THERMOCHEMISTRY OF 5,10,15,20-TETRAPHENYLPORPHYRIN

Lev S. Kudin*, Anatoly M. Dunaev, Vladimir B. Motalov

*Ivanovo State University of Chemistry and Technology, 153000, Ivanovo,
Av. Sheremetevsky, 7, Ivanovo 153000, Russia*

Luigi Cavallo

*KAUST Catalysis Center (KCC), King Abdullah University of Science and
Technology, Thuwal-23955-6900, Saudi Arabia*

Yury Minenkov

*Moscow Institute of Physics and Technology, Institutskiy Pereulok 9,
Dolgoprudny, Moscow Region 141700, Russia*

Saturated vapor pressure of 5,10,15,20-tetraphenylporphyrin (TPP) was determined by Knudsen effusion mass spectrometry technique. The temperature dependence of the vapor pressure is described by the equation $\ln p/\text{Pa} = - (23.45 \pm 0.26) \cdot 10^3/T + 37.32 \pm 0.47$ in the temperature range 490 – 615 K. The specific heat capacity measurements of TPP were performed in the temperature range 169 – 568 K. Quantum-chemical calculations of the structure and force field of the TPP molecule were carried out. These data were used to calculate thermodynamic functions of TPP in the solid and gas states. The enthalpy of sublimation of triclinic form of TPP was determined by the second and third laws of thermodynamics. The value $\Delta_s H^\circ(298.15 \text{ K}) = 220 \pm 12 \text{ kJ} \cdot \text{mol}^{-1}$ was recommended. The reaction based Feller-Peterson-Dixon approach predicts the gas phase TPP formation enthalpy $\Delta_f H^\circ(298.15 \text{ K}) = 1004 \pm 10 \text{ kJ} \cdot \text{mol}^{-1}$. A combination of the two last values results in the formation enthalpy of the TPP triclinic form $\Delta_f H^\circ(298.15 \text{ K}) = 784 \pm 15 \text{ kJ} \cdot \text{mol}^{-1}$.

Keywords: *tetraphenylporphyrin, Knudsen effusion mass spectrometry, vapor pressure, enthalpy of sublimation, formation enthalpy, quantum-chemical calculations, thermodynamic functions*

* Corresponding author.

E-mail address: lkudin@yandex.ru (L.S. Kudin).

I. INTRODUCTION

Porphyrins are macrocycles formed by four pyrrole rings connected in the α -positions by four methine groups. A specific function of each porphyrin is determined by the variety of their substituents and by their capacity for coordination with many metallic ions or atoms. Porphyrins play an exceptional role in the natural biochemical and biophysical processes^{1,2}. Many important biological, photochemical, and enzymatic processes occur with their participation, including but not limited to photosynthesis, oxygen transfer, electron transfer etc. Currently, various functional materials based on porphyrins, such as photosensitizers and optical materials, information storage elements, oxygen and toxic gas sensors, molecular switches, liquid crystals, organic semiconductors, catalysts, and drugs, are widely used in chemistry, molecular electronics, pharmacology, and medicine.

Despite the widespread use of porphyrins, knowledge of their thermochemical properties is neither complete nor reliable. For instance, the sublimation enthalpy of 5,10,15,20-tetraphenylporphyrin (TPP), one of the main precursors of porphyrins and their substituted derivatives, obtained by various authors, is highly contradictory. The first value of the TPP sublimation enthalpy $\Delta_s H^\circ(633 \text{ K}) = 111 \pm 5 \text{ kJ}\cdot\text{mol}^{-1}$ was determined in 1970 by Bonderman et al.³ using the Knudsen effusion technique from the temperature dependence of saturated vapor pressure. About that time, Edwards et al.⁴ studied the gas-phase absorption spectrum of TPP and calculated the TPP enthalpy of sublimation $\Delta_s H^\circ(668 \text{ K}) = 146.4 \text{ kJ}\cdot\text{mol}^{-1}$. Much later, the saturated vapor pressure of TPP was measured by Golubchikov et al.⁵ using the inert gas flow method. These authors reported four different sublimation enthalpy values: $\Delta_s H^\circ(598 \text{ K}) = 267 \pm 9 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_s H^\circ(653 \text{ K}) = 185 \pm 10 \text{ kJ}\cdot\text{mol}^{-1}$ for sublimed TPP and $\Delta_s H^\circ(558 \text{ K}) = 370 \pm 40 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_s H^\circ(628 \text{ K}) = 170 \pm 5 \text{ kJ}\cdot\text{mol}^{-1}$ for TPP recrystallized from benzene. In later publications^{6,7} the same authors have reconsidered their initial interpretation, giving the value $\Delta_s H^\circ(588 \text{ K}) = 240 \pm 7 \text{ kJ}\cdot\text{mol}^{-1}$ for TPP in tetragonal modification obtained by vacuum sublimation, and the value $\Delta_s H^\circ(578 \text{ K}) = 207 \pm 10 \text{ kJ}\cdot\text{mol}^{-1}$ for triclinic TPP, grown from benzene solution. In 2002 Torres et al.⁸ determined the TPP sublimation enthalpy $\Delta_s H^\circ(550 \text{ K}) = 171 \pm 2 \text{ kJ mol}^{-1}$ by the Knudsen effusion method using a quartz crystal microbalance. In 2004 Stefanov et al.⁹, studying fluorescence on molecular diluted beams, determined the enthalpy of sublimation of TPP, $\Delta_s H^\circ(667 \text{ K}) = 142 \pm 3 \text{ kJ mol}^{-1}$. Finally, in 2007 Deachapunya et al.¹⁰ using Knudsen effusion mass spectrometry (KEMS) measured the temperature dependence of the ion current $\text{C}_{44}\text{H}_{30}\text{N}_{4+}$, formed by electron-impact ionization of the effusive molecular beam, and obtained the TPP sublimation enthalpy as $\Delta_s H^\circ(642 \text{ K}) = 160 \pm 3 \text{ kJ}\cdot\text{mol}^{-1}$.

Thus, the TPP sublimation enthalpies determined by different authors using different techniques are inconsistent forming a wide range of individual values from 111 to 370 $\text{kJ}\cdot\text{mol}^{-1}$. To rationalize the available experimental data, new measurements of saturated vapor pressure of TPP were performed by KEMS. Unlike previous studies,

in which the processing of experimental data was carried out exclusively according to the second law of thermodynamics, the third law method was also applied in this work.

II. EXPERIMENTAL

A. Sample

5,10,15,20-tetraphenylporphyrin (Fig. 1) was synthesized by condensation of pyrrole with benzaldehyde according to the improved method of Semeykin et al.¹¹. The MALDI spectrum of the synthesized sample showed that the peak with $m/z = 614$, corresponding to the molecular ion TPP, is dominant. The purity of TPP according to high performance liquid chromatographic analysis was rated no worse than 98%. X-ray analysis of the obtained TPP powder (Fig. 2) shows that the crystalline system has a triclinic structure (space group P1) with the following unit cell parameters: $a = 6.4309(4) \text{ \AA}$, $b = 10.4711(6) \text{ \AA}$, $c = 12.4165(8) \text{ \AA}$, $\alpha = 95.865(4)^\circ$, $\beta = 99.296(3)^\circ$, $\gamma = 101.162(3)^\circ$, which agree well with the literature data¹². The ^1H NMR TPP spectrum (Fig. 3) is completely consistent with the reference data¹³ and does not show any related impurity compounds in measurable amounts. The electron absorption spectra of the initial sample and its residue after mass spectrometric experiment, given in Fig. 4, did not reveal any differences and corresponds to the literature data^{14,15}. Fig. 3 and 4 point out that TPP does not decompose during evaporation in the studied temperature range.

