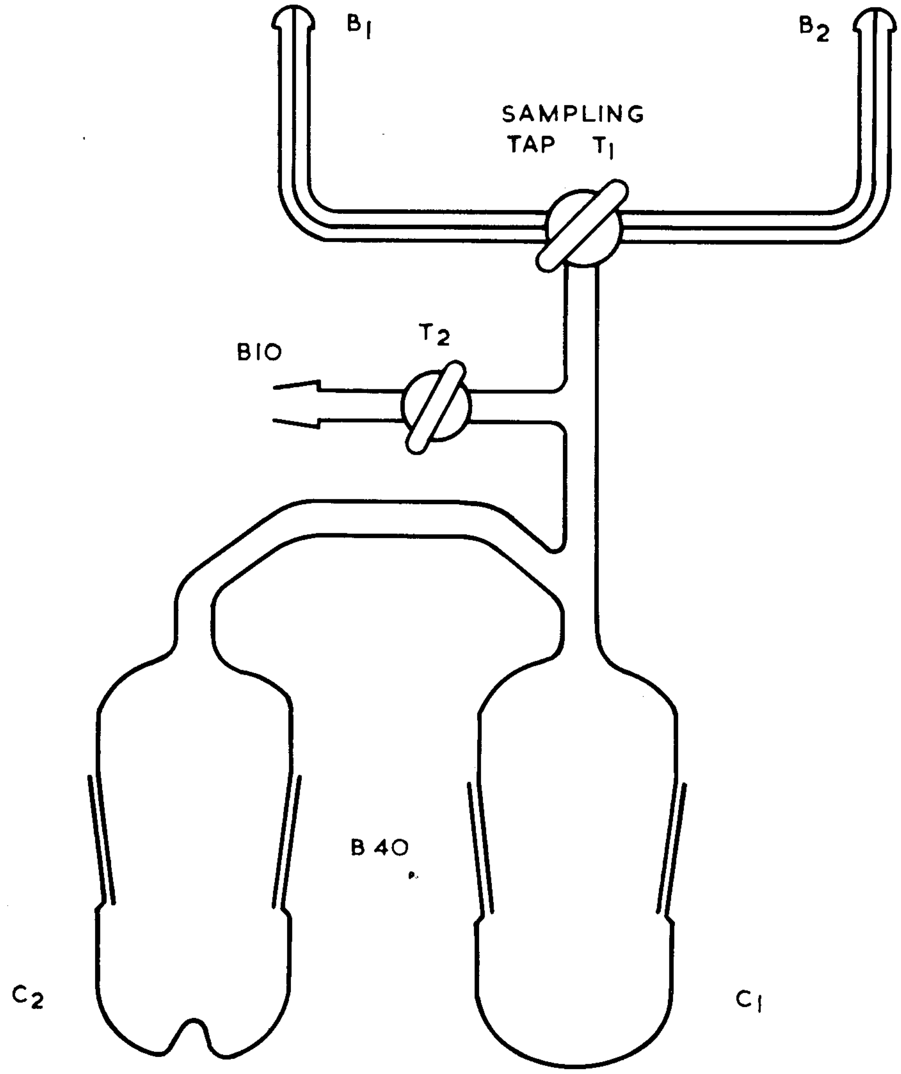

FIGURE I. REACTION VESSEL

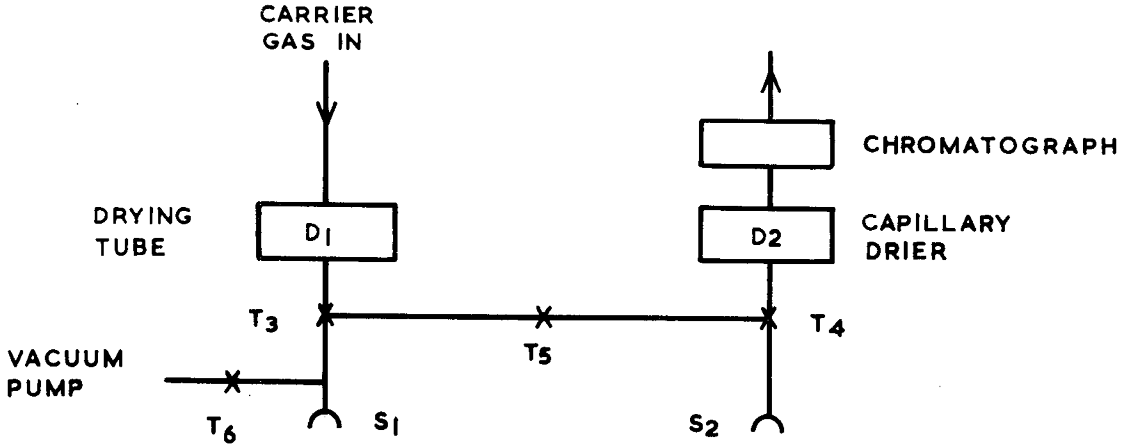

