

# The effect of temperature on the kinetic parameters of $\text{TeF}_6$ production

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## Abstract

This study examined the kinetics of the reaction between tellurium oxide ( $\text{TeO}_2$ ) and fluorine gas ( $\text{F}_2$ ) to produce tellurium hexafluoride gas ( $\text{TeF}_6$ ). This investigation was conducted between 150 and 250 °C and between 1 and 2 bar of pressure. To achieve this, a volumetric method was used in 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 make up the three primary components of this laboratory system. To obtain the kinetic parameters, the Arrhenius form of the reaction rate was used. The obtained results showed that the fluorination reaction of tellurium oxide is a first-order reaction between 150 to 200 °C and a second-order reaction at 250 °C. The AARE values were calculated 0.57% and 0.46%, respectively, which indicates the excellent ability of kinetic models to predict the reaction kinetics of  $\text{TeF}_6$  gas production.

**Keywords:** Volumetric method, Fluorination,  $\text{TeF}_6$ , Kinetic study

## 1. Introduction

Tellurium isotopes have many applications in the field of medicine, so enrichment of them 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  $\text{TeF}_6$  gas is required for the enrichment of these isotopes[2]. Since the production of this gas requires the reaction kinetic data to design and construct a reactor system, it is necessary to drive the kinetic parameters of  $\text{TeF}_6$  production. Stated differently, reaction kinetics are necessary to apply lab-scale research to large-scale reactors.[3].

The interaction of  $\text{F}_2$  gas with  $\text{TeO}_2$  is one way to produce  $\text{TeF}_6$ . The solid material is shaped into a pellet in this type of solid-gas reaction, and it is brought into contact with the gas at the predetermined temperature and pressure. The product of the reaction may be gas (such as  $\text{TeF}_6$  production) or solid (such as the desulfurization of sulfides)[4].

So far, most of the published reports in this field have focused on reactions whose product is solid (such as metal oxidation processes). A few data is available regarding the reactions in which a gaseous product is produced, such as the fluorination reaction of tellurium, molybdenum, and so on [5].

The following two groups of techniques can be applied 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 done, which is known as the gravimetric method. This is the most common technique for the study of heterogeneous solid-gas reactions [6]. For example, Labaton et al. studied the reaction of uranium tetrafluoride and fluorine gas by measuring the weight changes of the solid phase [7]. In another work, Barbour et al. designed a system in controlled atmospheres for studying the kinetics of gas-solid reactions [8]. The kinetic of zinc oxide reduction,  $\text{CaO}$  carbonation, and  $\text{CO}_2$  adsorption on a solid amine sorbent were also investigated using the gravimetric method [9-11].

In the second method, measuring gas pressure changes is used to determine kinetic parameters, which is called 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 certain 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 with time. In this method, the sealing of the system is very important. So, before starting the

operation, the leakage of the system must be checked carefully. Also, before starting the reaction, the temperature of the reactor chamber must be set at a certain value. The attractive feature of the volumetric method is its simplicity, stability, and relatively low cost [12].

Since working with F<sub>2</sub> gas and its compounds is very dangerous, to study the kinetics of these reactions, it is necessary to use methods in which the exposure to F<sub>2</sub> gas reaches zero. So, in this research work, a laboratory system based on the volumetric method was designed and built. The kinetic study of the reaction for the production of TeF<sub>6</sub> was done in this system. One of the methods for producing TeF<sub>6</sub> is the reaction between TeO<sub>2</sub> and F<sub>2</sub> gas at 150 to 300 °C as follows [13]:



As reported by R. Campbell and P.L. Robinson, if this reaction occurs at 150 and 250 °C, the main product will be TeF<sub>6</sub> [13].

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

## 2. Experimental

### 2.1. Materials

TeO<sub>2</sub> and sodium fluoride (NaF) were purchased from Sigma Aldrich. The chemical properties of them were presented in our previous work [18]. Water-free and laboratory-grade mixture of F<sub>2</sub> and N<sub>2</sub> gas capsule (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 kinetic of solid-gas reactions (Fig. 1). This system consists of three main parts:

- 1- Supply of feed gases (N<sub>2</sub> and mixture of N<sub>2</sub> / F<sub>2</sub>)
- 2- Fluorination reactor
- 3- Collecting the product and removing the unreacted gases

Based on the  $F_2$  gas compatibility table, temperature, and pressure range, all equipment, such as valves, pipes, pressure transmitter, connections, etc., were selected from stainless steel 316 material [14].