FIG. 1. 5,10,15,20-tetraphenylporphyrin (TPP) structure

FIG. 2. X-ray diffraction pattern of TPP

FIG. 3. ¹H NMR spectrum of TPP: (a) – initial sample, (b) – residue after mass spectrometric experiment

FIG. 4. Electron absorption spectrum of initial sample (1) and its residue after mass spectrometric experiment (2)

B. Mass spectrometric analysis

A magnetic sector type mass spectrometer MI201 (90°, 200 mm curvature radius) reconstructed for high-temperature studies was used. The sample of TPP was placed into a molybdenum Knudsen cell; the diameter and the channel length of the effusion orifice were 0,7 mm and 0,4 mm correspondingly; the vaporization-to-effusion area ratio was about 400. A resistance furnace was utilized for heating of the cell. The temperature of the cell was measured by a tungsten-rhenium thermocouple calibrated by silver to ± 5 K accuracy in the separate experiment. Molecular beam formed by effusing species reached ionization chamber and intersected electron beam of specified energy. Electrons with an energy of 40 eV was used. The cathode current was adjusted to provide a constant emission current of 0.25 mA between the cathode and ionization chamber. The special software “HTMSLab” was used to control experimental parameters, collect and process the data, and export the results into the database. Detailed description of the apparatus is given elsewhere^{16,17-19}.

C. Thermal analysis and heat capacity measurements

Thermal analysis of TPP samples was carried out on a Netzsch STA 449 F3 Jupiter thermal analyzer. Measurements of mass loss and heat flow were performed

in the temperature range 300–1023 K with rates of 5 and 10 K min⁻¹ in an argon atmosphere. The sample was placed in a platinum pan.

The standard specific heat capacity C_p of TPP in solid state was measured by differential scanning calorimetry (DSC) in the temperature range 169 – 568 K. The DSC 204 F1 Phoenix (169 – 302 K) and DSC 404C Pegasus (328 – 568 K) heat calorimeters (NETZSCH, Germany) with the highly sensitive sensors were used in combination with the Proteus software for Windows.²⁰ High purity (>99.999%) materials C₆H₁₂ (melting temperature 280 K), Hg (234 K), Pb (327 K), C₁₂H₁₀ (342 K), In (430 K), Bi (545 K), C₆H₅COOH (396 K), RbNO₃ (583 K), KClO₄ (683 K), Ag₂SO₄ (933 K) and CsCl (919 K) were used to calibrate the temperature when operating the DSC experiments in the studied temperature range. Sample was heated with a rate of 10 K min⁻¹ in argon atmosphere. The cooling system is provided with liquid nitrogen. The pre-dried sample (3-5 mg) was placed in an aluminum pan and heat flow was measured by comparison with that for an empty control aluminum pallet depending on temperature. The specific heat capacity C_p of TPP samples was determined relative to sapphire. The precision of the specific heat capacity determination was estimated to be less than 5 % within the studied temperature ranges.

III. RESULTS AND DISCUSSION

A. Thermal analysis

The results of thermal analysis of TPP (Fig. 5) indicate the absence of any structural changes in the studied temperature range. Fig. 5 suggests a noticeable mass loss of the sample starting at a temperature of about 700 K. The decomposition temperature was determined to be 760±30 K. The peak on the heat flow curve corresponds to the melting temperature of 720 ± 6 K and the melting enthalpy $\Delta_m H^\circ = 17 \pm 5$ kJ mol⁻¹.

B. Mass spectra

Scanning of masses in the range of 2–1300 Da showed that the main peaks in the electron ionization mass-spectrum in the temperature range 490-615 K are ions with $m/z = 614$ (100) and $m/z = 307$ (13). The relative intensities of ion currents at $T = 523$ K are given in parentheses. It should be noted that no trace of ions with $m/z > 614$ was observed in the mass spectrum. The appearance energies (AE) of the registered ions, determined by the method of linear extrapolation of near-threshold portions of ionization efficiency curves (Fig. 6), are 8.2±0.5 eV and 20.8±0.5 eV, respectively. The energy scale was calibrated using the background signal of HI⁺ ($IE(\text{HI}) = 10.38$ eV₂₁). The low value of the appearance energy of the ion with $m/z = 614$ indicates that it is the molecular ion C₄₄N₄H₃₀⁺. High appearance energy of ion with $m/z = 307$ and its mass, which is two times less than that of C₄₄N₄H₃₀⁺,

allow to attribute it to double charged molecular ion. This interpretation is confirmed by similarity of slopes of the temperature dependencies of the registered ion currents shown in Fig. 7. These dependencies were reproducible in heating and cooling cycles pointing out that TPP sublimate congruently in the studied temperature range. This conclusion is consistent with the results of thermal analysis described above.

FIG. 5. Thermal analysis of TPP with a heat rate 10 K/min

C. Vapor pressure

The measured ion currents were converted into the vapor pressures (p) (Table I) using the standard KEMS equation

$$p = kIT, \quad (1)$$

where k is the mass spectrometer sensitivity constant, I is the total ion current of all ions formed from the TPP molecule, T is the temperature of the Knudsen cell.

The sensitivity constant k was calculated as $k = p/(IT)$, based on the TPP vapor pressure found in isothermal mass loss experiment according to the Hertz-Knudsen equation

$$p = \frac{\Delta m}{\Delta t} \cdot \frac{1}{cA} \sqrt{\frac{2\pi RT}{M}}, \quad (2)$$

where $\Delta m/\Delta t$ is the mass-loss rate, c is the Clausing factor, A is the area of effusion orifice, M is the molecular weight of TPP, R is the ideal gas constant. The total mass-loss rate $\Delta m/\Delta t$ was found by weighing the cell with the sample before and after vaporization. The effective area of the effusion orifice cA was determined by formula (2) in a separate experiment carried out for the same cell using Zn as a reference substance.

The determined vapor pressure (p) of TPP was approximated by the linear equation

$$\ln p/\text{Pa} = -(23.45 \pm 0.26) \cdot 10^3/T + (37.32 \pm 0.47), \quad (\Delta T = 490\text{-}615 \text{ K}). \quad (3)$$

In Fig. 8 the available literature data on TPP vapor pressure are compared. One can see that the values of TPP pressure of different authors agree well to each other at temperatures about 610-620 K. At the same time, the slopes of their temperature trends disagree significantly. Moreover, the temperature dependences in^{6,7} have an evidently expressed non-linear character. Note that our data were obtained in the wider low-temperature range.

FIG. 6. Ionization efficiency curves

FIG. 7. Temperature dependencies of ion currents:

$$1 - \ln I(\text{C}_{44}\text{N}_4\text{H}_{30+}) \cdot T = (-23.54 \pm 0.29) \cdot 10^3 / T + 32.71 \pm 0.53$$

$$2 - \ln I(\text{C}_{44}\text{N}_4\text{H}_{30++}) \cdot T = (-23.24 \pm 0.33) \cdot 10^3 / T + 30.14 \pm 0.61$$

TABLE I. Saturated vapor pressures¹ of TPP

T / K	p / Pa	T / K	p / Pa
595	$1.34 \cdot 10^{-1}$	537	$1.62 \cdot 10^{-3}$
594	$1.10 \cdot 10^{-1}$	544	$2.86 \cdot 10^{-3}$
550	$6.04 \cdot 10^{-3}$	557	$7.63 \cdot 10^{-3}$
551	$5.60 \cdot 10^{-3}$	560	$9.08 \cdot 10^{-3}$
539	$2.56 \cdot 10^{-3}$	577	$3.48 \cdot 10^{-2}$
536	$1.64 \cdot 10^{-3}$	588	$7.00 \cdot 10^{-2}$
498	$6.59 \cdot 10^{-5}$	615	$4.85 \cdot 10^{-1}$
490	$2.26 \cdot 10^{-5}$	612	$3.33 \cdot 10^{-1}$
523	$4.77 \cdot 10^{-4}$		

¹The overall uncertainty is estimated by a factor of 2.

