BULETINUL INSTITUTULUI POLITEHNIC DIN IAŞI
Publicat de
Universitatea Tehnică „Gheorghe Asachi” din Iaşi
Volumul 71 (75), Numărul 2, 2025
Secţia
CHIMIE şi INGINERIE CHIMICĂ
DOI: 10.5281/zenodo.15617712

APPLICATION OF THERMOGRAVIMETRIC ANALYSIS IN THE INVESTIGATION OF THE SUBLIMATION PROCESS

BY

CERASELA-IONELA CLEMINTE and GABRIELA LISA[*]

“Gheorghe Asachi” Technical University of Iaşi, “Cristofor Simionescu” Faculty of Chemical Engineering and Environmental Protection, Iaşi, Romania

Received: March 19, 2025
Accepted for publication: May 10, 2025

Abstract. Sublimation is essential in chemical vapor deposition (CVD), which is used to obtain thin material layers with applications in semiconductor manufacturing, integrated circuits, or photovoltaic panels. By optimizing the sublimation process, advanced materials with unique properties can be obtained, revolutionizing fields such as electronics, optics, and the aerospace industry.

This study evaluates the influence of temperature on the sublimation rate of naphthalene, frequently used as a standard for studying the sublimation of aromatic hydrocarbons. For this purpose, thermogravimetric analysis was applied under isothermal conditions, using air as a carrier gas at temperatures of 40, 50, 60, and 70°C, with different naphthalene layer thicknesses. The processing of thermogravimetric curves allowed the determination of the mass loss percentage over time. The sublimation rate was determined from the slope of these curves. The mass loss rate of naphthalene followed zero-order kinetics. The study demonstrated that isothermal thermogravimetric analysis provides a simple method for determining kinetic parameters such as activation energy and pre-exponential factor.

Keywords: naphthalene, activation energy, sublimation process, thermogravimetric analysis.

[*]Corresponding author; *e-mail*: gabriela.lisa@academic.tuiasi.ro

1. Introduction

Sublimation is a physical process by which a substance passes directly from the solid state to the gaseous state, without passing through the liquid phase. This phenomenon occurs when the heat energy added to a substance exceeds the energy required to break the bonds between molecules in the solid state without reaching the melting point.

The thermogravimetric analysis is a simple but very accurate method of measuring mass variation and temperature (Cleminte *et al*., 2022; Postolache *et al*., 2024). The use of thermogravimetric analysis for the study of the sublimation process has experienced an intense development in recent years. Most researchers have used this technique to evaluate sublimation enthalpy and less sublimation rate and mass and heat transfer. Sublimation involves the loss of mass of the solid by releasing molecules in the gaseous state. In a thermogravimetric analysis, this mass loss is recorded as a function of the applied temperature.

The sublimation process mechanism includes the following stages: (1) thermal energy transfer into the solid, (2) breaking of intermolecular bonds in the crystal lattice leading to the formation of free molecules and (3) carrying and taking vapours to the surface. Sublimation kinetics may be controlled by the rate of any of these processes. In the case of the sublimation process evaluated by thermogravimetric analysis, it can be considered that the rate-determining step is the second stage, in which the breaking of intermolecular bonds in the crystalline network occurs (Krongauz *et al*., 2007). In modern thermogravimetric analysis equipment, small sample quantities on the order of milligrams are used. Therefore, heat transfer to the powdered sample is sufficiently rapid. The thickness of the substance layer introduced into the analysis crucible is a few millimeters, so the sublimation rate is not affected by this variation, and we can consider that the sublimation process is partially influenced by the diffusion process (Lähde *et al*., 2009; Li *et al*., 2006).

The technique of naphthalene sublimation is an experimental method used to determine heat transfer coefficients in convection flows. The fundamental characteristic of this technique is that the heat transfer problem to be investigated is replaced by an analogous mass transfer problem. In the laboratory, only mass transfer experiments are conducted, and then heat transfer results are obtained by exploring the concept of analogy between heat and mass transfer. Naphthalene ($C_{10}H_8$) is used in mass transfer experiments due to some of its properties, such as sublimation at room temperature, relatively low toxicity compared to other compounds, and good casting and processing properties.

