



Experimental enthalpies of formation and sublimation of urea compounds: An accuracy assessment

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ABSTRACT

The thermochemical network of 91 isodesmic and other balanced reactions was used to adjust simultaneously the enthalpies of formation of 14 urea compounds. The experimental enthalpies of formation of these compounds were treated as unknowns in the least-squares minimization of deviations between the theoretically predicted enthalpies of reaction and experimental values. A result of a least-squares fit confirms the accuracy of experimental enthalpies of formation of 8 ureas, whereas the experimental measurements for 6 urea compounds require re-examination. The gas-phase standard enthalpies of formation of 8 ureas were used as a consistent basis to obtain values for other 15 ureas through isodesmic reactions. To estimate the enthalpies of formation in crystalline state, the sublimation enthalpies were predicted using the molecular electrostatic potential model.

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1. Introduction

The thermochemical properties of urea and its derivatives, such as enthalpy of formation ($\Delta_f H_m^\circ$) and enthalpy of sublimation ($\Delta_{cr} H_m^\circ$) or vaporization ($\Delta_v H_m^\circ$), have received much attention because these compounds have a number of different applications. A great contribution to these thermochemical studies has been made by Professor Kabo and his co-workers who have investigated the urea and 18 its derivatives [1–9]. The sublimation enthalpy was measured more than once and often by different authors. However, the condensed phase enthalpy of formation of most of the compounds was reported only once and it is desirable to have an additional confirmation of the accuracy of these quantities. In the present work, to check the consistency of experimental data on enthalpies of formation, enthalpies of sublimation, and enthalpies of vaporization, an isodesmic reaction network based on experimental determinations of $\Delta_f H_m^\circ(g)$ was used. Recently, the same approach has been applied to analyse the accuracy of experimental data for adamantanes [10].

The reliability of experimental data on alkyl substituted ureas was validated earlier by Emel'yanenko et al. [9] using group additivity scheme. This scheme is based on the value of $\Delta_f H_m^\circ(\text{urea}, g) = -(237.6 \pm 0.8) \text{ kJ} \cdot \text{mol}^{-1}$ determined by the authors

from experimental measurements of $\Delta_f H_m^\circ(\text{urea}, cr)$ and $\Delta_{cr} H_m^\circ$. It is interesting that this value is significantly lower than that calculated at a high CCSD(F12*)(T) level ($-231.0 \pm 2.8 \text{ kJ} \cdot \text{mol}^{-1}$) [11]. Considering such a large discrepancy, in this work the enthalpy of formation of urea was used in simultaneous least-squares adjustment together with enthalpies of formation of urea derivatives. In addition to isodesmic reaction network, which involves the $\Delta_f H_m^\circ(g)$ values of urea and substituted ureas, the enthalpy of formation of urea was also calculated from a set of working reactions in which the urea derivatives are not used as the reference species. Thus, the purpose of the present work is (1) to establish whether the experimental enthalpy of formation of urea [9] is of benchmark quality and (2) to check the consistency of available experimental data for urea derivatives. To accomplish these tasks, we used the isodesmic and other balanced reactions whose enthalpies were calculated by G4 method [12]. This approach is widely used in thermochemical calculations. It was shown that, compared to DFT, MP2 and other composite methods, the G4 method provides reasonably accurate results even for non-isodesmic reactions [13].

2. Computational details

Preliminary geometry optimization, vibrational frequency calculation, and conformational analysis were carried out at the B3LYP/6-31G(d,p) density functional level. To study the conformational behavior of the molecules, the series of one dimensional

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potential energy profiles were calculated for each internal rotation degree of freedom. The minima were located by the inspection of the calculated torsional profiles, unconstrained optimizations, and frequency calculation. The scan procedure went on until no new potential minima were detected. For some complex molecules (*n*-propylurea, *n*-butylurea, and 3-benzoyl-1,1-diethylurea), the GMMX conformational searching methodology implemented in GaussView 6 [14] was also used for conformational search. Both search methods predict the same most stable conformers, however, a small difference is observed concerning higher energy conformers. The most stable conformers were used to calculate the G4 enthalpies [12] of working reactions. Although some molecules have many conformations, their contribution to the enthalpy of formation was ignored because the products in these working reactions are conformationally similar to the reagent structures and that leads to the cancellation of errors associated with the conformational contribution to the computed enthalpy of formation. Moreover, it was shown that the effect of Boltzmann conformational averaging on the computed enthalpies is partially compensated by neglect of anharmonicity of low frequency torsional motions in the calculation of ZPVEs (zero-point vibrational energies) [15]. All quantum chemical calculations were performed using the Gaussian 16 package of programs [16].