D. Sublimation enthalpy

The vapor pressures allow to calculate the sublimation enthalpy of TPP using approaches of the second and third laws of thermodynamics.

The second law calculation is based on the Clausius-Clapeyron equation

$$\ln p/p^\circ = - \frac{\Delta_s H^\circ(T)}{RT} + \frac{\Delta_s S^\circ(T)}{R}, \quad (4)$$

where $p^\circ = 0.1$ MPa is a standard pressure, $\Delta_s H^\circ(T)$ and $\Delta_s S^\circ$ are the enthalpy and entropy of sublimation. It is important to emphasize that in this method the sublimation enthalpy for the average temperature range can be determined from the slope of temperature dependence not only for absolute vapor pressure but also for any experimentally measured quantity, proportional to pressure.

FIG. 8. Temperature dependence of TPP vapor pressure (polymorphic modification is given in parentheses): 1 – triclinic (our data); 2 – tetragonal₇; 3 – not specified₃; 4 – triclinic₆; 5 – presumably tetragonal₄

The calculations according to the third law are performed using absolute vapor pressures in accordance with the equation

$$\Delta_s H^\circ(298.15 \text{ K}) = T(\Delta_s \Phi^\circ(T) - R \ln p/p^\circ), \quad (5)$$

where $\Phi^\circ = - (G^\circ(T) - H^\circ(298.15 \text{ K})) / T$ is a reduced Gibbs energy.

The thermodynamic functions of TPP in the gas and crystalline phases, necessary for these calculations, were obtained from quantum chemical computations and experimental measurements of heat capacity (see below).

The results of processing of all the experimental data are given in Table II. As can be seen, the $\Delta_s H^\circ$ and $\Delta_s S^\circ$ values obtained by the different authors are largely scattered. The observed deviations are far beyond of the limits of the evaluated errors. Let us try to analyze the possible causes of such strong discrepancies. As for the second law values, there are many different factors such as: a sample purity, type of crystal lattice, magnitude of temperature range studied, thermal stability of crystal phase, etc., which turn out a noticeable effect on the value of sublimation enthalpy. According to the authors of^{22,23}, recrystallization of TPPs from a solution leads, depending on the solvent, to the formation of porphyrin sponges (clathrate lattices) of various polymorphic modifications. Therefore, it is important to conduct a preliminary control of the crystalline phase of the studied samples, which was not done, with exception of this work, by the authors of the works discussed here. The enthalpy of sublimation obtained by Golubchikov et al.⁶ for triclinic ($\Delta_s H^\circ(578 \text{ K}) = 207 \pm 10 \text{ kJ mol}^{-1}$) and Perlovich et al.⁷ for tetragonal ($\Delta_s H^\circ(588 \text{ K}) = 240 \pm 7 \text{ kJ mol}^{-1}$) modifications should be considered as rough estimates due to the mentioned above nonlinearity of temperature dependences. The enthalpy of sublimation $\Delta_s H^\circ(550 \text{ K}) = 171 \pm 2 \text{ kJ mol}^{-1}$, determined by Torres et al.⁸, cannot be considered to be reliable due to too narrow temperature range (12 K). In the work⁴ the temperature range in which the measurements were performed is missing, and the absolute vapor pressure is given only at one temperature ($T = 668 \text{ K}$). The sublimation enthalpies obtained in^{3,9,10} do not have a definite meaning since it is unclear which TPP modification they relate to. At the same time it should be noted, that for the results with known or suggested TPP modification (this work and the data^{4,6,7,8}), no relation between the sublimation enthalpy and modification is observed.

Processing according to the third law, based on absolute vapor pressure, was performed for the data from^{3,4,6,7} and this work. Since the vapor pressures for different authors agree with each other within one order of magnitude, the third law enthalpies are also close and lie in the range of 212–220 kJ mol⁻¹. At the same time, comparison of $\Delta_s H^\circ(298.15 \text{ K})$ and $\Delta_s S^\circ(T)$ calculated according to the third and second laws shows a good agreement only for our data, in contrast to literature data, where they either disagree^{3,4} or their concordance much worse^{6,7}. Moreover, as can be seen from Fig. 9, a weak temperature trend of the third law value $\Delta_s H^\circ(298.15 \text{ K})$

is observed in the case of our data unlike the data from^{3,6,7}. This indicates a high reliability of the values obtained in this work. Thus, all of the above allows us to recommend the value $\Delta_s H^\circ(298.15 \text{ K}) = 220 \pm 12 \text{ kJ mol}^{-1}$ for the trigonal form of TPP. The overall error given with a "±" sign includes statistical (standard deviation) and systematic uncertainties (5 % from $\Delta_s H^\circ$ value).

E. Thermodynamic functions

1. The thermodynamic functions of TPP in the solid state

The thermodynamic functions of TPP in the solid state (Table III) were calculated based on measurements of specific heat capacity (Fig. 10, Table SI in Supplementary Material). In our opinion, a small peak in the range from 270 to 280 K can be caused by the presence of water, sorbed by the sample when loaded into the effusion cell under atmospheric conditions. The experimental data C_p in the temperature range 300–700 K, used in calculations of thermodynamic functions, were approximated by the equation

$$C_p/(\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) = -90.32 + 2.830 \cdot T - 7.161 \cdot 10^{-4} \cdot T^2 \quad (6)$$

The standard absolute entropy $S^\circ(298.15 \text{ K}) = 679 \text{ J mol}^{-1} \text{ K}^{-1}$ was estimated using the correlation equation from²⁴ and The standard absolute entropy $S^\circ(298.15 \text{ K}) = 679 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ estimated by the correlation equation²⁴

$$S^\circ(298.15 \text{ K})_{\text{solid}}/(\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) = 1.285 \left[\frac{M}{\rho} / (\text{cm}^3 \cdot \text{mol}^{-1}) \right] + 57 \quad (7)$$

2. The thermodynamic functions of TPP in an ideal gas state

The thermodynamic functions of TPP in an ideal gas state were obtained from density functional theory (DFT) simulations. All spatial molecular structures were exposed to geometry optimization with the hybrid generalized gradient approximation (GGA) functional of Perdew and co-workers PBE0^{25,26,27} using the Gaussian 09 software²⁸. The choice of the PBE0 is attributed to low errors obtained for this particular DFT model in reproducing of experimental molecular geometries free from collective interactions^{29,30,31}. The def2- tzvp³² sets of nuclear-centered Gaussian functions developed in the Karlsruhe group were employed for all the elements. Built-in Gaussian 09 criteria were applied for the convergence of the self-consistent-field (SCF) scheme. The “tight” internal Gaussian 09 geometry optimization stopping criteria were utilized: maximum gradient = $1.5 \cdot 10^{-5}$ a.u., RMS gradient = $1.0 \cdot 10^{-5}$ a.u., maximum displacement = $6.0 \cdot 10^{-5}$ Å, and RMS displacement = $4.0 \cdot 10^{-5}$ Å. The exchange-correlation potential was integrated numerically using the “ultrafine” pruned grid (99 radial shells and 590 angular points per shell) to get rid of any numerical noise. All optimized spatial structures were

indicated as stable potential energy surface (PES) minima by the eigenvalues of the electronic energy second derivatives matrix computed analytically.