FIGURE 2. SAMPLE INJECTION SYSTEM

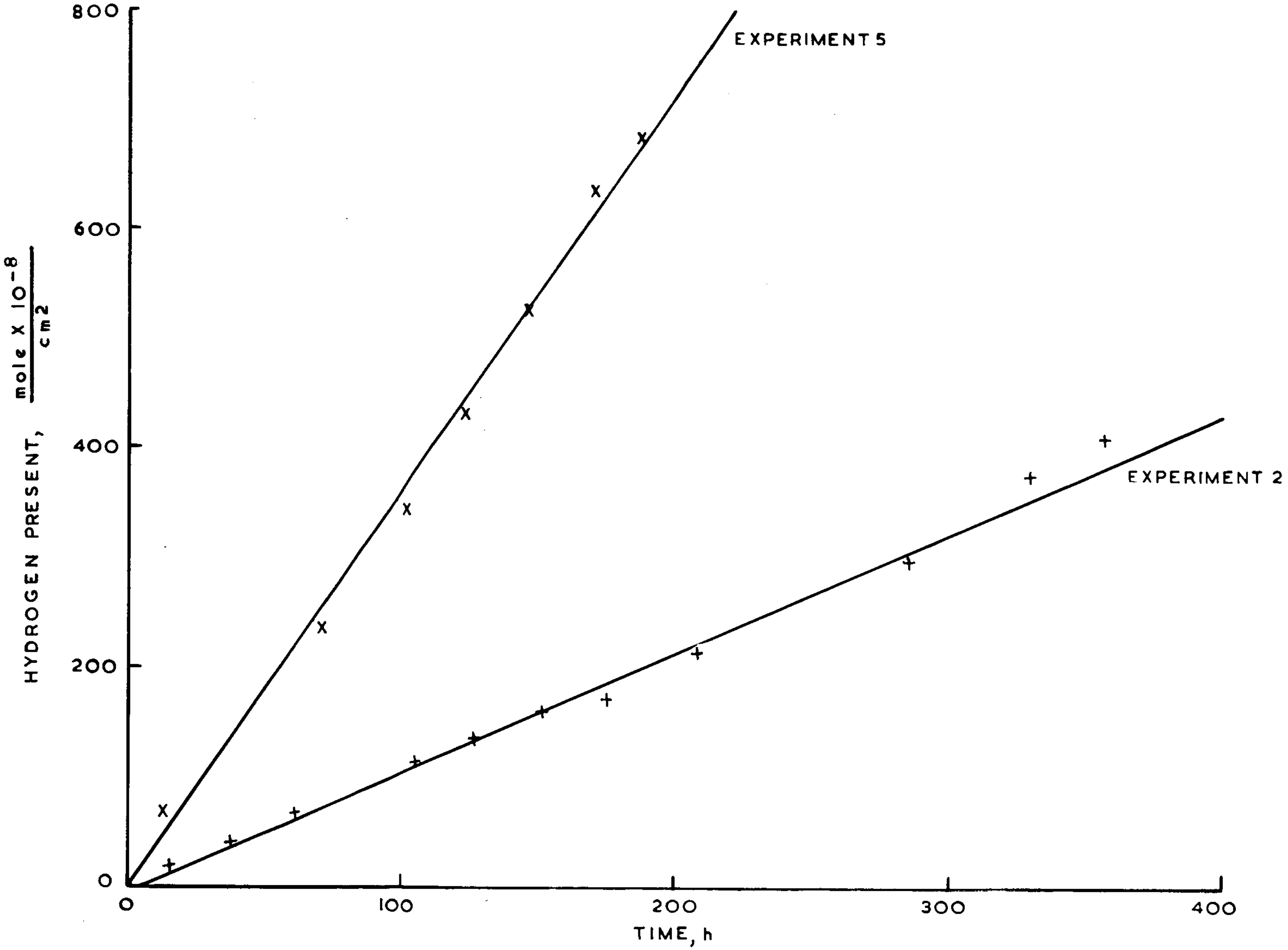

FIGURE 3. URANIUM-WATER VAPOUR REACTION. TYPICAL HYDROGEN-PRODUCTION GRAPHS