The gas-phase enthalpy of formation of urea was estimated using a set of isogyric, isodesmic, and other balanced reactions with reference species from ATcT [17] (Table S1 of Supplementary material) and by isodesmic reaction network (Table S2 of Supplementary material). An isodesmic reaction network containing 14 experimental enthalpies of formation was created to check the accuracy and internal consistency of experimental enthalpies of formation of urea and its derivatives. A total of 91 balanced reactions was used in the thermochemical network calculations. The enthalpies of formation of 14 ureas were refined by the method of least squares to minimize the discrepancy between the calculated and experimental enthalpies of working reactions. The enthalpies of formations of other species involved in working reactions were fixed; their values were taken from ATcT [17] for the most of compounds. The details of isodesmic reaction calculation are given in Ref. [10]. An optimum set of enthalpies of formation was determined using Generalized Reduced Gradient method available in Microsoft Office Excel Solver. The result was supported by the use of an unconstrained minimization algorithm in MATLAB. The difference in results of two minimization methods is from (0.9 to 1.5) kJ·mol^{−1}. Since the thermochemical network used in this work is highly overdetermined, the preliminary analysis was carried out using different available experimental values of enthalpies of formation and different number of ureas to check the system for overall consistency. The best result was achieved using 14 ureas.

In order to be able to estimate the $\Delta_f H_m^\circ(\text{cr})$ values for urea derivatives not yet studied or for which experimental data are unreliable, the sublimation enthalpies were also calculated in this work. Following ideas introduced by Politzer and co-workers [18], who have shown that sublimation enthalpy may be expressed in terms of molecular descriptors defined from the molecular electrostatic potential (MEP), we proposed the following equation for estimation of sublimation enthalpy [19]:

$$\Delta_{\text{cr}}^{\text{g}} H_m^\circ = a\rho + bA_s + cV_s + d(\sigma_{\text{tot}}^2 v) + e\Pi + f \quad (1)$$

where ρ is the crystal density, A_s is the surface area, V_s is the average value of the potential on the surface, σ_{tot}^2 indicates the variability of the potential on the molecular surface, v is the degree of the balance between positive and negative regions, and Π is the measure of local polarity.

The DFT/B3LYP/6-311++G(3df,2p) method was used to optimize geometries and determine the densities for generating the electro-

static potentials. All descriptors in Eq. (1) were calculated using the program Multiwfn [20]. The coefficients a , b , c , d , e , and f were determined from least-squares fitting to reliable experimental values of sublimation enthalpies of 14 ureas. The computed values of descriptors and coefficients a , b , c , d , e , and f involved in Eq. (1) are given in Table S3 of Supplementary material.

3. Results and discussion

3.1. Urea

Experimental and theoretical values of gas-phase enthalpy of formation of urea are collected in Table 1. In agreement with CCSD(F12*)(T) result [11], the values calculated in this work are somewhat larger than the most recent experimental value of -237.6 kJ·mol^{−1} [9], and only one of 20 working reactions used to calculate the enthalpy of formation of urea (Table S1 of Supplementary material) gives the $\Delta_f H_m^\circ(\text{g})$ value close to the experimental result. It can be also seen from Table 1 that the average value calculated from 20 working reactions not involving urea derivatives (-233.3 kJ·mol^{−1}) agrees well with the value obtained by simultaneous least-squares adjustment of enthalpies of formation of 14 ureas (-233.8 kJ·mol^{−1}). Thus, theoretical calculations give preference to the earlier experimental value (-235.5 kJ·mol^{−1}) determined by Kabo et al. [5], rather than the value of -237.6 kJ·mol^{−1} [9].

The enthalpy of formation of crystalline urea has been determined by three research groups [22,23,2] and, as seen from Table 2, two experimental values are in excellent agreement. The sublimation enthalpy of urea has been determined by four research groups. The values obtained by Suzuki et al. (87.7 kJ·mol^{−1}) [24] and Ferro et al. (90.9 kJ·mol^{−1}) [26] seem to be underestimated. Wit et al. [25] give the value of 98.6 kJ·mol^{−1}, whereas slightly smaller values from (95.5 to 97.6) kJ·mol^{−1} were reported by Kabo et al. [1,5,8,9]. Results of theoretical calculations show that the higher experimental $\Delta_{\text{cr}}^{\text{g}} H_m^\circ$ values [25,5] lead to better agreement between experimental and calculated $\Delta_f H_m^\circ(\text{g})$ values. It is also interesting to note that the gas-phase enthalpy of formation and sublimation enthalpy predicted in this work lead to the value of $\Delta_f H_m^\circ(\text{cr})$ in good agreement with the experimental data [22,2] (Table 2).

3.2. Simultaneous adjustment of experimental enthalpies of formation of ureas 1–14

The results of simultaneous least-squares solution of a thermochemical network of 91 working reactions connecting enthalpies of

Table 1
Experimental and theoretical gas-phase enthalpies of formation of urea.