On basis of calculated molecular parameters (Table S2, S3 in Supplementary Material) the thermodynamic functions of TPP in the state of ideal gas were computed in the “Rigid Rotator - Harmonic Oscillator” (RRHO) approximation by the StatThermo software³³. The calculations were performed for the ground electronic state of TPP. A preliminary estimate of the contribution of the low-lying excited electronic states as has been shown to be negligible. The molecule of TPP refers to a point group of symmetry C_{2v} . However, because of NH tautomerism^{5,34}, the two central hydrogen atoms are distributed between the four nitrogen atoms so quickly that it cannot be detected in NMR experiments. Thus, from this point of view, the TPP molecule can be formally attributed to the symmetry group C_{4v} . For this reason, the symmetry number $\sigma = 4$ was used in the calculations. The thermodynamic functions of the TPP molecule were computed in the range of 298–700 K and are shown in Table III.

FIG. 9. Dependence of the third law sublimation enthalpy of TPP versus the temperature: 1 – our data; 2; 3; 4 – the works^{7,3,6} respectively

FIG. 10. Temperature dependence of the heat capacity of TPP

Table II. Enthalpies $\Delta_s H^\circ$ (kJ·mol⁻¹) and entropies $\Delta_s S^\circ$ (J·mol⁻¹ K⁻¹) of TPP sublimation

ΔT / K	$\langle T \rangle$ / K	II law ^a			III law ^b		Modification	Method ^c	Ref.
		$\Delta_s H^\circ(T)$	$\Delta_s S^\circ(T)$	$\Delta_s H^\circ(298.15)_d$	$\Delta_s H^\circ(298.15)$	$\Delta_s S^\circ(T)$			
490–615	557	195±2	214±4	220±2	217±60	207±60	triclinic	KEMS	This work
573–673	578	207±10	243±15	245±10	212±60	195±60	triclinic	IGF	[6]
543–555	550	171±2		197±2			presumably triclinic	KE	[8]
543–633	588	240±7	278±10	275±7	220±60	191±60	tetragonal	IGF	[7]
	668	146		196	212±60		presumably tetragonal	VPAS	[4]
588–678	633	111±5	87±3	152±5	219±60	180±60	not specified	KE	[3]
626–707	667	142±3		191±3			not specified	FMDB	[9]
618–665	642	160±3		203±3			not specified	IGF	[10]

^a A standard deviation is given with the “±” sign.

^b Evaluation of the systematic error is given with the “±” sign. The latter is mainly determined by the uncertainty of thermodynamic functions.

^c Methods: KE is the Knudsen effusion, VPAS vapor phase absorption spectroscopy, IGF inert gas flow, FMDB fluorescence on molecular diluted beams, KEMS Knudsen effusion mass spectrometry.

^d The literature data of $\Delta_s H^\circ(T)$ were recalculated onto $\Delta_s H^\circ(298.15)$ using thermodynamic function from this work (see Table III).

Table III. Thermodynamic functions of TPP

T/K	S° $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$\Phi^{\circ'}$	$H^\circ(T)-H^\circ(298.15)$ $\text{kJ}\cdot\text{mol}^{-1}$	S° $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$\Phi^{\circ'}$	$H^\circ(T)-H^\circ(298.15)$ $\text{kJ}\cdot\text{mol}^{-1}$
		gas			crystal	
298.15	946.8	946.5	0.0	679.0	679.0	0.0
400	1160.7	973.8	75.4	915.7	709.1	82.5
500	1369.3	1032.3	167.9	1145.8	773.4	186.2
600	1567.2	1105.0	276.2	1373.0	854.5	311.1
700	1753.4	1184.4	398.3	1595.4	944.5	455.7

The uncertainties in the thermodynamic functions were estimated as 5% in accordance with the procedure discussed in Ref.³⁵.

F. TPP gas phase formation enthalpy

The TPP heat of formation in an ideal gas state was derived via the reaction-based methodology^{36,37}. In this approach, the TPP heat of formation is expressed through the difference between accurate reference heats of formation and enthalpy change of ad hoc composed chemical reactions. The next reference $\Delta_f H^\circ(298.15)$ data in $\text{kJ}\cdot\text{mol}^{-1}$ retrieved from the Active Thermochemical Tables at Argonne national laboratory web-page³⁸ were utilized in our research: 228.26 ± 0.13 (C_2H_2), 52.36 ± 0.12 (C_2H_4), -45.56 ± 0.03 (NH_3), 88.34 ± 0.62 (CH_3N), 129.27 ± 0.09 (HCN), 83.11 ± 0.23 (C_6H_6), 50.01 ± 0.34 (C_7H_8). For pyrrole the experimental gas phase heat of formation of 108.3 ± 0.5 kJ mol^{-1} ³⁹ was adopted as it reasonably matches the theoretically predicted value of 109.2 ± 2.3 kJ mol^{-1} ⁴⁰.

Total theoretical reaction enthalpies ($\Delta_r H^\circ$) at 298.15 K were calculated from the following modified Feller-Peterson-Dixon (FPD) method^{41,42,43,44,45,46} presented in equation (7) with Δ referring to the difference between the reactants and products for each enthalpy component:

$$\Delta_r H^0(298.15 \text{ K}) = \Delta E_{CBS} + \Delta H_{CORR} + \Delta E_{AUG} + \Delta E_{CV} + \Delta E_{IT} + \Delta E_{PNO} \quad (8)$$

The ΔE_{CBS} term was evaluated as a difference between the single-point (SP) energies of the reactants and the products. All SP energies were obtained with the domain based local pair natural orbital (DLPNO) coupled cluster CCSD(T) approach,^{47,48,49} as a part of the ORCA software.⁵⁰ The DLPNO-CCSD(T) approach yielded more accurate enthalpies of reactions comparing to popular DFT models.^{51,52} The default “NormalPNO” DLPNO settings were adopted. Triple and quadruple- ζ correlation consistent Gaussian nuclear centered basis sets were employed. Hydrogen, carbon and nitrogen atoms were described with the Gaussian-type cc-pVnZ basis sets of Dunning⁵³. Only valence electrons of H, C, N were correlated following the “frozen core” ORCA defaults. The extrapolation to an infinite basis set was performed separately for the HF and the CCSD(T) correlation energies using the two-point (TZ/QZ) scheme proposed by Helgaker and co-authors.^{54,55,56}

Additional corrections to the DLPNO-CCSD(T)/CBS reaction energy ΔE_{CBS} are requested to attain higher accuracy. The PBE0/def2-tzvp molecular spatial structures and unscaled harmonic vibrational frequencies were exerted to compute the enthalpic correction (H_{CORR}) for all individual compounds. The impact of diffuse functions on reaction energies, ΔE_{AUG} , was estimated via the difference in DLPNO-CCSD(T) reaction energies obtained with aug-cc-pVTZ and cc-pVTZ basis sets. The core-valence energy correction on reaction energies, ΔE_{CV} , was approximated by the difference in DLPNO-CCSD(T) reaction energies obtained with cc-pwCVTZ basis sets (cc-pVTZ on H) and all electrons (AE) correlated, and

cc-pVTZ basis sets and the default “frozen core” framework. The effect of iterative triples correction on reaction energies, ΔE_{IT} , was estimated via the difference in DLPNO-CCSD(T1) reaction energies obtained with iterative (T1) and the default DLPNO-CCSD(T) with semi-canonical (T) and cc-pVTZ basis sets. Finally, the impact of tighter PNO settings, ΔE_{PNO} , was estimated via comparison DLPNO-CCSD(T)/cc-pVTZ reaction energies obtained with TightPNO (TCutPairs = 10^{-5} , TCutPNO = 10^{-7} , and TCutMKN = 10^{-3}) and default NormalPNO settings. For all but the AE simulations, the correlation fitting basis sets ((aug-)cc-pVnZ/C) worked out by Hättig et al.⁵⁷ mandatory for the resolution of identity (RI) approximation which is at root of the DLPNO approach were utilized. The AutoAux⁵⁸ option was employed for automatic initiation of correlation fitting Gaussian basis sets requested for for the AE computations. The ideal gas TPP formation enthalpies are collected in Table IV.

