The Effect of Temperature on the Kinetic Parameters of TeF₆ Production

P. Zaheri*, A. Charkhi, I. Dehghan

Nuclear Fuel Cycle Research School, Nuclear Science and Technology Research Institute, P.O. Box: 11365-8486, Tehran, Iran.

(Received: 13 November 2023, Revised: 27 January 2024, Accepted: 21 February 2024)

A B S T R A C T
This study examined the kinetics of the reaction between tellurium oxide (TeO₂) and fluorine gas (F₂) to produce tellurium hexafluoride gas (TeF₆). This investigation was conducted between 150 and 250 °C and between 1 and 2 bar of pressure. To achieve this, a volumetric method was utilized for the design and construction of a laboratory system. The supply of feed gases, the fluorination reactor, and the collection and removal of the unreacted gases constitute the three primary components of this laboratory system. To obtain the kinetic parameters, the Arrhenius form of the reaction rate was used. The results obtained indicate that the fluorination reaction of tellurium oxide is a first-order reaction between 150 and 200 °C and a second-order reaction at 250 °C. The AARE values were calculated as 0.57% and 0.46%, respectively, which indicates the excellent capability of kinetic models to predict the reaction kinetics of TeF₆ gas production.

Keywords: Volumetric method, Fluorination, TeF₆, Kinetic study.

1. Introductions
Tellurium isotopes have many applications in the field of medicine, so their enrichment is of great importance. For example, iodine radionuclides were produced using different tellurium isotopes, which are useful in the treatment of hyperthyroidism thyroid cancers, kits necessary for the treatment and diagnosis of adrenal cancer, and so on [1]. The TeF₆ gas is required for the enrichment of these isotopes [2]. Since the production of this gas requires the reaction kinetics data to design and construct a reactor system, it is necessary to determine the kinetic parameters of TeF₆ production. Stated differently, reaction kinetics are necessary to apply laboratory-scale research to large-scale reactors [3].

The interaction between F₂ gas and TeO₂ represents a pathway for the generation of TeF₆. In this type of solid-gas reaction, the solid material is formed into a pellet and
subsequently exposed to the gas at predetermined temperature and pressure conditions. The resulting reaction yields either a gaseous product, as seen in TeF₆ production, or a solid product, exemplified by the desulfurization of sulfides [4].

To date, the majority of published studies in this field have concentrated on reactions yielding solid products, such as metal oxidation processes. Limited data is available on reactions generating gaseous products, including the fluorination reaction of tellurium, molybdenum, and similar elements [5]. The following two groups of techniques can be determined to ascertain the kinetic parameters of gas-solid reactions:

1. Recording of changes in the solid phase
2. Recording of changes in the gas phase

In the first method, the continuous measurement of the weight of the solid phase is employed, which is known as the gravimetric method. This method stands as the most prevalent technique utilized in the investigation of heterogeneous solid-gas reactions [6]. For example, Labaton et al. studied the reaction between uranium tetrafluoride and fluorine gas by measuring the weight changes of the solid phase [7]. Additionally, Barbour et al. developed a controlled atmosphere system to examine the kinetics of gas-solid reactions [8]. Furthermore, the kinetic of zinc oxide reduction, CaO carbonation, and CO₂ adsorption on a solid amine sorbent were also investigated using the gravimetric method [9-11].

In the second method, gas pressure changes are measured to determine kinetic parameters, known as volumetric method [4]. This method is based on gas expansion between a reference volume and the reactor chamber (containing the solid sample). First, the gas pressure in the reference volume is set at a specific value. Then, the valve is opened, and after reaching a certain pressure in the reactor, the valve is closed. When the reaction starts, the pressure changes in the reactor chamber are recorded over time.

In this method, ensuring the system is sealed is very important. Therefore, before starting the operation, the system must be checked carefully for leaks. Additionally, before beginning the reaction, the temperature of the reactor chamber must be set at a specific value. The attractive features of the volumetric method is its simplicity, stability, and relatively low cost [12].