The sublimation of naphthalene particles into the air was used by Atmakidis and Kenig to validate the simulation results of mass transfer in a fixed-bed reactor. The authors obtained results that enable the improvement of the packed bed's performance as well as a better understanding of the fundamental transport phenomena in such a reactor (Atmakidis and Kenig, 2012). A similar study was also carried out by Bale et al to highlight the limitation of mass transfer at the wall in a laminar flow (Re 100) perforated bed reactor (Bale *et al*., 2017).

The naphthalene sublimation technique was also used by Kwon and co-workers to analyze heat and mass transfer in an experimental setup that was designed and built for low-speed test conditions. The plant consists of four parts: the settling chambers, the temperature control system, the flow control system and the test section. This allowed evaluation of the Sherwood criterion as a function of channel depth and Reynolds number for flows ranging from laminar to turbulent. The minimum depth tested (h/H) ranged from 0.2 to 0.4 (Kwon *et al*., 2011).

Considering that numerous studies in the literature present experimental values for the vapor pressure of naphthalene at different temperatures, it can be used as a reference material for determining the vapor pressure and sublimation rate for a wide range of materials for which data is not available in the literature, using thermogravimetric analysis (Goldfarb, 2013). Ramos and others used thermogravimetric analysis to determine the sublimation and vaporization enthalpies for a set of organic compounds. To test and validate the proposed methodology, they determined the molar sublimation enthalpies of a set of ten compounds whose values had been previously reported in the literature. The compounds used were: pyrene, phenanthrene, anthracene, benzoic acid, ferrocene, 2-furoic acid, 2-thiophenecarboxylic acid, methyl 4-hydroxybenzoate, hydantoin, and 2-thiohydantoin. The authors demonstrated that thermogravimetric analysis is indeed a suitable and reliable method for determining vaporization or sublimation enthalpies (Ramos *et al*., 2017). Recently, Treviño Kaufmann and others developed an improved method to determine the sublimation enthalpies of solid organic compounds using isothermal thermogravimetric analysis. The method involves measuring the mass loss rate as a function of temperature from isothermal experiments within a temperature range of 10 to 20 K below the melting temperature of the sample (Treviño-Kaufmann *et al*., 2024).

In this study, thermogravimetric analysis is applied to evaluate the influence of temperature, carrier gas velocity, and material layer height in the crucible on the sublimation rate of naphthalene. The kinetic study of naphthalene sublimation, conducted using thermogravimetric analysis under isothermal conditions, also allowed for the assessment of kinetic parameters. The original aspects of the study lie in the fact that naphthalene sublimation was used to evaluate the sublimation process in thermogravimetric analysis equipment, paving the way for future studies that will enable the assessment of sublimation rates and mass transfer for a range of organometallic compounds, which serve as precursors for chemical vapor deposition.

2. Materials and methods

The study of naphthalene sublimation was conducted using a Mettler Toledo TGA-SDTA 851^e equipment, which provides highly accurate results when analyzing mass and temperature changes.

Experimental determinations were carried out at the following temperatures: 40, 50, 60 and 70ºC, at various material thicknesses in the crucible (0.5; 1; 1.5 and 2 mm) and at 0.003; 0.012 and 0.024 m/s air rates (air being the carrying agent). The sublimation process was assessed for one hour, regardless of temperature and material thickness. Several readings were recorded in the same experimental conditions in order to check data reproducibility. Figure 1 presents the samples after the sublimation process study in the equipment. It can be observed that the material retains its shape, indicating that the sublimation surface remained constant throughout the experiment and matches the crucible surface: $1.96 \cdot 10^{-5}$ m².

Fig. 1 – Samples of naphthalene that remained in the crucible after the sublimation process.

