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The effect of the failure of isotropy of a gas in an effusion cell on the vapor pressure and enthalpy of sublimation for alkyl derivatives of carbamide

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Abstract

The divergence of the values of enthalpy of sublimation for urea, methylurea, ethylurea, 1,1-dimethylurea, 1,3-dimethylurea, (1-methylethyl)urea, *n*-butylurea, (1-methylpropyl)urea, (1,1-methylethyl)urea, 1,1-diethylurea, 1,3-diethylurea, 1,3-bis(1,1-dimethylethyl)urea obtained calorimetrically and from the effusion measurements [Izv. Akad. Nauk SSSR. Ser. Khim. 4 (1990) 750] was analyzed. The results of the calorimetric measurements were shown to be independent of the evaporation rate. The influence of the isotropy failure of a gas on the effusion results was analyzed. The vapor pressures and enthalpies of sublimation were corrected according to the proposed technique. The decrease of divergence of the values of enthalpies of sublimation for alkyl derivatives of carbamide from effusion and calorimetric measurements while taking into account the isotropy failure of a gas was shown.

The average weighted value of enthalpy and entropy of sublimation were evaluated. The additive scheme for enthalpy of sublimation was proposed.

Keywords: Alkyl carbamides; Vapor pressure; Effusion

1. Introduction

Alkyl derivatives of carbamide (AC) are used as intermediates in the synthesis of medicines, herbicides, high-temperature solvents, dyes and antistatic agents [2,3]. The wide practical use of these compounds stimulates the great interest in their thermodynamic properties. In paper by Kabo et al. [4], the data on the thermodynamic properties of AC crystals in the temperature range of 5–300 K and their enthalpies of combustion were reported. Additivity of their properties was also shown [4]. The vapor pressure (p_{sat} (Pa)) was studied by the torsion effusion method by Della Gatta and co-workers [5–7].

The vapor pressure and enthalpy of sublimation $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^{\mathrm{o}}$, were also systematically studied by the authors [8] using the integral Knudsen method and a Calvet type microcalorimeter. The results [1] are shown in Table 1. The p_{sat} values were found as

$$p_{\mathrm{sat}} = \frac{\Delta m}{ks\tau}\sqrt{\frac{2\pi RT}{M}} \qquad (1)$$

where Δm is a mass loss of a sample (kg) during time τ (s); M the molar weight of the vapor (kg mol^{-1}); s the area of the orifice (m^2); k the transmission probability,

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Table 1
Enthalpies of sublimation for alkyl derivatives of carbamide

Substance	a^*[a]	b (K)[a]	T_m (K)[a]	$\Delta_{cr}^{g}H_m^o$ (T)[a] (kJ mol^{-1})	$\Delta_{cr}^{g}C_p$ (J K^{-1} mol^{-1})	T_m[b] (K)	$\Delta_{cr}^{g}H_m^o$ (T) (kJ mol^{-1})	$\Delta_{cal}^{eff}\Delta_{cr}^{g}H_m^o$ (350 K) (kJ mol^{-1})
Urea	32.66 ± 1.25	11846 ± 275	370	98.49 ± 2.3	−27.0	354	94.6 ± 0.5	
			350	99.03 ± 2.3		350	94.6 ± 0.5	4.4
Methylurea	34.92 ± 0.27	11951 ± 95	343	99.36 ± 0.7	−39.0	337	94.9 ± 0.4	
			350	99.24 ± 0.7		350	94.4 ± 0.4	4.8
Ethylurea	35.31 ± 0.24	12066 ± 81	344	100.3 ± 0.7	−48.0	337	97.0 ± 1.1	
			350	100.0 ± 0.7		350	96.4 ± 1.1	3.6
1,1-Dimethylurea	35.62 ± 0.3	11913 ± 107	348	99.05 ± 0.9	−27.1	353	93.2 ± 0.5	
			350	99.00 ± 0.9		350	93.3 ± 0.5	5.7
1,3-Dimethylurea	33.68 ± 0.37	11091 ± 130	347	92.22 ± 1.1	−34.4	354	86.4 ± 0.5	
			350	92.12 ± 1.1		350	86.6 ± 0.5	5.5
(1-Methylethyl)urea	34.47 ± 0.48	11984 ± 173	353	99.64 ± 1.4	−19.7	354	97.1 ± 0.6	
			350	99.70 ± 1.4		350	97.2 ± 0.6	2.5
Butylurea	35.55 ± 0.81	12609 ± 290	354	104.8 ± 2.6	−66.3	354	100.3 ± 0.4	
			350	105.1 ± 2.6		350	101.1 ± 0.4	4.5
(1-Methylpropyl)urea	35.67 ± 0.29	12776 ± 103	355	106.2 ± 0.9	−33.4	354	102.1 ± 0.5	
			350	106.4 ± 0.9		350	102.4 ± 0.5	4.2
(1,1-Dimethylethyl)urea	34.78 ± 0.40	12108 ± 140	353	100.7 ± 1.2	−22.6	354	94.2 ± 0.9	
			350	100.8 ± 1.2		350	94.4 ± 0.9	6.4
1,1-Diethylurea	37.90 ± 0.40	12014 ± 131	324	99.89 ± 1.1	−24.1	320	95.5 ± 0.2	
			350	99.23 ± 1.1		350	94.7 ± 0.2	4.6
1,3-Diethylurea	34.73 ± 0.32	11653 ± 115	358	96.89 ± 1.0	−58.2	364	94.8 ± 0.6	
			350	97.36 ± 1.0		350	95.6 ± 0.6	1.8
1,3-bis(1,1-Dimethylethyl)urea	33.67 ± 0.33	11503 ± 115	348	95.64 ± 1.0	−20.1	354	89.6 ± 1.0	
			350	95.60 ± 1.0		350	90.0 ± 1.0	5.6
Average of absolute deviations								4.5

[a] Values of a^*, b^* for eqation $\ln(p^*_{sat}) = a^* - (b^*/T)$; $\Delta_{cr}^{g}H_m^o$ (T) from effusion data [1]; p^*_{sat}: effective values of vapor pressure [1], where k is calculated by Eq. (2).

[b] $\Delta_{cr}^{g}H_m^o$ obtained calorimetrically by the ampoule technique [1].

which is dimensionless; $R = 8.31447\,\mathrm{J\,mol^{-1}\,K^{-1}}$; and T is the temperature (K).