Since working with F₂ gas and its compounds is very dangerous, to study the kinetics of these reactions, it is necessary to use methods that eliminate exposure to F₂ gas. Therefore, in this research, a laboratory system based on the volumetric method was designed and built. The kinetic study of the reaction for the production of TeF₆ was conducted using this system. One method for producing TeF₆ is the reaction between TeO₂ and F₂ gas at 150 to 300 °C, as follows [13]:

\[
\text{TeO}_2 + 3\text{F}_2 / N_2 \rightarrow \text{TeF}_6 + O_2 + N_2
\]

As reported by R. Campbell and P.L. Robinson, if this reaction occurs at 150 and 250 °C, the main product will be TeF₆ [13].

So far, no data about the kinetic of this reaction has been reported.

2. Experimental

2.1. Materials

TeO₂ and sodium fluoride (NaF) were purchased from Sigma Aldrich. The chemical properties of these compounds were presented in our previous work [18]. A water-free, and laboratory-grade mixture of F₂ and N₂ gas (40% fluorine) was provided by Sooreh Company in Iran.

2.2. Apparatus and methods

A laboratory system was designed and constructed based on the volumetric method to study the kinetics of solid-gas reactions (Fig. 1). This system consists of three main parts:
1. Supply of feed gases (N$_2$ and a mixture of N$_2$ / F$_2$)  
2. Fluorination reactor  
3. Collection of the product and removal of unreacted gases

Based on the F$_2$ gas compatibility table, temperature, and pressure range, all equipment, such as valves, pipes, pressure transmitters, and connections, etc., were selected from stainless steel 316 material [14].

Before the installation and commissioning of the system, all valves, pipes, fittings, and equipment were cleaned with acid and detergent, and then thoroughly dried [15]. After that, the system equipment was installed, and all connections were carefully checked for leaks to ensure the system maintained stable pressure in the absence of any reaction. In the next step, passivation was carried out step by step by increasing the pressure of F$_2$ gas, allowing a film of metal fluoride to develop on the stainless steel 316 surface and thus preventing any further corrosion [14].

2.2.1. Supply of feed gases

The mixture of N$_2$/F$_2$ gas was passed through a packed column containing NaF granules to absorb any possible moisture and HF in the gas before entering the reactor [7]. The N$_2$ gas capsule was also used for purging the remaining F$_2$ gas from the system.

2.2.2. Fluorination reactor

The fluorination reactor was made of a stainless steel 316 tube with a diameter of 1 inch and a length of 11 inches. The reactor temperature was raised to the desired level by a heater. To increase the contact between the gas and the solid sample and minimize the mass transfer resistance, the heater was installed in the lower part of the reactor where the TeO$_2$ was placed. This ensures that, the heated gas in the lower part of the reactor is regularly replaced with the cold gas in the upper part of the reactor, promoting gas mixing.

2.2.3. Collecting the product and removing the unreacted gases

The product of the fluorination reaction was collected using a cold trap in the exhaust gas flow path. Subsequently, a dry scrubber filled with activated alumina, and a wet scrubber containing NaOH solution were used to remove the unreacted gases [16].

![Fig. 1. The schematic of the laboratory system.](image-url)
2.2.4. Calculating the volume of the reactor

Since the volumetric method is based on the volume and pressure of the reactor, determining the exact volume of the reactor, including the volume of the reaction chamber, the volume of the terminal, and its connections (including valves and pressure transmitter), is essential. This work was carried out by following the steps outlined (Fig. 2):

**Step 1:**
First, N\textsubscript{2} gas at a certain pressure entered chamber V\textsubscript{1} by opening valve 5. Then, valve 7 opened, and the gas expanded to fill the entire volume (V\textsubscript{3}, V\textsubscript{2}, and V\textsubscript{1}). The pressure indicated (P\textsubscript{1}) was recorded. Afterward, valve 7 was closed, and the reactor chamber (V\textsubscript{1} and V\textsubscript{2}) was evacuated. Valve 7 was then opened, allowing the remaining gas in chamber V\textsubscript{3} to expand throughout the entire volume again. The indicated pressure (P\textsubscript{2}) was recorded. This process was repeated for up to 10 times.

