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Kinetic investigation of tellurium hexafluoride production using the volumetric method

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HIGHLIGHTS

- The kinetic reaction of tellurium hexafluoride synthesis was studied using the volumetric method.
- A laboratory system was designed and constructed for the volumetric method.
- The fluorination of tellurium oxide was a first-order reaction in the temperature of 204 ± 1 °C.

ABSTRACT

Since the production of tellurium hexafluoride gas requires the design of a suitable reactor system, so the study of tellurium oxide fluorination kinetics is of great importance. For this purpose, a novel laboratory system was designed and constructed to study the fluorination reactions by the volumetric method. Fluorine gas was injected into the reactor containing a tellurium oxide pellet, and the reaction was studied by following the changes in pressure of the gas phase using a pressure transmitter instrument. In this volumetric system, the kinetic parameters of the reaction between tellurium oxide pellet and fluorine gas have been derived for a pressure range of 137.9 and 181.2 kPa by monitoring the gas phase pressure. The reaction temperature was adjusted to 204 ± 1 °C using a heater. The results showed that the fluorination reaction of tellurium oxide is a first-order reaction. The reaction rate constant is calculated to be $6.86 \times 10^{-4} \text{ s}^{-1}$.

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1 Introduction

Due to the use of stable tellurium isotopes, enrichment of these isotopes has been considered as one of the goals of the Atomic Energy Organization. For example, different tellurium isotopes are used to produce iodine radionuclides, which are used in the treatment of hyperthyroidism, thyroid cancers, treatment and diagnostic kits for adrenal cancers, and so on (Williams Jr, 1948). The primary method of enrichment of these isotopes is the gas centrifuge method, in which tellurium hexafluoride gas is injected into the centrifuge and separated (Benedict et al., 1981). Since the production of this gas requires the design of a suitable reactor system, so the study of tellurium fluorination reaction kinetics is of great importance.

To measure the reaction rate in solid-gas systems, the solid is usually formed into a pellet and contacted with the gas stream under controlled temperature and pressure. The product of the reaction may be gaseous (such as the production of tellurium hexafluoride) or solid (such as the desulfurization of sulfides) (Szekely, 2012).

The reports of gas-solid reactions indicate that most studies have focused on reactions that produce solid products (such as metal oxidation processes). Instead, few studies have been done on the processes that lead to a gaseous product, such as the fluorination reaction of tellurium, molybdenum, and so on (Labaton and Johnson, 1959).

The methods that can be used to examine the progress of the solid-gas reactions are classified into two groups:

1. Measurement of changes in solid,
2. Measurement of changes in the gas phase.

The techniques used in the first group include continuous measurement of solid weight (gravimetric method). In the second group, it is possible to measure the changes in gas pressure to study the reaction kinetic (volumetric method) (Szekely, 2012).

The basis of the volumetric method is the expansion of the gas between the reference volume and the reactor chamber, which includes a solid sample. First, the gas

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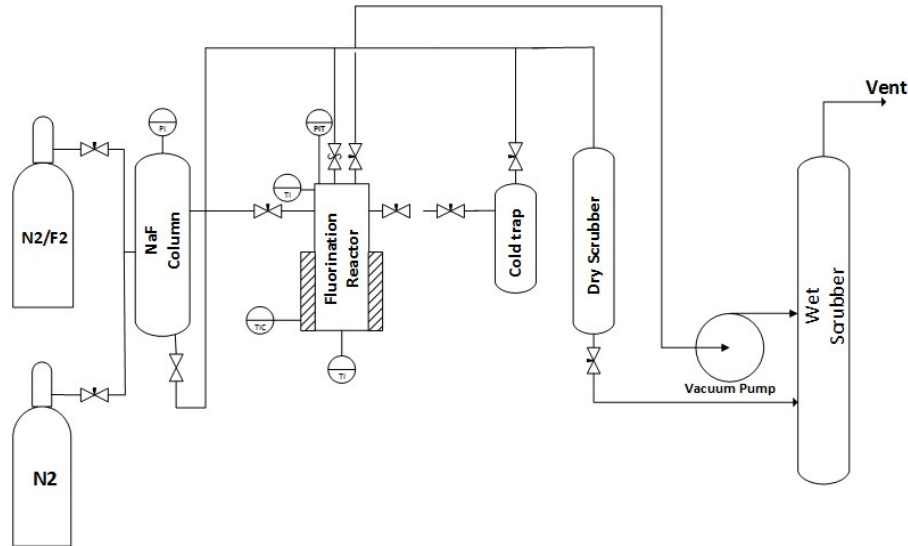


Figure 1: The schematic of the laboratory system.

pressure is adjusted to the reference volume, and then the valve is opened. After a certain pressure is reached in the reactor chamber, the valve closes, and the reaction begins. Pressure changes in the reactor are recorded over time. In this method, the type of valve used and the pressure transmitter must be selected correctly. Also, to increase the accuracy of the volumetric method, the system leakage rate should be carefully checked and reach zero. Temperature control is also important, and the system must reach thermal equilibrium before the reaction can begin. The attractive feature of the volumetric method is its robustness and relatively low cost (Wang et al., 2021).