$\Delta_f H_m^\circ(\text{g})$ / kJ·mol ^{−1}	Comments	Reference
-235.5 ± 1.2	Experiment	[5]
-237.6 ± 0.8	Experiment	[9]
-235.7 ± 1.4	Dissociative photoionization energy measurements combined with W1 and CBS-APNO calculations	[21]
-231.0 ± 2.8	CCSD(F12)/(T)/cc-pVTZ-F12//CCSD(T)/cc-pVTZ ^a	[11]
-232.2 ± 4.0	G4, atomization reaction	This work
-232.4 ± 4.0	G4, bond separation reaction ^a	This work
-233.3 ± 3.0	G4, average of 20 working reactions not involving urea derivatives ^b	This work
-233.8 ± 2.5	G4, thermochemical network of 91 reactions connecting $\Delta_f H_m^\circ(\text{g})$ values for 14 ureas ^c	This work

^a Applied to bond separation reaction $\text{NH}_2\text{C}(\text{O})\text{NH}_2 + 2 \text{CH}_4 = 2 \text{CH}_3\text{NH}_2 + \text{HC}(\text{O})\text{H}$.

^b See Table S1 of Supplementary material.

^c See Table S2 of Supplementary material.

Table 2

Experimental and theoretical enthalpies of formation in both condensed and gaseous phases and enthalpies of sublimation or vaporization of urea and its derivatives.

Compound	$\Delta_f H_m^\circ(\text{cr})$ or $\Delta_f H_m^\circ(\text{l})/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_{\text{cr}}^\circ H_m^\circ$ or $\Delta_l^\circ H_m^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_f H_m^\circ(\text{g})/\text{kJ}\cdot\text{mol}^{-1}$ ^a	Reference ^b
1 Urea (cr)	–333.4 ± 0.2			[22]
	–320.2 ± 2.0			[23]
	–333.1 ± 0.7			[2]
		87.7 ± 0.9		[24]
		98.6		[25]
		90.9 ± 1.9 (381 K)		[26]
		97.6 ± 1.0 (386 K)		[1]
	–333.1 ± 0.7	97.6 ± 1.0	–235.5 ± 1.2	[5]
		96.0 ± 0.5		[8]
		95.5 ± 0.3		[9]
	–333.6 ± 0.6 ^c	96.0 ± 0.5 ^d	–237.6 ± 0.8	[9]
	–334.3 ± 6.0 ^e	100.5 ± 4.5	–233.8 ± 3.5	Calc, this work
2 Methylurea (cr)	–327.8 ± 1.4			[27]
	–332.8 ± 0.8			[2]
		87.3 ± 1.9 (348 K)		[26]
		93.2 ± 1.1 (355 K)		[28]
	–332.8 ± 0.8	99.3 ± 0.7	–233.5 ± 1.0	[5]
	–332.8 ± 0.8	97.1 ± 0.4	–235.7 ± 0.9	[7]
		96.3 ± 0.4		[8]
		95.5 ± 0.5		[9]
	–327.8 ± 1.4 ^f	95.9 ± 0.5 ^d	–231.9 ± 1.5	[9]
	–324.7 ± 6.0 ^e	95.0 ± 4.5	–229.7 ± 3.5	Calc, this work
3 1,1-Dimethylurea (cr)	–319.1 ± 0.7			[2]
	–319.1 ± 0.7			[5]
		99.1 ± 0.9	–220.0 ± 1.1	[26]
		89.1 ± 1.9 (347 K)		[28]
		92.5 ± 1.3 (357 K)		[8]
		94.9 ± 0.4		[9]
	–319.1 ± 0.7	93.5 ± 0.3	–225.6 ± 0.8 ^g	[9]
	–315.0 ± 6.0 ^e	93.5 ± 0.3	–226.2 ± 3.5	Calc, this work
		88.8 ± 4.5		[29]
4 1,3-Dimethylurea (cr)	–326.5 ± 0.4			[5]
	–313.7 ± 1.2			[30]
	–312.1 ± 2.8			[26]
		85.2 ± 1.9 (344 K)		[28]
		87.2 ± 0.6 (353 K)		[8]
		88.3 ± 0.4		[9]
	–313.7 ± 1.2	88.8 ± 0.4 ^d	–224.9 ± 1.3	[9]
	–316.8 ± 6.0 ^e	91.5 ± 4.5	–225.3 ± 3.5	Calc, this work
5 Tetramethylurea (l)	–262.2 ± 1.1			[2]
		52.8 (320 K)		[31]
	–262.2 ± 1.1	53.4	–208.8	[4]
	–262.2 ± 1.1	56.6 ± 0.8	–205.6 ± 1.3	[5]
	–274.5			GA, [32]
	–270.5 ± 4.0 ^e	56.6 ± 0.8 ^c	–213.8 ± 3.5	Calc, this work
6 Ethylurea (cr)	–357.8 ± 0.7			[2]
	–357.8 ± 0.7			[5]
		100.3 ± 0.7	–257.5 ± 1.0	[26]
		86.0 ± 1.9 (346 K)		[28]
		91.8 ± 1.2 (354 K)		[8]
		99.3 ± 0.8		[9]
	–357.8 ± 0.7 ^c	99.3 ± 0.8 ^h	–258.5 ± 1.1	[9]
	–357.7 ± 6.0 ^e	96.5 ± 4.5	–260.6 ± 3.5	Calc, this work
7 1,1-Diethylurea (cr)	–372.2 ± 1.1			[2]
	–372.2 ± 1.1			[5]
		99.9 ± 1.1	–272.3 ± 1.6	[8]
		95.9 ± 0.2		[9]
		95.7 ± 0.7		[9]
	–372.2 ± 1.1	95.8 ± 0.5 ^d	–276.4 ± 1.2	[9]
		95.6 ± 4.5		Calc, this work
	–382.7 ± 4.0 ^e	95.8 ± 0.5 ^d	–286.8 ± 3.5	Calc, this work
8 1,3-Diethylurea (cr)	–379.8 ± 1.8			[5]
		96.9 ± 0.9	–282.9 ± 2.0	[26]
		96.6 ± 1.9 (346 K)		[28]
		96.8 ± 0.9 (361 K)		[8]
		97.6 ± 0.5		[9]
		95.4 ± 0.3		[9]
	–379.8 ± 1.8	97.1 ± 0.3	–284.5 ± 1.8	[9]
	–385.7 ± 6.0 ^e	98.2 ± 4.5	–287.5 ± 3.5	Calc, this work
9 Isopropylurea (cr)	–389.5 ± 1.3			[2]
	–389.5 ± 1.3			[5]
		99.7 ± 1.4	–289.8 ± 1.9	[28]
		100.6 ± 1.3 (389 K)		