**Step 2:**
In this step, a piece of metal with a specific volume (V) was placed inside the reactor, and the procedure of step 1 was repeated. Then, using the ideal gas law, the following relations were solved simultaneously. Finally, the total volume of the reactor was calculated to be 140.62 mL.

\[ P_1 V_1 = P_2 (V_1 + V_2 + V_3) \]  \hspace{1cm} (2)

\[ P_2 V_1 = P_3 (V_2 + V_2 + (V_3 - V)) \]  \hspace{1cm} (3)

2.2.5. A sample runs

First, TeO\textsubscript{2} fine powder was weighed and pressed to form a pellet with a uniform cross-section. Then, TG analysis was performed to ensure that the weight change of the pellet is insignificant in the temperature range of 150 to 250 °C. After that, the pellet was placed inside the fluorination reactor and degassed under vacuum conditions at a temperature of 150°C. The degassed pellet was weighed again and quickly placed in the reactor. The system was washed several times with N\textsubscript{2} gas and then evacuated. After that, a mixture of N\textsubscript{2}/F\textsubscript{2} gas (40% F\textsubscript{2}) was passed through the NaF column and directed into the reactor (including a TeO\textsubscript{2} pellet) until a certain pressure. From this moment, the reactor pressure started to decrease, which indicates the start of the reaction and gas consumption. The changes in
the reactor pressure was measured by a diaphragm-type pressure transmitter (-1 to +1 barg, accuracy of 0.25% of full scale) and recorded in computer memory every half second. After a certain time, the pressure changes inside the reactor reaching zero, which indicates the end of the reaction. At this time, the gas inside the reactor was discharged and collected in the cold trap. The unreacted gas was then swept into a dry scrubber containing activated alumina and a wet scrubber containing NaOH solution before being ventilated. After complete purging of N₂ gas in the system, the TeO₂ pellet is removed from the reactor and its weight was measured.

2.3. Kinetic equations

TeO₂ reacts with three moles of F₂ gas to produce one mole of TeF₆ gas. If n₀ is the initial mole of feed (40% F₂ and 60% N₂) and m is the molar amount of TeF₆ at time t, according to the reaction stoichiometry, the following molar balance obtains:

$$n₀ - 3m = 0.6n₀$$

The molar amount of various components in the reactor at time t is written as follows:

$$n_T = n₀ - m$$

$$n_{TeF₆} = n₀ - n_T$$

$$n_{F₂} = 0.4n₀ - 3(n₀ - n_T) = 3n_T - 2.6n₀$$

Since the reactor is composed of three chambers with different temperatures (as shown in Fig. 3), the temperatures of all three zones were carefully measured during the tests during the tests and considered in the calculations.

The production rate of TeF₆ gas at a given temperature can be written as [17]:

$$\frac{1}{w} \frac{dn_{TeF₆}}{dt} = kC_{F₂}^n$$

By assuming the ideal gas law and using Eqs. 4 and 6:

$$n_T = \frac{p_T}{R} \left( \frac{V₁}{T₁} + \frac{V₂}{T₂} + \frac{V₃}{T₃} \right)$$

$$n_{F₂} = \frac{1}{R} \left( \frac{V₁}{T₁} + \frac{V₂}{T₂} + \frac{V₃}{T₃} \right) (3P_T - 2.6P₀)$$

To determine the degree of reaction, the left-hand side of Eq. 9 is plotted against the right-hand side within the bracket. The slope of the line represents the degree of reaction (n), and the intercept represents the logarithm of the rate constant (k). The Arrhenius form of the
reaction rate to propose a correlation for the reaction rate in terms of temperature, as follows [17]:

\[ k = k_0 e^{-\frac{E}{RT}} \]  

(10)

E is the reaction activation energy.

3. Results and discussion

3.1. Calibration

As sealing the system in the volumetric method is essential, the leakage of the system was determined by injecting F₂ gas into the reactor without any reactant (TeO₂ pellet) under reaction conditions. The changes in reactor pressure were recorded each time. According to the obtained results, which were presented in our previous work [18], the leakage rate of gas was approximately 0.6 Pa/s. This amount of leakage was considered in the calculation of kinetic parameters.

The TG analysis of TeO₂ pellet was reported in Fig. 4. The result shows that in the temperature range required for the production of TeF₆ (150 to 250 °C), the weight change of TeO₂ pellet is insignificant.

