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THE OXIDATION OF URANIUM TETRACHLORIDE

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Abstract—The oxidation of uranium tetrachloride was investigated by thermo-analytical and X-ray diffraction methods. It proceeds in the presence of oxygen at atmospheric pressure via uranyl chloride (UO_2Cl_2) as an intermediate product:

$$UCl_4 + O_2 \rightarrow UO_2Cl_2 + Cl_2$$
$$3UO_2Cl_2 + O_2 \rightarrow U_3O_8 + 3Cl_2$$

The conversion at the surface of the crystal initially sets the rate. The activation energy and the frequency factor of the surface reaction were calculated. After a coat of reaction products has grown the diffusion of oxygen through the interface controls the continued oxidation process. The thermal decomposition of uranyl chloride becomes noticeable from 400°C on, accelerating the reaction at reduced pressure and causes a change in the kinetics.

INTRODUCTION

THE stable uranium tetrachloride is an important reactant for the preparation of numerous uranium compounds.(1,2) In many cases the substance provides the tetravalent uranium ion required for electrolytic conversions in molten salts.(3) Uranium tetrachloride also exists as an intermediate product in the chlorination processing of nuclear oxide fuels.(4–8) In this process it is converted by oxidation with oxygen into the original oxide after separation from the fission product chlorides.

The residual amount of chlorine and chloride in the oxide certainly depends on the progress of the oxidation. It should be extremely low, because the strong corrosive action of chlorine causes a destruction of the fuel cladding. Moreover, a renewed activation in the reactor would generate the long-lived beta activity of chlorine-36 (3×10^5 a).

The applications mentioned above require a high degree of chemical purity of the basic material and, for the method mentioned last,(5) also of the final product.

Small contaminations of the chloride by oxichlorides and uranyl chloride and its hydrates, respectively, can be avoided in the preparation process only with special precautions because the reaction of the substance with vapour and oxygen of the air already occurs at low temperatures.

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(1) R. K. STEUNENBERG and R. C. VOGEL, *Reactor Handbook* Vol. II, p. 250. Interscience, New York (1961).

(2) P. PASCAL, *Nouveau Traité de Chimie Minerale*, Tome XV, Chapitre III: M. OXLEY, Combinaison Chlorées de l'Uranium, p. 135–160.

(3) M. D. BRODSKY and B. G. F. CARLESON, *J. inorg. nucl. Chem.* **24**, 1675 (1962).

(4) J. J. GROCE, Report NAA-SR-Memo-8465.

(5) J. SCHMETS and PH. SPEECKAERT, Report EURAEC-81 (1960).

(6) D. NAUMANN, *Kernenergie* **5**, 118 (1962); **6**, 73, 116, 173, 243 (1963).

(7) J. H. GOODE, Report ORNL-TM-828.

(8) H. PARTHEY, *Nukleonik* **7**, 8, 473 (1965).

In an earlier paper[9] the reaction of UCl_4 with oxygen of the air was investigated by determination of the released chlorine. Later on VAN WAZER and JOHN[10] found that uranyl chloride is an intermediate product, which can be visually recognized because of the colour change of the material:

$$UCl_4 \text{ (green)} + O_2 \rightarrow UO_2Cl_2 \text{ (yellow)} + Cl_2 \qquad T < 230°C \qquad (1)$$

$$3UO_2Cl_2 + O_2 \rightarrow U_3O_8 \text{ (black)} + 3Cl_2 \qquad T < 250°C \qquad (2)$$

The activation energy for the first step of the reaction (1) was calculated to be 12 kcal/mole, for the second step (2) it was calculated to 45 kcal/mole from the rate of conversion which has been optically measured.

These are the steps of the reaction which were regarded as possibly controlling the rate:

1. Transport of oxygen to the reacting surface.
2. Diffusion of the oxygen into the crystal surface covered with oxidation products.
3. Rate of oxidation in the interface between initial and final product.

The authors assumed the last process to be the rate controlling step.

As detailed data on the kinetics have not been available, a renewed investigation seemed to be appropriate because of the importance of the substance as indicated above and in view of the possible dependence of the chlorine content in the final oxidation product on the conditions of the oxidation.

