

## Thermodynamic properties of cadmium compounds from quantum chemical evaluations

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By the PM3 method, standard entropies, heats and free energies of formation for some cadmium compounds have been computed. Quantitative relationships  $P_{\text{exper}}$  vs,  $P_{\text{theor}}$ , where  $P$  is any of the mentioned properties, have been established.

*Keywords:* cadmium compounds, thermodynamic properties, quantum chemical evaluation, theory-experiment correlation.

### INTRODUCTION

Cadmium is used for corrosion-preventive coatings on metals, for the production of pigments, solders and alloys, semiconducting materials, plastic stabilizers.<sup>1</sup> Cadmium electrodes are used in batteries and Weston cells.<sup>1</sup> Inorganic compounds of cadmium serve as catalysts in organic synthesis, stabilizers of photoemulsions, sorbents in gas chromatography, semiconducting and optical materials, components of glass, luminophors, explosive compositions, tone compositions in photography, lubricants, mordants on fabrics dyeing and solid electrolytes in chemical power sources.<sup>1</sup> Organocadmium compounds are used for the synthesis of ketones from chloroanhydrides and anhydrides of carboxylic acids, for obtaining hydroperoxides by oxidation of cadmium dialkyl derivatives with oxygen in organic solvents, as well as catalysts for the polymerization of unsaturated substances.<sup>1</sup>

Cadmium and its compound are toxic.<sup>1</sup>

Research into the resistivity of cadmium compounds, as well as into their reactivity, mechanisms of chemical reactions (including those constituting the basis of practical applications) and toxic effects, calls for information on relevant thermodynamic properties. Experimental difficulties are experienced in the measurement of the latter which are not always feasible, and the corresponding methods have substantial restrictions.

It is of value to show the possibility of *a priori* estimation of the above characteristics, namely to reveal the possibility of theoretical reproduction of the quantities considered, and to establish quantitative interrelations between experimental and theoretical manifestations of the thermodynamic properties and study.

#### METHODS

The computations were performed by of the usual PM3 (Parametric Method 1) routine<sup>2,3</sup> using software from the MOPAC package<sup>4,5</sup> with complete geometry optimization (Broyden – Fletcher – Goldfarb – Shanno function minimizer<sup>6</sup>) involving Thiel's fast minimization algorithm.<sup>7</sup> The preliminary optimization was realized by the molecular mechanics method (the MMX procedure)<sup>8</sup> with the software of the PCMODEL complex.<sup>8</sup> Subsequently, bond lengths, valence angles and dihedrals were subjected to correction according to literature data.<sup>3,9</sup> In the quantum chemical computations, the condition that the gradient norm should not exceeding 0.084 kJ/(mol Å) was preset.

The RHF (Restricted Hartree-Fock) and UHF (Unrestricted Hartree-Fock) formalisms<sup>5,10</sup> were used.

In calculating the rotational contributions to the thermodynamic functions, the symmetry number was taken as unity, in order to provide a universal approach for any compound without any restrictions on symmetry.

The regression analysis was performed with the confidence level of 0.95.

#### RESULTS AND DISCUSSION

For evaluating energy characteristics, the methods of quantum chemistry are promising. As for *ab initio* computations, in relation to compounds of cadmium and other heavy elements, only a low level of sophistication is available in a number of cases. Consequently, the results of such treatment depend significantly and not always monotonically on the selected basis and consideration of correlation effects.<sup>10,11</sup> Let, however, the fruitful performance of parallel TURBOMOLE for DFT (Density Functional Theory) geometries (not thermodynamics) computations of cadmium-containing species, be mentioned.<sup>12</sup> Using the relativistic pseudopotential, at the theory level of CCSD(T) (Coupled-Cluster Singles, Doubles, and Triples) with large valence basis sets, the Cd–C bond dissociation energies were reproduced for the Cd(CH<sub>3</sub>)<sub>2</sub> and Cd(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> molecules.<sup>13</sup> The paper by Antes and Frenking<sup>13</sup> contains references to earlier works on *ab initio* considerations of cadmium compounds.