Before 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 the leakage of all connections was checked carefully to ensure the system had stable pressure in the absence of any reaction. In the next step, the passivation was done 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 the possible moisture and HF of the gas before entering the reactor [7].

The  $N_2$  gas capsule was also used for purging the remaining  $F_2$  gas in the system.

### **2.2.2. Fluorination reactor**

The fluorination reactor was made of stainless steel 316 tube with a diameter of 1 in and a length of 11 in. The reactor temperature was raised to the desired temperature 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). Therefore, the heated gas in the lower part of the reactor is regularly replaced with the cold gas in the upper part of the reactor, and a gas mixing occurs.

### **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. In the following, a dry scrubber (filled with activated alumina), and a wet scrubber (containing NaOH solution) were used to remove the unreacted gases [16].

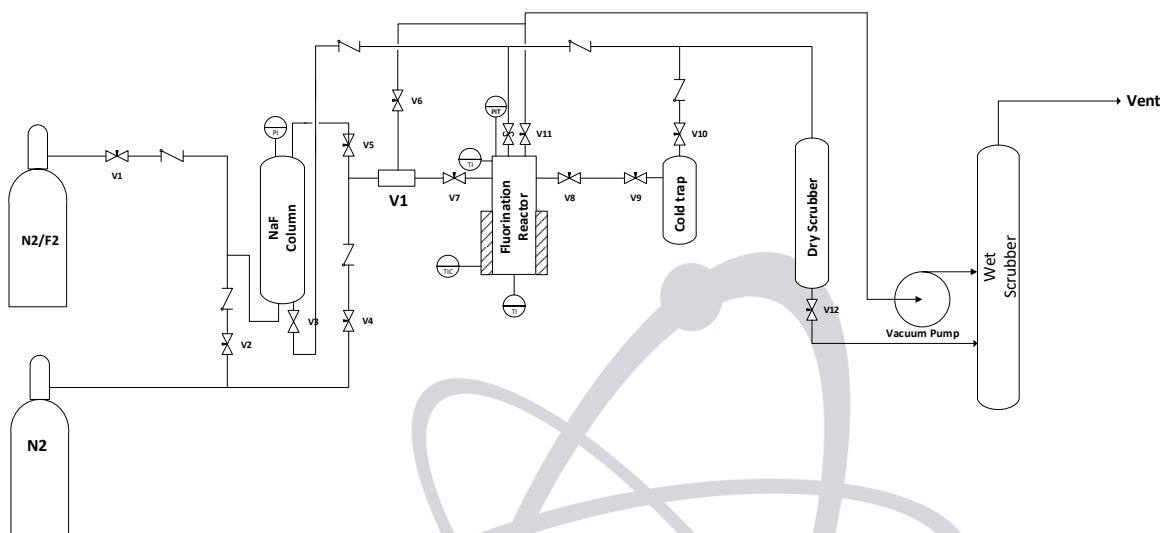


Fig. 1. The schematic of the laboratory system.

#### 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 (the connection of valves and pressure transmitter), is essential. This work was done by following steps (Fig. 2):

Step 1:

First,  $N_2$  gas at a certain pressure entered the chamber  $V_1$  by opening the valve 5. Then, valve 7 opened, and the gas expanded in the entire volume ( $V_3$ ,  $V_2$ , and  $V_1$ ). The indicated pressure ( $P_1$ ) was recorded. After that, valve 7 was closed, and the reactor chamber ( $V_1$  and  $V_2$ ) was evacuated. The valve 7 was opened, and the remaining gas in the chamber  $V_3$  expanded in the entire volume again. The indicated pressure ( $P_2$ ) was recorded. This process was repeated 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.