3. Results and discussions

The experimental determinations conducted with the Mettler Toledo equipment allowed the evaluation of the influence of temperature, naphthalene layer height, and carrier gas velocity on the sublimation process.

The percentage mass losses were obtained as a function of time, which are presented in Figs. 2a, b, c and d. It is observed that, as expected, the percentage mass loss increases with increasing temperature, which favors the sublimation process.

The time dependence of the sublimated naphthalene mass change (Figs. 2a, b, c and d) was linear at each temperature, which proves that the naphthalene sublimation process exhibits zero-order kinetics.

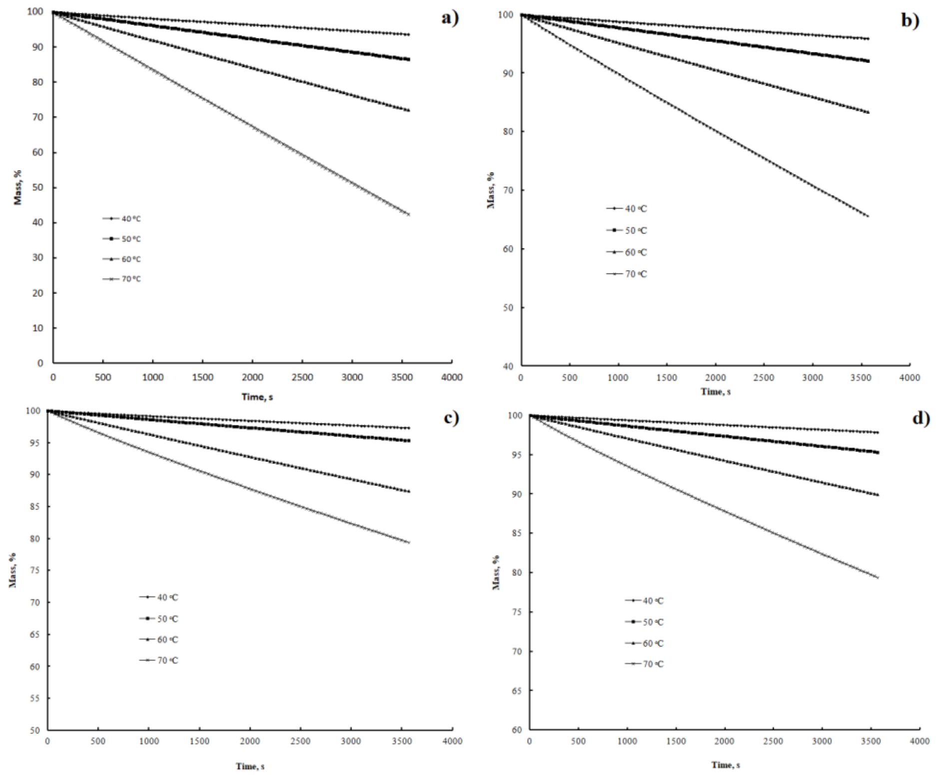

Fig. 2 – Percentage loss of mass over time, at various temperatures and a naphthalene layer height of 0.5 mm a), 1mm b), 1.5 mm c) and 2 mm d).

At the temperature of 70ºC, the influence of the driving agent, respectively the air rate, on the naphthalene sublimation process was also analyzed. The percentage mass losses at different entrainer flow rates are represented in Figs. 3 a, b, c and d. An intensification of the sublimation process is observed as the rate of the entrainer increases.

The sublimation rate is constant, at constant temperature, the Eq. (1):

$$r_{subl} = \frac{dm}{dt} = k \quad (1)$$

The temperature dependence of the sublimation rate constant may be described by an Arrhenius equation:

$$k = A \cdot e^{-\frac{Ea}{RT}} \quad (2)$$

where A is the pre-exponential factor, Ea is the activation energy, R is the universal gas constant and T – is temperature expressed in K.