For obtaining rather simplified property evaluations and predictive quantitative relations, it would be reasonable to use the semiempirical quantum chemical methods. Good evaluations of the heats of formation (not entropies and free energies of formation) of cadmium species were obtained by means of the MNDO/d method.<sup>14</sup>

For a series of organic compounds, the correctness of the reproduction of the most important thermodynamic and molecular characteristics by the MNDO, AM1 and PM3 methods,<sup>15–22</sup> as well as of the electronegativity, inductive and mesomeric parameters of the atomic groups.<sup>23</sup> have been established. Whereby the PM3 scheme<sup>2,3</sup> is the only method among the mentioned ones which involves a set of parameters for cadmium.<sup>3</sup> Using the PM3 method, Stewart<sup>3</sup> computed the heats of formation for four Cd-containing molecular systems and indicated that the average absolute error of the quantum chemical evaluation is 10.9 kJ/mol.

All the aforesaid lead to the choice of the PM3 method<sup>2,3</sup> for solving the problems considered in the present work, which was aimed at the evaluation of the standard gaseous-phase heats of formation ( $\Delta H_f$ ), entropies ( $S$ ) and free energies of formation ( $\Delta G_f$ ) of cadmium compounds in order to establish correlations, having a predictive power, between the computed and experimental ones.

It must be stressed that in this paper not only  $P = \Delta H_f$  (values usually treated), but also  $P = S, \Delta G_f$ , estimations of which are reported in only a few papers,<sup>15–22</sup> have been considered. For cadmium-containing species, only the heats of formation were tested earlier.<sup>3</sup>

In this work, the  $\Delta H_f$  and  $S$  quantities were generated directly by the MOPAC package.

It is of importance to explain how the  $S$  values were computed.

The contributions of the separate degrees of freedom for translational, rotational and vibrational motions, to the entropy were computed using the rigid molecule approximation (barriers of rotation and inversion far exceed  $kT$ ) with no allowance made for vibration anharmonicity. The translational contributions were calculated without using quantum chemical computations, but the rotational contributions relied on data of the equilibrium internuclear distances obtained in the course of a quantum chemical treatment. Finally, the contributions of the vibrational component of entropy were evaluated on the basis of normal vibrations frequencies computed by the quantum chemical method. For computing the frequencies after geometric optimization, second-order derivatives of the total energy in natural coordinates (force constants) were preliminary computed.<sup>24</sup>

The  $\Delta G_f$  values were calculated from the relationship:

$$\Delta G_f = \Delta H_f - T\Delta S_f,$$

where the standard entropies of formation  $\Delta S_f$  were calculated using the equation:

$$\Delta S_f = S - \sum S_i$$

in which  $S_i$  are the entropies of the elements constituting the molecule in their standard state<sup>9,24–26</sup> in view of chlorine, bromine, iodine being two-atomic molecules;  $T = 298.15$  K.

The compounds, for which acceptable values of  $\Delta H_f$ ,  $S$  and  $\Delta G_f$  were obtained by the PM3 method, are presented.

Deviations  $\Delta H_{f \text{ theor}} - \Delta H_{f \text{ exper}}$  corresponding to the RHF and UHF computations are negative for all the compounds listed in Table I, except for dimethylcadmium and diethylcadmium. For elementary cadmium, the  $\Delta H_{f \text{ theor}} - \Delta H_{f \text{ exper}}$  quantity is equal to zero.

Positive and negative values of  $S_{\text{theor}} - S_{\text{exper}}$  occur with approximately equal frequency but the positive deviations are much larger, especially for  $\text{CdI}_2$ .

For  $P = \Delta G_f$ , all the values  $P_{\text{theor}} - P_{\text{exper}}$  are negative and exceed those for  $P = \Delta H_f, S$ .

