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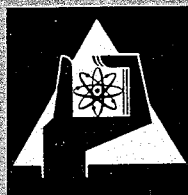
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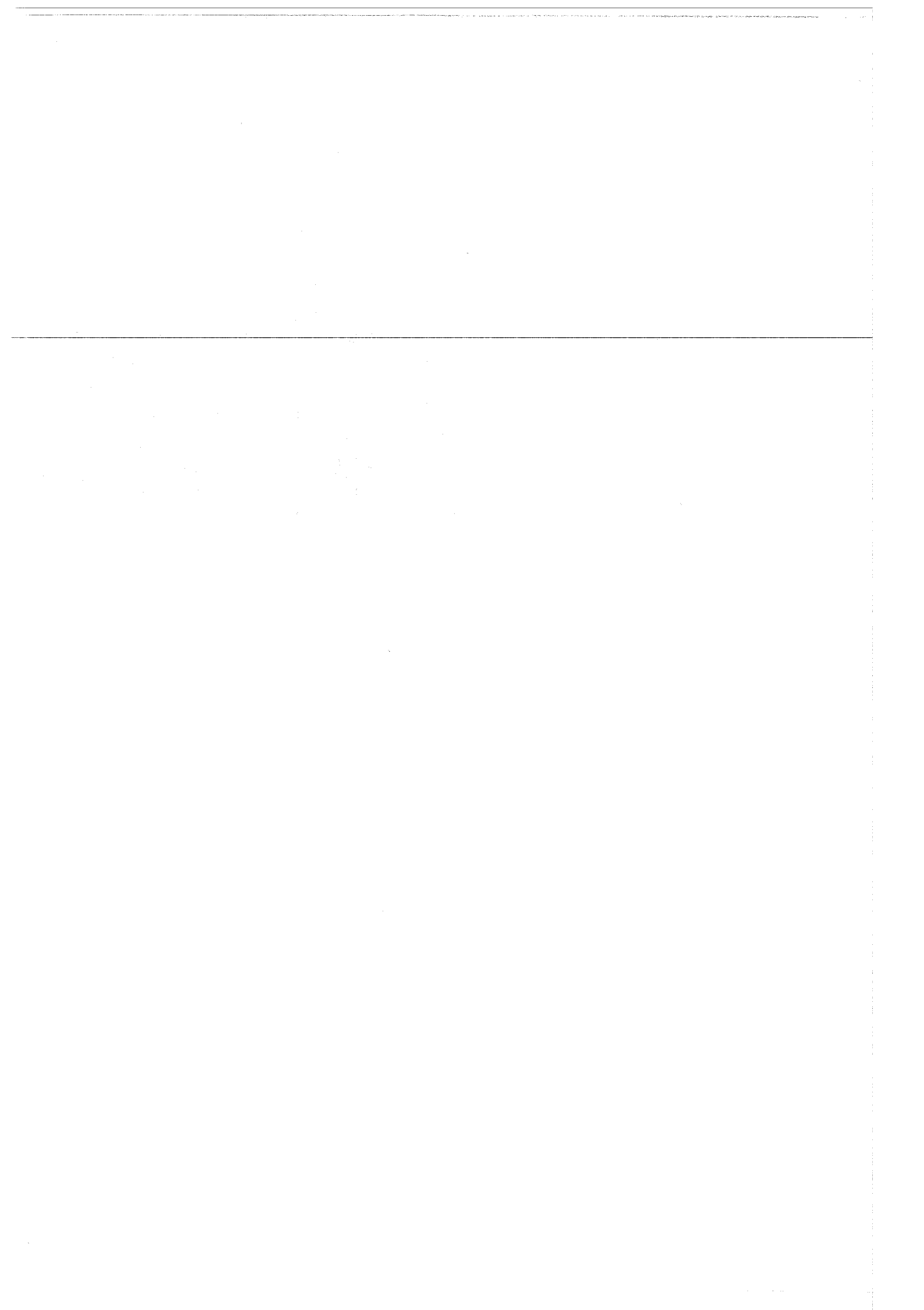
Institut für Heiße Chemie

The Oxidation of Uranylchloride

B. Kanellakopoulos, H. Parthey



**GESELLSCHAFT FÜR KERNFORSCHUNG M. B. H.
KARLSRUHE**



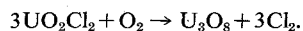
THE OXIDATION OF URANYLCHLORIDE

B. KANELLAKOPOLOS and H. PARTHEY

Nuclear Research Centre, Karlsruhe, Germany

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Abstract—The oxidation of uranylchloride was investigated by thermoanalytical and X-ray diffraction methods. UO_2Cl_2 reacts with oxygen according to



The surface reaction controls the rate. The activation energy and the frequency factor of the reaction were calculated.