Table 2 (continued)

Compound	$\Delta_f H_m^c(\text{cr})$ or $\Delta_f H_m^c(\text{l})/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_{\text{cr}}^g H_m^c$ or $\Delta_f^g H_m^c/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_f H_m^c(\text{g})/\text{kJ}\cdot\text{mol}^{-1}$ ^a	Reference ^b
10	<i>n</i> -Butylurea (cr)	98.1 ± 0.6		[8]
		98.1 ± 0.6 ^h		[9]
		98.6 ± 4.5	–291.4 ± 1.4	Calc, this work
		–389.5 ± 1.3	–295.4 ± 3.5	
		–394.0 ± 6.0 ^e		
		–419.5 ± 3.2		[2]
11	sec-Butylurea (cr)	105.9 ± 2.6	–313.6 ± 4.2	[5]
		99.0 ± 4.0 (345 K)		[28]
		104.0 ± 0.4		[8]
		105.8 ± 0.7		[9]
		106.7 ± 0.7	–314.5 ± 3.4	[9]
		104.8 ± 4.5		Calc, this work
12	tert-Butylurea (cr)	104.9 ± 0.7 ^d	–304.4 ± 3.5	Calc, this work
		–409.3 ± 4.0 ^e		
		–413.2 ± 1.5		[2]
		–413.2 ± 1.5		[5]
		106.2 ± 0.9	–307.0 ± 1.8	[8]
		104.6 ± 0.4		[9]
13	Biuret (cr)	101.9 ± 0.5	–311.3 ± 1.6	[9]
		101.9 ± 0.5		Calc, this work
		103.9 ± 4.5		Calc, this work
		103.3 ± 0.5 ^d	–317.2 ± 3.5	
		–420.5 ± 4.0 ^e		
		–414.7 ± 0.9		[2]
14	Acetylurea (cr)	100.7 ± 1.2	–314.0 ± 1.5	[5]
		101.6 ± 0.7 (379 K)		[28]
		97.3 ± 0.6		[8]
		98.2 ± 0.4		[9]
		97.8 ± 0.5 ^d	–316.9 ± 1.0	[9]
		98.5 ± 4.5		Calc, this work
15	Trimethylurea (cr)	97.8 ± 0.5 ^d	–327.7 ± 3.5	Calc, this work
		–425.5 ± 4.0 ^e		
		–563.7 ± 2.1		[3]
		126.7 ± 1.9	–437.0 ± 2.8	[3]
		–559.5 ± 6.0 ^e	–430.0 ± 4.5 ⁱ	Calc, [11]
		124.3 ± 4.5	–435.2 ± 3.5	Calc, this work
16	Triethylurea (cr)	103.1 ± 0.7	–441.2 ± 0.9	[33]
		106.0 ± 4.5	–436.2 ± 3.5	Calc, this work
		–544.2 ± 0.5		
		–542.2 ± 6.0 ^e		
		–330.5 ± 4.1		[34]
		104.0 ± 2.0 (344 K)		[28]
17	Tetraethylurea (l)	88.6		GA, [32]
		89.2		GA, [9]
		88.0 ± 4.5	–221.6 ± 4.5	Calc, this work
		–309.6 ± 7.0 ^e		
		97.8		GA, [9]
		102.7 ± 4.5	–313.1 ± 5.0	Calc, this work
18	<i>n</i> -Propylurea (cr)	63.6 ± 0.6	–316.4 ± 5.0	[6]
			–326.0 ± 4.0	Calc, this work
		88.2 ± 1.9 (351 K)		[26]
		90.7 ± 1.0 (366 K)		[28]
		101.4 ± 0.6		[9]
		100.2 ± 4.5	–282.2 ± 4.5	Calc, this work
19	1,3-Dipropylurea (cr)	101.4 ± 0.6 ^j		Calc, this work
		107.0		GA, [9]
		110.4 ± 4.5	–331.6 ± 5.0	Calc, this work
		–442.0 ± 8.0 ^e		
		98.7		GA, [9]
		107.8 ± 4.5		Calc, this work
20	1,3-Diisopropylurea (cr)	99–108	–356.6 ± 5.0	Calc, this work
		–456 ÷ –465 ^e		
		101.1 ± 1.1 (377 K)		[28]
		103.6 ± 1.1		[9]
		104.0 ± 4.5		Calc, this work
		103.6 ± 1.1 ^j	–313.5 ± 4.5	Calc, this work
21	Isobutylurea (cr)	95.6 ± 1.0	–404.2 ± 4.3	[2]
		91.7 ± 0.7		[5]
		112.8 ± 4.5		[8]
		91.7 ± 0.7 ^h	–421.4 ± 4.0	Calc, this work
		–513.1 ± 4.0 ^e		Calc, this work
		–218.6 ± 2.4		[2]
22	1,3-Di-tert-butylurea (cr)	–231.5 ± 2.2		[29]
		136.0 ± 6.0 (406 K)		[35]
		102.4		GA, [32]
		113.0 ± 4.5		Calc, this work
		–218.6 ± 2.4 ^k	–103.6 ± 4.0	Calc, this work
		–211.5 ± 7.0 ^e	–104.9 ± 4.5	Calc, this work
23	Phenylurea (cr)	106.6 ± 4.5		
		–211.5 ± 7.0 ^e		
		106.6 ± 4.5		
		–211.5 ± 7.0 ^e		
		106.6 ± 4.5		
		–211.5 ± 7.0 ^e		
24	1-Methyl-1-phenylurea (cr)	106.6 ± 4.5		
		–211.5 ± 7.0 ^e		
		106.6 ± 4.5		
		–211.5 ± 7.0 ^e		
		106.6 ± 4.5		
		–211.5 ± 7.0 ^e		