$$P_1 V_1 = P_2 (V_1 + V_2 + V_3) \quad (2)$$

$$P_2 V_1 = P_3 (V_1 + V_2 + (V_3 - V)) \quad (3)$$

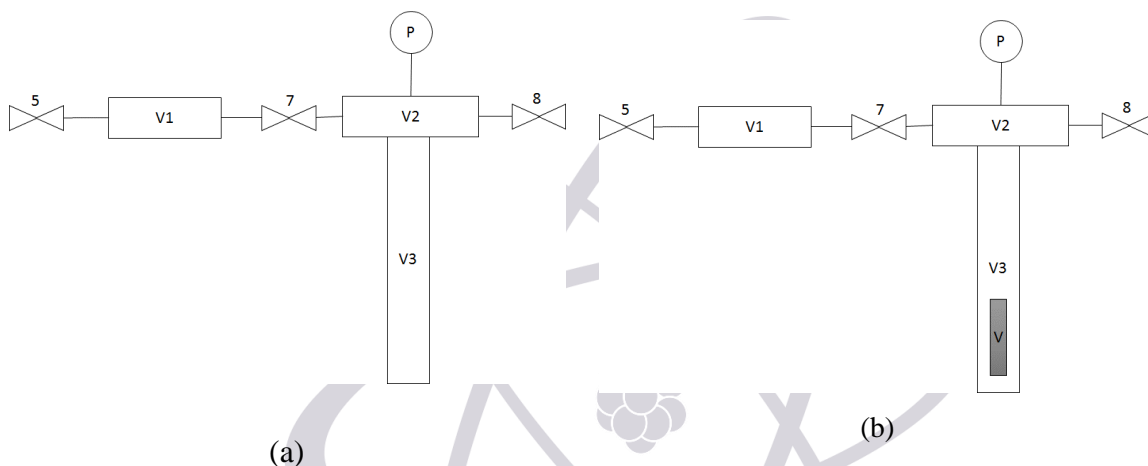


Fig.2. Method for calculating the volume of the reactor, (a) Step 1, (b) Step 2.

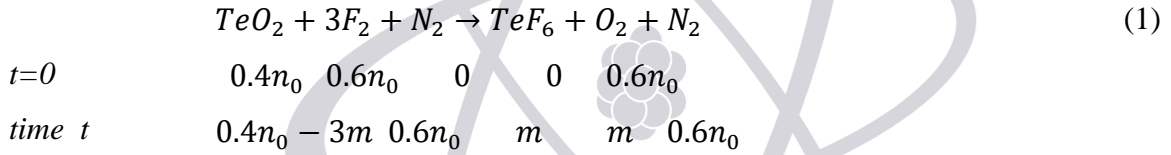
### 2.2.5. A sample run

First,  $\text{TeO}_2$  fine powder was weighed and pressed to form a pellet with a uniform cross-section. Then, TG analysis was performed to make sure 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, and a temperature of 150°C. The degassed pellet was weighed again and quickly placed in the reactor. The system was washed several times with  $\text{N}_2$  gas and then evacuated. After that, a mixture of  $\text{N}_2/\text{F}_2$  gas (40%  $\text{F}_2$ ) was passed through the NaF column and directed into the reactor (including a  $\text{TeO}_2$  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 were 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 reached 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 also

swept into a dry scrubber (containing activated alumina) and a wet scrubber (containing NaOH solution) and then ventilated. After complete purging of N<sub>2</sub> gas in the system, the TeO<sub>2</sub> pellet is removed from the reactor and its weight was measured.

### 2.3. Kinetic equations

TeO<sub>2</sub> reacts with three moles of F<sub>2</sub> gas to produce one mole of TeF<sub>6</sub> gas. If n<sub>0</sub> is the initial mole of feed (40% F<sub>2</sub> and 60% N<sub>2</sub>) and m is the molar amount of TeF<sub>6</sub> at time t, according to the reaction stoichiometry, the following molar balance obtains:



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

$$n_T = n_0 - m \tag{2}$$

$$n_{TeF_6} = n_0 - n_T \tag{3}$$

$$n_{F_2} = 0.4n_0 - 3(n_0 - n_T) = 3n_T - 2.6n_0 \tag{4}$$

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

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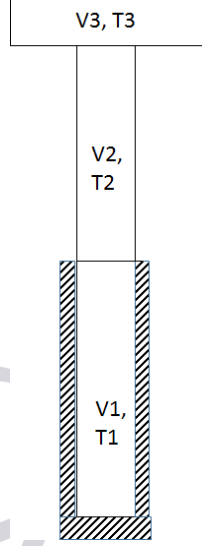


Fig. 3. The reactor with three different temperature zones.