An analysis of Table IV reveals that the largest impact on reaction energies were obtained from inclusion of diffuse Gaussian functions (ΔE_{AUG}) and using of iterative (T1) triples instead their semi-canonical counterparts, ΔE_{IT} . The significance of core-valence correction (ΔE_{CV}) and tightening of PNO frameworks (ΔE_{PNO}) were both noticed to be less important. The resulting heats of formation were detected to vary considerably on chemical reaction applied. The averaged over 10 reactions ΔH_f° (298.15 K) amounts 1004 ± 10 kJ mol⁻¹ (a doubled standard deviation is accepted as an error).

G. Enthalpy of formation of TPP in crystal state

The standard values of formation enthalpy of crystalline TPP were experimentally determined in works^{59,60,61}. The first of these $\Delta_f H^\circ(298.15 \text{ K}) = 621.3 \pm 8.5$ kJ·mol⁻¹ was obtained by Wu et al.⁵⁹ in 1989 using static bomb calorimeter. Then in 1999 Patino et al.⁶⁰ using combustion calorimeter measured the standard molar energy of combustion and calculated the formation enthalpy $\Delta_f H^\circ(298.15 \text{ K}) = 655 \pm 9$ kJ·mol⁻¹. The last value $\Delta_f H^\circ(298.15 \text{ K}) = 1174.8 \pm 33.7$ kJ·mol⁻¹ from work⁶¹ was calculated from the enthalpy of combustion found by the liquid calorimetry with isothermal shell. It is obvious that all the above results contradict to each other.

In this work, the formation enthalpy of crystalline TPP was obtained as the difference between the gas phase formation enthalpy and the enthalpy of sublimation. Our value $\Delta_f H^\circ(298.15 \text{ K}) = 784 \pm 15$ kJ·mol⁻¹ is within the range of the above literature values^{59,60,61}.

TABLE IV. Enthalpies of formation of TPP in the gaseous state as well as corresponding reaction enthalpies along with individual contributions in kJ mol⁻¹.

N	Reaction	ΔE_{CBS} ^a	ΔE_{AUG} ^b	ΔE_{CV} ^c	ΔE_{IT} ^d	ΔE_{PNO} ^e	ΔH_{CORR} ^f (298.15)	$\Delta H_{\text{r}}^{\circ}$ (298.15)	$\Delta H_{\text{f}}^{\circ}$ (298.15)
1	$4\text{C}_6\text{H}_6 + 10\text{C}_2\text{H}_4 + 2\text{N}_2 = \text{C}_{44}\text{H}_{30}\text{N}_4 + 17\text{H}_2$	484.6	-51.8	-5.1	-20.5	-1.8	-282.8	122.5	978.6
2	$7\text{C}_6\text{H}_6 + \text{C}_2\text{H}_2 + 4\text{NH}_3 = \text{C}_{44}\text{H}_{30}\text{N}_4 + 13\text{H}_2$	677.3	-9.6	-1.9	-15.9	0.9	-247.9	402.9	1030.7
3	$6\text{C}_6\text{H}_6 + 2\text{C}_2\text{H}_4 + 4\text{HCN} = \text{C}_{44}\text{H}_{30}\text{N}_4 + 9\text{H}_2$	52.6	-46.0	1.8	-14.2	0.7	-125.6	-130.7	989.8
4	$4\text{C}_6\text{H}_6 + 4\text{C}_4\text{NH}_5 + 2\text{C}_2\text{H}_4 = \text{C}_{44}\text{H}_{30}\text{N}_4 + 11\text{H}_2$	391.5	-24.4	-0.4	-16.7	3.5	-211.6	141.8	1012.2
5	$4\text{C}_6\text{H}_6 + 4\text{C}_4\text{NH}_5 + 2\text{C}_2\text{H}_2 = \text{C}_{44}\text{H}_{30}\text{N}_4 + 9\text{H}_2$	-21.9	-24.7	2.3	-15.6	3.0	-154.1	-211.0	1011.2
6	$4\text{C}_7\text{H}_8 + 4\text{C}_4\text{NH}_5 = \text{C}_{44}\text{H}_{30}\text{N}_4 + 11\text{H}_2$	641.0	-17.2	-0.8	-16.8	5.4	-228.5	383.0	1016.3
7	$4\text{C}_7\text{H}_8 + 4\text{CH}_2\text{NH} + 6\text{C}_2\text{H}_4 = \text{C}_{44}\text{H}_{30}\text{N}_4 + 19\text{H}_2$	545.1	-27.9	-11.0	-21.2	0.5	-354.3	131.2	998.8
8	$4\text{C}_7\text{H}_8 + 4\text{CH}_2\text{NH} + 6\text{C}_2\text{H}_2 = \text{C}_{44}\text{H}_{30}\text{N}_4 + 13\text{H}_2$	-695.0	-28.7	-3.1	-17.8	-0.7	-181.8	-927.1	995.9
9	$6\text{C}_6\text{H}_6 + 2\text{C}_2\text{H}_4 + 4\text{CH}_3\text{N} = \text{C}_{44}\text{H}_{30}\text{N}_4 + 13\text{H}_2$	336.1	-31.8	-6.5	-16.5	1.2	-236.8	45.7	1002.4
10	$6\text{C}_6\text{H}_6 + 2\text{C}_2\text{H}_2 + 4\text{CH}_3\text{N} = \text{C}_{44}\text{H}_{30}\text{N}_4 + 11\text{H}_2$	-77.3	-32.0	-3.8	-15.4	0.7	-179.3	-307.1	1001.5
Average									1004$\pm$5 ^g

^a ΔE DLPNO-CCSD(T) reaction energy obtained from cc-pVTZ/cc-pVQZ CBS extrapolation; ^b the effect of diffuse functions obtained as a difference between DLPNO-CCSD(T)/aug-cc-pVTZ and DLPNO-CCSD(T)/cc-pVTZ reaction energies; ^c the effect of core-valence correlation obtained as a difference between AE DLPNO-CCSD(T)/cc-pwCVTZ (cc-pVTZ on H) and FC DLPNO-CCSD(T)/cc-pVTZ reaction energies; ^d the effect of iterative triples obtained as a difference between DLPNO-CCSD(T1)/cc-pVTZ and the default DLPNO-CCSD(T)/cc-pVTZ reaction energies; the effect of tightening of PNO settings obtained as a difference between Tight PNO DLPNO-CCSD(T)/cc-pVTZ and Normal PNO DLPNO-CCSD(T)/cc-pVTZ reaction energies; ^f the effect of enthalpic correction on reaction energies to arrive at reaction enthalpies; ^g a standard deviation is given with the “ $\pm$ ” sign.