(continued on next page)

Table 2 (continued)

Compound		$\Delta_f H_m^{\circ}(\text{cr})$ or	$\Delta_{\text{cr}}^{\circ} H_m^{\circ}$ or	$\Delta_f H_m^{\circ}(\text{g})/\text{kJ}\cdot\text{mol}^{-1}$ ^a	Reference ^b
		$\Delta_f H_m^{\circ}(\text{l})/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_{\text{l}}^{\circ} H_m^{\circ}/\text{kJ}\cdot\text{mol}^{-1}$		
25	1,1-Diphenylurea (cr)	–122.7 ± 3.4 –113.2 ± 7.0 ^e	132.1 ± 4.5	18.9 ± 4.5	[36] Calc, this work
26	1,3-Diphenylurea (cr)	–116.8 ± 4.4	152.0 ± 6.0 (464 K) 108.1 136.5 ± 4.5 138.8 ^e	22.0 ± 4.5	[2] [35] GA, [32] Calc, this work Calc, this work
27	3-Benzoyl-1,1-diethylurea (cr)	–479.2 ± 4.8 –462.6 ± 5.0 ^e	132.2 ± 2.8 134.8 ± 4.5 132.2 ± 2.8 ^l	–347.0 ± 5.6 –330.4 ± 4.5	[37] Calc, this work Calc, this work
28	Diaminourea (cr)	–101.6 ± 10.0 ^e –103.8 ± 8.0 ^e	107.4 ± 10.0 ^m 105.5 ± 4.5	5.8 ± 3.0 ⁿ 1.7 ± 5.0	Calc, [38] Calc, this work
29	Triuret (cr)	–777.1 ± 12.0 ^e	149.9 ± 4.5	–620.3 ± 6.3 ⁱ –621.8 ⁱ –627.2 ± 9.5	Calc, [11] Calc, this work Calc, this work

^a Recommended $\Delta_f H_m^{\circ}(\text{g})$ values are given in bold.