INTRODUCTION

URANYLCHLORIDE (UO_2Cl_2) is a secondary product in the course of the chlorination of UO_2 [1, 2], to UCl_6 and an intermediate product [3, 4] in the course of the oxidation of uraniumtetrachloride (UCl_4) to uraniumoxide (U_3O_8). Consequently the behaviour of UO_2Cl_2 strongly influences the chlorination and oxidation process. The processing of nuclear oxide fuels by chlorination includes as well the chlorination of UO_2Cl_2 to UCl_6 as the oxidation of UCl_4 to U_3O_8 . Hence all factors influencing reaction rate, yield, and purity of the products should be known well. It was the purpose of this work to obtain more information about the behaviour of UO_2Cl_2 in order to establish the design of such processes and their installations.

EXPERIMENTAL

The UO_2Cl_2 -powder was prepared by the reaction of hydrochloric acid with uranyl nitrate [5]. The product was carefully dried and screened. All manipulations were carried out in a dry box. Vacuum sublimation was not possible because of decomposition. The DTA-investigations were conducted on a Netzsch-apparatus. The TGA-measurements were performed on a Sartorius-thermobalance as formerly described [4].

Usually 30–40 mg of UO_2Cl_2 (150–250 μ particle size) were oxidised in a Pt-crucible by dry oxygen at 760 torrs. After the run every sample was examined by X-ray diffraction investigations.

RESULTS

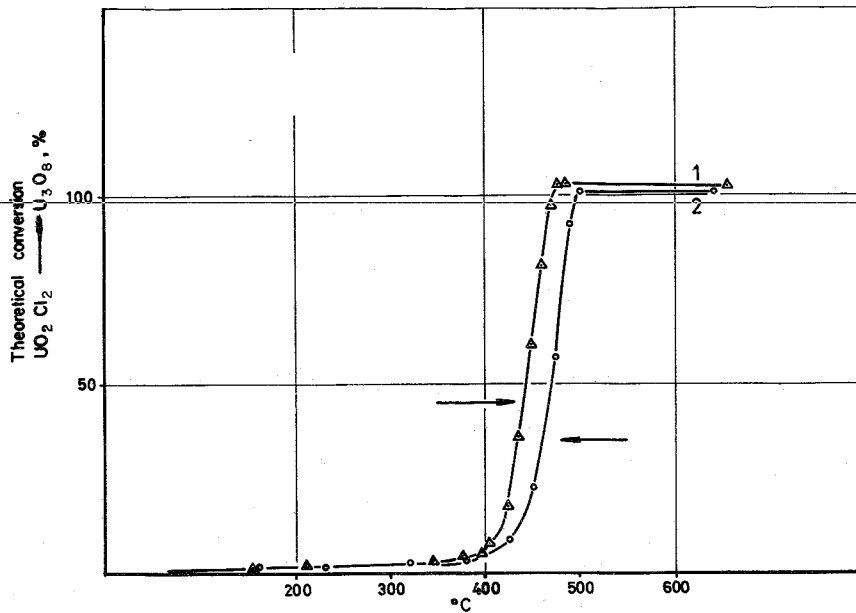
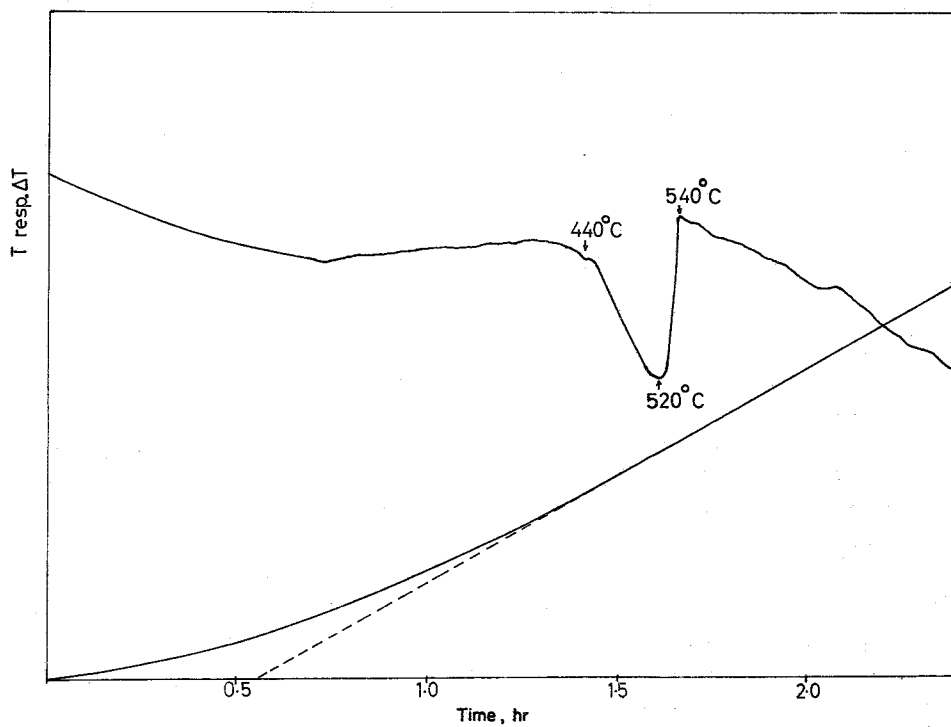
Figure 1 shows the TGA-curve of the oxidation of UO_2Cl_2 to U_3O_8 . The weight loss of the samples up to 120°C was attributed to the desorption of adsorbed gases.