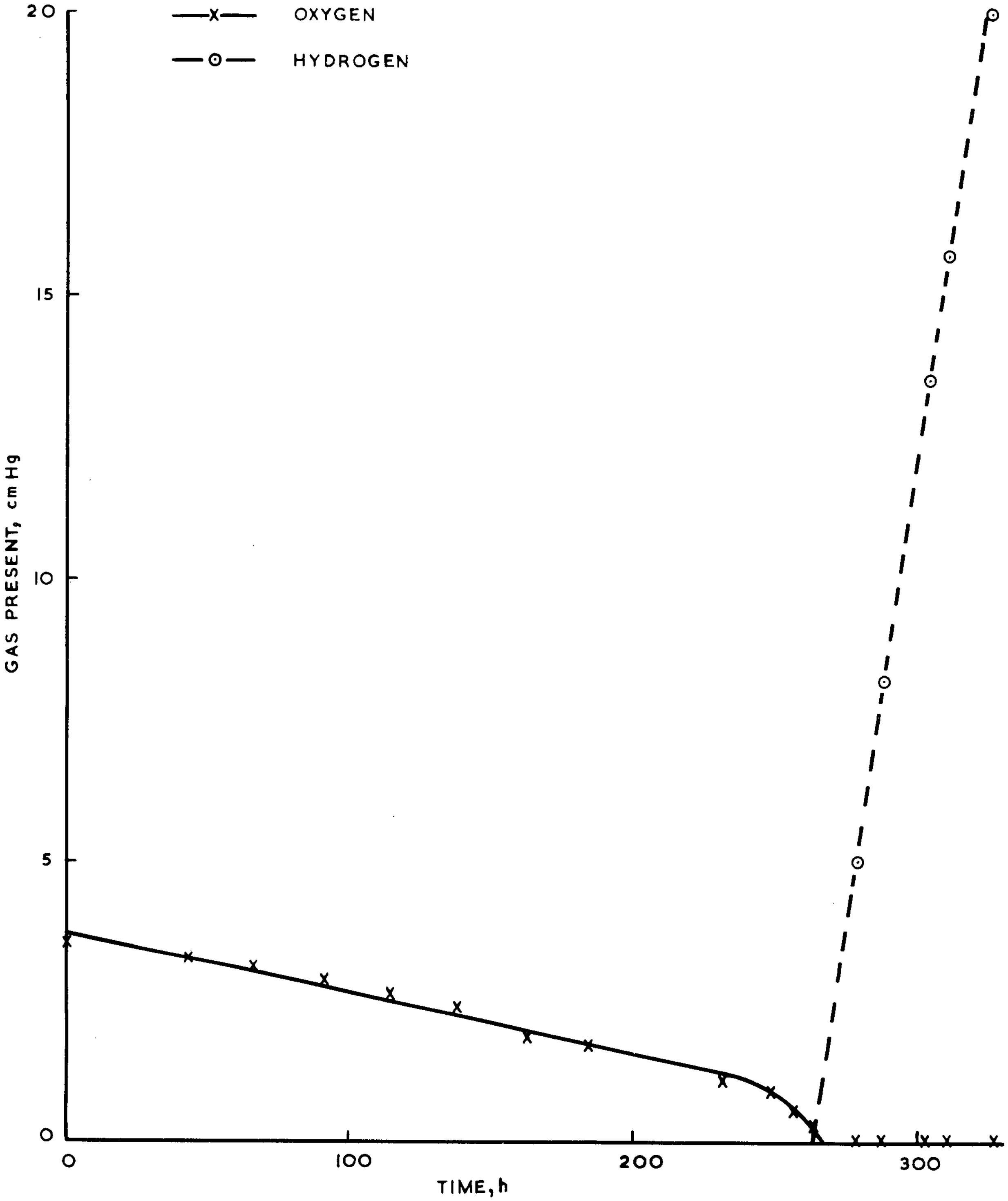

FIGURE 4. OXYGEN INHIBITION. TYPICAL GRAPHS OF OXYGEN CONSUMPTION