EXPERIMENTAL

Experiments to study the oxidation of UCl_4 to U_3O_8 were conducted on a Netzsch DTA-apparatus and on a Sarorius thermobalance. The measurable change in weight was limited to some ± 0·1 mg primarily by the thermal diffusion of the gas in the balance vessel at a pressure of 10–760 torr. At pressures of 10^{-1} torr and below this effect diminishes. It is surpassed, however, by the so-called radiometer effect. The accuracy of the indicated absolute temperature can be stated to be ±15°. The relative temperature measurements were considerably more accurate (±3°).

Our experiments as described below were carried out using samples of screened powders which were equally pre-treated.

The uranium tetrachloride was purified by vacuum sublimation and always stored in sealed capsules in a dry box because it reacts rapidly with moisture.[1]

The screening of the powders into fractions of different particle size as well as the preparation of X-ray samples was also carried out in this box.

Usually 40 mg of UCl_4 powder in a Pt-crucible were quickly introduced into the apparatus filled with dry oxygen. Afterwards, the apparatus was heated up.

For isothermal experiments the sample was introduced into the furnace chamber after the desired temperature had been reached.

RESULTS

Figure 1 indicates the typical curves of non-isothermal oxidation of screened UCl_4-powders to U_3O_8. The initial conversion of all the samples at about 100°C up to 10 per cent of the theoretical conversion into U_3O_8 corresponds to the desorption of adsorbed gases and moisture, as is evident also from exceeding the conversion more than 100 per cent. The oxidation of the coarser powder at atmospheric pressure starts at about 400°C reaching a maximum conversion at 450°C.

The reaction at reduced pressure starts already at 200°C and reaches a first maximum at about 320°C, probably indicating a change in kinetics.

[9] J. BOOHER and A. DE HAAN, JR., Report RL-4.6.6 (1942).

[10] J. R. VAN WAZER and G. S. JOHN, *J. Am. chem. Soc.* **70**, 1207 (1948); Report MDDC-1322.