^b Only references are given for experimental data. The values estimated by group additivity method are marked as GA. “Calc, this work” means that the gas-phase enthalpies of formation are obtained from isodesmic and other balanced reactions and the sublimation enthalpies are estimated by MEP model; for compounds **1–14**, the uncertainty of $\Delta_f H_m^{\circ}(\text{g})$ is defined as one and a half times the root-mean-square deviation (RMSD) of calculated values from the experimental values for compounds **1–4**, **6**, **8**, **9**, **13**; for compounds **15–29**, the uncertainty of $\Delta_f H_m^{\circ}(\text{g})$ is defined as two times the RMSD of calculated values from the average of all working reactions; the uncertainty of $\Delta_{\text{cr}}^{\circ} H_m^{\circ}$ is defined as two times the RMSD of calculated values from the experimental.

^c Ref. [5].

^d Average value from Refs. [8,9].

^e Estimated in this work using the relationship between condensed and gas phase enthalpies of formation.

^f Ref. [27].

^g This value is equal to the sum of $\Delta_f H_m^{\circ}(\text{cr})$ and $\Delta_{\text{cr}}^{\circ} H_m^{\circ}$ given in Ref. [9]. The value of –224.2 kJ·mol^{–1} given in [9] seems to be erroneous.

^h Ref. [8].

ⁱ Calculated from bond separation reaction (NH₂C(O)NHC(O)NHC(O)NH₂ + 6 CH₄ + 2 NH₃ → 3 HC(O)H + 6 CH₃NH₂) using CCSD(F12*)(T)/cc-pVTZ-F12//xB97X-D/cc-pVTZ enthalpies.

^j Ref. [9].

^k Ref. [2].

^l Ref. [37].

^m Estimated by MEP model using hydrazine derivatives.

ⁿ Estimated using working reactions with hydrazine derivatives.

formation of 14 ureas are presented in Table 3. As can be seen, the deviations between experimental and calculated enthalpies of formation do not exceed 4.0 kJ·mol^{–1} for eight compounds, **1–4**, **6**, **8**, **9**, and **13** (hereinafter, the compound's numbers are given according to Table 2), and experimental data for these ureas are

considered as accurate. The corresponding $\Delta_f H_m^{\circ}(\text{g})$ values are marked in bold in Table 2.

Since isodesmic reaction network calculations (Table 3) show a large difference from (5.0 to 10.4) kJ·mol^{–1} between experimental and theoretical values for six compounds (**5**, **7**, **10–12**, and **14**), the

Table 3

Comparison of experimental gas-phase enthalpies of formation of urea and its derivatives with those determined from isodesmic reaction network.^a

Compound		$\Delta_f H_m^{\circ}(\text{g, exp})$ /kJ·mol ^{–1}	$\Delta_f H_m^{\circ}(\text{g, calc})$ /kJ·mol ^{–1}	$\Delta_f H_m^{\circ}(\text{g, exp}) - \Delta_f H_m^{\circ}(\text{g, calc})$ /kJ·mol ^{–1}
1	Urea	–235.5 ± 1.2 –237.6 ± 0.8	–233.8	–1.7 –3.8
2	Methylurea	–231.9 ± 1.5	–229.7	–2.2
3	1,1-Dimethylurea	–225.6 ± 0.8	–226.2	0.6
4	1,3-Dimethylurea	–224.9 ± 1.3	–225.3	0.4
5	Tetramethylurea	–205.6 ± 1.3	–213.8	8.2
6	Ethylurea	–258.5 ± 1.1	–260.6	2.1
7	1,1-Diethylurea	–276.4 ± 1.2	–286.8	10.4
8	1,3-Diethylurea	–284.5 ± 1.8	–287.5	3.0
9	Isopropylurea	–291.4 ± 1.4	–295.4	4.0
10	n-Butylurea	–314.5 ± 3.4	–304.4	–10.1
11	sec-Butylurea	–311.3 ± 1.6	–317.2	5.9
12	tert-Butylurea	–316.9 ± 1.0	–327.7	10.8
13	Biuret	–437.0 ± 2.8	–435.2	–1.8
14	Acetylurea	–441.2 ± 0.9	–436.2	–5.0
	RMSD ^b	8.3	0.3	

^a References to experimental values are given in Table 2. Values in bold are internally self-consistent enthalpies of formation recommended from the solution of isodesmic reaction network.

^b Root-mean-square deviation (RMSD) between enthalpies of 91 working reactions calculated using G4 energies (Table S2 of Supplementary material) and those obtained with experimental or calculated enthalpies of formation listed in this table.

experimental data are assumed to be inaccurate and theoretical $\Delta_f H_m^\circ(g)$ values are recommended in Table 2 for these compounds.

The values of vaporization enthalpy of tetramethylurea (**5**) reported in Refs. [31,4,5] are in close agreement, and so a large difference of $8.2 \text{ kJ}\cdot\text{mol}^{-1}$ between experimental and theoretical $\Delta_f H_m^\circ(g)$ values may be the result of error in the experimental value of $\Delta_f H_m^\circ(l)$. Note that the liquid-phase enthalpy of formation of tetramethylurea (**5**) estimated in Table 2 ($-270.5 \text{ kJ}\cdot\text{mol}^{-1}$) using calculated in this work value of $\Delta_f H_m^\circ(g)$ and experimental vaporization enthalpy [5] is close to that predicted by group additivity method [32].

