

kinetic investigation of tellurium hexafluoride production using volumetric method

Parisa Zaheri, Amir Charkhi*, Iman Dehghan, Amjad Sazgar

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

*Email: acharkhi@aeoi.org.ir

Abstract

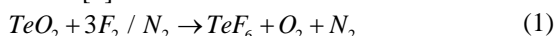
A novel laboratory system was designed and constructed to study the fluorination reactions by the volumetric method. In this system, the kinetic parameters of the reaction between tellurium oxide and fluorine have been derived for a pressure range of 137.9 and 181.2 kPa by monitoring the gas phase pressure. The reaction temperature was adjusted to 204 ± 1 °C. The results showed that the fluorination reaction of tellurium is a first-order reaction and its reaction constant is $6.86 \times 10^{-4} \text{ s}^{-1}$.

Keywords: Volumetric method, Fluorination, Tellurium hexafluoride, Kinetic parameters

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 [1]. 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 [2]. 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. 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. In a volumetric experiment, the pressure variation in time is the measured quantity. The attractive feature of this method is its robustness and relatively low cost [3].

Tellurium hexafluoride can be prepared by the reaction between tellurium oxide and fluorine at 150 to 300 °C as follow [4]:



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

Experimental

Materials

Tellurium oxide (TeO_2) and sodium fluoride (NaF) powder were purchased from Sigma Aldrich. Fluorine gas was provided by Soreh company in Iran.

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 [5]. After cleaning the system, leak tests were carried out to ensure that the system had a 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 a 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.

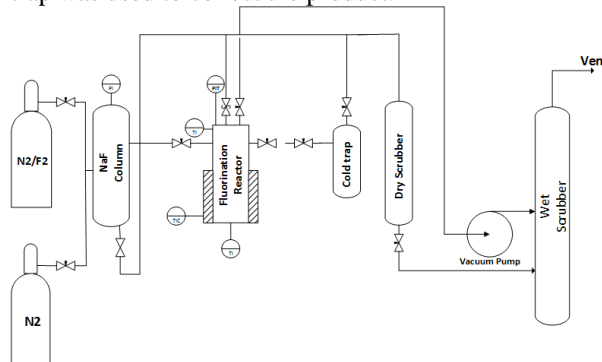


Fig. 1. The schematic of the *laboratory system*.

Results and discussion

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. 2. 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:



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

S is the surface area of the TeO₂ pellet, and n_{TeF₆} is the mole of TeF₆ gas. K and C_{F₂} are the rate constant and fluorine gas concentration, respectively.

According to Eq. (1), the system pressure change is written as Eq. (3).

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

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

P₀ 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-2.6P₀). The results in Fig. 3 shows that the fluorination reaction of tellurium is a first- order reaction. The rate constant determined for this reaction was 6.86e-4 s⁻¹.

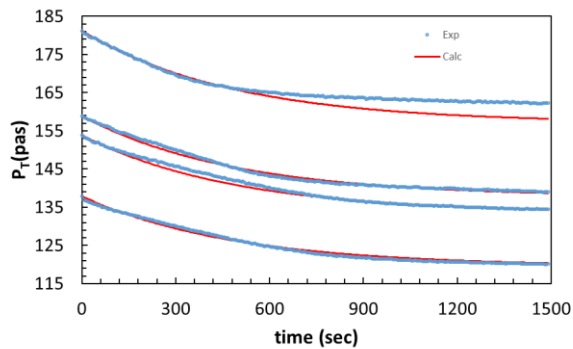


Fig. 2. *The experimental and calculated pressure changes with time.*

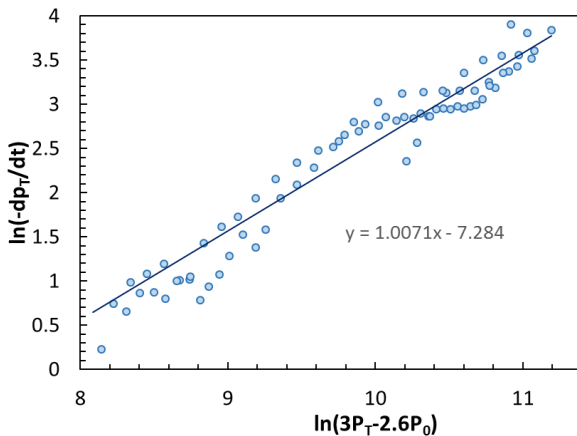


Fig. 3. *ln(-dP_T/dt) vs. ln(3P_T-2.6P₀)*

To examine the accuracy of the obtained results, P_T was calculated and compared with experimental data using the average absolute relative error (ARRE) equation.

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

n is the number of experimental points.

The AARE (%) value was calculated to be 0.56%. This shows that there is a good agreement between experimental and calculated values.

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 rate of reaction depends on the pressure in 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 6.86e-4 s⁻¹

References

- [1] Jr, R.R.W. Nuclear Chemistry of Tellurium: Chemical Effects of Isomeric Transition. The Journal Of Chemical Physics, 1948. 16: p. 513-519.
- [2] Benedict, Manson, Thomas H. Pigford, and Hans Wolfgang Levi. Nuclear chemical engineering. McGraw-Hill Education, 1981.
- [3] Wang, Jin-Yu, et al. "A review of common practices in gravimetric and volumetric adsorption kinetic experiments." Adsorption 27.3 (2021): 295-318.
- [4] Campbell, R. and P.L. Robinson, The Fluorination of Tellurium. Ditellurium Decajuoride and Tellurium Oxyjuorides. 1956.
- [5] Barbe, J., et al. "Code of practice-Compressed fluorine and mixtures with inert gases." (2007).