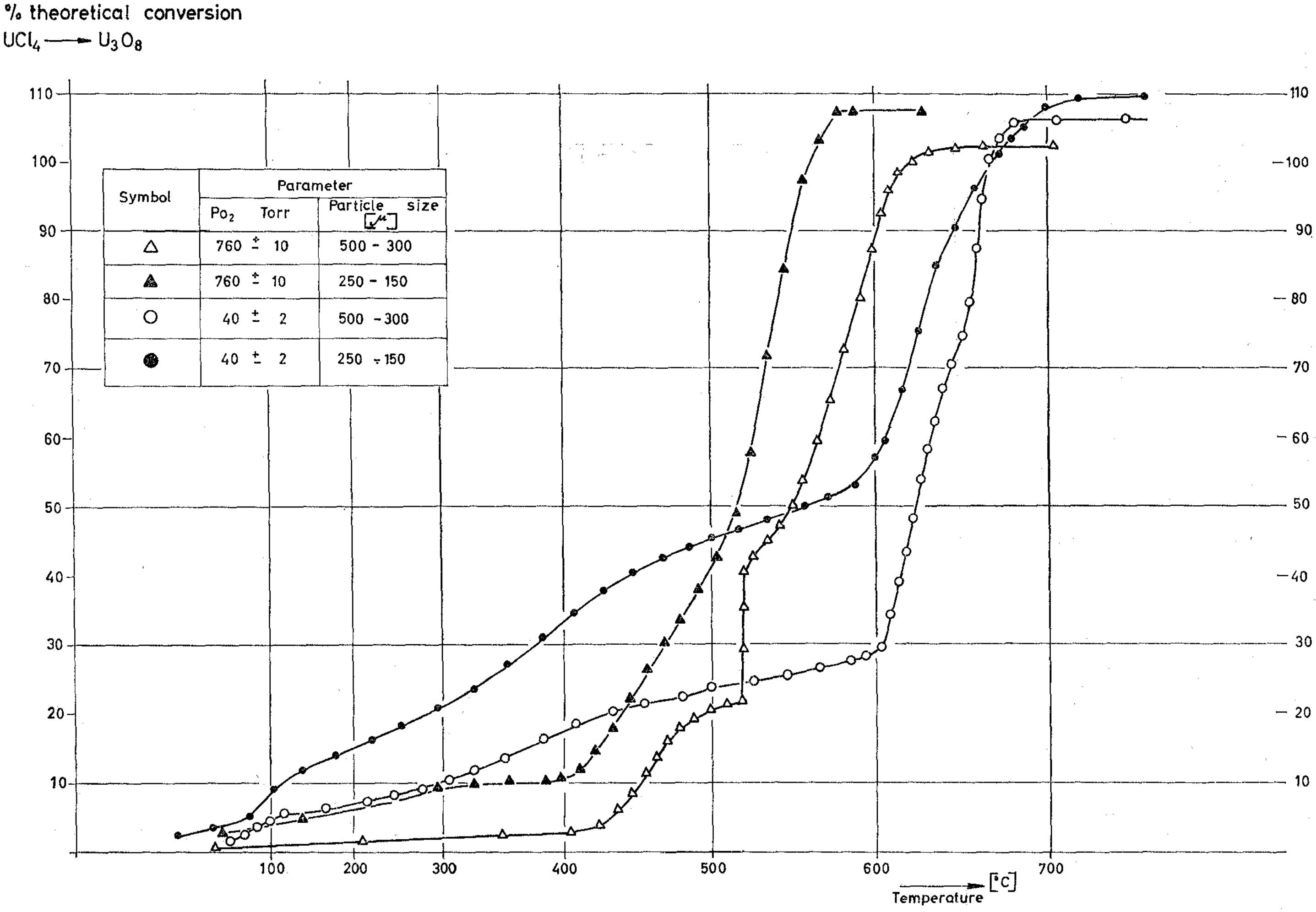

FIG. 1.—TGA-curves of the oxidation of UCl_4 to U_3O_8.

The shape of the curve at atmospheric pressure apparently starts to change at 500°C, at reduced pressure, however, not before 600°C.

The conversions reached up to these temperatures are almost twice as high for the powder of a smaller particle size, which proves the dependence of the reaction on surface area. The conversion of the coarser powder (300–500 μ) at atmospheric pressure is delayed intermittently; we will refer to this phenomenon further below.

The DTA-curve of a fine powder at atmospheric pressure (Fig. 2) shows a good agreement with the results indicated above. The first exothermal peak at 460°C was followed by an endothermal peak at 550°C.

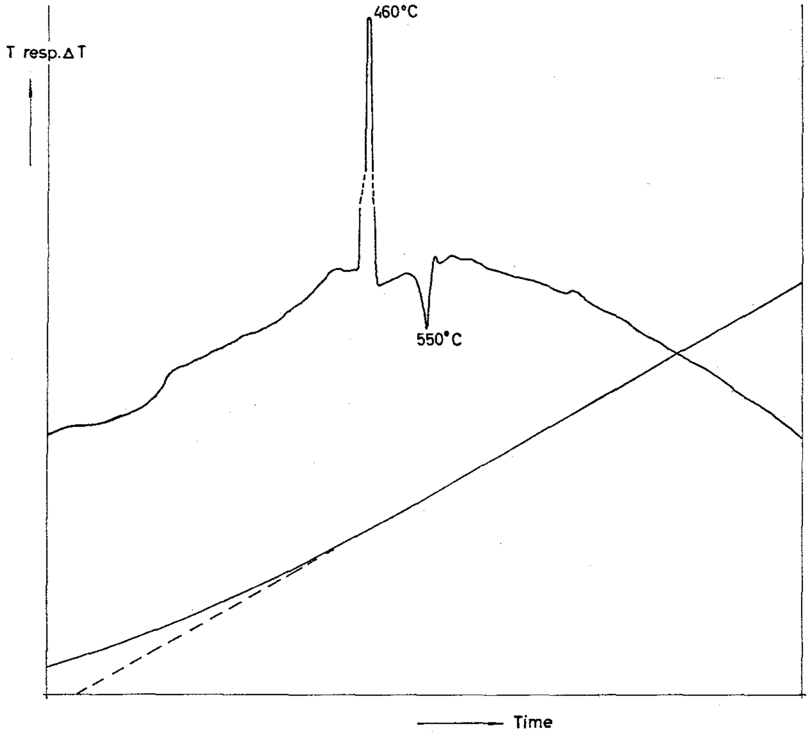

FIG. 2.—DTA-curve of the oxidation of UCl_4-powder to U_3O_8.