FOLLOWED BY HYDROGEN PRODUCTION

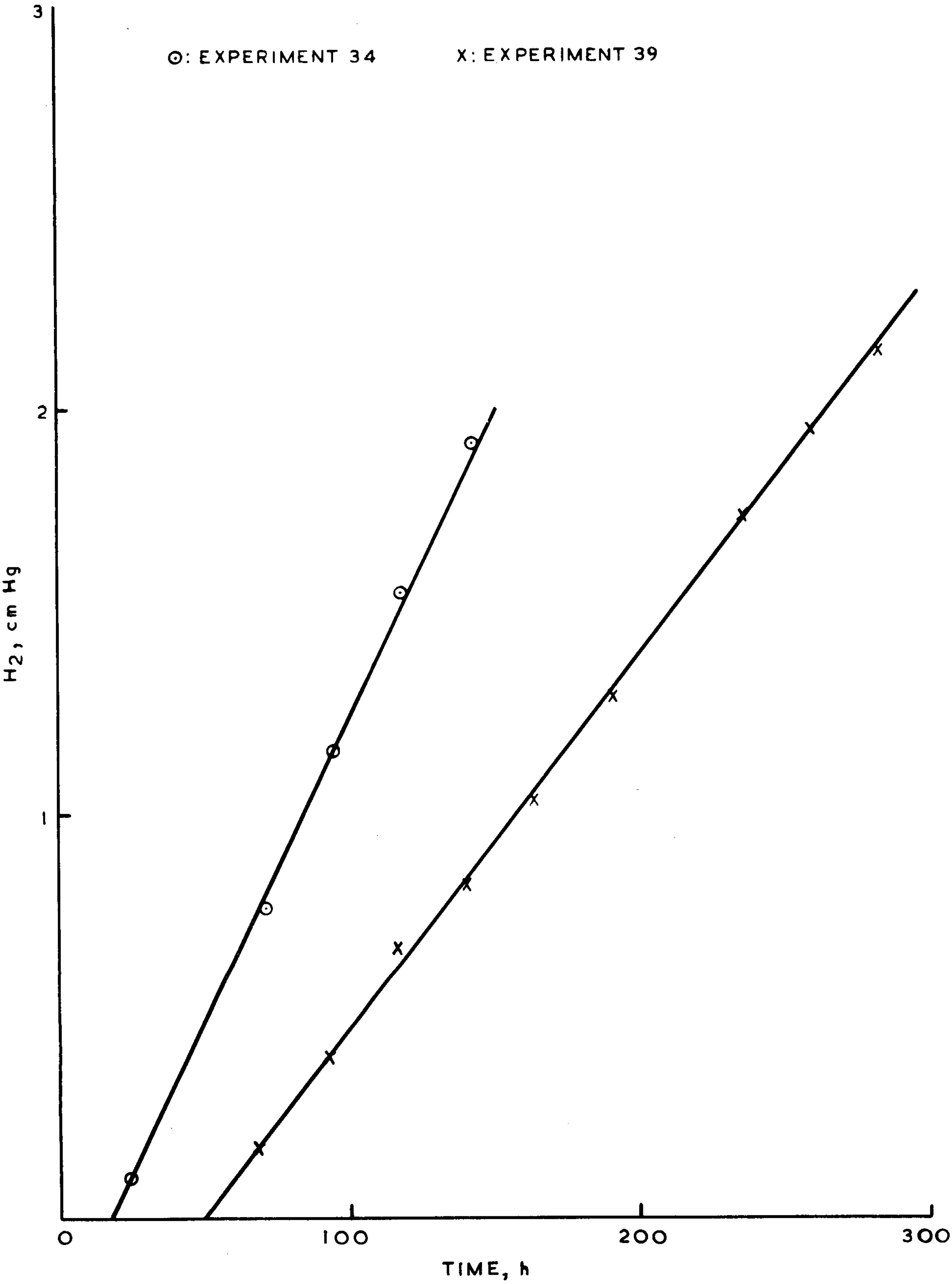

FIGURE 5. OXYGEN INHIBITION. RENEWAL OF HYDROGEN