The transmission probability k_C was calculated using the theory of a molecular stream forming in the effusion cell according to Clausing [9]:

$$k_C = \frac{1}{1 + (l/2r)} \tag{2}$$

where l is the thickness of the membrane (m) and r is the radius of the orifice (m).

The values of $\Delta_{cr}^{g}H_m^o$ were evaluated from the linear approximation $\ln(p_{sat}) = a - (b/T)$. The use of the nonlinear equation $\ln(p_{sat}) = a - (b/T) + (\Delta_{cr}^{g}C_p/R)\ln(T/350\,\mathrm{K})$ does not decrease the uncertainty of $\Delta_{cr}^{g}H_m^o$ and $\Delta_{cr}^{g}S_m^o$.

The values of the isobaric heat capacity of the crystals and the ideal gases [4,10] were used to adjust $\Delta_{cr}^{g}H_m^o$ both from the effusion and calorimetric measurements for AC to 350 K, the average temperature of the measurements. As one can see from Table 1, the values of $\Delta_{cr}^{g}H_m^o$ for AC for the same samples from effusion measurements are systematically on an average 4.5 kJ mol^{-1} higher than those obtained calorimetrically. Such a deviation is much higher than the total random errors of the two methods.

The aim of this work is to elucidate the reasons for such a deviation. The influence of the evaporation rate on the results of calorimetric measurements was studied and found to have little influence on the sublimation enthalpies. A procedure for more accurate evaluation of p_{sat} from effusion data developed by Wahlbeck to account for loss of gas isotropy occurring in the transition between molecular flow and hydrodynamic flow has been applied to the data and the results are reported.

2. Calorimetric study of $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$ for AC

The calorimetric values of $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$ shown in Table 1 was obtained in a Calvet type differential microcalorimeter using the “ampoule technique” described in [8]. Hereafter, the original calorimetric cell for $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$ determination (Fig. 1) was developed [11]. It was shown [11] that calibration of the calorimeter (ampoule technique) against substances with essentially differing evaporation rates: water, naphthalene, benzoic acid did not change the thermal constants of the calorimetric cells significantly. During calibration,

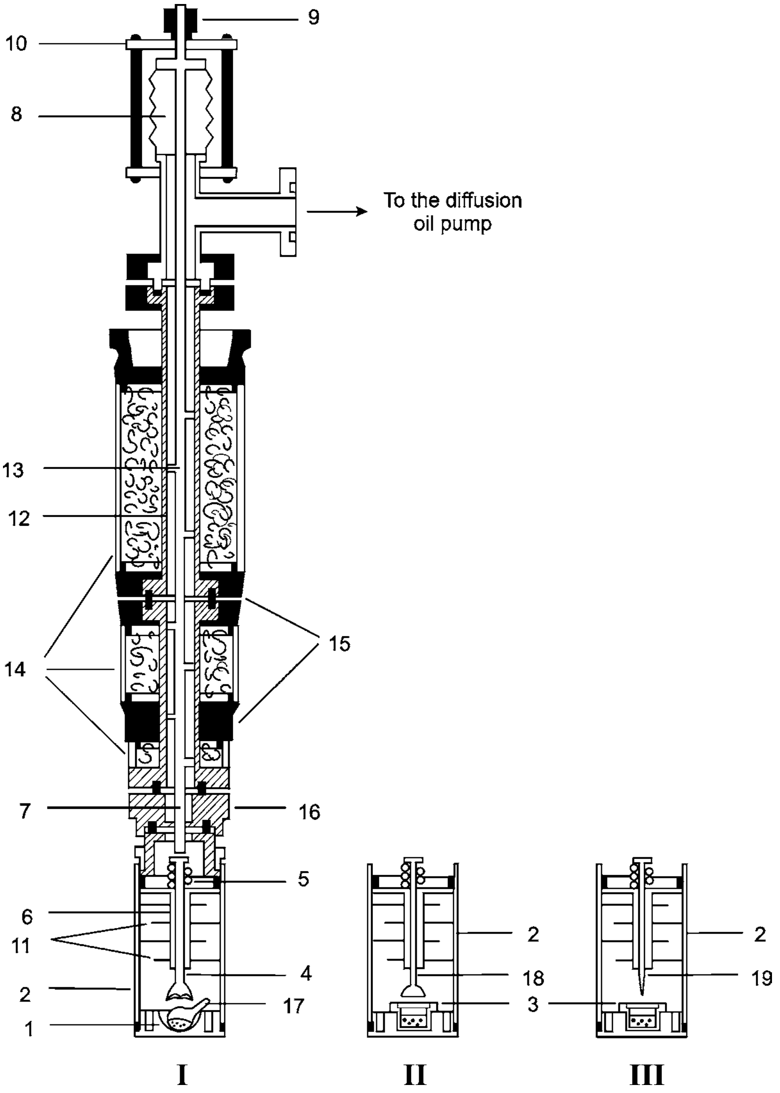


Fig. 1. The scheme of the calorimetric cell for the differential microcalorimeter: (1) the lower lid; (2) evaporation chamber; (3) effusion cell with a sample; (4) metal rod; (5) spring; (6) directing channel; (7) subsidiary rod; (8) bellows; (9) fixing screw; (10) limiting strap; (11) metal shields; (12) Teflon tube; (13) segmental shields; (14) thermoisolating coats; (15) and (16) metal contacts for thermostating; (17) glass cell; (18) metal rod with a seal band; (19) metal rod with a spire; (I) evaporation chamber with crushed ampoule; (II) evaporation chamber with effusion cell closed by metal rod; (III) evaporation chamber with effusion cell obtained by piercing the membrane.

the following values of $\Delta_{\rm cr}^{\rm g} H_{\rm m}^{\rm o}$ (298.15 K) and $\Delta_{\rm cr}^{\rm g} C_p$ for the standard substances were used: water, 44 016 J mol^{-1} and -42 J K^{-1} mol^{-1}; naphthalene, 72 295 J mol^{-1} and -34 J K^{-1} mol^{-1}; benzoic acid, -90 536 J mol^{-1} and -49 J K^{-1} mol^{-1}.