3.2. Kinetics of reaction

To measure the kinetics of TeF₆ production, the reaction temperature was selected between 150 and 250 °C. The TeF₆ product has high purity within this temperature range [13]. First, using the experimental data, the kinetic parameters were calculated by Eq. 9. Then, these parameters were fitted with Eq. 10 to derive a correlation for the reaction rate. The results indicate that the data in the temperature range of 150 to 200 °C can be fitted by a kinetic equation, while the data at 250 °C are not well predicted, while the data at 250 °C are not well predicted. The reason could be a change in the reaction mechanism at higher temperatures. Accordingly, two kinetic equations were presented: one for the temperature range of 150 to 200 °C and the other for the temperature of 250 °C (Table 1). The results of data fitting with the proposed models are also presented in Figs 5. and 6. According to these Figs. and the AARE values, it is clear that the kinetic models have the ability to predict the kinetics of the reaction.

![Fig. 4. The TG analysis of TeO₂ pellet.](image)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Order of reaction (n)</th>
<th>Rate constant (k) (mol·m⁻³)⁻¹·s⁻¹·g⁻¹</th>
<th>Activation energy (E) (j/mol)</th>
<th>AARE (%)²</th>
</tr>
</thead>
<tbody>
<tr>
<td>150-200</td>
<td>1</td>
<td>2.76×10⁻⁶</td>
<td>123478</td>
<td>0.57</td>
</tr>
<tr>
<td>150-200</td>
<td>1.09</td>
<td>3.59×10⁻⁶</td>
<td>14046.4</td>
<td>0.55</td>
</tr>
<tr>
<td>250</td>
<td>2</td>
<td>1.18×10⁻⁸</td>
<td></td>
<td>0.46</td>
</tr>
</tbody>
</table>

1 \( \frac{dn_{TeF_6}}{dt} = k_0 e^{-\frac{E}{RT}} C_{F_2} \)

\[ [C_{F_2}] = \frac{mol}{m^3} \]

2 \( \text{AARE} (%) = \frac{\sum_{i=1}^{n} |Exp_i - Cal_i|}{\sum_{i=1}^{n} Exp_i} \)
4. Conclusions

In this study, a volumetric method was used to derive the kinetics of TeF$_6$ production by the reaction of TeO$_2$ and F$_2$ gas. After calibrating the system, F$_2$ gas was introduced into the reactor, containing a TeO$_2$ pellet, at different initial pressures (1 to 2 bar) and temperatures (150 to 250 °C). Upon starting the reaction, pressure changes in the reactor were measured using a pressure transmitter at different times and recorded in a computer system. The obtained data were fitted to the Arrhenius form of the reaction rate. The results showed that the reaction kinetics are first-order for the temperature range of 150 to 200 °C and second-order at 250 °C. The rate constant values were calculated to be 2.76×10$^{-6}$ m$^3$g$^{-1}$s$^{-1}$ and 1.18×10$^{-8}$ (m$^3$)molg$^{-1}$s$^{-1}$, respectively. To evaluate the accuracy of the proposed models, the AARE values were calculated to be 0.57 and 0.46%, respectively indicating the excellent ability of the kinetic models to predict the reaction kinetics of TeF$_6$ production.

5. Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>Pressure (Pa)</td>
</tr>
<tr>
<td>V</td>
<td>Volume (m$^3$)</td>
</tr>
<tr>
<td>T</td>
<td>Temperature (K)</td>
</tr>
<tr>
<td>R</td>
<td>Ideal gas constant (m$^3$·Pa·K$^{-1}$·mol$^{-1}$)</td>
</tr>
<tr>
<td>t</td>
<td>Time (sec)</td>
</tr>
<tr>
<td>C</td>
<td>Concentration (mol/m$^3$)</td>
</tr>
<tr>
<td>E</td>
<td>Activation energy (J/mol)</td>
</tr>
<tr>
<td>K</td>
<td>Reaction rate constant ((mol)$^{1-n}$·(m$^3$)$^n$·s$^{-1}$·g$^{-1}$)</td>
</tr>
<tr>
<td>n</td>
<td>Order of reaction</td>
</tr>
<tr>
<td>w</td>
<td>TeO$_2$ weight (g)</td>
</tr>
<tr>
<td>$n_T$</td>
<td>Total moles at time t</td>
</tr>
<tr>
<td>$n_0$</td>
<td>Initial moles at t=0</td>
</tr>
<tr>
<td>$n_{TeF_6}$</td>
<td>Moles of TeF$_6$ gas</td>
</tr>
<tr>
<td>$n_{F_2}$</td>
<td>Moles of F$_2$ gas</td>
</tr>
</tbody>
</table>

Conflict of interest

The authors declare no potential conflict of interest regarding the publication of this work.

References