Experiments at atmospheric pressure interrupted at different conversions undoubtedly yielded uranyl chloride as the intermediate product, as could be verified by X-ray diffraction analysis.

In addition, the U_3O_8 often showed a broadened lattice in mixtures of uranyl chloride and U_3O_8.

Therefore the first exothermal peak is caused by the formation of UO_2Cl_2, and the subsequent endothermal peak is due to the oxidation of UO_2Cl_2 to U_3O_8.

Thermochemical calculations resulted in figures of —51·7 and +55·2 kcal/mole, respectively, for the enthalpy of these reactions under standard conditions.

The isothermal experiments were restricted to the temperature range of 400–450°C. Beyond that range the uranium tetrachloride already started to evaporate. Below 390°C the reaction was sluggish.

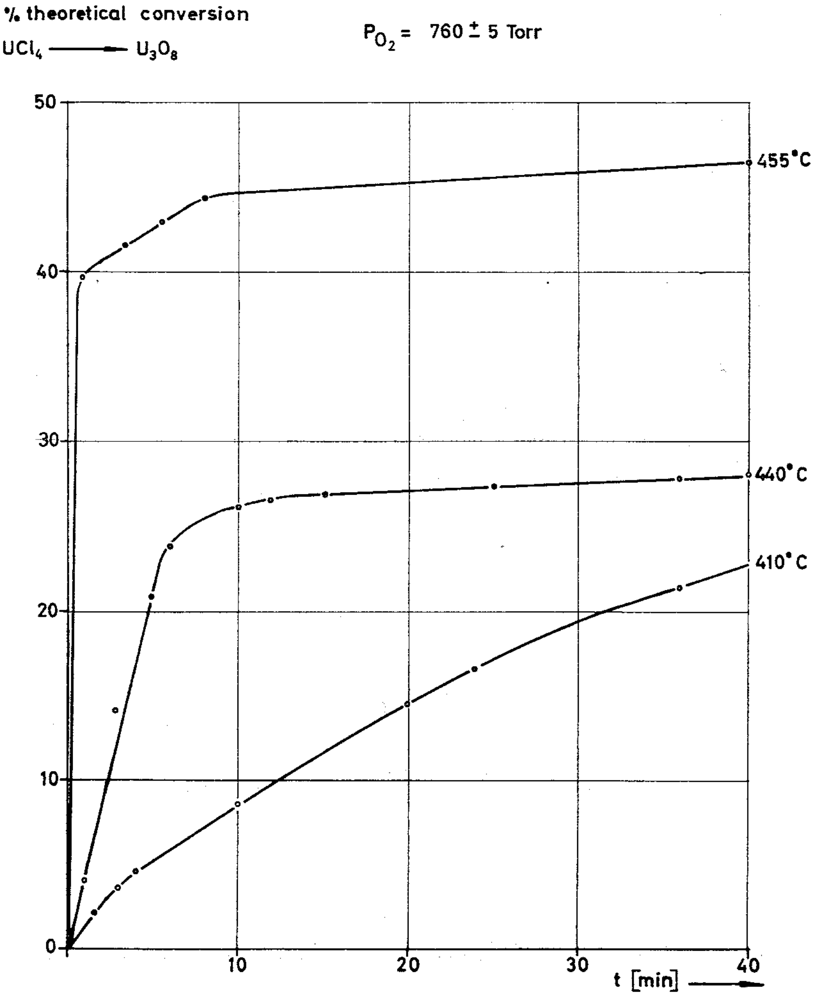

FIG. 3.—Isothermal oxidation of UCl_4 to U_3O_8

Figure 3 shows the TGA-curves of powders of the particle size 150–250 μ at different temperatures under oxygen of atmospheric pressure.