For the investigation of the effect of evaporation rate on $\Delta_{\rm cr}^{\rm g} H_{\rm m}^{\rm o}$, the special evaporation chambers where the sample evaporated from effusion cells with different orifice diameters (Fig. 1) were made. The evaporation process was initiated by either opening of the orifice or piercing of the membrane. In the first case, the membranes with orifice diameters of 3.0 ± 0.1 mm and 0.83 ± 0.001 mm were used. The energy of the opening–closing process averaged $(6 \pm 3) \times 10^{-2}$ J and $(5 \pm 3) \times 10^{-2}$ J for the membrane piercing. These values were taken into account while obtaining thermal constants of the calorimetric cells. The results of $\Delta_{\rm cr}^{\rm g} H_{\rm m}^{\rm o}$ determination for 1,1-dimethylurea are given in Table 2. The values of $\Delta_{\rm cr}^{\rm g} H_{\rm m}^{\rm o}$ were adjusted to 350 K with the help of the isobaric heat capacity of the crystal and the ideal gas from [4,10]. They are 93.28 ± 0.5 kJ mol^{-1} using the ampoule technique, 93.23 ± 1.4 kJ mol^{-1} using an effusion cell with 3.0 mm orifice, and 93.72 ± 1.0 kJ mol^{-1} using an effusion cell with 0.83 mm orifice. These values coincide with each other within uncertainties of the measurements. Thus, the value of $\Delta_{\rm cr}^{\rm g} H_{\rm m}^{\rm o}$ obtained from calorimetric investigations in a Calvet type differential microcalorimeter was found to be independent on the evaporation rate under the conditions studied. The authors suppose that the use of evaporation chamber with effusion cell membrane pierced (Fig. 1) by spire rod was worth.

3. Vapor pressure determination by the integral Knudsen method

The technique of vapor pressure determination by the integral Knudsen method was described earlier [12]. The cylindrical effusion cell with the internal diameter 10 mm, height 10 mm and wall thickness 1 mm was used. The membrane thickness was 0.05 mm and orifices diameters 0.8254 ± 0.0001 mm and 0.2579 ± 0.0001 mm. The temperature was kept constant within ±0.01 K. The cell was inflated with helium up to 1 atm and preliminary thermostated during 30 min. After that the cell was vacuumed to the residual pressure 1×10^3 Pa. When the exposition time was up, the cell was filled with helium in order to stop the vaporization. Then the cell was left on air for 30 min to get the constant weight and weighted with the accuracy 1×10^{-5} g. The exposition was corrected with respect to the unsteady conditions in the beginning of the experiment.

The values of $\Delta_{\rm cr}^{\rm g} H_{\rm m}^{\rm o}$ for AC were evaluated from the vapor pressures [1] calculated using Eqs. (1) and

Table 2
Calorimetric study of 1,1-dimethylurea

	m (g)	T (K)	$\int_{\tau=0}^{\tau} \Delta E\, {\rm d}\tau$ (mV s)	$K_{\rm A}$, $K_{\rm B}$[a] (mV W^{-1})	ΔH (J)	$\Delta_{\rm cr}^{\rm g} H_{\rm m}^{\rm o}$ (kJ mol^{-1})
Orifice diameter $d = 0.83 \pm 0.001$ mm						
1	0.01245	339.56	2495.98	184.84	13.50	95.50
2	0.04742	351.26	10231.35	202.57	50.51	93.79
3	0.05656	352.68	12173.11	202.57	60.09	93.56
4	0.01206	339.52	2593.05	202.57	12.80	93.46
5	0.01606	347.65	3498.52	202.57	17.27	93.67
6	0.01441	347.41	3072.22	202.57	15.17	92.66
7	0.01500	347.76	3189.35	202.57	15.74	92.41
Average						93.72 ± 1.0
Orifice diameter $d = 3.0 \pm 0.1$ mm						
8	0.07074	347.71	15245.84	184.84	75.26	93.70
9	0.03495	347.56	7478.90	202.57	36.92	93.02
10	0.06268	347.13	13278.58	202.57	65.55	92.10
11	0.06434	347.71	12705.95	202.57	68.74	94.09
Average						93.23 ± 1.4

[a] $K_{\rm A}$, $K_{\rm B}$ are the thermal constants of the calorimetric cells.

(2). Because of rather narrow temperature interval (50 K on average), the linear approximation was used (Table 1). The values of the isobaric heat capacity of the crystal and ideal gas [4,10] were used to adjust values of $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^{\mathrm{o}}$ both from effusion and calorimetric measurements for AC to 350 K. As one can see from Table 1, the values of $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^{\mathrm{o}}$ for AC for the same samples from effusion measurements were on an average 4.5 kJ mol^{-1} higher than those obtained calorimetrically. Such a deviation is much higher than the collective random errors of the two methods (calorimetry and effusion).

A possible explanation of these deviations might be due to the isotropy failure of the effusing gas. This problem has been investigated by different authors [12–16]. The approach by Wahlbeck seems to be well-grounded [16]. It is based on a large amount of the experimental data of the influence of the evaporation conditions on the effusing gas isotropy. According to Wahlbeck, the isotropy assumption assumed for a given locus that the number of molecules moving toward that point in all directions in all velocity ranges are equal. For the molecules near orifice this assumption cannot be true. He demonstrated [16] that the transmission probability can be evaluated using

$$k_{\mathrm{W}} = 2(C + DA) + G\left(1 + \frac{(B/3) - (AD)}{0.5 - C}\right) \tag{3}$$

where A is an isotropy failure function for the vacuum-side opening and B is an isotropy failure function for the gas-side opening of the orifice. The value of A is calculated using

$$A = \frac{1}{\lambda}\int_{l}^{\infty}\left(1 - \frac{L}{(L^2 + r^2)^{1/2}}\right)\exp\left(-\frac{L}{\lambda}\right)\mathrm{d}L \tag{4}$$

where l is the membrane thickness (m); λ the mean free path of a molecule (m); and r is the orifice radius (m). The value of B is calculated using Eq. (4) with the lower integration limit set equal to zero. The C and D parameters do not have obvious physical meaning and are calculated using

$$C = \int_{0}^{\pi/2}\cos(x)\sin(x)\,R(P)\,\mathrm{d}x \tag{5}$$

$$D = \int_{0}^{\pi/2}\cos^2(x)\sin(x)\,R(P)\,\mathrm{d}x \tag{6}$$

where x is the angle of the molecules getting into the orifice in radians and $R(P)$ is a cutoff function. The cutoff function takes into account the decrease in orifice area available to these molecules leaving the effusion cell without colliding with the orifice wall. It is calculated as

$$\begin{aligned} R(P) &= \frac{2}{\pi}(\arccos(P) - P\sqrt{1 - P^2}), \quad \text{for } P = 1 \\ R(P) &= 0, \quad \text{for } P > 1 \end{aligned} \tag{7}$$

The P-value is calculated from:

$$P = \frac{l\tan(x)}{d} \tag{8}$$

where l is the membrane thickness (m) and d is the orifice diameter (m).