IV. CONCLUSION

In the course of a comprehensive investigation of the evaporation of 5,10,15,20-tetraphenylporphyrin (TPP), the following new results were obtained:

- (1) TPP evaporates congruently in the molecular form $C_{44}N_4H_{30}$ in the temperature range 490–615 K.
- (2) TPP begins to decompose at a temperature of about 700 K. The melting temperature and the enthalpy of melting are 720 ± 6 K and 17 ± 5 kJ·mol⁻¹, respectively.
- (3) The saturated vapor pressure was measured and the sublimation enthalpy $\Delta_s H^\circ(298.15\text{ K}) = 220 \pm 12$ kJ mol⁻¹ for the triclinic form of TPP was recommended.
- (4) The formation enthalpy $\Delta_f H^\circ(298.15\text{ K}) = 1004 \pm 10$ kJ mol⁻¹ of gaseous TPP molecules was determined using a high quality reaction-based Feller-Peterson-Dixon DLPNO-CCSD(T) approach.
- (5) The formation enthalpy of crystalline TPP $\Delta_f H^\circ(298.15\text{ K}) = 784 \pm 15$ kJ was obtained based on the gas phase formation enthalpy and the enthalpy of sublimation.
- (6) The specific heat capacity of TPP in the solid state was measured and quantum-chemical calculations of the structure and force field of TPP molecules were performed. The results obtained made it possible to calculate the thermodynamic functions of TPP in the solid and gaseous states.

SUPPLEMENTARY MATERIAL

The atomic coordinates, vibrational frequencies and IR-intensities of the TPP molecule obtained as a result of quantum-chemical calculations are summarized in Tables S1, S2 and S3 in Supplementary Material.

ACKNOWLEDGEMENTS

This work was supported by the Ministry of science and higher education of the Russian Federation in the framework of Government order (№ FZZW-2020-0007).

The authors are grateful to Ph.D. N.L. Pechnikova and Dr. V.V. Aleksandriiskii (Research Sharing Center of the Ivanovo State University of Chemistry and Technology) for the synthesis of TPP and the study of the NMR spectrum,

respectively, Ph.D. D.V. Tyurin (Department of Chemistry and Technology of Higher Molecular Compounds of the Ivanovo State University of Chemistry and Technology) for the MALDI spectrum of TPP and Ph.D. A.A. Gushchin (Department of Industrial Ecology of the Ivanovo State University of Chemistry and Technology) for the analysis of TPP sample by the high performance liquid chromatography. The authors also thank Ph.D. M.S. Gruzdev (Research Sharing Center of the Institute of Solution Chemistry RAS, Ivanovo) and Ph.D. D.N. Sergeev (Forschungszentrum Jülich, IEK-2, Germany) for measuring the heat capacity of TPP in the temperature ranges 169–302 K and 328–568 K, respectively.

REFERENCES

- ¹E.K.M. Kadish, K.M. Smith, and R. Guillard, *The Porphyrin Handbook*, Academic Press, San Diego, 2003, Vols.1–20.
- ²“Chemistry of biologically active natural compounds (carbohydrate-protein complexes, chromoproteins, lipids, lipoproteins, metabolism)”, ed. by N. A. Preobrazhenskij and R. P. Evstigneeva, Chemistry, Moscow, 1976. [in Russian]
- ³D. Bonderman, E.D. Cater, W.E. Bennett, Vapor pressures, mass spectra, magnetic susceptibilities, and thermodynamics of some phthalocyanine compounds, *J. Chem. Eng. Data*, 15 (1970), pp. 396-400. DOI: <https://doi.org/10.1021/je60046a004>
- ⁴L. Edwards, D.H. Dolphin, M. Gouterman, A.D. Adler, Porphyrins XVII. Vapor absorption spectra and redox reactions: tetraphenylporphins and porphin, *J. Mol. Spectrosc.*, 38 (1971), pp. 16-32. DOI: [https://doi.org/10.1016/0022-2852\(71\)90090-7](https://doi.org/10.1016/0022-2852(71)90090-7)
- ⁵O.A. Golubchikov, G.L. Perlovich, B.K. Naneishvilli, Termodinamika sublimacii tetrafenilporfirina (Sublimation thermodynamics of tetraphenylporphyrin) *Zh. Fiz. Khim.*, 68 (1994), pp. 2120-2123. [in Russian]
- ⁶O.A. Golubchikov, G.L. Perlovich, Termodinamika sublimacii porfirinov, In: “Advances in chemistry of porphyrins”, Ed. by Golubchikov O.A., Vol. 1, Ch. 10, St. Petersburg State University, 1997, pp. 223-245. [in Russian]
- ⁷G. L. Perlovich, O.A. Golubchikov, M.E. Klueva, Thermodynamics of porphyrin sublimation, *J. of Porphir. Phthalocyanines*, 4 (2000), pp. 699-706. DOI: [10.1002/1099-1409\(200012\)4:8<699::AID-JPP284>3.0.CO;2-M](https://doi.org/10.1002/1099-1409(200012)4:8<699::AID-JPP284>3.0.CO;2-M)
- ⁸L.A. Torres, M. Campos, E. Enriquez, R. Patino The enthalpy of sublimation of 5,10,15,20-tetraphenylporphine and 5,10,15,20-tetrakis(4-methoxyphenyl)porphine, *J. Chem. Thermodynamics*, 34 (2002), pp. 293-302. DOI: <https://doi.org/10.1006/jcht.2001.0920>