The oxidation reactions started at 390°C. Near 450°C the slope of the curves were changed a little as marked by two arrows.

The curves indicate that isothermal experiments can be performed between 390° and 490°C.

The DTA-curve (Fig. 2) shows an endothermal peak in the range of 440–540°C in agreement with the results indicated above. Electrochemical

1. H. Parthey, *Nukleonik* **7**, 8, 473 (1965).
2. B. Kanellakopoulos and H. Parthey, *Nukleonik* **8**, 7, 363 (1966).
3. J. R. van Wazer and G. S. John, *J. Am. chem. Soc.* **70**, 1207 (1948); *Report MDDC-1322*.
4. B. Kanellakopoulos and H. Parthey, *J. inorg. nucl. Chem.* **28**, 2541 (1966).
5. G. Brauer, *Handbuch der präp. anorg. Chemie*, p. 1257. F. Enke, Stuttgart (1962).

Fig. 1. TGA-curves of the oxidation of UO_2Cl_2 to U_3O_8 .Fig. 2. DTA-curve of the oxidation of UO_2Cl_2 -powder to U_3O_8 .

measurements gave +45 kcal/mole for the enthalpy of the reaction at standard conditions [6].

The isothermal curves are illustrated in Fig. 3. At 400°C the reaction was sluggish and only small amounts of U_3O_8 were formed at the surface of the particles. The reaction reached appreciable rates at about 410°C and proceeded very rapidly at 490°C. Figure 4 gives a plot of $\log 1/(1-x)$ (x = per cent of conversion of UO_2Cl_2) against time. In any case the curves started as straight lines which indicates a first order reaction with respect to UO_2Cl_2 .

After some minutes the slope of the lines increased suddenly; that means a second first order reaction followed somewhat faster to about 90 per cent completion of the reaction.

Up to 440°C the reactions were strongly delayed by a diffusion process which followed the two first order reactions. At temperatures higher than 440°C the curves started also as straight lines for a few minutes. Later on they were no longer linear and increased more and more in dependence on reaction temperature.

From the curves the activation energy was calculated to be 39.9 ± 0.2 kcal/mole and 43.9 ± 0.2 kcal/mole. The frequency factor was estimated to be 10^{11} and the diffusion coefficient to be 10^{-8} cm²/sec [7].