The theoretical gas-phase enthalpies of formation of ureas **7** and **10–12** differ from the experimental values by $(6\text{--}11) \text{ kJ}\cdot\text{mol}^{-1}$. The sublimation enthalpies of these compounds were determined repeatedly and their values agree well with each other and with the values estimated in this work by MEP model (Table 2). This, in turn, suggests that some revision of the enthalpies of formation of crystalline ureas **7** and **10–12** may be necessary. The $\Delta_f H_m^\circ(\text{cr})$ values that are consistent with the calculated gas-phase enthalpies of formation and experimental sublimation enthalpies are given in Table 2. As can be seen, these values are about $10 \text{ kJ}\cdot\text{mol}^{-1}$ higher or lower than the experimental $\Delta_f H_m^\circ(\text{cr})$ values.

The calculated gas-phase enthalpy of formation of acetylurea (**14**) differs from the experimental value by only $5 \text{ kJ}\cdot\text{mol}^{-1}$. It is seen from Table 2 that a little change in the reported values of $\Delta_f H_m^\circ(\text{cr})$ and $\Delta_{\text{cr}}^g H_m^\circ$ [33] leads to agreement with theoretical result. Therefore, the experimental data are of reasonable accuracy but are not sufficiently reliable for deriving an accurate gas-phase enthalpy of formation that can be considered as benchmark in isodesmic reaction calculations. Because of this the theoretical $\Delta_f H_m^\circ(g)$ value is preferred for **14** in Table 2.

Thus, eight accurate and reliable values of gas-phase enthalpies of formation of urea and its derivatives (**1–4**, **6**, **8**, **9**, and **13**) were selected within the framework of an isodesmic reaction network approach. These values were used to estimate the enthalpies of formation of ureas for which experimental data were not reported or determined with large uncertainty (Section 3.4).

The system of equations used in isodesmic reaction network does not have a unique solution. However, the close agreement between enthalpy of formation of urea determined by isodesmic reaction network and that estimated from working reactions not including urea derivatives as a reference species (Table S1 of Supplementary material) supports the reliability of the result obtained in this work.

3.3. Estimation of sublimation enthalpies

The comparison between experimental enthalpies of sublimation and those calculated by Eq. (1) is given in Table S3 of Supplementary material. As can be seen, the difference between experimental and calculated values for compounds **1–14** vary from $(0.2 \text{ to } 4.7) \text{ kJ}\cdot\text{mol}^{-1}$ with the root-mean-square deviation of $2.3 \text{ kJ}\cdot\text{mol}^{-1}$, which is a satisfactory accuracy. We used the estimated $\Delta_{\text{cr}}^g H_m^\circ$ values in some cases to resolve the discrepancy between the available experimental data or predict the enthalpy of formation in the crystalline state for unexplored compounds.

3.4. Estimation of enthalpies of formation of ureas **15–29**

Experimental data for ureas **15–29** were not reported or determined with large uncertainty. The gas-phase enthalpies of formation of these compounds were estimated in this work from reactions where urea and its derivatives (**1–4**, **6**, **8**, **9**, and **13**) are

used as the reference species (Table S4 of Supplementary material). The accuracy of experimental data for **1–4**, **6**, **8**, **9**, and **13** was confirmed by isodesmic reaction network calculations (section 3.2). The sublimation enthalpies were calculated using Eq. (1) with parameters determined by fitting to existing experimental sublimation enthalpy data for **1–14** (see Table S3 of Supplementary material).

Both enthalpy of formation in condensed state and sublimation or vaporization enthalpy were determined experimentally for urea derivatives **15**, **17**, **22**, **23**, **26**, and **27**, however, there are doubts about the reliability of these data. The experimental sublimation enthalpy of trimethylurea (**15**) [28] is much more than that estimated by group additivity [32,9] or MEP model (Table 2). Assuming the experimental $\Delta_{\text{cr}}^g H_m^\circ$ value is overestimated, the enthalpy of formation of crystalline **15** is suggested to be about $20 \text{ kJ}\cdot\text{mol}^{-1}$ greater than the reported experimental value (Table 2).

The gas-phase enthalpy of formation of tetraethylurea (**17**) is about $10 \text{ kJ}\cdot\text{mol}^{-1}$ more negative than the experimental value [6]. This discrepancy may be due to the error in experimental value of $\Delta_f H_m^\circ(l)$ or $\Delta_f^g H_m^\circ$. Using the value $\Delta_f H_m^\circ(g)$ calculated in this work for 1,3-di-tert-butylurea (**22**) and experimental sublimation enthalpies [5,8], we can suggest that experimental enthalpy of formation of crystalline **22** is overestimated by $(13\text{--}17) \text{ kJ}\cdot\text{mol}^{-1}$.