The kinetics of naphthalene sublimation was estimated using the logarithmic form of the Arrhenius equation:

$$ln\frac{dm}{dt} = lnA - \frac{Ea}{RT} \quad (3)$$

where *dm*/*dt* is the sublimation rate constant (k).

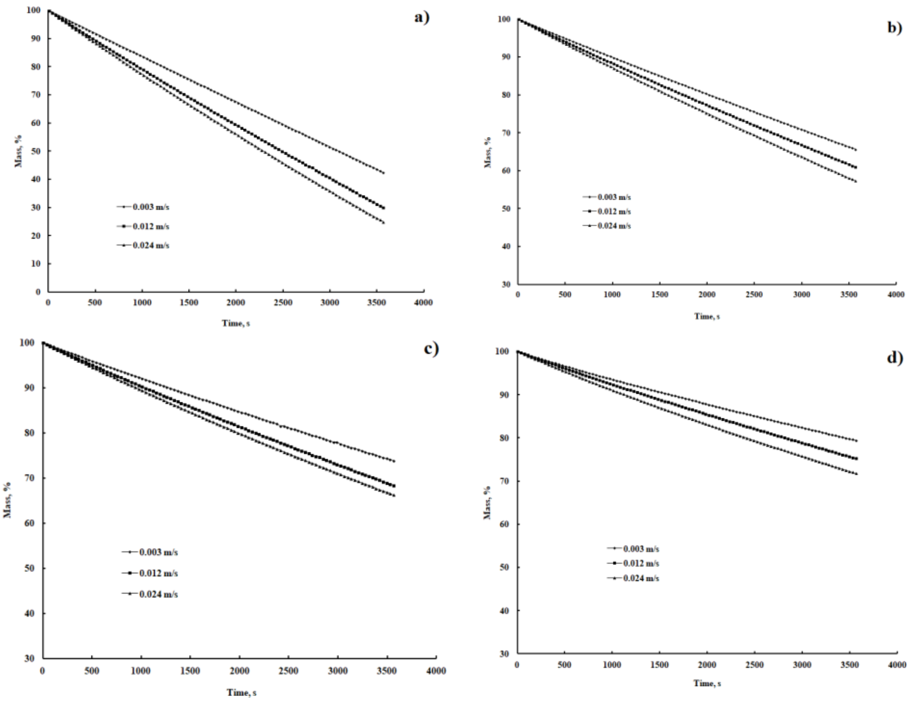

Fig. 3 − The percentage loss of mass over time, at different flow rates of the entrainer, at a temperature of 70ºC and a naphthalene layer height of 0.5 mm a), 1mm b), 1.5 mm c) and 2 mm d).

As shown in Figs. 4a, b, c and d, linear dependences are determined by the graphical representation of *ln*(*dm*/*dt*) dependence on 1/*T*. The activation energy was calculated using the inclination of the lines obtained, while the origin intercept revealed the pre-exponential factor. The results obtained are shown in Table 1.