PRODUCTION AFTER REMOVAL OF OXYGEN INHIBITOR

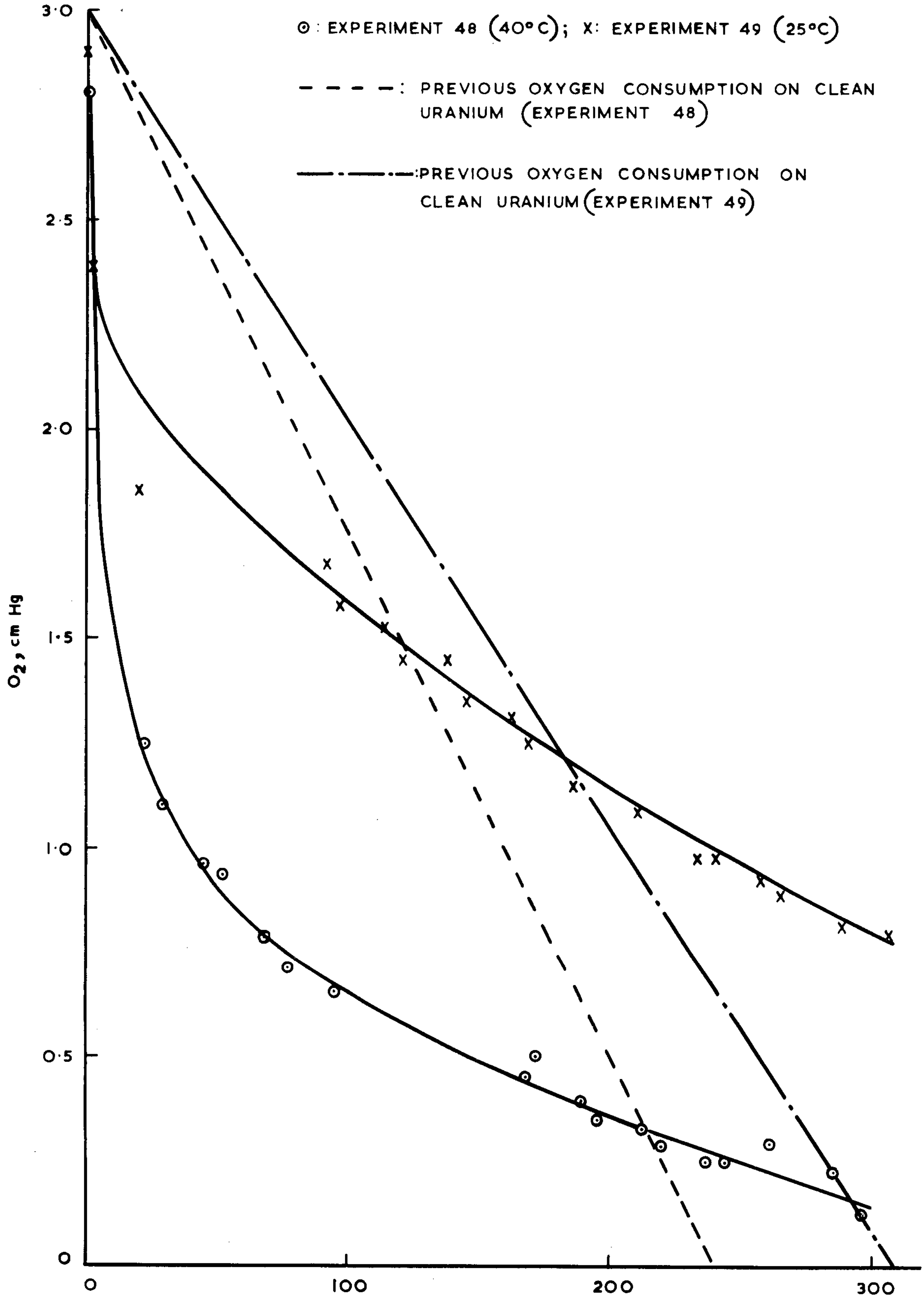

FIGURE 6. RENEWAL OF OXYGEN