Initially the rapid reaction is of zero order followed by a transition range with a first-order reaction corresponding to UCl_4. Afterwards, the reaction was controlled by a diffusion process, which can be concluded from the $\sqrt{(t)}$ dependence of the conversion.

The curve at 410°C markedly differs from that obtained at higher temperatures. Already after 1 min the diffusion controls the reaction, proceeding more rapidly than at higher temperatures, because the coating of uranyl chloride is only thin.

Yet, the crystal surface was passivated in practically all experiments by the formation of a uranyl chloride surface coat, as is shown by the slow increase of the conversion into U_3O_8 from 20 per cent on, corresponding to 50 per cent conversion into UO_2Cl_2.

From the measured rates of reaction the activation energy of the zero order reaction was calculated to be 51 ± 9 kcal/mole, in contrast to the value by VAN WAZER

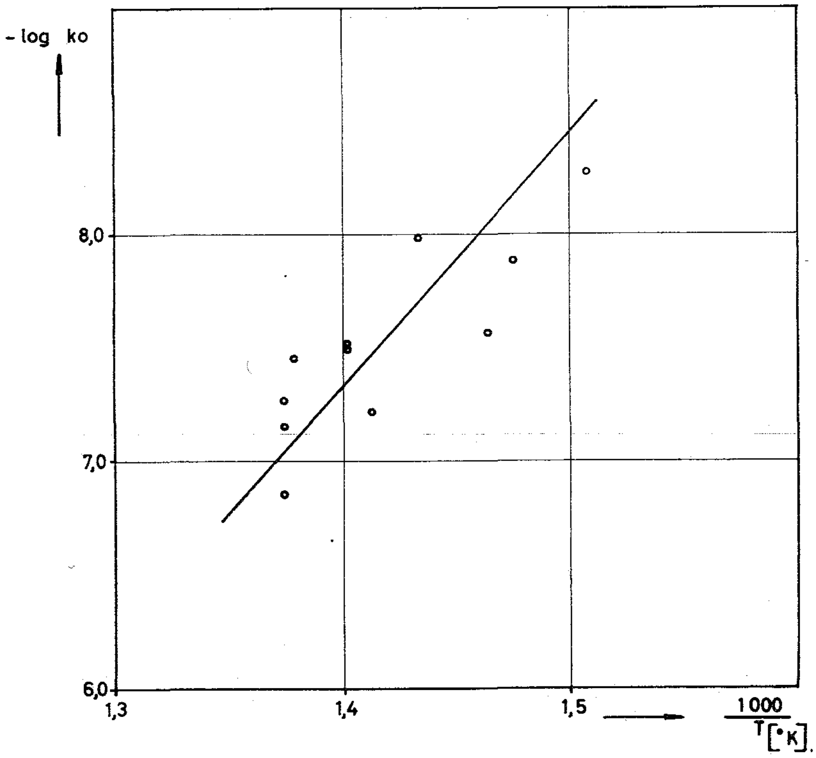

FIG. 4.—Arrhenius plot of the reaction rate constants.

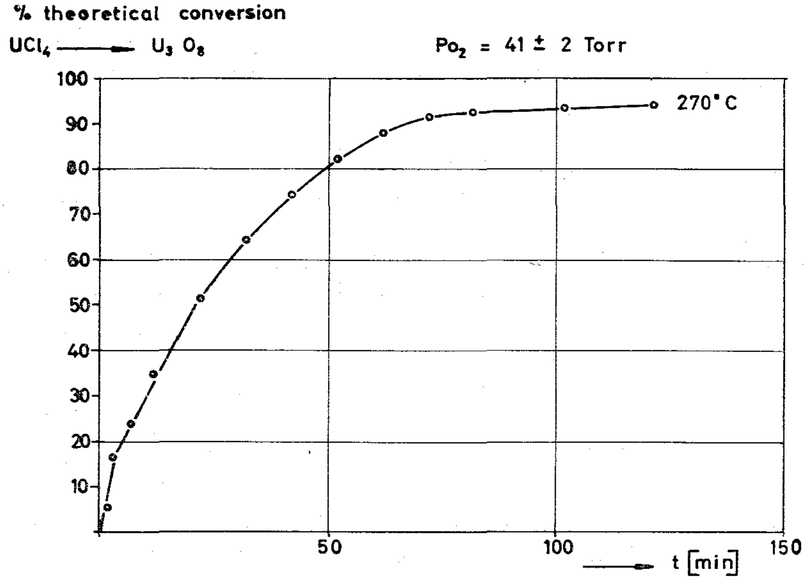

FIG. 5.—Isothermal oxidation of UCl_4 at reduced oxygen pressure.

and JOHN. The frequency factor was calculated to be 10^8 (Fig. 4). The diffusion coefficient was estimated to be 10^{-10}–10^{-9} cm²/sec.

