

**SUBLIMATION THERMODYNAMICS  
OF SOME PHENYL-SUBSTITUTED PORPHYRINS**

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Porphyrins belong to a broad class of tetrapyrrole macrocyclic compounds with unique properties, such as the ability to form complexes with most chemical elements, high chemical stability, etc. Materials based on porphyrins are used to create active layers for sensors, photo- and electrocatalysts, solar cells, etc.

Thermodynamic parameters of porphyrin evaporation, such as saturated vapor pressure and sublimation enthalpy, are of interest due to the possibility of forming thin films of functional materials by vapor deposition methods.

In this work, the thermodynamic parameters of sublimation of 5,15-diphenylporphyrin (**H<sub>2</sub>DPhP**) and 5,10,15,20-tetrakis(4-methylphenyl)porphyrin (**H<sub>2</sub>T(4-MePh)P**) were determined by the Knudsen effusion mass spectrometry method. Sublimation of porphyrins was carried out in the temperature ranges of 443-527 K for **H<sub>2</sub>DPhP** and 542-620 K for **H<sub>2</sub>T(4-MePh)P**. The mass spectra of both compounds contain two main peaks corresponding to the M<sup>+</sup> and M<sup>++</sup> (M is the monomer molecule).

The saturated vapor pressures of porphyrins were determined using the Knudsen effusion method in combination with mass spectrometric measurements of ion currents. The obtained data are described using the following linear equations:

$$\ln(p/\text{Pa}) = -(20.24 \pm 0.19) 10^3/T + (35.80 \pm 0.39), \text{H}_2\text{DPhP}, 443\text{-}527 \text{ K};$$

$$\ln(p/\text{Pa}) = -(27.50 \pm 0.22) 10^3/T + (41.85 \pm 0.37), \text{H}_2\text{T(4-MePh)P}, 542\text{-}620 \text{ K}.$$

The sublimation enthalpy at the harmonic mean temperature ( $T_{\text{hm}}$ ) of measurements was found from the slope of the temperature dependence of vapor pressure and recalculated to 298.15 K in according to [1].

The values determined in this work and in [2] are listed in Table and show an increase in enthalpy with increasing complexity of molecular structure of the considered structural analogs.

Sublimation enthalpy,  $\Delta_{\text{sub}}H^\circ(T) / \text{kJ}\cdot\text{mol}^{-1}$

Compound	$\Delta T / \text{K}$	$T_{\text{hm}} / \text{K}$	$\Delta_{\text{sub}}H^\circ(T_{\text{hm}})$	$\Delta_{\text{sub}}H^\circ(298.15 \text{ K})$
<b>H<sub>2</sub>DPhP</b>	443-527	487	168 ± 2	183 ± 8
<b>H<sub>2</sub>TPhP [2]</b>	490-615	557	195 ± 2	220 ± 12
<b>H<sub>2</sub>T(4-MePh)P</b>	542-620	583	227 ± 2	263 ± 17

1. Acree W.Jr., Chickos J.S. J Phys. Chem. Ref. Data. 2016. 45. 033101.

2. Kudin L. S., Dunaev A. M., Motalov V. B., Cavallo L., Minenkov Y. J. Chem. Thermodyn. 2020, 151. 106244.

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