-
- ⁹A.A. Stefanov, A. Stibor, A. Dominguez-Clarimon, M. Arndt, Sublimation enthalpy of dye molecules measured using fluorescence, *J. Chem. Phys.*, 121 (2004), pp. 6935-6940. DOI: <https://doi.org/10.1063/1.1792551>
- ¹⁰S. Deachapunya, A. Stefanov, M. Berninger, H. Ulbricht, E. Reiger, N.L. Doltsin, M. Arndt, Thermal and electrical properties of porphyrin derivatives and their relevance for molecule interferometry, *J. Chem. Phys.*, 126 (2007), pp. 164304-1-164304-7. DOI: <https://doi.org/10.1063/1.2721563>
- ¹¹A.S. Semeikin, O.I. Koifman, B.D. Berezin, Improved method for synthesis of substituted tetraphenylporphyrins *Chem. Heterocycl. Compd*, 22 (1986) pp. 629-632.
- ¹²S.J. Silvers, A. Tulinsky, The crystal and molecular structure of triclinic tetraphenylporphyrin, *J. Amer. Chem. Soc.*, 89 (1967) pp. 3331-3337. DOI: [10.1021/ja00989a036](https://doi.org/10.1021/ja00989a036)
- ¹³K.M. Smith, D.A. Goff, R.J. Abraham, J.E. Plant, The NMR spectra of porphyrins: 22 — Ring current effects in chlorins versus porphyrins, *Org. Magn. Reson.*, 21 (1983), pp. 505-511. DOI: <https://doi.org/10.1002/omr.1270210811>.
- ¹⁴J.L. Soret, Analyse spectrale: sur le spectre d'absorption du sang dans la partie violette et ultraviolette, *Compt. Rend*, 97 (1883), pp. 1269-1273. [in French]
- ¹⁵M. Biesaga, K. Pyrzynska, M. Trojanowicz, Porphyrins in analytical chemistry. A review., *Talanta*, 51 (2000), pp. 209-224. DOI: [10.1016/s0039-9140\(99\)00291-x](https://doi.org/10.1016/s0039-9140(99)00291-x)
- ¹⁶A.M. Pogrebnoi, L.S. Kudin, A.Yu. Kuznetsov, M.F. Butman, Molecular and ionic clusters in saturated vapor over lutetium trichloride, *Rapid Commun. Mass Spectrom.*, 11 (1997), pp. 1536–1546. DOI: [https://doi.org/10.1002/\(SICI\)1097-0231\(199709\)11:14<1536:AID-RCM31>3.0.CO;2-D](https://doi.org/10.1002/(SICI)1097-0231(199709)11:14<1536:AID-RCM31>3.0.CO;2-D)
- ¹⁷A.M. Dunaev, V.B. Motalov, L.S. Kudin, A high-temperature mass-spectrometric method for determination of the electron work function of ionic crystals: Lanthanum, cerium, and praseodymium triiodides, *Russ. J. Gen. Chem.*, 87 (2017), pp. 632-638. DOI: [10.1134/S1070363217030410](https://doi.org/10.1134/S1070363217030410)
- ¹⁸A.M. Dunaev, A.S. Kryuchkov, L.S. Kudin, M.F. Butman, Avtomatizirovanny kompleks dlya vysokotemperaturnykh issledovaniy na baze mass-spektrometra MI1201 (Automated complex for high temperature research based on the mass spectrometer MI1201), *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.*, 54 (2011), pp. 73-77. [in Russian]
- ¹⁹D.N. Sergeev, A.M. Dunaev, D.A. Ivanov, Y.A. Golovkina, G.I. Gusev, Automation of a mass spectrometer for determination of ionization efficiency functions, *Russ. Instrum. Exp. Tech.*, 1 (2014), pp. 139-140. DOI: [10.7868/S0032816214010200](https://doi.org/10.7868/S0032816214010200)
- ²⁰G. Della Gatta, M.J. Richardson, S.M. Sarge, S. Stølen, Standards, calibration, and guidelines in microcalorimetry. Part 2. Calibration standards for differential scanning calorimetry (IUPAC Technical Report), *Pure Appl. Chem.*, 78 (2006), pp. 1455-1476. DOI: <https://doi.org/10.1351/pac200678071455>
- ²¹K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki, S. Iwata “Handbook of HeI Photoelectron Spectra of Fundamental Organic Compounds”, Japan Scientific Society Press, Tokyo, 1981.

-
- ²²O.R. Simonova, V.B. Sheinin. Thermodynamics of Formation of Porphyrin Sponge in the Etioporphyrin III-Methanol System, *Russ. J. Gen. Chem.* 78 (2008), pp. 1268-1272. DOI: [10.1134/S1070363208060297](https://doi.org/10.1134/S1070363208060297)
- ²³M.P. Byrn, C.J. Curtis, Yu Hsiou, S.I. Khan, P.A. Sawin, S.K. Tendick, A. Terzis, C.E. Strouse. Porphyrin Sponges: Conservation of Host Structure in over 200 Porphyrin-Based Lattice Clathrates, *Am. Chem. Soc.*, 115 (1993), pp. 9480-9491. DOI: <https://doi.org/10.1021/ja00074a013>
- ²⁴L. Glasser, H.D.B. Jenkins, Standard absolute entropies, S°_{298} , from volume or density: Part II. Organic liquids and solids, *Thermochim. Acta*, 414 (2004), pp. 125–130. DOI: <https://doi.org/10.1016/j.tca.2003.12.006>
- ²⁵J.P. Perdew, K. Burke, M. Ernzerhof, Generalized Gradient Approximation Made Simple, *Phys. Rev. Lett.*, 77 (1996), pp. 3865-3868. DOI: <https://doi.org/10.1103/PhysRevLett.77.3865>
- ²⁶J.P. Perdew, K. Burke, M. Ernzerhof, Generalized Gradient Approximation Made Simple [*Phys. Rev. Lett.* 77, 3865 (1996)], *Phys. Rev. Lett.*, 78 (1997), pp. 1396. DOI: <https://doi.org/10.1103/PhysRevLett.78.1396>
- ²⁷C. Adamo, V. Barone, Toward reliable density functional methods without adjustable parameters: The PBE0 model, *Chem. Phys.*, 110 (1999), pp. 6158-6170. DOI: <https://doi.org/10.1063/1.478522>
- ²⁸*Gaussian 09*, Gaussian / Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J., Inc.: Wallingford, CT, USA, 2009.
- ²⁹Y. Minenkov, L. Cavallo, Ground-State Gas-Phase Structures of Inorganic Molecules Predicted by Density Functional Theory Methods, *ACS Omega*, 2 (2017), pp. 8373-8387. DOI: <https://doi.org/10.1021/acsomega.7b01203>
- ³⁰I. Minenkova, V.V. Sliznev, L. Cavallo, Y. Minenkov, Gas Phase Silver Thermochemistry from First Principles, *Inorg. Chem.*, 58 (2019), pp. 7873-7885. DOI: <https://doi.org/10.1021/acs.inorgchem.9b00556>
- ³¹G.V. Girichev, N.I. Giricheva, O.I. Koifman, Y.V. Minenkov, A.E Pogonin, A.S. Semeikin, and S.A. Shlykov, Molecular structure and bonding in octamethylporphyrin tin(ii), *SnN4C28H28*, *Dalton Trans.*, 41 (2012), pp. 7550-7558. DOI: [10.1039/C2DT12499H](https://doi.org/10.1039/C2DT12499H)