A typical TGA-curve obtained under reduced pressure at 270°C, is illustrated in Fig. 5.

After a short initial reaction caused by the heat-up of the sample there was a first-order reaction corresponding to UCl_4 up to about 90 per cent of the conversion. Afterwards, the diffusion again controlled the reaction.

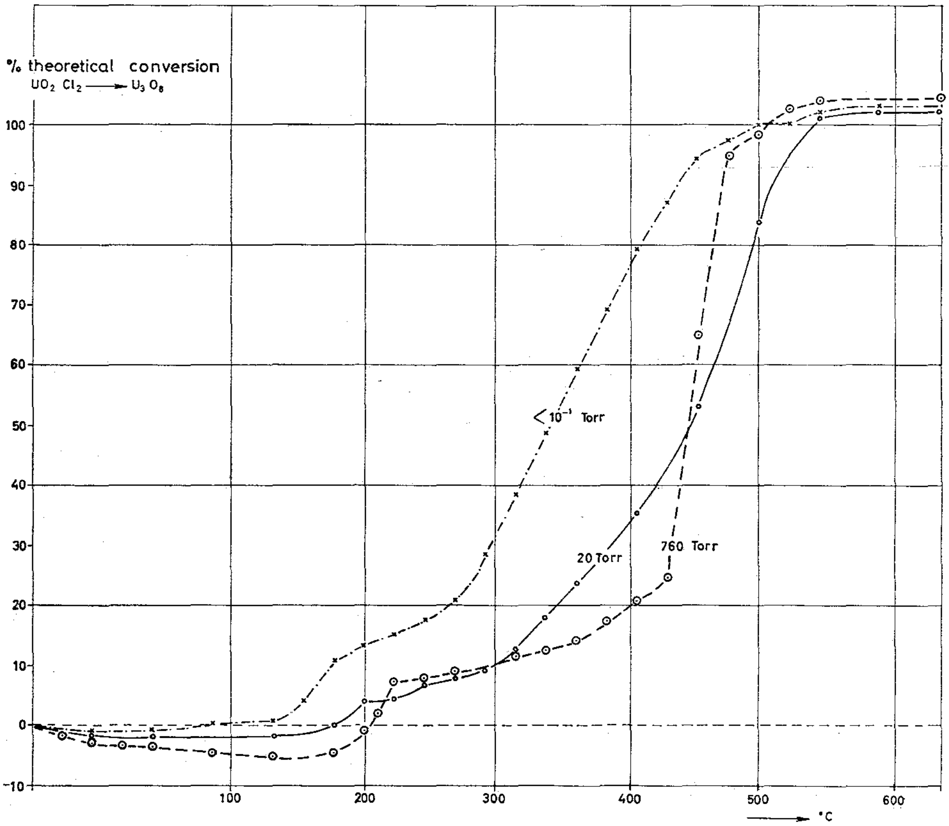

FIG. 6.—TGA-curves of the oxidation of UO_2Cl_2 to U_3O_8.

The whole progress of oxidation at reduced pressure could not be reproduced perfectly, as in the case of the experiments carried out at atmospheric pressure. However, it was possible to obtain a conversion of 80 per cent within 50 min at a considerably lower temperature, more about which will be said below. The reaction stopped at a conversion of about 95 per cent.

The strongly delayed conversion towards the end of the reaction resulted in remarkable contents of uranyl chloride and chlorine, respectively, in the final product.

Some tentative experiments to study the oxidation of UO_2Cl_2 to U_3O_8 (particle size 150–250 μ) at different oxygen pressures are illustrated in Fig. 6.

