[CONTRIBUTION FROM THE DIVISION OF CHEMICAL RESEARCH AND DEVELOPMENT, TENNESSEE EASTMAN CORP., CLINTON ENGINEERING WORKS]

A Kinetic Study of the Oxidation of Uranium Tetrachloride

BY JOHN VAN WAZER AND GEORGE JOHN

A novel method for kinetic studies of solid–gas reactions in which the solid undergoes a color change has been used in this Laboratory for determining the activation energy for oxidation of uranium tetrachloride. The oxidation process consists of two independent steps which can be described by the equation

$$UCl_4(\text{green}) + O_2 \longrightarrow UO_2Cl_2(\text{yellow}) + Cl_2 \quad (1)$$

$$3UO_2Cl_2(\text{yellow}) + O_2 \longrightarrow U_3O_8(\text{black}) + 3Cl_2 \quad (2)$$

There is also a side reaction in which the uranium tetrachloride reacts with the chlorine evolved to form volatile uranium pentachloride.

Experimental

Working in a dry box a thin layer of uranium tetrachloride was dusted on the top of a rectangular copper bar which could be heated electrically at one end and cooled by a water coil at the other (see Fig. 1). The bar was then put into an airtight glass envelope and purified helium was passed over it while the temperature of the hot end was raised to about 600°. The temperatures were measured by the thermocouples soldered to the bar at several points along its length. Then oxygen instead of helium was allowed to stream over the bar. This caused the green uranous chloride to change into yellow uranyl chloride at the hot end of the bar and a boundary separating the green from the yellow region was seen to move at an approximate velocity of 1 cm. in several seconds from the hot toward the cold end of the bar. This boundary was soon followed by another separating the yellow region from one of black uranium oxide. These boundaries were quite sharply defined and the kinetics of the reaction was studied by measuring the velocity at which the boundaries moved.

Interpretation of Results

The rate constant for either of the over-all reactions is inversely proportional to the time, t, required for the material to undergo a given color change at any particular temperature. Thus the rate constant in the Arrhenius equation can be replaced by B/t to give

$$t = (B/A)e^{E/RT} = Ke^{E/RT}$$

where E is the activation energy and A is the frequency factor. As the positions of the boundaries along the bar are determined as a function of time and each position corresponds to a definite temperature, values of time and temperature can be found which when substituted in the above equation will give the activation energy. Since time in these experiments was measured from the instant oxygen was allowed to flow into the system, the time origin was displaced from experiment to experiment and the data were best interpreted by plotting $\log t$ against $1/T$.

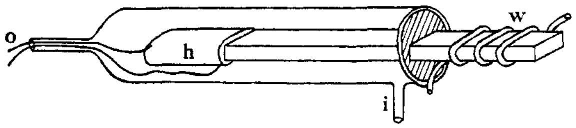

Fig. 1.—Reaction bar: w, water coil for cooling; i, gas inlet; h, heating element; o, gas outlet with wires to heating element.

In the oxidation of uranium tetrachloride to uranyl chloride the activation energy was found to be 12 (±2) kcal. and the lowest temperature for measurable reaction is 230 ± 5°. In the conversion of uranyl chloride to the black oxide the activation energy was 45 (±5) kcal. and the lowest temperature for observable reaction is 250 ± 10°. The mechanism of these reactions can be divided into three steps: (1) transport of oxygen to the reacting surface, (2) diffusion of oxygen into a uranium tetrachloride particle coated over with oxidation product, and (3) the rate at which oxidation will occur when the oxygen molecules reach the unreacted solid. From kinetic theory it can be shown that step (1) does not determine the rate. Also, since varying the rate of gas flow over the bar did not change the oxidation rate, diffusion of oxygen through a concentration gradient of chlorine near the surface does not affect the measured rate.

Diffusion of the oxygen through a thick surface layer is probably not the rate determining process either since the color of such a surface layer is used as the criterion of completion of the reaction. It also seems doubtful that a tight skin such as is found on passive metals can be formed over a salt. Thus it appears that step (3) is the rate determining process and that plenty of oxygen is available for the reaction.

Acknowledgment.—We wish to thank Dr. C. E. Larson for his permission to undertake this problem and his interest in it. This document is based on work performed under Contract No. W-7401-eng-23 for the Atomic Energy Project at the Tennessee Eastman Corporation, Oak Ridge, Tennessee.

Summary

A simple procedure for studying the kinetics of a heterogenous reaction involving color change of the solid phase has been applied to the investigation of uranium tetrachloride oxidation.

OAK RIDGE, TENN. RECEIVED SEPTEMBER 30, 1947