Equilibria and kinetics of the reaction of phosgene with thorium oxide

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Equilibria and kinetics of the reaction of phosgene with thorium oxide

Abstract
The reaction of phosgene with thorium oxide has been shown to be a good method for preparing thorium tetrachloride. The equilibria of the reaction showed that nearly complete utilization of phosgene could be attained in a properly designed reactor. The kinetics of the reaction could not be represented by a simple rate law but the effects of bed depth, particle size, mode of oxide preparation and temperature on the rate of reaction were established. The depth of the bed of thorium oxide and the particle size of the oxide did not affect the initial rate of reaction. At high conversions the rate of the reaction was probably controlled by the slow solid state diffusion of oxygen to the surface of the thorium tetrachloride crystals and the highest conversion of thorium oxide to thorium tetrachloride obtained was approximately 91 o/o. The size of the crystallites in the thorium oxide particles increased as the temperature at which thorium oxalate was calcined to thorium oxide was increased. The resulting decrease in surface area decreased the initial rate of reaction. The temperature coefficient of the reaction rate was small and a temperature increase of approximately 200° C was required to double the rate of reaction.

Disciplines
Chemical Engineering
EQUILIBRIA AND KINETICS OF THE REACTION OF PHOSGENE WITH THORIUM OXIDE

by

D. T. Peterson and D. J. Sundquist

IOWA STATE UNIVERSITY

AMES LABORATORY

RESEARCH AND DEVELOPMENT REPORT

U.S.A.E.C.

PHYSICAL SCIENCES READING ROOM
UNITED STATES ATOMIC ENERGY COMMISSION

Research and Development Report

EQUILIBRIA AND KINETICS OF THE REACTION OF PHOSGENE WITH THORIUM OXIDE

by

D. T. Peterson and D. J. Sundquist

July, 1964

Ames Laboratory

at

Iowa State University of Science and Technology

F. H. Spedding, Director
Contract W-7405 eng-82
This report is distributed according to the category Engineering and Equipment (UC-38) as listed in TID-4500, June 1, 1964.

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IS-917
EQUILIBRIA AND KINETICS OF THE REACTION
OF PHOSGENE WITH THORIUM OXIDE

D. T. Peterson and D. J. Sundquist

ABSTRACT

The reaction of phosgene with thorium oxide has been shown to be a good method for preparing thorium tetrachloride. The equilibria of the reaction showed that nearly complete utilization of phosgene could be attained in a properly designed reactor. The kinetics of the reaction could not be represented by a simple rate law but the effects of bed depth, particle size, mode of oxide preparation and temperature on the rate of reaction were established. The depth of the bed of thorium oxide and the particle size of the oxide did not affect the initial rate of reaction. At high conversions the rate of the reaction was probably controlled by the slow solid state diffusion of oxygen to the surface of the thorium tetrachloride crystals and the highest conversion of thorium oxide to thorium tetrachloride obtained was approximately 91%. The size of the crystallites in the thorium oxide particles increased as the temperature at which thorium oxalate was calcined to thorium oxide was increased. The resulting decrease in surface area decreased the initial rate of reaction. The temperature coefficient of the reaction rate was small and a temperature increase of approximately 200°C was required to double the rate of reaction.

INTRODUCTION

High purity thorium metal can be prepared by the magnesium reduction of thorium tetrachloride by a process developed at the Ames Laboratory.\(^1\) The purity of the thorium metal produced by this process