For all the molecular systems, both the RHF and UHF formalisms were used, according to the demand of universality. It was not clear *a priori*, whether the RHF or the UHF approaches would yield the better results.

TABLE I. Experimental and computed values of standard heats of formation

Compound	$\Delta H_f^{\text{exper}}/4.184 \text{ kJ mol}^{-1}$	Ref.	$\Delta H_f^{\text{theor}}/4.184 \text{ kJ mol}^{-1}$	
			RHF	UHF
Cd	26.72	27	26.72	26.72
Cd <sub>2</sub>	51.4	14	53.44	53.44
CdCl	6.548	26	4.96	3.55
CdCl <sub>2</sub>	-46.5	25	-48.52	-48.52
CdBr	15.885	26	4.14	3.17
CdBr <sub>2</sub>	-33.45	9,26	-37.45	-37.45
CdI <sub>2</sub>	-14.4	9,26,28	-23.52	-23.52
Cd(CH <sub>3</sub> ) <sub>2</sub>	25.8	3	30.60	30.60
Cd(CH <sub>3</sub> ) <sub>2</sub> <sup>+</sup>	223.2	3	212.78	211.98
Cd(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	25.5	3	25.92	25.92

It is shown that for the heats and free energies of formation of cadmium compounds, the error of the quantum chemical UHF computations expressed through MS (mean signed) and MU (mean unsigned) (Table IV) are higher than the results of RHF evaluations. In contrast, in the case of the entropies, the MS and MU values are somewhat higher when RHF consideration were applied.

TABLE II. Experimental and computed values of standard entropies

Compound	$S_{\text{exper}}/4.184 \text{ J mol}^{-1} \text{ K}^{-1}$	Ref.	$S_{\text{theor}}/4.184 \text{ J mol}^{-1} \text{ K}^{-1}$	
			RHF	UHF
CdH	50.76	27	48.93	48.96
CdO	56.3	25	56.88	56.89
CdF	57.7	25,27	57.69	57.70
CdF <sub>2</sub>	63.4	26	66.27	66.12
CdS	59.1	26	58.86	58.87
CdCl	60.36	27	59.48	59.52
CdCl <sub>2</sub>	68.3	26	72.19	71.99
SdSe	62.1	26	61.73	61.75
SdBr	62.9	26	62.27	62.31
CdBr <sub>2</sub>	74.0	26	77.82	77.72
CdI	64.7	26	64.32	-
CdI <sub>2</sub>	77.8	26	86.04	83.64

For  $P = \Delta H_f, S, \Delta G_f$  we have established linear dependences of the type

$$P_{\text{exper}} = bP_{\text{theor}}$$

In Table IV the values of  $b$ , the correlation coefficients  $r$ , as well as the following conventional quantities: MS (mean signed) – average value for  $P_{\text{theor}} - P_{\text{exper}}$ , and MU (mean unsigned) – average value for  $P_{\text{theor}} - P_{\text{exper}}$  are shown.

TABLE III. Experimental and computed values of standard free energies of formation

Compound	$\Delta G_{\text{f exper}}/4.184 \text{ kJ mol}^{-1}$	Ref.	$\Delta G_{\text{f theor}}/4.184 \text{ kJ mol}^{-1}$	
			RHF	UHF
CdCl	0.262	26	-4.84	-6.25
CdCl <sub>2</sub>	-47.286	26	-54.16	-54.10
CdBr	6.243	26	-9.01	-9.98
CdBr <sub>2</sub>	-40.978	26	-49.81	-49.78
CdI <sub>2</sub>	-25.631	26	-40.90	-40.18

As it may seem at first, the slope  $b$  and the correlation coefficient can be misleading as to the actual magnitudes of the discrepancies. Seeming contradiction between Tables I–III on the one hand and Table IV on the other is connected with the fact that the MU and MS values are mean quantities. The fact that the slope  $b$  for the dependences  $P_{\text{exper}} = bP_{\text{theor}}$  for  $P = \Delta H_{\text{f}}$  and  $S$  is 1, with little uncertainty, indicates that the PM3 was parameterized well, so that it fails on the high side just as frequently as it fails on the low side. The considerable number of points in the correlation equations may shadow some effects when determining  $b$  and  $r$ ; but the MU and MS values provide more local and detailed information on the accuracy of the computations.