The G function takes into account the contribution to gas flow from molecules leaving the orifice that collide with walls of the orifice.

$$\begin{aligned} G = {} & \int_{0}^{f} 2\cos(x)\sin(x)\left(\frac{2}{\pi}\alpha(\arcsin(P) + P\sqrt{1 - P^2}) \right. \\ & \left. + \frac{4}{3\pi}(1 - 2\alpha)\frac{(1 - (\sqrt{1 - P^2})^3)}{3}\right)\mathrm{d}x \\ & + \int_{f}^{\pi/2} 2\cos(x)\sin(x)\left(\alpha + \frac{4(1 - 2\alpha)}{2\pi P}\right)\mathrm{d}x \end{aligned} \tag{9}$$

The value of α in Eq. (9) characterizes the membrane and is calculated from Clausing theory:

$$\alpha = \frac{\sqrt{l^2 + 4r^2} - l}{2r + (4r^2/\sqrt{l^2 + 4r^2})} \tag{10}$$

The integrals C, D, G depend only on membrane parameters.

Wahlbeck [16] and Wey [17] showed that the procedure described above can be used for Knudsen number, $Kn = (\lambda/d_{\mathrm{orifice}})$, larger than 0.2. In the region $Kn > 10$, the values of k_{W} (Eq. (3)) are very close to those calculated from Clausing theory (2).

Examples of the p_{sat} calculations from effusion measurement with transmission probabilities calculated from Clausing k_{C} and Wahlbeck k_{W} are listed below.

1. Carbamide sample mass loss in the experiment was 0.02751 g over a period of $\tau = 1799$ s. The thermostat temperature was $T = 398.05$ K. The membrane

was characterized by the following parameters: $d = 0.0008254\,\mathrm{m}$, $l = 0.00005\,\mathrm{m}$, $C = 0.443342$, $D = 0.307967$, $G = 0.056591$, $k_C = 0.9432$.

The effective value of the vapor pressure p^*_{sat} without corrections due to failure of isotropy is calculated using Eqs. (1) and (2).

$$p^*_{\mathrm{sat}} = \frac{2.751\times10^{-5}}{0.9429\times3.1416\times(4.127\times10^{-4})^2\times1799} \times\sqrt{\frac{2\times3.1416\times8.31447\times398.05}{0.060}} = 17.84\,\mathrm{Pa} \qquad (14)$$

2. The calculation of the transmission probability is carried out using an iteration algorithm.

   The mean free path of a molecule is calculated from the effective vapor pressure:

$$\lambda = \frac{k_B T}{\pi\sigma^2 p^*_{\mathrm{sat}}\sqrt{2}} \qquad (15)$$

where k_B is a Boltzmann constant equal to $1.38\times10^{-23}\,\mathrm{J\,s}$ and σ is an effective diameter of the molecule (collision diameter). The later is calculated as

$$\sigma = \left(\frac{3V}{4\pi}\right)^{1/3} \qquad (12)$$

where V is a molecular volume calculated from its MM3 [18] geometry using Van der Waals radii from [19]. The value of the diameter is obtained from Van der Waals volume assuming a spherical shape of the molecule.

For carbamide, σ is equal to $4.440\times10^{-10}\,\mathrm{m}$. Inserting this value into Eq. (15) gives:

$$\lambda = \frac{1.38\times10^{-23}\times398.05}{3.1416\times(4.440\times10^{-10})^2\times17.84\sqrt{2}} = 3.580\times10^{-4}\,\mathrm{m} \qquad (16)$$

3. The value λ is used to evaluate integrals A and B (Eq. (4)). Following integration, one obtains $A = 0.46652$ and $B = 0.49900$.

Now one can calculate k_W using A, B, C, D, G in Eq. (3):

$$k_W = 2\times(0.443342+0.307967\times0.46652) + 0.056591 \times\left(1+\frac{(0.49900/3)-(0.46652\times0.307967)}{0.5-0.443342}\right) \qquad (17)$$

$$k_W = 1.2533 \qquad (18)$$

The new value of the transmission probability is used to evaluate the new value of the vapor pressure.

$$p^*_{\mathrm{sat}} = \frac{2.751\times10^{-5}}{1.2533\times3.1416\times(4.155\times10^{-4})^2\times1799} \times\sqrt{\frac{2\times3.1416\times8.31451\times398.05}{0.060}} = 13.24\,\mathrm{Pa} \qquad (19)$$

The new value of the vapor pressure is used to recalculate the mean free path and transmission probability. The iterative procedure was terminated when the entire cycle changed the vapor pressure value by less than 0.001%. As a result of the calculation, one

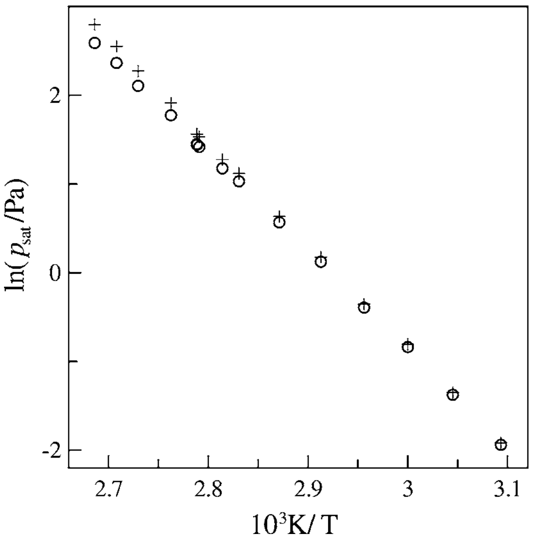


Fig. 2. Temperature dependence of vapor pressures of 1,3-bis(1,1-dimethylethyl)urea: (+) effective values of p^*_{sat} obtained by Knudsen method, (○) p_{sat} values corrected taking into account the isotropy failure of a gas in the effusion cell.