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\(^1\)This report is based on an M.S. thesis submitted by Donald J. Sundquist to Iowa State University, Ames, Iowa, July, 1964.
depends primarily on the purity of the thorium tetrachloride. Cuthbert\textsuperscript{2} has reviewed the methods of producing thorium tetrachloride and has indicated that the chlorination of thorium oxide is the most feasible method for production of large quantities. For example, Peterson \textit{et al.}\textsuperscript{3} have used the reaction of chlorine with thorium oxide - carbon mixtures to produce large quantities of thorium tetrachloride. The advantages of this reaction were the high rate of reaction and ready availability of the reactants. However, subsequent purification of the product was necessary because it was impossible to balance the carbon and thorium oxide compositions to arrive at a carbon free product. The non-volatility of carbon and thorium oxide enabled the thorium tetrachloride to be separated by sublimation. The reaction was found to be very slow at 575°C and a temperature of 600°C was necessary to obtain a satisfactory rate of reaction. At 600°C, thorium tetrachloride has a significant vapor pressure and volatilization and subsequent condensation of thorium tetrachloride produced a sintered product. At temperatures above 600°C, the charge sintered rapidly into a solid mass which was not sufficiently porous to permit complete conversion. Chlorine corrosion of Inconel, the only metal found suitable as a construction material, was significant at 600°C and became severe at slightly higher temperatures. The high enthalpy of reaction made overheating of the reaction charge a constant problem.

In 1901, Matignon and Delépine\textsuperscript{4} reported that phosgene, COCl\textsubscript{2}, would react with thorium oxide to produce thorium tetrachloride. The
The purpose of this research was to study the reaction of phosgene with thorium oxide as a method of producing pure thorium tetrachloride. This was accomplished by studying the equilibria and kinetics of the reaction. The equilibrium study established the completeness of reaction from the standpoint of phosgene utilization. The results of the kinetic study would permit the design of a suitable reactor and prediction of the optimum operating conditions of the reactor.

The reaction of phosgene with thorium oxide proceeds by the formation of thorium oxychloride, \( \text{ThOCl}_2 \), and the reaction of this compound to form thorium tetrachloride. The existence of thorium oxychloride had been reported by several investigators and was confirmed by Novikov et al.\(^5\) in 1963.

The overall reaction can be represented by the following equations:

\[
\text{ThO}_2(s) + \text{COCl}_2(g) \rightleftharpoons \text{ThOCl}_2(s) + \text{CO}_2(g) \quad (1)
\]

and

\[
\text{ThOCl}_2(s) + \text{COCl}_2(g) \rightleftharpoons \text{ThCl}_4(s) + \text{CO}_2(g) \quad (2)
\]

When two solid phases are present, the equilibrium constants are

\[
K_1 = \frac{P_{\text{CO}_2}}{P_{\text{COCl}_2}}
\]
and

$$K_2 = \frac{P_{CO_2}}{P_{PCCl_2}},$$

where $K_1$ and $K_2$ are the equilibrium constants for the first and second reactions respectively and $p$ is the partial pressure of each component in the equilibrium gas.

Equilibria in the reaction of phosgene with thorium oxide is made slightly more complicated by the dissociation of phosgene at elevated temperatures. Bodenstien \(^6\) has reported that at 600°C phosgene is 91% dissociated. Therefore, the following reaction also takes place during the reaction of phosgene with thorium oxide:

$$CO + Cl_2 \rightleftharpoons COCl_2.$$  \hspace{1cm} (3)

The equilibrium constant for this reaction would be

$$K_3 = \frac{P_{COCl_2}}{P_{CO}P_{Cl_2}}.$$

Consequently, $K_1$ and $K_2$ can be expressed as

$$K_1 = \frac{P_{CO_2}}{K_3P_{CO}P_{Cl_2}},$$

and

$$K_2 = \frac{P_{CO_2}}{K_3P_{CO}P_{Cl_2}}.$$
The partial pressure of carbon monoxide and chlorine are equal and the composition of the gas can be determined by analyzing for chlorine and phosgene.

The equilibrium constants for the reaction of phosgene with thorium oxide were determined by passing phosgene through a bed of thorium oxide and determining the composition of the gas leaving the bed. If the phosgene flow rate is sufficiently small, the gas leaving the bed should have the equilibrium composition set by the phases present at the top of the bed.

The study of the kinetics of heterogeneous reactions can be quite complex. In addition to the chemical reaction-rate kinetics, the kinetic behavior of several physical steps must be considered. The activity of a given component in a phase remains constant as long as that phase is present so that the free energy of reaction, the driving force, may not change as the reaction proceeds. However, the rate at which the reaction proceeds will usually depend on the amount and state of aggregation of the condensed reactant and product phases. The steps in the reaction of a gas with a bed of solid particles are the following:

1. Diffusion of the gaseous reactant into the bed of particles and into each particle.
2. Absorption of the gaseous reactant at the reaction site.
3. Chemical reaction at the site.
5. Diffusion of gaseous products from the reaction site to the bulk gas stream.
Often one of these steps is the rate controlling step of the reaction and information about this step aids in the formulation of a mathematical description of the kinetics of the reaction.