The production rate of  $\text{TeF}_6$  gas at a given temperature can be written as [17]:

$$\frac{1}{w} \frac{dn_{\text{TeF}_6}}{dt} = k C_{F_2}^n \quad (5)$$

$$-\frac{1}{w} \frac{dn_T}{dt} = k \left( \frac{n_{F_2}}{V_1 + V_2 + V_3} \right)^n \quad (6)$$

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

$$n_T = \frac{P_T}{R} \left( \frac{V_1}{T_1} + \frac{V_2}{T_2} + \frac{V_3}{T_3} \right) \quad (7)$$

$$n_{F_2} = \frac{1}{R} \left( \frac{V_1}{T_1} + \frac{V_2}{T_2} + \frac{V_3}{T_3} \right) (3P_T - 2.6P_0) \quad (8)$$

$$\begin{aligned} \ln \left( -\frac{1}{w} \frac{dP_T}{dt} \right) + \ln \left( \frac{V_1}{T_1} + \frac{V_2}{T_2} + \frac{V_3}{T_3} \right) \\ = \ln k + n \left[ \frac{1}{(V_1 + V_2 + V_3)} \left( \frac{V_1}{T_1} + \frac{V_2}{T_2} + \frac{V_3}{T_3} \right) (3P_T - 2.6P_0) \right] \end{aligned} \quad (9)$$

To determine the degree of reaction, the left expression of Eq. 9 is drawn versus the right expression inside the bracket. The line slope is the degree of reaction (n), and the intercept is the logarithm of the rate constant (k). The Arrhenius form of the reaction rate



is used to propose a correlation for the reaction rate in terms of temperature, as follows [17]:

$$k = k_0 e^{-\frac{E}{RT}} \quad (10)$$

E is the reaction activation energy.

### 3. Results and discussion

#### 3.1. Calibration

As the sealing of the system in the volumetric method is very essential, the leakage of the system was determined by injecting the F<sub>2</sub> gas into the reactor without any reactant (TeO<sub>2</sub> pellet) and under reaction conditions. The changes in the reactor pressure were recorded every time. According to the obtained results, which was 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 TeO<sub>2</sub> pellet was reported in Fig. 4. The result shows that in the temperature range required for the production of TeF<sub>6</sub> (150 to 250 °C), the weight change of TeO<sub>2</sub> pellet is insignificant.

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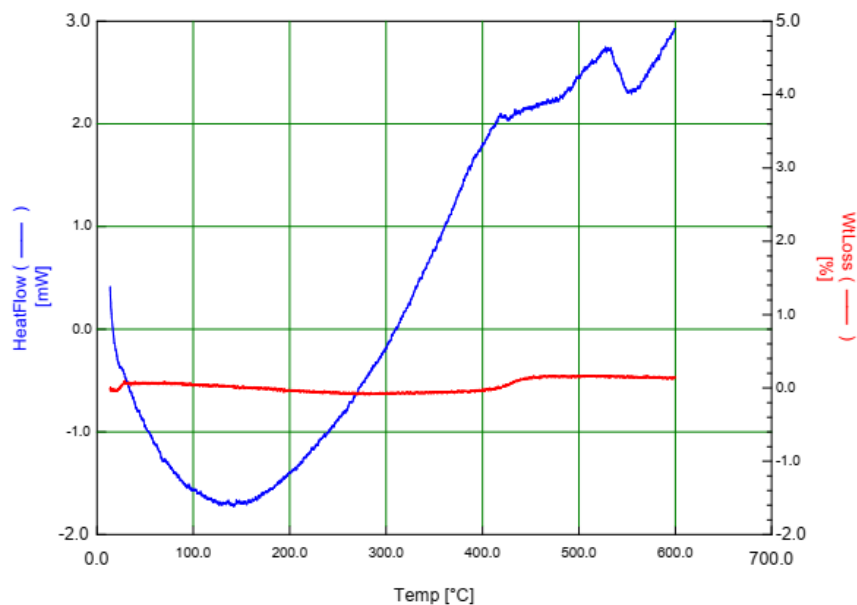


Fig.4. The TG analysis of TeO<sub>2</sub> pellet.