As formerly reported [4] the TGA-curves of the oxidation of UO_2Cl_2 to U_3O_8

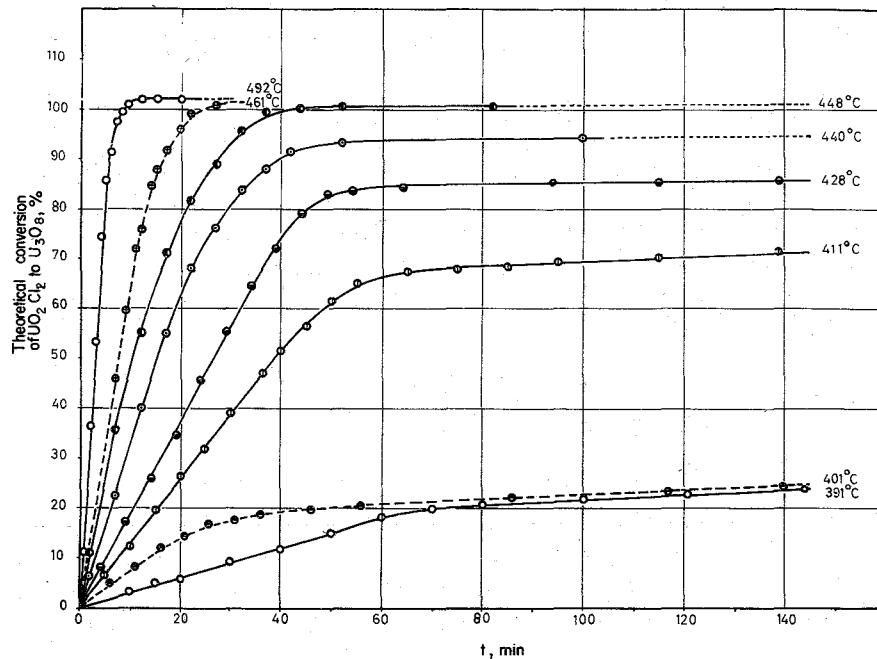


Fig. 3. Isothermal oxidation of UO_2Cl_2 to U_3O_8 .

6. E. F. Westrum, Jr. and F. Grønfold, in *Thermodynamics of Nuclear Materials*, p. 3. IAEA, Vienna 1962.
7. H. D. Ünwald and C. Wagner, *Z. phys. Chem.* **24**, 53 (1934).

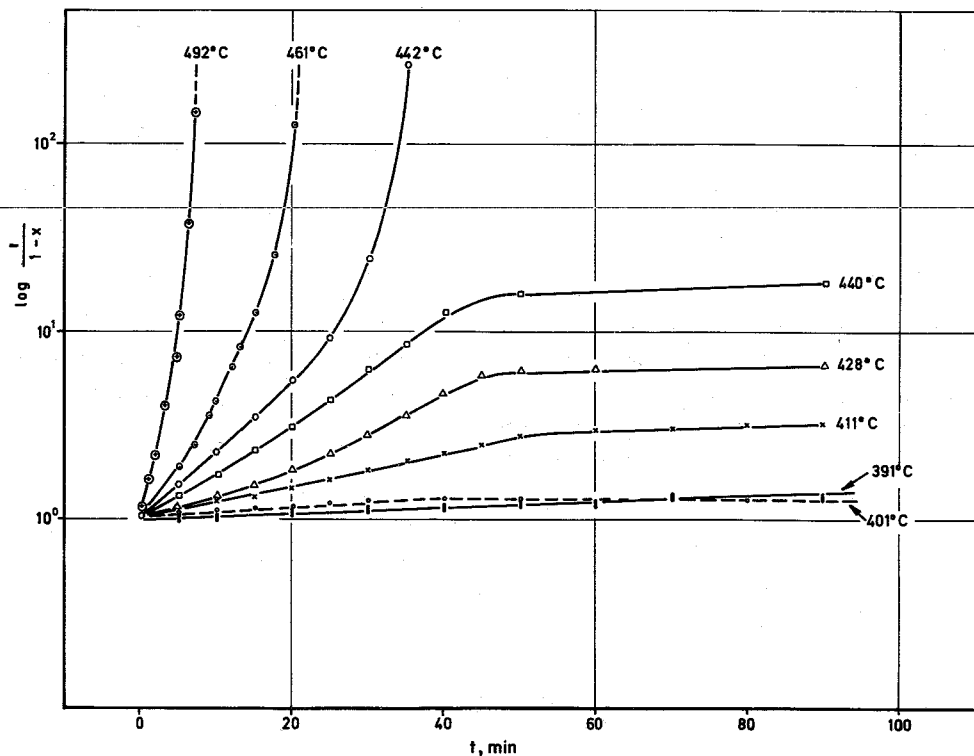
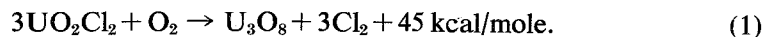