In this research work, a laboratory system was designed and built. In this system, the kinetic parameters of the tellurium hexafluoride production were derived by the volumetric method.

Tellurium hexafluoride can be prepared by the reaction between tellurium oxide and fluorine at 150 to 300 °C as follow (Campbell and Robinson, 1956):



Before this study was made, no fundamental data on the kinetics of this reaction were available.

2 Experimental

2.1 Materials

Tellurium oxide (TeO_2) and sodium fluoride (NaF) powder were purchased from Sigma Aldrich (Table 1). The mixture of fluorine and nitrogen gas capsule (40% fluorine) was provided by Soreh company in Iran.

Table 1: The properties of TeO_2 and NaF.

Properties	Molar mass ($\text{g}\cdot\text{mol}^{-1}$)	Appearance	Density ($\text{g}\cdot\text{cm}^{-3}$)
TeO_2	159.60	white solid	5.670
NaF	41.98	white solid	2.558

2.2 Apparatus and methods

A laboratory system was designed and used for kinetic studying (Fig. 1). Based on the fluorine gas reactivity, allowable temperature, and pressure limits, all apparatus, valves, and instruments in this system were made of stainless steel 316 (Barbe et al., 2007). After cleaning the system, leak tests were carried out to ensure that the system had stable pressure. Then, passivation was done in stages by increasing concentrations and pressure of fluorine, allowing the metal fluoride film to develop on the metal surface and thus preventing any further fluorine reaction. The system was vacuumed, then a mixture of nitrogen and fluorine gas (40% fluorine) was passed through a column packed with NaF granules to remove HF of the gas. After that, the gas is injected into the reactor (containing TeO_2 pellet with a specific weight) until a certain pressure. The reactor was heated by a furnace with adjustable temperature. The reaction was followed by observing changes in the pressure of the reactor, and these changes were recorded by a pressure recorder at different times. At the end of the reaction, the gas was directed into a dry scrubber (containing activated alumina) and then a wet scrubber (containing NaOH solution) to remove all gases. A cold trap was used to collect the product.

3 Results and discussion

3.1 Calibration

To determine the leakage rate of the system, fluorine gas was injected into the reactor without reactant (TeO_2 pellet) under reaction conditions. The leakage rate was calculated by recording changes in reactor pressure over time. According to the presented results in Fig. 2, the leakage rate of fluorine gas from the reactor is approximately $0.6 \text{ Pa}\cdot\text{s}^{-1}$, which was considered in calculating the reaction kinetics.

3.2 Measuring the volume of the reactor

Since the volumetric method is used to study the reaction kinetics, it is essential to determine the exact volume of the reactor. This volume includes the volume of the reactor, the volume of the terminal, the volume of dead spaces between the valves, pressure gauge, and terminal connections. For this purpose, nitrogen gas pressure changes were measured after injection into the vacuumed reactor several times. Using the ideal gas law, the volume of the reactor was calculated to be 145.3 ml.

3.3 Kinetics of the reaction

The experiments were done at four initial pressure of 181.2, 158.9, 153.9, and 137.9 kPa. The temperature of the reactor was adjusted to 204 ± 1 °C in all experiments. The pressure changes recorded over a period of 25 minutes are shown in Fig. 3. As expected from Eq. (1), the pressure in the system decreases with the reaction between fluorine and tellurium oxide. To determine the kinetics of the reaction, TeF_6 production rate was considered as follows:

$$\frac{1}{S} \frac{dn_{\text{TeF}_6}}{dt} = K C_{\text{F}_2}^a \quad (2)$$

where S is the surface area of the TeO_2 pellet, and n_{TeF_6} is the mole of TeF_6 gas. K and C_{F_2} are the rate constant and fluorine gas concentration, respectively.

According to Eq. (1), the system pressure changes are written as Eq. (3):

$$\frac{dP_T}{dt} = K'(3P_T - 2.6P_0)^a \quad (3)$$

$$\ln\left(-\frac{dP_T}{dt}\right) = \ln(K') + a \times \ln(3P_T - 2.6P_0) \quad (4)$$

where P_0 and P_T are the pressure at $t = 0$ and $t = t$, respectively.