### 3.2. Kinetics of reaction

To measure the kinetics of TeF<sub>6</sub> production, the reaction temperature was selected between 150 and 250 °C. The TeF<sub>6</sub> product has high purity in 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 drive 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. The reason could be a change in the reaction mechanism at high 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.

Table 1. Kinetic equation<sup>1</sup> parameters for TeF<sub>6</sub> production using TeO<sub>2</sub> and F<sub>2</sub> gas.

Temperature (°C)	Order of reaction (n)	Rate constant (k) ((mol) <sup>1-n</sup> (m <sup>3</sup> ) <sup>n</sup> s <sup>-1</sup> g <sup>-1</sup> )	Activation energy (E) (j/mol)	AARE (%) <sup>2</sup>
150-200	1	2.76×10 <sup>-6</sup>	12347.8	0.57
150-200	1.09	3.59×10 <sup>-6</sup>	14046.4	0.55
250	2	1.18×10 <sup>-8</sup>	-	0.46

$$^1 \frac{1}{w} \frac{dn_{TeF_6}}{dt} = k_0 e^{-\frac{E}{RT}} C_{F_2}^n, \quad [C_{F_2}] = \frac{mol}{m^3}$$

$$^2 AARE(\%) = \frac{\sum_{i=1}^n |Exp_{-i} - Cal_{-i}| / Exp_{-i}}{n}$$

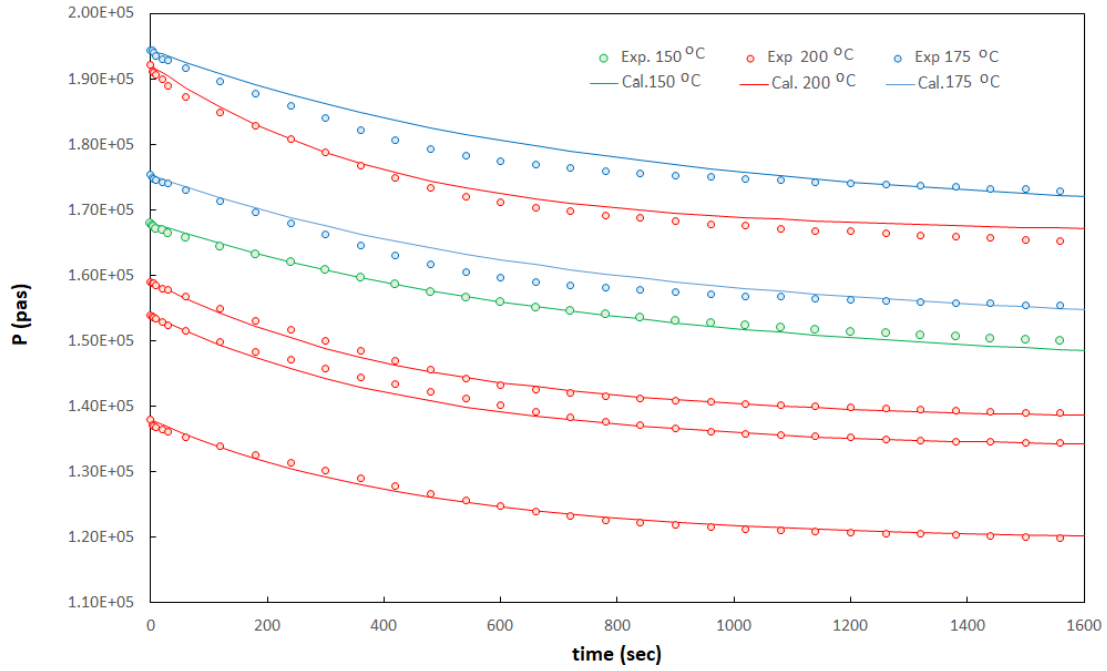


Fig. 5. Pressure changes inside the reactor at 150-200 °C – Order of reaction: 1.0.