The sublimation enthalpies of phenylurea (**23**) and 1,3-diphenylurea (**26**) were determined with large uncertainty by Ferro et al. [26] and these values are substantially larger than those estimated by group additivity and MEP model (Table 2). Combining the calculated in this work gas-phase enthalpies of formation of **23** and **26** with the experimental crystalline-phase enthalpies of formation [2] yields the values of sublimation enthalpies which agree well with those obtained by the MEP model. This result supports the experimental data on enthalpies of formation of **23** and **26** [2] and suggests that predictions of sublimation enthalpies seem to be accurate enough, although the phenylureas were not used in calibration of the MEP model (see Table S3 of Supplementary material).

A large difference between experimental [37] and calculated gas-phase enthalpy of formation of 3-benzoyl-1,1-diethylurea (**27**) can only be explained by errors in the experimental data. Since the sublimation enthalpy estimated in this work agrees well with the experimental one, we can assume an error in the enthalpy of formation of crystalline **27**, rather than in sublimation enthalpy. Combination of calculated ($\Delta_f H_m^\circ(g)$) and experimental ($\Delta_{\text{cr}}^g H_m^\circ$) data is used in Table 2 to estimate the enthalpy of formation in crystalline state. As seen from Table 2, the estimated $\Delta_f H_m^\circ(\text{cr})$ value is larger than the experimental one by $16.6 \text{ kJ}\cdot\text{mol}^{-1}$.

For the remaining compounds in Table 2 (**16**, **18–21**, **24**, **25**, **28**, and **29**), the experimental enthalpy of formation in crystalline state or sublimation enthalpy or both these properties are not reported. The missing properties were estimated using values of $\Delta_f H_m^\circ(g)$ and $\Delta_{\text{cr}}^g H_m^\circ$ calculated in this work.

Only sublimation enthalpies were reported for **18** and **21**. As can be seen from Table 2, the values calculated by MEP model are in good agreement with the experimental data by Emel'yanenko et al. [9]. The values of $\Delta_f H_m^\circ(\text{cr})$ for **18** and **21** were estimated using these experimental data and gas-phase enthalpies of formation calculated in this work.

Sublimation enthalpy was not measured for 1,1-diphenylurea (**25**). The use of $\Delta_{\text{cr}}^g H_m^\circ$ value estimated by MEP model yields the enthalpy of formation in crystalline state which is about $10 \text{ kJ}\cdot\text{mol}^{-1}$ greater than the experimental value (Table 2). Note, that the result of similar estimation for 1,3-diphenylurea (**26**)

agrees well with the experiment and it does not exclude an error in the experimental enthalpy of formation of **25**.

The experimental measurements were not reported for **16**, **19**, **20**, **24**, **28**, and **29**. The sublimation enthalpies of **16** and **19** estimated by MEP model are in good agreement with the values estimated by group additivity scheme [9], whereas the difference of about 10 kJ·mol⁻¹ is observed for **20**. Taking into account this difference, a larger inaccuracy in $\Delta_f H_m^\circ(\text{cr})$ is suspected for **20**.

The thermochemical properties of diaminourea (**28**) were evaluated earlier by the similar approach using hydrazine derivatives as reference species [38]. As can be seen from Table 2, the results of two predictions are close to each other. The gas-phase enthalpy of formation of triuret (**29**) was calculated by CCSD(F12*)(T) for bond separation reaction [11]. Almost the same value is obtained by G4 method for this reaction in the present work (Table 2). However, a little lower value is recommended for gas-phase enthalpy of formation of **29** in Table 2; this value is calculated using eight working reactions (Table S4 of Supplementary material).

4. Conclusions

The consistent set of enthalpies of formation of ureas was found by simultaneous least-squares solution of a thermochemical network containing 91 isodesmic and other balanced reactions. The solution of this network produces an internally consistent set of enthalpies of formation of 14 ureas. These data are a combination of calculated values and experimentally confirmed values (Table 3). The experimental values were confirmed for 8 compounds (**1–4**, **6**, **8**, **9**, and **13**, see Table 3); these values may be used in estimating the enthalpies of formation of new ureas by isodesmic reaction approach. In addition, the least-squares fit of the network helped to identify measurements that require re-examination.

The calculations carried out in this work show that the most recent gas-phase enthalpy of formation of urea, $-(237.6 \pm 0.8)$ kJ·mol⁻¹ [9], seems to be underestimated. An earlier value reported by Kabo et al., $-(235.5 \pm 1.2)$ kJ·mol⁻¹ [5], is in a better agreement with the results of calculations. Moreover, one can expect even a little higher value than the experimental ones.

The sublimation enthalpies calculated by MEP model agree well with the experimental values. Thus, this model, when applied to structurally similar compounds, may be useful in estimating enthalpies of formation in crystalline state.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jct.2018.11.008>.

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