-
- ³²F. Weigend, R. Ahlrichs, Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy, *Phys. Chem. Chem. Phys.*, 7 (2005), pp. 3297-3305. DOI: 10.1039/B508541A
- ³³A.M. Dunaev, L.S. Kudin, *Izv. Vyss. Uchebn. Zaved. Khim. Khim. Tekhnol.*, 2017, **60**, 40-46. <https://doi.org/10.6060/tcct.2017604.5490>
- ³⁴Y. Niwa, H. Kobayashi, T. Tsuchiya, X-ray photoelectron spectroscopy of tetraphenylprophine and phthalocyanine, *J. Chem. Phys.*, 60 (1974), pp. 799-807. DOI: <https://doi.org/10.1063/1.1681153>
- ³⁵L.V Gurvich, I.V. Veyts, C.B. Alcock, *Thermodynamic properties of individual substances*, 4th ed., Vol.1, Hemisphere Publishing Corp., New York, 1989.
- ³⁶D.H. Bross, K.A. Peterson, Composite thermochemistry of gas phase U(VI)-containing molecules, *J. Chem. Phys.*, 141 (2014), pp. 244308. DOI: <https://doi.org/10.1063/1.4904721>
- ³⁷Y. Minenkov, V.V. Sliznev, L. Cavallo, *Accurate Gas Phase Formation Enthalpies of Alloys and Refractories Decomposition Products*, *Inorg. Chem.*, 2017, **56**, 1386-1401, DOI: 10.1021/acs.inorgchem.6b02441.
- ³⁸B. Ruscic, R.E. Pinzon, G. von Laszewski, D. Kodeboyina, A. Burcat, D. Leahy, D. Montoya, A. F.Wagner, *Active Thermochemical Tables: Thermochemistry for the 21st Century*, *J. Phys. Conf. Ser.*, 16 (2005), pp. 561-570. DOI: <https://doi.org/10.1088/1742-6596/16/1/078>
- ³⁹D.W. Scott, W.T. Berg, Ia Hossenlo, W.N. Hubbard, J.F. Messerly, S.S. Todd, D.R. Douslin, McCullou. Jp, G. Pyrrole Waddingt, *Pyrrole: chemical thermodynamic properties*, *J. Phys. Chem.*, 71 (1967), pp. 2263-2270. DOI: <https://doi.org/10.1021/j100866a046>
- ⁴⁰J.M. Simmie, *A Database of Formation Enthalpies of Nitrogen Species by Compound Methods (CBS-QB3, CBS-APNO, G3, G4)*, *J. Phys. Chem. A.*, 119 (2015), pp. 10511-10526. DOI: <https://doi.org/10.1021/acs.jpca.5b06054>
- ⁴¹D. Feller, K.A. Peterson, D.A. Dixon, A survey of factors contributing to accurate theoretical predictions of atomization energies and molecular structures, *J. Chem. Phys.*, 129 (2008), pp. 204105. DOI: <https://doi.org/10.1063/1.3008061>
- ⁴²D. Feller, K.A. Peterson, D.A. Dixon, Further benchmarks of a composite, convergent, statistically calibrated coupled-cluster-based approach for thermochemical and spectroscopic studies, *Mol. Phys.* 110 (2012), pp. 2381-2399. DOI: <https://doi.org/10.1080/00268976.2012.684897>
- ⁴³K.A. Peterson, D. Feller, D.A. Dixon, Chemical accuracy in ab initio thermochemistry and spectroscopy: current strategies and future challenges, *Theor. Chem. Acc.* 131 (2012), pp. 1-20. DOI: <https://doi.org/10.1007/s00214-011-1079-5>
- ⁴⁴D.A. Dixon, D. Feller, K.A. Peterson, Chapter One - A Practical Guide to Reliable First Principles Computational Thermochemistry Predictions across the Periodic Table, *Annu. Rep. Comput. Chem.*, 8 (2012), pp. 1-28. DOI: <https://doi.org/10.1016/B978-0-444-59440-2.00001-6>
- ⁴⁵D. Feller, K.A. Peterson, D.A. Dixon, Chapter Two - The Impact of Larger Basis Sets and Explicitly Correlated Coupled Cluster Theory on the Feller–Peterson–

-
- Dixon Composite Method, *Annu. Rep. Comput. Chem.*, 12 (2016), pp. 47-78.
DOI: <https://doi.org/10.1016/bs.arcc.2016.02.001>
- ⁴⁶M. Vasiliu, D.J. Grant, D. Feller, D.A. Dixon, Heats of Formation of MH_xCly (M = Si, P, As, Sb) Compounds and Main Group Fluorides from High Level Electronic Structure Calculations, *J. Phys. Chem. A*, 116 (2012), pp. 3717-3727.
DOI: <https://doi.org/10.1021/jp2119229>
- ⁴⁷C. Riplinger, F. Neese, An efficient and near linear scaling pair natural orbital based local coupled cluster method, *J. Chem. Phys.*, 138 (2013), pp. 034106. DOI: <https://doi.org/10.1063/1.4773581>
- ⁴⁸C. Riplinger, B. Sandhoefer, A. Hansen, F. Neese, Natural triple excitations in local coupled cluster calculations with pair natural orbitals, *J. Chem. Phys.*, 139 (2013), pp. 134101. DOI: <https://doi.org/10.1063/1.4821834>
- ⁴⁹C. Riplinger, P. Pinski, U. Becker, E.F. Valeev, F. Neese, Sparse maps—A systematic infrastructure for reduced-scaling electronic structure methods. II. Linear scaling domain based pair natural orbital coupled cluster theory, *J. Chem. Phys.*, 144 (2016), pp. 024109. DOI: <https://doi.org/10.1063/1.4939030>
- ⁵⁰F. Neese, The ORCA program system, *WIREs Comput. Mol. Sci.*, 2 (2012), pp. 73-78. DOI: <https://doi.org/10.1002/wcms.81>
- ⁵¹Y. Minenkov, E. Chermak, L. Cavallo, Accuracy of DLPNO-CCSD(T) Method for Noncovalent Bond Dissociation Enthalpies from Coinage Metal Cation Complexes, *J. Chem. Theory Comput.*, 11 (2015), pp. 64-4676, DOI: <https://doi.org/10.1021/acs.jctc.5b00584>
- ⁵²R. Credendino, Y. Minenkov, D. Liguori, F. Piemontesi, A. Melchior, G. Morini, M. Tolazzi, L. Cavallo, Accurate experimental and theoretical enthalpies of association of TiCl₄ with typical Lewis bases used in heterogeneous Ziegler-Natta catalysis, *Phys. Chem. Chem. Phys.*, 19 (2017), pp. 26996-27006, DOI: 10.1039/c7cp04047d
- ⁵³T.H. Dunning, Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen, *J. Chem. Phys.*, 90 (1989), pp. 1007-1023. DOI: <https://doi.org/10.1063/1.456153>
- ⁵⁴Halkier, T. Helgaker, P. Jørgensen, W. Klopper, H. Koch, J. Olsen, A.K. Wilson, Basis-set convergence in correlated calculations on Ne, N₂, and H₂O, *Chem. Phys. Lett.*, 286 (1998), pp. 243-252. DOI: [https://doi.org/10.1016/S0009-2614\(98\)00111-0](https://doi.org/10.1016/S0009-2614(98)00111-0)
- ⁵⁵T. Helgaker, W. Klopper, H. Koch, J. Noga, Basis-set convergence of correlated calculations on water, *J. Chem. Phys.*, 106 (1997), pp. 9639-9646. DOI: <https://doi.org/10.1063/1.473863>
- ⁵⁶A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, J. Olsen, Basis-set convergence of the energy in molecular Hartree-Fock calculations, *Chem. Phys. Lett.* 302 (1999), pp. 437-446. DOI: [https://doi.org/10.1016/S0009-2614\(99\)00179-7](https://doi.org/10.1016/S0009-2614(99)00179-7)
- ⁵⁷F. Weigend, Efficient use of the correlation consistent basis sets in resolution of the identity MP2 calculations, *J. Chem. Phys.*, 116 (2002), pp. 3175, DOI: <https://doi.org/10.1063/1.1445115>

-
- ⁵⁸G.L. Stoychev, A.A. Auer, F. Neese, Automatic Generation of Auxiliary Basis Sets, *J. Chem. Theory Comput.*, 13 (2017), pp. 554-562. DOI: <https://doi.org/10.1021/acs.jctc.6b01041>
- ⁵⁹D.Q. Wu, G.U. Xu, S.S. Qu, R.S. Xue, C.G. Gu, F. Zhang, Standard enthalpies of combustion and formation of porphyrin derivatives, *Thermochim. Acta*, 154 (1989), pp. 233-245. DOI: [https://doi.org/10.1016/0040-6031\(89\)85460-7](https://doi.org/10.1016/0040-6031(89)85460-7)
- ⁶⁰R. Patino, L.A. Torres, M. Campos, The standard molar enthalpies of formation of 5,10,15,20-tetraphenylporphine and 5,10,15,20-tetrakis(4-methoxyphenyl)porphine by oxygen bomb combustion calorimetry, *J. Chem. Thermodyn.*, 31 (1999), pp. 627-634. DOI: <https://doi.org/10.1006/jcht.1998.0469>
- ⁶¹D.R. Zakirov, D.V. Solomin, A.V. Volkov, A.S. Semeikin, M.I. Bazanov, Standard Enthalpies of Combustion and Formation of Tetraphenylporphin, *Russ. J. Phys. Chem.*, 73 (1999), pp. 2058-2059 [in Russian]