A mathematical description of the kinetic behavior of a reaction greatly simplifies the problem of designing a reactor in which to perform the reaction. An empirical analytical expression could fit the kinetic data but have a somewhat limited value in that it would provide no information concerning the effect of the amount or state of aggregation of the solid phases on the rate of reaction. A more satisfactory description can sometimes be obtained by selecting a physical model that closely represents the actual reaction mechanism and developing a mathematical expression from the model. The resulting expression permits the effect of various parameters on the rate of reaction to be predicted but does not always establish the correct rate controlling step of the reaction.

In many cases a simple model does not represent the actual physical phenomena and a more complex model must be used. Unfortunately, this usually results in a rate law which involves mathematical difficulties and which includes parameters which cannot easily be measured by independent means. For example, if the rate controlling step is associated with some geometric property of irregularly shaped particles of an unknown size distribution, an exact mathematical description of the rate is not possible. Also, the rate controlling step can change as the reaction proceeds. All of these factors were present in the reaction of phosgene with thorium oxide and, although a rate expression could not be formulated, the kinetic
study was valuable in determining the optimum conditions for producing thorium tetrachloride.

EQUILIBRIUM STUDY

Apparatus and Experimental Procedure

The apparatus used to study the equilibria consisted of a reactor and a gas analyzing system. The apparatus is represented schematically in Fig. 1. Approximately 50 g of thorium oxide, prepared by calcining thorium oxalate at 316°C, were introduced into the reactor. A carbon diffusion plate was fixed in place to support the sample and the tapered joint at the bottom was sealed with Apiezon W wax. The loaded reactor was placed in the furnace and heated to 600°C. As the temperature increased, a significant amount of water vapor was evolved which was allowed to escape through the top of the reactor. When the evolution of water vapor stopped, the tube at the top of the reactor was sealed in place with Apiezon W wax. The flow of phosgene was started and the samples of the exit gas were taken at 5 to 15 min intervals for 3 to 4 h. The samples were obtained by withdrawing a known volume of gas with a syringe and forcing the gas through a potassium iodide solution and then through a sodium hydroxide solution.

The chlorine in the gas sample reacted with iodide ion to form free iodine. The chlorine content was determined by titrating the iodine with sodium thiosulfate. The phosgene reacted with the sodium hydroxide
Fig. 1. Equilibrium study apparatus.
solution to form sodium chloride and sodium carbonate. The amount of phosgene was determined by titrating the chloride ion with silver nitrate solution using an absorption indicator. Analysis of samples of known composition indicated that the partial pressure of each component in the gas could be determined within 0.02 - 0.04 atm.

Results and Discussion

The equilibria in the chlorination of thorium oxide with phosgene were studied at 600°C. The gas leaving the reactor bed was sampled and analyzed at 5 to 15 min intervals as the reaction proceeded. If equilibrium were established in the bed, as should be the case at sufficiently slow flow rates, this gas should have the equilibrium composition corresponding to the solid phases in the top section of the bed. The composition of the gas leaving the bed initially should be that corresponding to equilibrium with thorium oxide and thorium oxychloride. The partial pressures of phosgene and chlorine in the exit gas from the reaction bed during the initial stages of the reaction decreased as the phosgene flow rate was decreased. At flow rates less than 5 cc/min, phosgene and chlorine could not be detected until a considerable fraction of the bed had been converted to thorium tetrachloride. This established that the equilibrium constant for the thorium oxychloride formation reaction was greater than 5 x 10^3. This large equilibrium constant would allow nearly 100% utilization of phosgene in a properly designed reactor.
As the reaction proceeded, a sharply defined yellow band moved up the reaction bed. This band was first believed to correspond to the thorium oxychloride phase. However, determination of the chloride content as a function of bed depth indicated that the chloride content of this yellow band did not correspond to the composition of thorium oxychloride. Indeed, a region of constant chloride content did not exist in the bed. The results of one such analysis are presented in Fig. 2. The yellow band was probably due to the chlorination of iron oxide impurities in the thorium oxide.