TABLE IV. Coefficients  $b$  in equations  $P_{\text{exper}} = bP_{\text{theor}}$  and the  $r$ , MU, MS values

$P$	Formalism	Number of compounds	$b$	$r$	Error	
					MU	MS
$\Delta H_{\text{f}}$	RHF	10	1.0282±0.0591	0.9973	4.62	-3.16
$\Delta H_{\text{f}}$	UHF	10	1.0312±0.0625	0.9971	4.93	-3.48
$S$	RHF	12	0.9751±0.0262	0.9894	1.98	1.26
$S$	UHF	11	0.9774±0.0232	0.9941	1.85	1.16
$\Delta G_{\text{f}}$	RHF	5	0.7777±0.2648	0.9803	10.27	-10.27
$\Delta G_{\text{f}}$	UHF	5	0.7773±0.2776	0.9833	10.58	-10.58

The agreement between the experimental value of the  $\Delta H_{\text{f}}$  for the elementary substance Cd with the semi-empirical computations is not surprising and originates from the parameterization of the method. The following should be noted: the tendencies in the change of the experimental and theoretical entropies, heats and free energies of formation of cadmium compounds agree with each other ( $r > 0.98$ ).

## CONCLUSION

The existence of quantitative relations  $P_{\text{exper}} = bP_{\text{theor}}$  ( $P = \Delta H_f, S$ ) featured by  $b$  close to unity, high  $r$  values and narrow confidence limits about the slope, the above consideration being different from previous<sup>2,3,14,29-37</sup> qualitative analysis of the absolute errors by data of the MNDO (Modified Neglect of Differential Overlap), MNDO/d (MNDO extended to take the d-orbitals into account), AM1 (Austin Model 1), PM3 SAM1 (Semi-*Ab-Initio* Model 1) methods, shows that the semi-empirical quantum chemical PM3 method does reproduce correctly trends in the alteration of the heat of formation cadmium compounds and the entropies.

The aforesaid is also valid with respect to the free energies of formation, with the only difference being that the value of  $b$  differ noticeably from unity, and the confidence limits are wider.

Using the established correlations, could be predicted the  $P = \Delta H_f, S$  quantities, not always available to experimental measurement. In doing so, the computed values have to be corrected by the multiplier  $b$ .

With the present availability of experimental data arrays of free energy values for cadmium compounds, the relationships  $\Delta G_{f\text{exper}} = b\Delta G_{f\text{theor}}$  would appear to be more reliable and, maybe, also predictive.

The collection of experimental and computed data on the thermodynamic properties of cadmium compounds will favour the enhancement of the reliability of the corresponding quantitative relationships.

*A priori* evaluation of the said parameters by quantum chemical methods is important for the molecular design of cadmium-containing compounds with given properties, may serve as a base for expert decision on the feasibility of a synthesis which is sometimes labour- and time-consuming, requiring complicated equipment, rigid conditions, expensive and toxic chemicals.

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## ИЗВОД

## КВАНТНО-ХЕМИЈСКО ИЗРАЧУНАВАЊЕ ТЕРМОДИНАМИЧКИХ ВЕЛИЧИНА ЗА ЈЕДИЊЕЊА КАДМИЈУМА

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Користећи РМ3 методу израчунате су стандардне ентропије, енталпије и Гибсове енергије стварања неких једињења кадмијума. Утврђени су квантитативни односи  $P_{\text{exper}}$  vs.  $P_{\text{theor}}$  где је  $P$  нека од претходно поменутих величина.

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