Fig. 4. Plot of $\log 1/(1-x)$ (x = per cent of conversion of UO_2Cl_2 to U_3O_8) against time.

at 80 and 760 torrs showed no marked differences. Thus the influence of the oxygen pressure at the reaction rate constant and activation energy can be neglected in the range of 80–760 torrs and 20–500°C. X-ray examinations showed different amounts of UO_2Cl_2 and U_3O_8 which corresponded to the degree of conversion. UO_2 could not be detected but at reduced pressure it is formed very rapidly at 300°C [4, 8, 9].

DISCUSSION

UO_2Cl_2 reacts with oxygen according to:



The controlling steps are two successive first order reactions with respect to UO_2Cl_2 which indicates that the surface reaction controlled the rate. The second first order reaction proceeded somewhat faster. This acceleration was caused by an optically observed destruction of the particles which increased their specific surface.

Near 440°C the decomposition:



8. O. Johnson, *Report CC-1781* (1944).

9. C. A. Kraus, *Report N-1789* (1943).

started and surpassed the rate of the oxidation reaction in agreement with the behaviour in the course of the oxidation of UCl_4 to U_3O_8 and literature statements [8, 10]. Usually the velocity of a spontaneous decomposition depends on nucleus formation and crystal growth which follow an induction time [11, 12] as observed in this case too.

According to investigations of several authors the oxidation of UO_2 to U_3O_8 is very fast at 390°C [13–15]. This explains the absence of UO_2 in the X-ray diagrams. However, in a few special cases there were indications that some UO_2 was present.

Nevertheless, a marked different activity of UO_2Cl_2 must be stated. As previously described [4] the coating of UO_2Cl_2 is stable below 450°C . In this work UO_2Cl_2 reacted slowly up to 400°C . Therefore, it may be concluded that the UO_2Cl_2 formerly formed indeed a very regular and tight layer on the UCl_4 -particles which prevented the oxidation. As additionally reported [4] the oxidation of UCl_4 -particles (particle size $300\text{--}500\ \mu$) was very sluggish and did not form a tight and coloured layer. In this case the oxidation of UO_2Cl_2 to U_3O_8 reached the same rate as the oxidation of UCl_4 to UO_2Cl_2 . Hence, the change of colour (black-green to yellow) did not occur.

CONCLUSION

Concerning the problem of handling UO_2Cl_2 in a chlorination process of reactor oxide fuels the present knowledge allows now to predict and to govern the behaviour of UO_2Cl_2 . In contrast to UO_2 the UO_2Cl_2 reacts slowly with a mixture of Cl_2/CCl_4 [1]. Therefore, the concentration of UO_2Cl_2 increases at the end of the chlorination reaction. This concentration could be decreased by interrupting the chlorination followed by a thermal decomposition of UO_2Cl_2 above 440°C or at 300°C and reduced pressure (~ 20 torrs). The same method may be applied during the oxidation of UCl_4 to U_3O_8 when the reaction is delayed by a layer of UO_2Cl_2 . In any case this procedure will supply a renewed active surface of the material and a shorter reaction time.

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10. R. K. Steunenberg and R. C. Vogel, *Reactor Handbook*, Vol. 2, p. 267. Interscience, New York (1961).
11. P. W. M. Jacobs and F. C. Tompkins, In *Chemistry of the solid state* (Edited by W. E. Garner), p. 184. Butterworths, London (1955).
12. D. Dollimore, J. Dollimore and D. Nicholson, In *Reactivity of Solids* (Edited by J. H. de Boer *et al.*), pp. 627–637. Elsevier, Amsterdam (1961).
13. H. R. Hoekstra, A. Sartoro and S. Siegel, *J. inorg. nucl. Chem.* **18**, 166 (1961).
14. P. Imris, *J. inorg. nucl. Chem.* **28**, 99 (1966).
15. H. Landsperky and M. Voboril, *J. inorg. nucl. Chem.* **29**, 250 (1967).