If equilibrium were established in a short length of the bed, the width of the thorium oxychloride band would depend on the completeness with which phosgene could react with thorium oxychloride to form thorium tetrachloride. If the equilibrium constant for this latter reaction were large, very little phosgene would be left unconsumed to react with thorium oxide and develop a thick band of thorium oxychloride. The fact that a region of thorium oxychloride did not exist in the reaction mixture indicated the equilibrium constant for the reaction of phosgene with thorium oxychloride was equal to or greater than unity.

From the thermodynamic data of Coughlin\textsuperscript{9} and Hamer \textit{et al.}\textsuperscript{10} the standard free energy change for the overall reaction was calculated to be $-77.0$ kcal. The standard free energy of formation of thorium oxychloride is not known. If the equilibrium constant for the individual reactions are nearly equal, the standard free energy change for the individual reactions will also be equal and the equilibrium constants would both be greater than $5 \times 10^9$. 

Fig. 2. Chloride content as a function of bed depth.
The small phosgene flow rates required to approach equilibrium in the reaction bed and the incomplete conversion of the bed to thorium tetrachloride indicated that the kinetics of the reaction were slow. Information about the kinetics of the reaction would be required to design a reactor in which an efficient utilization of phosgene and a high conversion of thorium oxide to thorium tetrachloride could be obtained.

KINETIC STUDY

Apparatus and Experimental Procedure

A thermobalance, represented schematically in Fig. 3, was used to measure the rate of reaction of phosgene with the thorium oxide bed. A magnetically dampened analytical balance with a projected scale permitted the weight on the pan to be read directly within 0.1 mg. Class S metric weights were used. The phosgene flow past the reaction pan did not change the balance reading in the range of flow rates used in the kinetic experiments. The force produced by the exhaust duct did change the rest point of the balance, but the force was constant and did not affect the change-in-weight measurements.

A known amount of thorium oxide was placed in the Vycor reactor pan and the pan was placed in the reactor. Alignment of the balance and reactor was checked to insure that the sample was freely suspended in the reactor. The Vycor pan, thorium oxide and Inconel rod were counterbalanced and the weight recorded. The temperature of the reactor was increased to the desired value and the weight again recorded. The sample
Fig. 3. Kinetic study apparatus.
decreased in weight by approximately 3% on heating to the reaction temperature. This weight loss was assumed to be due to water absorbed on the thorium oxide.

Phosgene was introduced at a flow rate of 100 cc/min. This flow rate was approximately eight times the rate of consumption of phosgene during the initial part of the reaction. Consequently, an atmosphere of nearly pure phosgene was maintained above the reaction bed. The weight of the reaction pan was recorded at 5 to 30 min intervals. At the completion of each run, the entire system was swept with nitrogen to remove the excess phosgene. From the initial weight of thorium oxide placed in the reaction pan, the weight increase corresponding to complete conversion to thorium tetrachloride was calculated. The fractional conversion was calculated by dividing the observed weight increase by the expected weight increase.

Results and Discussion

The initial rate of reaction was rapid and 50% conversion was achieved at 500°C in approximately 30 min. However, the rate of reaction decreased in increasing conversion and became very slow at 80-90% conversion. Obviously some factor was limiting the rate of reaction.

In the range of bed depths investigated, diffusion of phosgene into the bed of thorium oxide was not the rate controlling step of the reaction. This was established by observing the rate of reaction of a bed of particles 1 cm deep and of a bed consisting of only one layer of particles.
The particle size of the thorium oxide was 35/40 U. S. Standard Sieve and the reaction temperature was 500°C. The results are presented graphically in Fig. 4. Although the depth of the bed was changed by a factor of approximately 20, the percent conversion vs time curves were not significantly different. The small difference was probably due to a small phosgene concentration gradient in the thicker bed.