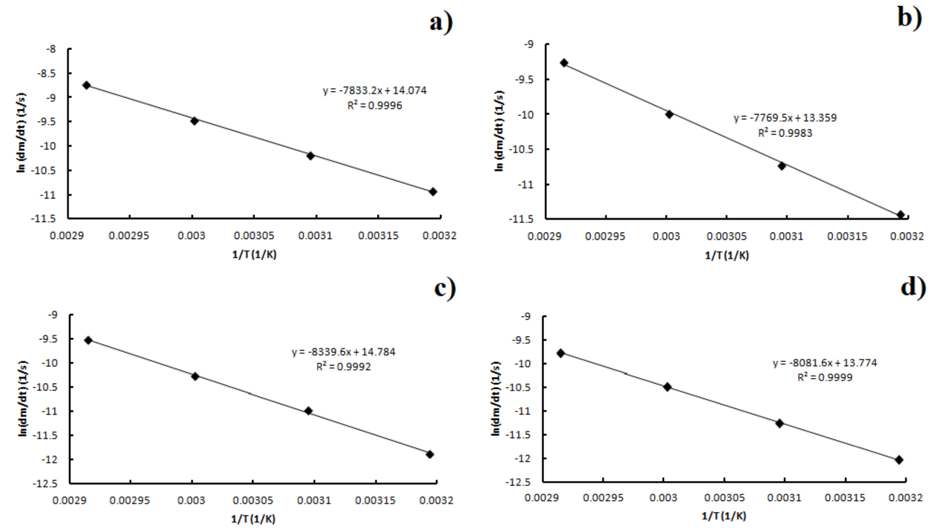

Fig. 4 – Calculation of Arrhenius equation parameters for a naphthalene layer height of 0.5 mm a), 1mm b), 1.5 mm c) and 2 mm d).

Table 1
Kinetic parameters in the Arrhenius equation

Material thickness	0.5 mm	1 mm	1.5 mm	2 mm
Ea, kJ/mol	65.125	64.595	69.335	67.190
lnA	14.074	13.359	14.784	13.774
r^2	0.9996	0.9983	0.9992	0.9999

Correlation coefficients greater than 0.99 were obtained by Xie and others for the linear dependence of $ln(dm/dt)$ as a function of $1/T$, applying thermogravimetric analysis in the study of the sublimation of a non-inhibitory reverse transcriptase nucleoside analogue for the HIV-1 retrovirus (DPC 963). The authors also obtained a sublimation enthalpy value of 29 ± 2 kcal/mol and highlighted that the determination of vapor pressure using thermogravimetric analysis provides sufficient accuracy to be used as a simple, rapid method and a good alternative to traditional vapor pressure determination methods, which require much more time and material consumption (Xie *et al.*, 2003). Thermogravimetric analysis has also proven useful in evaluating the sublimation process of explosive materials (Félix-Rivera *et al.*, 2011). Bhattacharia and others used this technique to assess the sublimation of pentaerythritol tetranitrate (PETN), an explosive widely used in military applications. The authors used benzoic acid and naphthalene as reference substances and demonstrated that the mass loss rate of the analyzed explosive materials follows zero-order kinetics, suggesting that the only process occurring during mass loss is sublimation (Bhattacharia *et al.*, 2013).

4. Conclusions

The study carried out confirms that the thermogravimetric analysis is suitable for evaluating the mass transfer process in sublimation.

Compared to other conventional techniques, these modifications of the analysis use have the advantage of a small quantity of materials and shorter experimental times.

The kinetic study of naphthalene sublimation performed using thermogravimetric analysis under isothermal conditions allowed the assessment of kinetic parameters. We find that the value of the activation energy and of the pre-exponential factor is little influenced by the thickness of the naphthalene layer in the crucible. The sublimation rate increased exponentially with temperature. The mass loss rate exhibited zero-order kinetics. The study conducted and described in this paper enabled us to prove that isothermal thermogravimetric analysis provides a simple way to determine the kinetic data of the sublimation process.

REFERENCES

Atmakidis T., Kenig E.Y., *Numerical analysis of mass transfer in packed-bed reactors with irregular particle arrangements*, Chem. Eng. Sci., **81,** 77-83 (2012).

Bale S., Sathe M., Ayeni O., Berrouk A.S., Joshi J., Nandakumar N., *Spatially resolved mass transfer coefficient for moderate Reynolds number flows in packed beds: Wall effects*, Int. J. Heat Mass Transf. **110,** 406-415 (2017).

Bhattacharia S.K., Maiti A., Gee R.H., Weeks B.L., *Sublimation properties of pentaerythritol tetranitrate single crystals doped with its homologs*, Propellants Explos. Pyrotech., **37**, 563-568 (2012).

Cleminte C.-I., Ionita D., Lisa C., Cristea M., Mamaliga I., Lisa G., *Evaluation of the sublimation process of some purine derivatives: sublimation rate, activation energy, mass transfer coefficients and phenomenological models*, Materials, **15**, 7376 (2022).