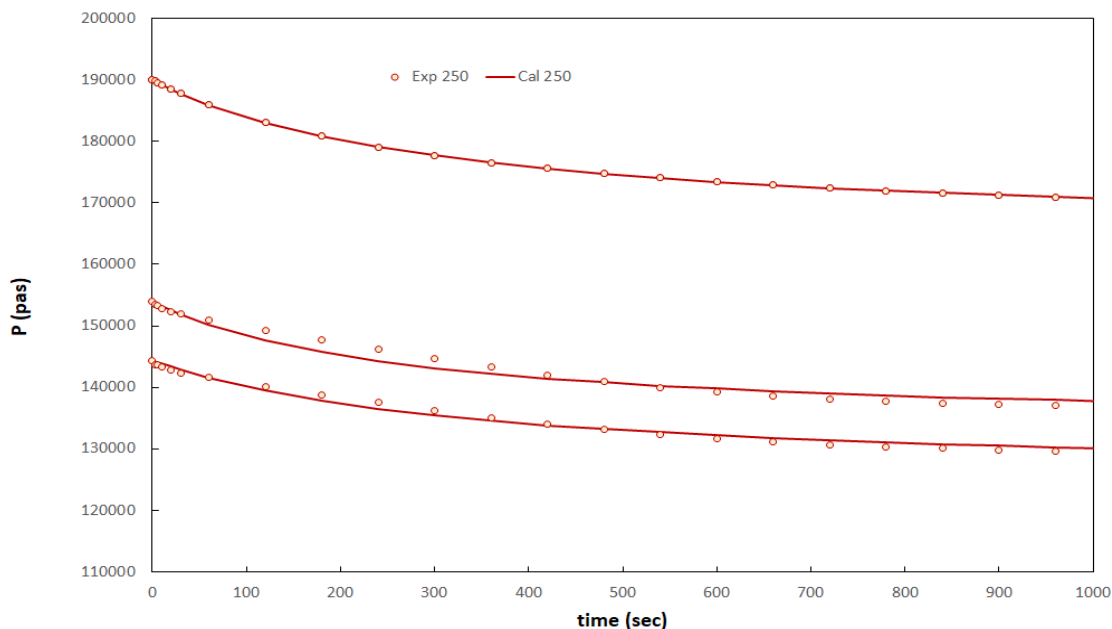


Fig. 6. Pressure changes inside the reactor at 250 °C – Order of reaction: 2.0.

#### 4. Conclusions

In this study, a volumetric method was used to drive the kinetic parameters of fluorination reactions. For this purpose, a system containing an absorption column, reactor, cold trap, and scrubber was designed and fabricated. This system was examined to study the kinetic of the  $\text{TeF}_6$  production by reactant of  $\text{TeO}_2$  and  $\text{F}_2$  gas. After calibrating the system,  $\text{F}_2$  gas was entered in the reactor, containing a  $\text{TeO}_2$  pellet, at different initial pressures (1 to 2 bar) and temperatures (150 to 250 °C). By beginning 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 by the Arrhenius form of the reaction rate. The results showed that the reaction kinetic is the first order for the temperature range of 150 to 200 °C and the second order for the temperature of 250 °C. The rate constant values were calculated to be  $2.76 \times 10^{-6} \text{ m}^3 \text{ g}^{-1} \text{ s}^{-1}$  and  $1.18 \times 10^{-8} (\text{m}^3)^2 \text{ mol g}^{-1} \text{ s}^{-1}$ , respectively. To evaluate the accuracy of the proposed models, the AARE values were calculated to be 0.57 and 0.46%, respectively, which indicates the excellent ability of the kinetic models to predict the reaction kinetics of  $\text{TeF}_6$  production.

## 5. Nomenclature

P	Pressure (Pa)
V	Volume ( $\text{m}^3$ )
T	Temperature (K)
R	Ideal gas constant ( $\text{m}^3 \cdot \text{Pa} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ )
t	Time (sec)
C	Concentration ( $\text{mol}/\text{m}^3$ )
E	Activation energy (J/mol)
K	Reaction rate constant ( $(\text{mol})^{1-n} (\text{m}^3)^n \text{s}^{-1} \text{g}^{-1}$ )
n	Order of reaction
w	$\text{TeO}_2$ weight (g)
$n_T$	Total moles at time t
$n_0$	Initial moles at t=0
$n_{\text{TeF}_6}$	Moles of $\text{TeF}_6$ gas
$n_{\text{F}_2}$	Moles of $\text{F}_2$ gas

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