The area through which the phosgene diffused was constant in both cases; and the flux, at equal times, into the bed should have been the same if the conditions leading to the parabolic rate law had been fulfilled. This would have resulted in equal phosgene mass flow rates into the beds and complete conversion of the bed that was only one particle layer thick in the same time that the thicker bed was one twentieth converted. The fact that the conversion rates were nearly the same for two reaction beds differing so much in thickness eliminated diffusion of reactants or products into or out of the bed as rate controlling steps.

The effect of particle size on the rate of reaction was established to determine if the rate of diffusion of phosgene into the thorium particles was the rate controlling step. The rate of reaction of equal amounts of 35/40 and 230/325 U. S. Standard Sieve thorium oxide with phosgene was observed at 500°C. The results are presented in Fig. 5. The initial rate of the reaction was not changed by decreasing the size of the particles by a factor of ten. Consequently, a rate law based on diffusion into the particles or a rate law based on the external surface area of the particles is not valid for the thorium oxide - phosgene reaction.
Fig. 4. Effect of bed depth on the rate of reaction.
Fig. 5. Effect of particle size on the rate of reaction.
The rate controlling process was not diffusion into the bed nor into the particles and, hence, it must be associated with some process within the thorium oxide particles. The decrease of the rapid initial reaction rate to nearly zero before complete conversion to thorium tetrachloride also was puzzling. To gain information about these problems as well as explain the negligible resistance to diffusion into the bed and into the particles, the packing array of the bed of particles and the structure of the particles were studied by optical microscopy, bulk density measurements, electron microscopy and x-ray diffraction analysis. The thorium oxide was observed by optical microscopy to consist of irregularly shaped particles in the size range of 50 - 500 µ depending on the sieve size of the thorium oxide. The bulk density of thorium oxide, determined by weighing a known volume of the particles, was 1.84 g/cc for the 35/40 U. S. Standard Sieve particles and 1.37 g/cc for the particles less than 325 U. S. Standard Sieve. Zachariasen has reported the density of thorium oxide as 11.39 g/cc. From these values the void fraction of the bed was calculated to be 0.82 - 0.88. The unusually large void fraction helped explain the negligible resistance to diffusion in the bed.

The extremely large void volume of the bed indicated that the particles must be porous. The void fraction in the most inefficiently packed bed of spherical particles in contact with one another would be approximately 0.5. This is the ratio of the volume of a sphere to the volume of a cube that encloses it. The void fraction of the particles must, therefore, be greater than 0.64 - 0.76.
Electron photomicrographs showed that the thorium oxide particles were comprised of small crystallites. An electron photomicrograph at a magnification of 7000 is presented in Fig. 6. The electron photomicrograph showed crystallites in the size range of approximately 0.05 to 0.1 μ and particles 3 to 6 μ in diameter which were porous aggregates of the small crystallites. Optical microscopy studies showed that the surface of the 50 - 500 μ particles was continuous, so the 3 to 6 μ aggregates were probably fragments of the larger particles.

X-ray diffraction patterns were obtained of the thorium oxide particles. From the broadening of the diffraction lines, the size of the crystallites was calculated to be approximately 200 Å. The x-ray diffraction line broadening would measure the size of the smallest crystallities in the sample, so the crystallites shown on the electron photomicrograph are probably the same as these indicated by the line broadening. The fact that the particles were porous and consisted of small crystallites helped explain the negligible effect of particle size on the rate of reaction.

Several observations indicated that the rate controlling step of the reaction changed as the reaction proceeded. For example, the rate of the reaction decreased rapidly beyond 55 - 65% conversion. Also, although the size of the particles did not affect the initial rate of reaction, the final rate was influenced by the size of the particles and a higher conversion was obtained with the smaller particles. This observation was illustrated previously in Fig. 5.
Fig. 6. Electron photomicrograph at a magnification of 7000 illustrating the small crystallites in the thorium oxide particles.
Mooney\textsuperscript{12} has reported the density of thorium tetrachloride to be 4.60 g/cc. As thorium oxide is converted to thorium tetrachloride, a decrease in density occurs as well as an increase in mass. The combined effect of changing the density and mass means that a solid particle of thorium oxide, when converted to thorium tetrachloride, must increase in volume by a factor of approximately 3.5. This increase is approximately the volume increase required to completely fill the void space of the porous particles of thorium oxide.