INHIBITION. OXYGEN CONSUMPTION BY PREVIOUSLY CORRODED URANIUM

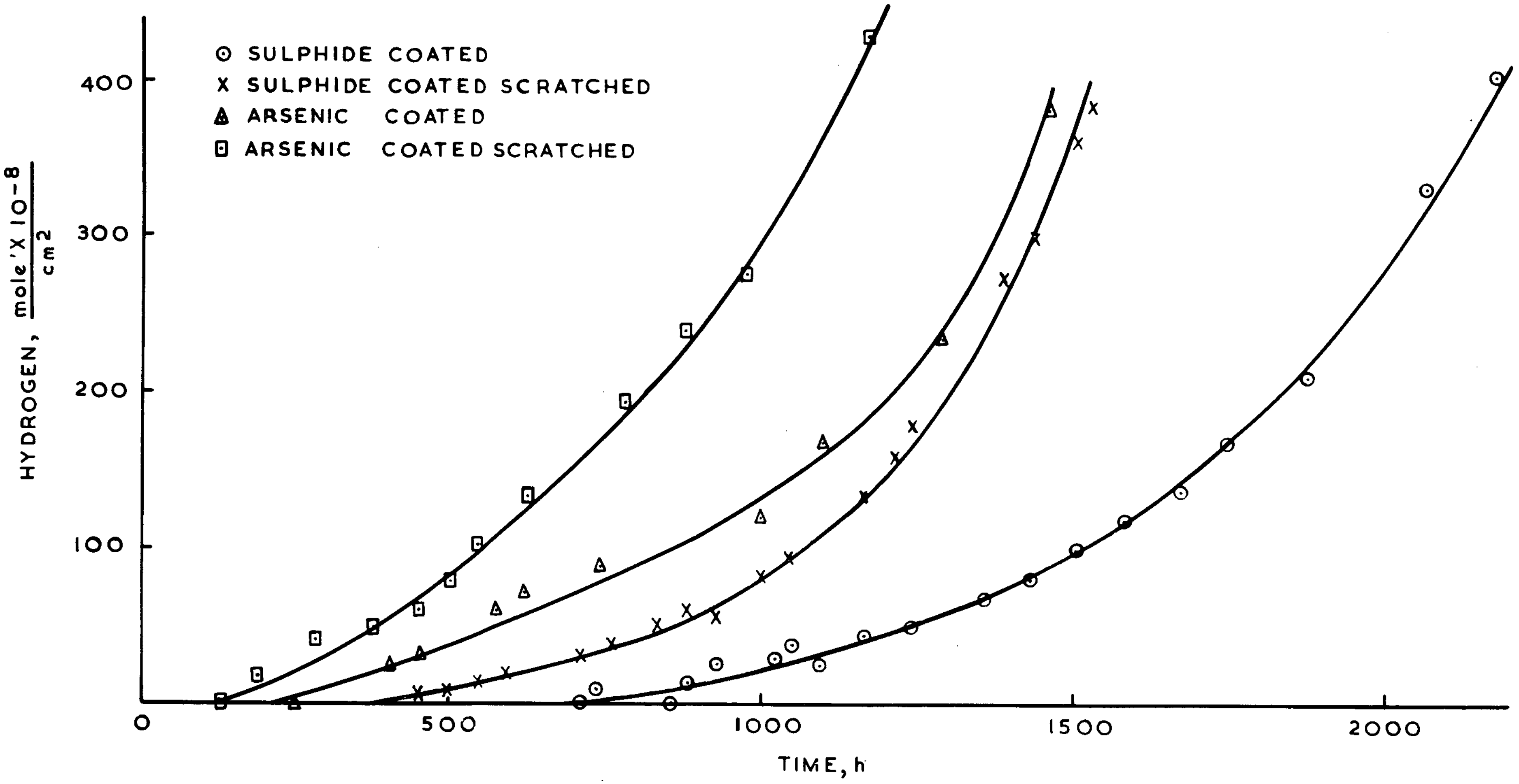

FIGURE 7. HYDROGEN