Table 3
Vapor pressures for alkyl derivatives of carbamide

T (K)	τ (s)	$\Delta m \times 10^6$ (kg)	Kn	k_W	p_{sat} (Pa)
Urea					
329.14	108230	3.93	164.7	0.9452	0.0379
335.76	86400	6.16	84.9	0.9459	0.0751
342.00	43219	5.34	49.6	0.9485	0.1310
352.10	20043	6.27	20.0	0.9571	0.3335
362.80	10808	10.19	6.9	0.9810	0.9954
367.35	7387	9.43	5.2	0.9921	1.341
371.02	8146	15.35	3.6	1.0104	1.953
378.45	1534	5.15	2.1	1.0467	3.393
381.20	3611	15.00	1.7	1.0632	4.148
386.33	2380	18.11	1.0	1.1192	7.266
388.92	3641	32.33	0.9	1.1351	8.388
389.20	3907	28.28	1.1	1.1137	6.972
398.05	1799	27.51	0.5	1.1947	13.89
403.10	1813	41.27	0.4	1.2388	20.06
Methylurea					
322.76	252000	2.81	128.2	0.8532	0.1212
327.69	263130	4.89	77.6	0.8546	0.2032
332.60	180000	5.71	45.9	0.8566	0.3486
337.05	101174	5.25	28.4	0.8598	0.5719
343.17	68908	6.67	15.5	0.8665	1.068
346.97	47172	6.73	10.6	0.8729	1.571
351.88	35100	7.80	7.0	0.8831	2.436
356.92	22377	8.33	4.3	0.9001	4.033
361.87	14752	8.34	2.9	0.9186	6.043
361.90	29641	16.92	2.9	0.9191	6.099
366.73	12689	10.74	2.0	0.9410	8.891
371.52	7345	9.71	1.3	0.9710	13.55
Ethylurea					
323.33	336000	4.31	104.1	0.8537	0.1279
327.32	230574	4.82	64.4	0.8550	0.2094
330.45	172800	5.00	46.8	0.8566	0.2907
335.27	119828	5.84	28.1	0.8599	0.4913
339.48	82829	6.37	18.0	0.8645	0.7760
343.63	64843	7.42	12.3	0.8703	1.154
347.87	39610	6.93	8.2	0.8789	1.758
351.48	38901	9.80	5.8	0.8890	2.515
355.73	27034	10.04	4.0	0.9029	3.673
360.78	20041	12.09	2.5	0.9258	5.860
364.12	12604	10.07	2.0	0.9420	7.662
1,1-Dimethylurea					
323.18	216767	6.12	46.7	0.8566	0.2805
328.17	115770	5.72	27.0	0.8602	0.4926
333.47	73800	6.31	15.8	0.8662	0.8533
338.06	43200	5.96	10.0	0.8743	1.374
343.14	29200	7.13	5.8	0.8888	2.409
348.21	18000	6.85	3.8	0.9050	3.715
353.12	10800	6.78	2.4	0.9295	6.008
359.83	7200	8.09	1.4	0.9666	10.44
363.39	5400	8.45	1.0	0.9915	14.24
368.17	4700	11.07	0.7	1.0245	20.88
372.32	3610	12.57	0.5	1.0566	30.10
1,3-Dimethylurea					
317.14	257664	7.27	43.0	0.9835	0.2418
321.16	172854	7.42	28.5	0.9870	0.3689
325.22	108054	6.92	19.3	0.9913	0.5514
329.31	83924	8.28	12.7	0.9982	0.8489
332.97	55933	7.74	9.2	1.0056	1.188
336.41	48768	9.42	6.7	1.0151	1.652
340.05	32470	8.72	4.9	1.0271	2.282
343.12	26657	9.54	3.7	1.0399	3.017
346.35	19634	10.43	2.6	1.0617	4.407
349.95	13810	9.34	2.1	1.0774	5.558
353.24	14099	13.09	1.5	1.1008	7.502
356.27	10912	12.06	1.3	1.1149	8.856
360.91	7099	12.08	0.9	1.1531	13.27
364.80	4552	11.81	0.6	1.1930	19.66
364.83	4555	11.97	0.6	1.1942	19.89
366.08	5470	15.05	0.6	1.1985	20.79
369.05	3654	13.16	0.5	1.2234	26.77
372.66	3654	16.74	0.4	1.2442	33.64
377.61	3787	25.21	0.3	1.2722	48.13
(1-Methylethyl)urea					
333.16	198465	4.74	54.0	0.8557	0.2240
338.10	158877	5.84	35.5	0.8582	0.3463
341.90	84600	4.84	23.0	0.8617	0.5398
345.85	87170	7.64	15.2	0.8668	0.8268
349.76	58088	7.11	11.0	0.8722	1.154
354.18	39601	7.42	7.3	0.8817	1.759
357.95	29549	8.05	5.1	0.8929	2.538
362.01	21600	8.50	3.6	0.9072	3.629
365.85	14492	8.00	2.3	0.9234	5.028
370.13	10800	8.62	1.9	0.9447	7.147
372.07	9000	8.37	1.6	0.9546	8.263
Butylurea					
339.28	173696	3.65	59.4	0.8553	0.1866
345.20	111658	4.68	30.2	0.8592	0.3737
348.14	87050	5.06	21.9	0.8623	0.519
351.08	68450	5.37	16.4	0.8657	0.700
354.20	43200	4.33	12.9	0.8693	0.895
357.02	37955	5.04	9.9	0.8745	1.183
360.12	31254	5.73	7.2	0.8820	1.626
363.23	22086	5.58	5.3	0.8915	2.23
363.42	32990	8.32	5.3	0.8915	2.22
366.32	19941	6.53	4.2	0.9009	2.87
368.08	18731	7.06	3.7	0.9067	3.29
(1-Methylpropyl)urea					
338.22	342000	4.67	91.1	0.8536	0.1213
343.22	297000	6.83	54.6	0.8556	0.2053
348.16	209289	8.04	33.1	0.8587	0.3442
350.72	126000	6.27	25.7	0.8608	0.4464

Table 3 (*Continued*)