Félix-Rivera H., Ramírez-Cedeno M.L., Sánchez-Cuprill R.A., Hernández-Rivera S.P., *Triacetone triperoxide thermogravimetric study of vapor pressure and enthalpy of sublimation in 303–338K temperature range*, Thermochim. Acta **514,** 37-43 (2011).

Goldfarb J.L., *Review of sublimation thermodynamics of polycyclic aromatic compounds and heterocycles*, J. Heterocyclic Chem., **50**, 1243-1263 (2013).

Krongauz V.V., Ling M.T.K., Woo L., Purohit U., *Kinetics of dihydro-dibenz[b, f]azepine derivatives sublimation*, Thermochim. Acta **457**, 35-40 (2007).

Kwon H.G., Hwang S.D., Cho H.H., *Measurement of local heat/mass transfer coefficients on a dimple using naphthalene sublimation*, Int. J. Heat Mass Transf. **54**, 1071-1080 (2011).

Lähde A., Raulaa J., Malmb J., Kauppinena E.I., Karppinen M., *Sublimation and vapour pressure estimation of l-leucine using thermogravimetric analysis*, Thermochim. Acta **482**, 17-20 (2009).

Li J., Wang Z., Yang X., Hu L., Liu Y., Wang C., *Decomposing or subliming? An investigation of thermal behavior of l-leucine*, Thermochim. Acta **447**, 147-153 (2006).

Postolache L-V, Palarii A., Nicuță A-M., Săvuc G-C., Smoc L-G., Lisa G., *Studies on energy recovery of textile waste*, Bul. Inst. Polit. Iaşi, **70(74)**, *2,* s. Chemistry and Chemical Engineering 9-18 (2024).

Ramos F., Ledo J.M., Flores H., Camarillo E.A., Carvente J., Amador M.P., *Evaluation of sublimation enthalpy by thermogravimetry: Analysis of the diffusion effects in the case of methyl and phenyl substituted hydantoins*, Thermochim. Acta **655**, 181-193 (2017).

Treviño-Kauffmann M.A., Esparza-Rivera D., Rojas A., *Sublimation enthalpies of organic compounds by isothermal thermogravimetry*, J. Therm. Anal. Calorim., https://doi.org/10.1007/s10973-024-12897-z (2024).

Xie M., Ziemba T.M., Maurin M.B., *Sublimation characterization and vapor pressure estimation of an HIV nonnucleoside reverse transcriptase inhibitor using thermogravimetric analysis*, AAPS PharmSciTech; **4**, *2*, 23 (2003).

APLICAREA ANALIZEI TERMOGRAVIMETRICE ÎN INVESTIGAREA PROCESULUI DE SUBLIMARE

(Rezumat)

Sublimarea este esențială în depunerea chimică din vapori (CVD), utilizată pentru obținerea straturilor subțiri de materiale cu aplicații în fabricarea semiconductorilor, a circuitelor integrate sau a panourilor fotovoltaice. Prin optimizarea procesului de sublimare, se pot obține materiale avansate cu proprietăți unice, revoluționând domenii precum electronica, optica și industria aerospațială. În această lucrare a fost evaluată influența temperaturii asupra vitezei procesului de sublimare a naftalinei utilizată frecvent ca etalon pentru studiul sublimării hidrocarburilor aromatice. În acest scop s-a aplicat analiza termogravimetrică în condiții izoterme utilizând aerul ca agent de antrenare, temperaturi de 40, 50, 60 și 70ºC și diferite înălțimi ale stratului de naftalină. Prelucrarea curbelor termogravimetrice a permis determinarea procentului de masă pierdut în timp. Folosind panta acestor drepte s-a determinat viteza de sublimare. Viteza de pierdere de masă a naftalinei a respectat o cinetică de ordin zero. Prin studiul realizat s-a demonstrat că analiza termogravimetrică izotermă oferă o modalitate simplă de determinare a parametrilor cinetici: energie de activare și factor preexponențial.