PRODUCTION FROM COATED URANIUM IN MOIST NITROGEN AT 40°C

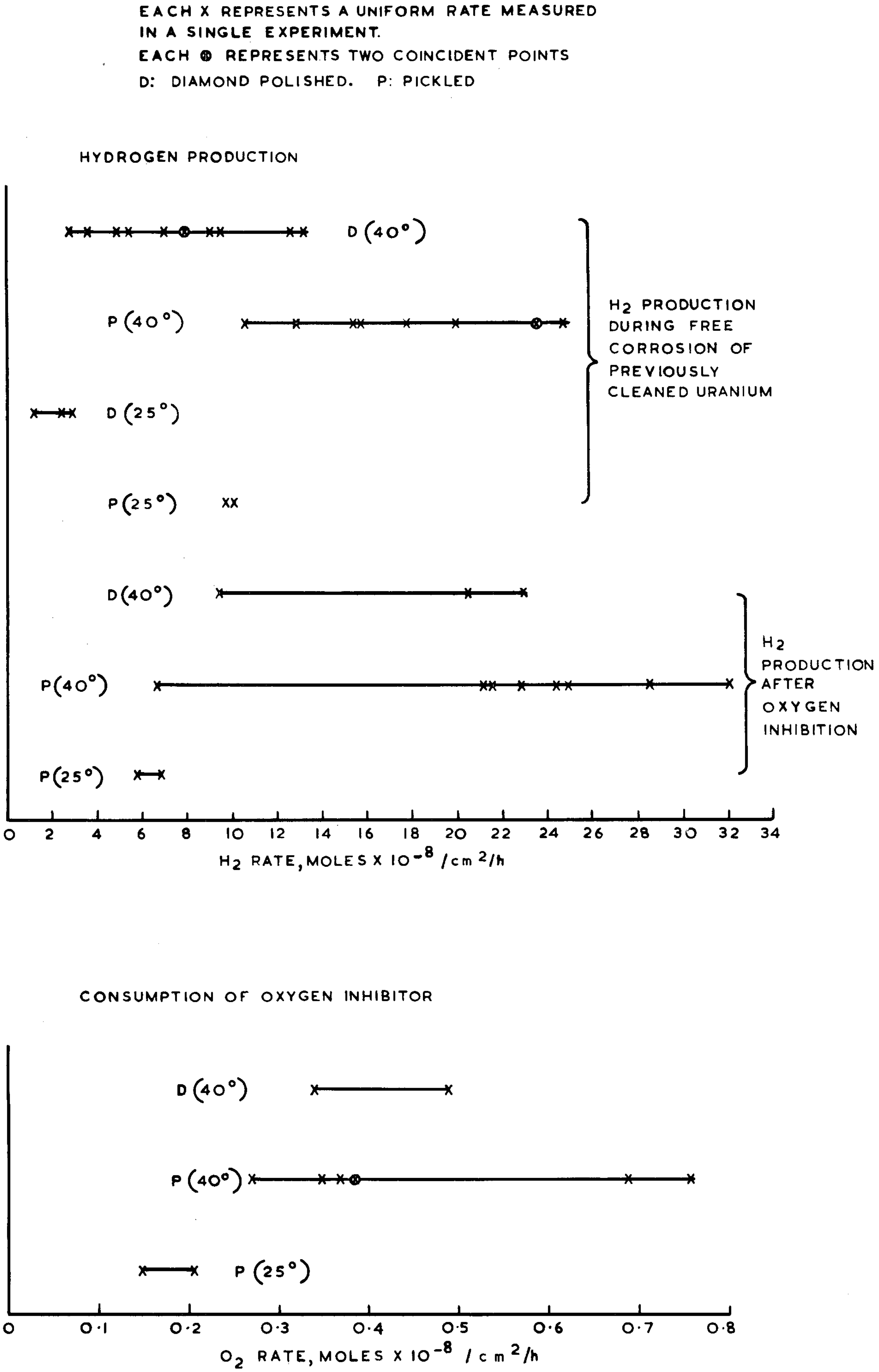

FIGURE 8. SPREAD OF RESULTS