T (K)	τ (s)	$\Delta m \times 10^6$ (kg)	Kn	k_W	p_{sat} (Pa)
353.24	109849	7.18	19.7	0.8635	0.5866
358.43	95404	10.41	12.0	0.8707	0.9783
361.54	41700	6.15	9.0	0.8766	1.319
364.95	18042	3.77	6.4	0.8855	1.859
367.46	27000	6.95	5.3	0.8920	2.281
369.25	23597	7.35	4.4	0.8988	2.746
372.17	18060	7.20	3.5	0.9090	3.489
(1,1-Dimethylethyl)urea					
333.24	217801	5.18	52.3	0.8561	0.2091
338.11	184202	7.50	30.9	0.8592	0.3593
342.25	126000	7.51	21.3	0.8625	0.5271
346.21	91802	8.17	14.4	0.8676	0.7870
350.15	68766	8.98	10.0	0.8742	1.153
354.37	43921	8.43	6.9	0.8833	1.687
358.62	30600	8.95	4.6	0.8968	2.547
363.06	19881	8.85	3.1	0.9145	3.824
366.15	14412	8.61	2.4	0.9297	5.070
369.23	10801	8.41	1.9	0.9455	6.524
372.15	9130	9.20	1.5	0.9627	8.325
1,1-Diethylurea					
305.11	250200	6.73	43.6	0.8568	0.2261
309.81	176412	8.59	24.4	0.8611	0.4104
314.23	110470	9.27	14.4	0.8676	0.7069
322.22	32400	6.85	5.9	0.8881	1.762
326.32	25331	8.36	3.9	0.9041	2.719
330.04	23400	11.32	2.7	0.9220	3.930
334.26	12819	9.84	1.8	0.9489	6.098
337.81	7344	8.26	1.3	0.9756	8.737
338.09	7372	8.59	1.2	0.9782	9.031
340.53	5436	8.38	0.9	1.0000	11.73
343.68	4498	9.85	0.7	1.0287	16.27
347.10	3602	10.77	0.5	1.0543	21.79
1,3-Diethylurea					
323.42	180054	6.73	38.6	0.8575	0.2699
328.41	127091	8.59	23.2	0.8616	0.4558
333.51	76288	9.27	13.4	0.8688	0.8021
338.26	43270	10.26	8.5	0.8779	1.286
343.22	32156	6.85	5.4	0.8911	2.050
347.77	28919	8.36	3.7	0.9063	3.036
353.33	18054	11.32	2.3	0.9326	5.031
358.98	11407	9.84	1.4	0.9669	8.315
362.86	6672	8.26	1.1	0.9901	11.13
368.16	6940	8.59	0.7	1.0287	17.39
368.19	4854	8.38	0.7	1.0298	17.60
372.84	3351	9.85	0.5	1.0593	24.69
378.52	2454	10.77	0.3	1.0949	38.87
383.30	1853	6.73	0.2	1.1160	54.85
384.73	2756	25.42	0.2	1.1251	66.30
384.73	1855	17.63	0.2	1.1269	68.21
1,3-bis(1,1-Dimethylethyl)urea					
323.28	303290	6.14	54.0	0.8559	0.1440
328.40	172747	6.12	31.3	0.8592	0.2530
333.33	115810	7.02	18.5	0.8642	0.4336
338.28	76655	7.25	12.0	0.8706	0.6765
343.31	57602	9.16	7.3	0.8818	1.131
348.29	36205	9.05	4.8	0.8957	1.763
353.26	21611	8.71	3.0	0.9158	2.801
355.35	21650	10.16	2.6	0.9235	3.243
358.30	14436	8.72	2.1	0.9377	4.129
358.58	21900	13.60	2.0	0.9394	4.239
358.63	14701	9.17	2.0	0.9396	4.257
361.98	11970	10.55	1.5	0.9622	5.901
366.35	9405	11.80	1.1	0.9883	8.227
369.28	5400	8.92	0.8	1.0103	10.64
372.28	4500	9.47	0.7	1.0301	13.35

τ: exposition time; Δm: mass loss; Kn: Knudsen number; k_W: Wahlbeck's transmission probability. For AC except urea: $d = 0.2579 \pm 0.0001$ mm, $C = 0.34010$, $D = 254917$, $G = 0.15810$.

gets $k_W = 1.1947$, $p_{sat} = 13.89$ Pa and $Kn = 0.55$. As one can see, the k_W value calculated by Wahlbeck theory is 27% higher than that obtained by Clausing theory; this results in the reduction of the vapor pressure by 28%. The effect of the isotropy failure for 1,3-bis(1,1-dimethylethyl)urea is shown in Fig. 2.

The results of the vapor pressure determination [1] were recalculated using Wahlbeck's transmission probabilities k_W, are shown in Table 3. The values of $\Delta_{cr}^{g} H_m^o$ for AC were calculated from new values of p_{sat} (Table 4). When using the Wahlbeck theory for p_{sat} calculations, agreement of $\Delta_{cr}^{g} H_m^o$ values from effusion and calorimetric measurements are better. The differences are within the experimental error of the methods.

The weighted average values of $\Delta_{cr}^{g} H_m^o$ (350 K) and $\Delta_{cr}^{g} H_m^o$ (350 K) were calculated from effusion and calorimetric measurements. These values were adjusted to 298.15 K with the help of the isobaric heat capacities of the crystal and ideal gas from [4,10].

Thus, Wahlbeck's theory for k_W calculation essentially raises the accuracy of p_{sat} and $\Delta_{cr}^{g} H_m^o$ determination by the integral Knudsen method.

For the purpose of checking the mutual agreement of $\Delta_{cr}^{g} H_m^o$ (298.15 K) for AC, a group additivity study was carried out. The method is based on incremental substitution of the H-atoms on nitrogen or carbon by a CH_3 group.

Table 4
Enthalpies of sublimation for the alkyl derivatives of carbamide

Substance	a[a]	b (K)[a]	T_m (K)[a]	$\Delta_{cr}^{g}H_m^o$ (T) (kJ mol^{-1})[a]	$\Delta_{cr}^{g}C_p$ (J K^{-1} mol^{-1})	$\Delta_{cr}^{g}H_m^o$ (350 K)[b] (kJ mol−1)	$\Delta_{cal}^{eff}\Delta_{cr}^{g}H_m^o$ (350 K) (kJ mol^{-1})
Urea	31.27 ± 0.70	11372 ± 260	370	94.55 ± 2.2	−27.0	94.6 ± 0.5	0.5
			350	95.09 ± 2.2			
Methylurea	34.00 ± 0.41	11654 ± 142	347	96.90 ± 1.2	−39.0	94.4 ± 0.4	2.4
			350	96.78 ± 1.2			
Ethylurea	34.47 ± 0.38	11796 ± 130	344	98.08 ± 1.1	−48.0	96.4 ± 1.1	1.4
			350	97.79 ± 1.1			
1,1-Dimethylurea	34.02 ± 0.47	11393 ± 163	348	94.73 ± 1.4	−27.1	93.3 ± 0.5	1.4
			350	94.68 ± 1.4			
1,3-Dimethylurea	31.82 ± 0.34	10537 ± 117	347	87.61 ± 1.0	−34.4	86.6 ± 0.5	0.9
			350	87.51 ± 1.0			
(1-Methylethyl)urea	33.40 ± 0.55	11632 ± 193	353	96.71 ± 1.6	−19.7	97.2 ± 0.6	−0.4
			350	96.77 ± 1.6			
Butylurea	34.78 ± 0.88	12350 ± 313	354	102.70 ± 2.8	−66.3	101.1 ± 0.4	1.9
			350	103.00 ± 2.8			
(1-Methylpropyl)urea	34.98 ± 0.27	12546 ± 96	355	104.30 ± 0.8	−33.4	102.4 ± 0.5	2.1
			350	104.50 ± 0.8			
(1,1-Dimethylethyl)urea	33.66 ± 0.25	11736 ± 90	353	97.58 ± 0.8	−22.6	94.4 ± 0.9	3.3
			350	97.65 ± 0.8			
1,1-Diethylurea	36.19 ± 0.31	11488 ± 100	324	95.52 ± 0.8	−24.1	94.7 ± 0.2	0.2
			350	94.86 ± 0.8			
1,3-Diethylurea	32.86 ± 0.31	11040 ± 110	358	91.79 ± 0.9	−58.2	95.6 ± 0.6	−3.3
			350	92.26 ± 0.9			
1,3-bis(1,1-Dimethylethyl)urea	32.29 ± 0.30	11053 ± 105	348	91.90 ± 0.9	−20.1	90.0 ± 1.0	1.9
			350	91.86 ± 0.9			
Average of absolute deviations							1.6