Individual particles of thorium oxide were photographed before and after exposure to phosgene at 500°C for 4 h. The size of the particles did not increase significantly so the volume increase accompanying the reaction must have occurred by filling the void space of each particle. This observation was supported by the fact that the bed did not expand during the reaction and was still a very loosely sintered mass of particles. Examination of reaction bed 86% converted to thorium tetrachloride showed solid appearing crystals of thorium tetrachloride of about the same size as the initial thorium oxide particles. These thorium tetrachloride crystals had some well developed crystal faces and a few were colorless transparent crystals. This change in the physical structure of the particles probably changed the rate controlling step of the reaction. Initially, the resistance to diffusion into or out of the particles was negligible and the rate of reaction was limited by the surface area of thorium oxide or oxychloride. At high conversions the rate controlling step was probably solid state diffusion of oxygen from dispersed thorium oxide or thorium
oxychloride crystallites to the surface of the thorium tetrachloride crystals. Information supporting this mechanism was obtained from x-ray diffraction patterns of a sample 85% converted to thorium tetrachloride which showed the presence of thorium oxychloride. Also, by grinding the highly converted product in an inert gas glove box and thus exposing more of the thorium oxide or thorium oxychloride crystallites, the rate of reaction of the sample increased significantly.

Beckett and Winfield\textsuperscript{13} have reported that the reactivity of thorium oxide depends on the temperature at which thorium oxalate is calcined to the oxide. To study this phenomenon, samples of thorium oxide were prepared by thermal decomposition of thorium oxalate at 316, 600 and 900°C. The resulting oxides, which were less than 325 U.S. Standard Sieve size were chlorinated with phosgene at 500°C. The rate of reaction data are presented in Fig. 7. A significant decrease in the initial rate of reaction was observed as the temperature of calcination was increased. The bulk densities of the oxides were also found to depend on the temperature at which the oxalate was decomposed. The bulk densities were 1.37, 1.56 and 2.09 g/cc for oxides prepared at 316, 600 and 900°C respectively. The void space in the low fired oxide particles was, therefore, greater than the void space in the high fired oxide particles. X-ray diffraction patterns obtained for each form of the thorium oxide powder indicated that the crystallites in the high fired oxide were larger than the crystallites in the low fired oxide. An increase in crystallite size would decrease the surface area. The effect of the decreased surface area could explain the lower initial rate of reaction observed with the high fired oxide.
Fig. 7. Effect of thorium oxalate decomposition temperature on the rate of reaction.
The effect of temperature on the rate of reaction was established by observing the rates of reaction of 35/40 U.S. Standard Sieve thorium oxide at 550, 500, 450 and 350°C. The results are presented in Fig. 8. At temperatures above 550°C the sublimation of thorium tetrachloride from the reaction pan was significant and accurate rate data at high conversion could not be obtained. However, the initial reaction rate at 600°C was the same as at 550°C. At 200°C temperature increase was required to increase the rate of reaction by a factor of two. The temperature dependence of this reaction rate is much smaller than that usually found for chemical reactions involving molecules or for reactions in which solid state diffusion is the rate controlling step. Chemical reactions of absorbed molecules on a surface often show a small temperature dependence because the increased rate of reaction at higher temperatures is partially compensated by a decreased surface concentration. This may be the explanation for the small temperature coefficient of the initial rate of this reaction. The small temperature dependence of the reaction rate has several valuable benefits. The reaction could be carried out at temperatures where the volatilization and condensation of thorium tetrachloride is negligible. This would result in less sintering of the charge and less difficulty in removing the product. Also, the problem of overheating and sintering of the reaction charge would be minimized at lower reaction temperatures. At temperatures below 550°C, the attack on Inconel is negligible and the deterioration of a reactor and contamination of the charge would be lessened.
Fig. 8. Effect of temperature on the rate of reaction.
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