The negative conversion at the beginning corresponded to the take up of water of the samples.

The water was discharged as a function of pressure between 150° and 200°C.

The shape of the curve in a vacuum $<10^{-1}$ torr strongly differs from that encountered at higher pressures. The reaction rate increases from 200°C on attaining a maximum conversion at 300°C. This seems to indicate the decomposition:

$$UO_2Cl_2 \rightarrow UO_2 + Cl_2 \qquad (3)$$

The reaction surpassed the rate of oxidation up to 300°C, which is in agreement with literature.(11,12)

DISCUSSION

The TGA-curves obtained at atmospheric pressure show that powders, which are quickly heated up to experimental temperature, do not start noticeable reactions with oxygen until the range between 400–450°C with the phase boundary reaction determining rate of reaction.

Primarily, the level of conversion of zero order (5–40 per cent) is a function of temperature, as the number of reacting surface sites usually increases with temperature.

In addition, there is also a dependence on the unknown specific surface area of the powder and the thickness of the uranyl chloride coat, respectively.

Afterwards, the reaction for a short time is of the first order with respect to uranyl chloride, probably caused by the thermal decomposition of uranyl chloride.

This assumption is supported also by the fact that the oxidation reactions of coarse uranium tetrachloride powders (300–500 μ) at reduced pressure were sluggish and the yellow colour of the intermediate product (UO_2Cl_2) repeatedly did not appear obviously because of difficulties of nucleus formation. Moreover, microscopic investigation of grains in some cases distinctly showed growth layers of U_3O_8 on top of UO_2Cl_2 which in turn covered UCl_4. Thus, the optical change in colour may not occur under certain conditions.

After the transition range the continued progress of the reaction seems to be dependent upon the diffusion of oxygen through the layer of oxidation products which strongly delayed the reaction. The conversion which may be attained remains below 50 per cent within 2 hr at 400–450°C.

At reduced pressure, however, considerable conversion is reached in a very much shorter time at considerably lower temperatures due to the change in kinetics.(4) The reason was the thermal decomposition of UO_2Cl_2 according to the Equation (3). Whereas the oxidation of UCl_4 to UO_2Cl_2 was delayed and in addition the progress of the reaction depends upon the reaction:

$$3UO_2 + O_2 \rightarrow U_3O_8 \qquad (4)$$

The impossibility of reproducing the experiments at reduced pressure could be explained in this way. The final conversion which could be attained in all cases was considerably below 100 per cent.

According to the experimental results a considerable content of chlorine or chloride, respectively, in the lattice has to be taken into account below 450°C, as was also shown by the determination of UO_2Cl_2 in the oxidation product by X-ray diffraction.

Numerous TGA-studies on powders of various particle sizes were interrupted at

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(11) O. JOHNSON, Report CC-1781 (1944).

(12) C. A. KRAUS, Report N-1789 (1943).

different degrees of oxidation to investigate the oxidation products by X-ray diffraction analysis. In all cases it was only possible to detect UO_2Cl_2 as the intermediate product.

The formation of higher chlorides of uranium (UCl_5 and UCl_6) could not be observed, contrary to statements in literature.(2,9)

CONCLUSION

Starting from the original problem it is now possible to establish the conditions (for a quantity of 500 mg) of avoiding major contents of chlorine in the ultimate product of oxidation of UCl_4 to U_3O_8:

Oxidation should be carried out on powders of a particle size less than 150 μ over a period of some 10 min at reduced oxygen pressure (about 10 torr) at 300°C so as to make a coat of uranyl chloride and oxide grow in order to avoid the evaporation of uranium tetrachloride.

Then the oxidation product will be subjected to a final oxidation over 60 min at about 500°C and at 1 atm of oxygen.

Because of the now thermally activated diffusion the increased temperature safeguards rapid oxidation of any uranium tetrachloride which might possibly still be present within the grains. The thermal decomposition of uranyl chloride and the oxidation of the solid decomposition products also occur, because the delayed nucleation and a slow growth rate were excluded.

An excellent crystallized U_3O_8 of the particle size of the initial product is obtained. The chloride content in this case is below 0·05 per cent (by weight).

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