[a] Values of a, b for the Eq. $\ln(p_{sat}) = a - (b/T)$ and $\Delta_{cr}^{g}H_m^o$ (T) from corrected effusion p_{sat} data.
[b] Calorimetric measurements $\Delta_{cr}^{g}H_m^o$ (T) [1].

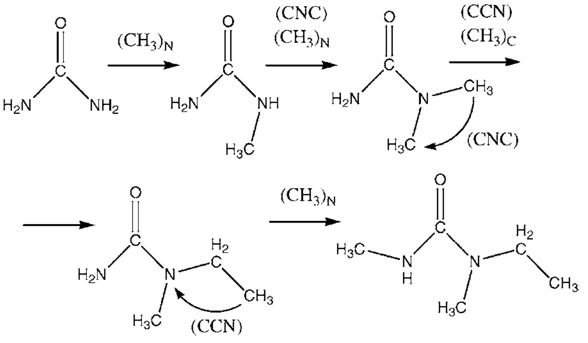
Table 5
Thermodynamic functions of sublimation for alkyl derivatives of carbamide

Substance	$\langle\Delta_{cr}^{g}H_{m}^{o}\rangle$ (350 K)p (kJ mol^{-1})	p_{sat} (350 K) (Pa)	$\Delta_{cr}^{g}S_{m}^{o}$ (350 K) (J mol^{-1} K^{-1})	$\langle\Delta_{cr}^{g}H_{m}^{o}\rangle$ (298.15 K) (kJ mol^{-1})	$\Delta_{cr}^{g}S_{m}^{o}$ (298.15 K) (J mol^{-1} K^{-1})
Urea	94.72 ± 0.51	0.295 ± 0.015	164.7 ± 1.5	95.97 ± 0.51	168.6 ± 1.5
Methylurea	94.64 ± 0.38	2.030 ± 0.10	180.6 ± 1.1	96.27 ± 0.38	185.5 ± 1.1
Ethylurea	97.07 ± 0.77	2.150 ± 0.11	188.0 ± 2.3	99.27 ± 0.77	194.8 ± 2.3
1,1-Dimethylurea	93.50 ± 0.42	4.340 ± 0.22	183.6 ± 1.3	94.91 ± 0.42	188.0 ± 1.3
1,3-Dimethylurea	86.79 ± 0.44	5.550 ± 0.28	166.5 ± 1.3	88.32 ± 0.44	171.2 ± 1.3
(1-Methylethyl)urea	97.15 ± 0.55	1.180 ± 0.06	183.2 ± 1.6	98.14 ± 0.55	186.3 ± 1.6
Butylurea	101.10 ± 0.40	0.603 ± 0.03	188.9 ± 1.2	104.00 ± 0.40	197.9 ± 1.2
(1-Methylpropyl)urea	103.00 ± 0.42	0.421 ± 0.02	191.4 ± 1.3	104.60 ± 0.42	196.2 ± 1.3
(1,1-Dimethylethyl)urea	96.20 ± 0.60	1.140 ± 0.06	180.2 ± 1.8	97.30 ± 0.60	183.6 ± 1.8
1,1-Diethylurea	94.73 ± 0.19	29.0 ± 1.5	202.9 ± 0.6	95.94 ± 0.19	206.7 ± 0.6
1,3-Diethylurea	94.60 ± 0.50	3.710 ± 0.19	185.5 ± 1.5	97.60 ± 0.50	194.8 ± 1.5
1,3-bis(1,1-Dimethylethyl)urea	91.05 ± 0.65	2.030 ± 0.10	170.3 ± 1.9	91.74 ± 0.65	172.4 ± 1.9

Table 6
Matrix of the group values and calculated values of enthalpies of sublimation for alkyl derivatives of carbamide

Substance	$\Delta_{cr}^{g}H_{m}^{o}$ (298.15 K) (kJ mol^{-1})	Matrix of the group values					$\Delta_{cr}^{g}H_{m}^{o}$ (298.15 K)$_{add}$ (kJ mol^{-1})	$\lvert\Delta_{add}^{exp}\Delta_{cr}^{g}H_{m}^{o}$ (298.15 K)$\rvert$ (kJ mol^{-1})
		$(CH_3)_N$	$(CH_3)_C$	(CCN)	(CNC)	(CCC)		
Methylurea	96.27	1	0	0	0	0	93.72	2.55
Ethylurea	99.27	1	1	1	0	0	96.77	2.50
1,1-Dimethylurea	94.91	2	0	0	1	0	92.37	2.54
1,3-Dimethylurea	88.32	2	0	0	0	0	91.46	3.14
(1-Methylethyl)urea	98.14	1	2	2	0	1	97.14	1.00
Butylurea	104.0	1	3	1	0	2	105.54	1.54
(1-Methylpropyl)urea	104.6	1	3	2	0	2	101.52	3.08
(1,1-Dimethylethyl)urea	97.30	1	3	3	0	3	94.82	2.48
1,1-Diethylurea	95.94	2	2	2	1	0	98.48	2.54
1,3-Diethylurea	97.60	2	2	2	0	0	97.58	0.02
1,3-bis(1,1-Dimethylethyl)urea	91.74	2	6	6	0	6	93.66	1.92
Average								2.12