Using the experimental data, $\ln(-dP_T/dt)$ was drawn in terms of $\ln(3P_T - 2.6P_0)$. The results in Fig. 4 show that the fluorination reaction of tellurium is a first-order reaction. The rate constant determined for this reaction was $6.86 \times 10^{-4} \text{ s}^{-1}$.

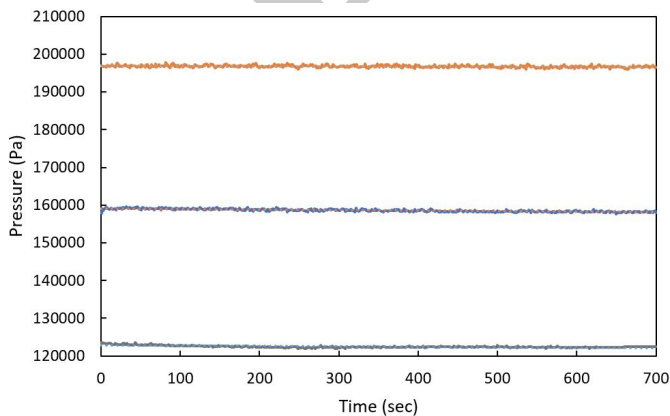


Figure 2: The results of leakage rate of the system.

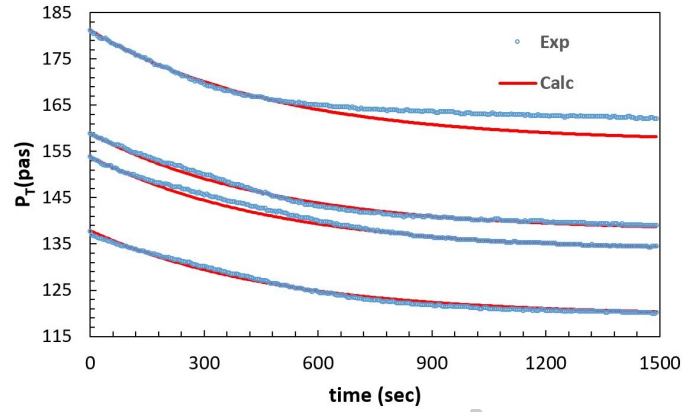


Figure 3: The experimental and calculated pressure changes with time.

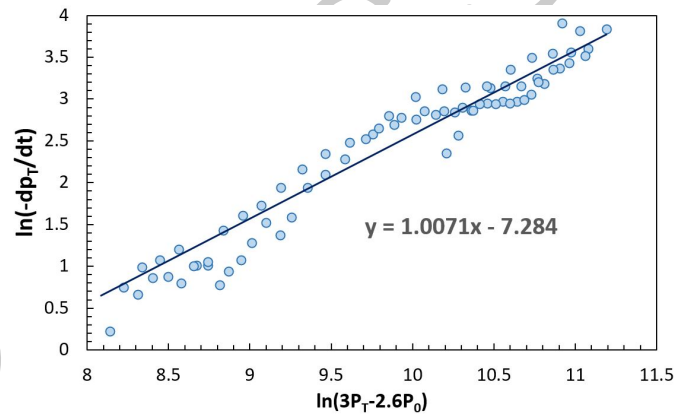


Figure 4: $\ln(-dP_T/dt)$ vs. $\ln(3P_T - 2.6P_0)$.

To examine the accuracy of the obtained results, P_T was calculated and compared with experimental data using the Average Absolute Relative Error (AARE) equation:

$$AARE(\%) = \frac{\sum_{i=1}^n \frac{|P_T^{\text{Exp.}} - P_T^{\text{Calc.}}|}{P_T^{\text{Exp.}}}}{n} \times 100 \quad (5)$$

in which n is the number of experimental points.

The AARE (%) value was calculated to be 0.56%. This shows a good agreement between experimental and calculated values, and the kinetic model can predict the reaction kinetics of tellurium oxide with fluorine gas at 204 ± 1 °C.

4 Conclusions

In this study, a laboratory system was designed and constructed to study the fluorination reactions by the volumetric method. This system was used to derive the kinetic parameters of the tellurium hexafluoride production for a pressure range of 137.9 and 181.2 kPa and reaction temperature of 204 ± 1 °C. Monitoring the gas phase pressure showed that the reaction rate depends on the pressure at a constant temperature. A linear relationship was shown

to exist between the reaction rate and pressure of fluorine. The rate constant determined for this reaction was $6.86 \times 10^{-4} \text{ s}^{-1}$.

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