According to Kabo et al. [4], carbamide was used as a basis. The other AC are obtained by subsequent substitutions:



The formula for the physical–chemical property calculations of AC was

$$\begin{aligned} P(AK) &= P(\text{urea}) + n_i\,\Delta P(CH_3)_N + n_j\,\Delta P(CH_3)_C \\ &\quad + n_k\,\Delta P(CNC) + n_l\,\Delta P(CNC) \\ &\quad + n_m\,\Delta P(CCC) \end{aligned} \qquad (20)$$

where $\Delta P(CH_3)_N$ is an increment of H → CH_3 substitutions on a nitrogen atom; $\Delta P(CH_3)_C$ is an increment of H → CH_3 substitution on a carbon atom. The mutual influence of the introduced CH_3 groups were taken into account through the three type of corrections by one to three interactions with polyvalent C and N atoms; n_i, n_j, n_k, n_l, and n_m are the

Table 7
Group values for the enthalpy of sublimation for alkyl derivative of carbamide at $T = 298.15\,\mathrm{K}$

Group contribution	Value
NH_2CONH_2 (urea)	95.97 ± 0.5
$(CH_3)_N$	−2.25 ± 3.0
$(CH_3)_C$	7.07 ± 4.1
(CCN)	−4.02 ± 4.0
(CNC)	0.91 ± 7.2
(CCC)	−2.69 ± 3.2

quantities of the corresponding increments and corrections.

The matrix of the coefficients, calculated values of $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^{\mathrm{o}}$ (298.15 K) and the divergence between experimental and additive values are listed in Tables 5–7. The average deviation between experimental and calculated values of $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^{\mathrm{o}}$ (298.15 K) was equal to $2.12\,\mathrm{kJ\,mol^{-1}}$. Such agreement seems to be satisfactory.

Acknowledgements

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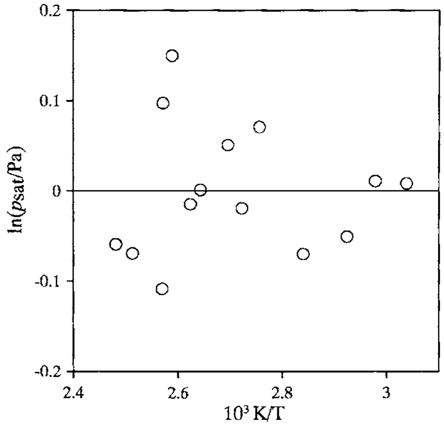
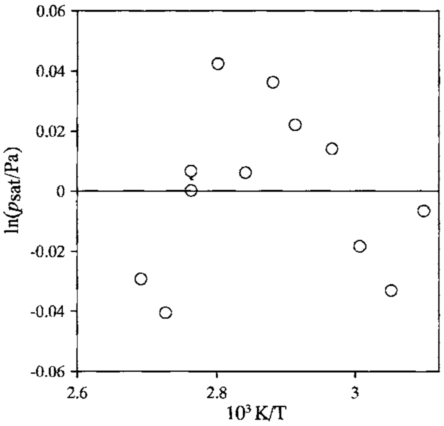
Appedix A

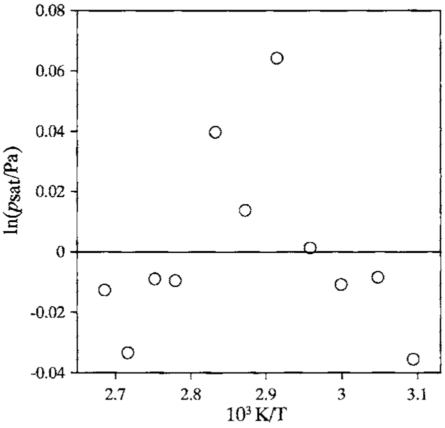
The dispersion of the experimental values $\ln(p_{\mathrm{sat}})$ from approximating equation $\ln(p_{\mathrm{sat}}) = a - (b/T)$.



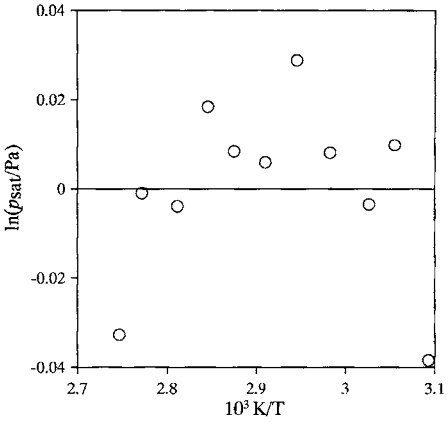
Urea



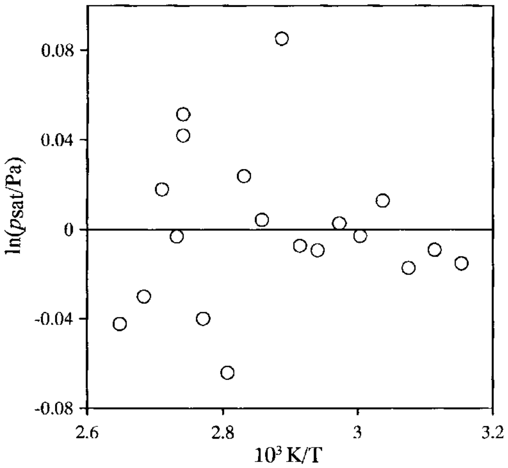
Methyl urea



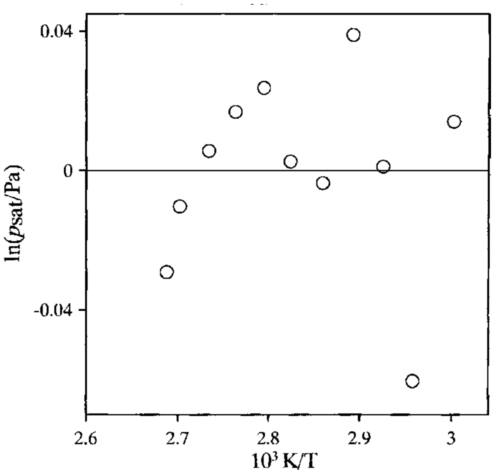
1,1-Dimethyl urea



Ethyl urea



1,3-Dimethyl urea



(1-Methylethyl)urea

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