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RELATIVE ENTHALPIES AND RELATED THERMODYNAMIC FUNCTIONS OF SOME ORGANIC COMPOUNDS BY DROP CALORIMETRY

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The values of thermodynamic functions of the following eight organic compounds under non-reacting conditions within the temperature range 298.15—550 K are given: N,N dimethylformamide, $CHO \cdot N(CH_3)_2$; 4-nitro-1-chlorobenzene, $Cl \cdot C_6H_4 \cdot NO_2$; sodium *p*-nitrophenoxide, $NO_2 \cdot C_6H_4 \cdot ONa$; 1-methyl-2-pyrrolidone, $CH_3 \cdot N \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH_2$; 4,4'-dinitrodiphenyl ether, $(NO_2 \cdot C_6H_4)_2O$; 4,4'-diaminodiphenyl ether, $(NH_2 \cdot C_6H_4)_2O$; bis-(4-aminophenyl)methane, $(NH_2 \cdot C_6H_4)_2CH_2$; bis(4-maleic acidimidphenyl)methane, $(C_6H_4 \cdot N \cdot CO \cdot CH : CH \cdot CO)_2CH_2$.

The relative enthalpy was obtained from calorimetric data by drop calorimetry. The heat capacity and relative entropy are functions derived from the foregoing. The equations of the temperature variation of the relative enthalphy were obtained by computer processing of the calorimetric data by the least squares method. The parameters of solid-liquid transitions were determined from the discontinuity of the temperature variation of the relative enthalpy.

For technological reasons it is very important to know the enthalpies of the reactions occurring in the industrial processes of pharmaceutical product preparation, dye fabrication and basic organic synthesis.

In the general case, for a reaction of the type

$$aA + bB \rightarrow rR + sS \tag{1}$$

the enthalpy of reaction, $\Delta_r H^\circ(T)$, is given by the difference between the enthalpies of the final and initial products:

$$\Delta_r H^\circ(T) = [r\, H^\circ(R, T) + s\, H^\circ(S, T)] - [a\, H^\circ(A, T] + b\, H^\circ(B, T)] \tag{2}$$

$H^\circ(T)$ can be estimated from the formula

$$H^\circ(T) = \Delta_f H^\circ(298.15\ K) + \int_{298.15}^{T} C_p^\circ\, dT = \Delta_f H^\circ(298.15\ K) + \{H^\circ(T) - H^\circ(298.15\ K)\} \tag{3}$$

in which $\Delta_f H^\circ$ (298.15 K) is the standard enthalpy of formation, and $\{H^\circ(T) - H^\circ(298.15\ K)\}$ is a thermodynamic function named the relative enthalpy. Standard enthalpies of formation can be estimated from thermal combustion data and the relative enthalpy can be estimated from the heat content data obtained by the drop calorimetric method. In this way one can obtain all the thermodynamic data for calculation of the enthalpy of reaction via Eqs 2 and 3.

To evaluate the thermodynamic properties of substances in a non-reacting state, a block-type calorimeter with isothermal jacket was used [1, 2]. With this apparatus we obtain the thermodynamic properties listed by the usual international tables:

(i) relative enthalpy, $\{H^\circ(T) - H^\circ(298.15\text{ K})\}$, as an explicit temperature function $f(T)$. This function has been obtained by least square computer processing of the data; use has been made of an improved variant of the Termox program [3], which allows direct finding of the equation for which deviation of the experimental points from the calculated curve is minimal; the final results are tabulated and both calculated and experimental curves are plotted;

(ii) heat capacity,

$$C_p^\circ = \frac{\partial}{\partial T}\{H^\circ(T) - H^\circ(298.15\text{ K}) \tag{4}$$

(iii) relative entropy,

$$\{S^\circ(T) - S^\circ(298.15\text{ K})\} = \int_{298.15}^{T} \frac{C_p^\circ}{T}\,\mathrm{d}T. \tag{5}$$

By examination of the discontinuity of the temperature variation of relative enthalpy, the parameters of the solid-liquid transition were obtained.

The operation ranges of the apparatus are: temperature: 300–1000 K, heat quantity: 70–5050 cal. The reproducibility of heat content measurements: 99.5–99.7%. Sensitivity: maximum: 0.7 cal, minimum: 12.2 cal. Accuracy of heat content measurements: 99.7%.

Results

The organic substances of technological importance which were examined by the drop calorimetric method are presented in Table 1.

The equations of the temperature variation of the relative enthalpy and related thermodynamic functions are as follows:

N,N-dimethylformamide

Liquid state: 298.15–429.15 K

$$\{\mathrm{H}^\circ(T) - \mathrm{H}^\circ(298.15\text{ K})\} = -\,8577.746 + 28.806\,(T/K)\text{ cal}\cdot\text{mole}^{-1} \tag{6}$$

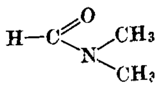
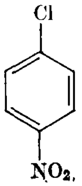
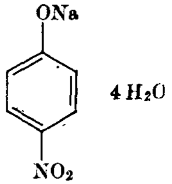
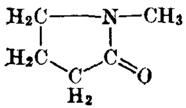
Standard deviation = ± 58.8 cal · mole^{-1}, that is ± 0.33 per cent.

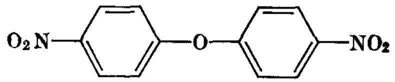
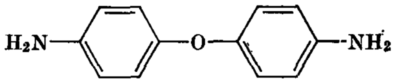
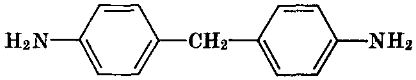
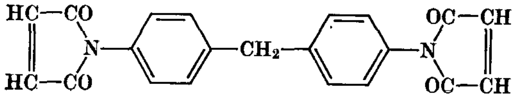
$$C_p^\circ = 28.806\text{ cal}\cdot\text{mole}^{-1}\cdot\text{K}^{-1} \tag{7}$$

$$\{S^\circ(T) - \mathrm{S}^\circ(298.15\text{ K})\} = -\,164\cdot 154 + 66.340\log(T/K)\text{ cal}\cdot\text{mole}^{-1}\cdot\text{K}^{-1} \tag{8}$$

Table 1

Organic substances studied by drop calorimetry

Name	Structural formula	Molecular weight	Temperature of melting, °C	
			literature	DTA
N,N-dimethyl--formamide*		73.09	– 60.48 : ref. [4] b.p. = 149 : ref. [4]	
4-nitro-1-chloro-benzene*		157.557	83.6 : ref. [4] 81–83 : ref. [5]	81.5 : ref. [6]
Sodium p-nitro-phenoxide*		197.13	*Observation:* lost two molecules of water at 36° and other two molecules at 120° [4]. In our determinations the compound was $C_6H_4.NO_2ONa.2H_2O$.	
1-methyl-2-pyrrolidone*		99.130	– 23 : ref. [4] b.p. = 202 : ref. [4]	

4,4'-dinitrodiphenyl ether*		260.21	144 : ref. [4] 142–143 : ref. [5]	145 ref. [6]
4,4'-diaminodiphenyl ether		200.24	186–187 : ref. [5] 190–192 : ref. [7]	192.3 : ref. [6]
Bis-(4-aminophenyl) methane*		198.27	93–94 : ref. [5] 92–93 : ref. [7]	90.5–90.6 : ref. [6]
Bis-(4-maleic acidimide, phenyl) methane		358.356		156.5–158.9 : ref. [6]

* Names approved by the International Union of Chemists (IUC) [4]

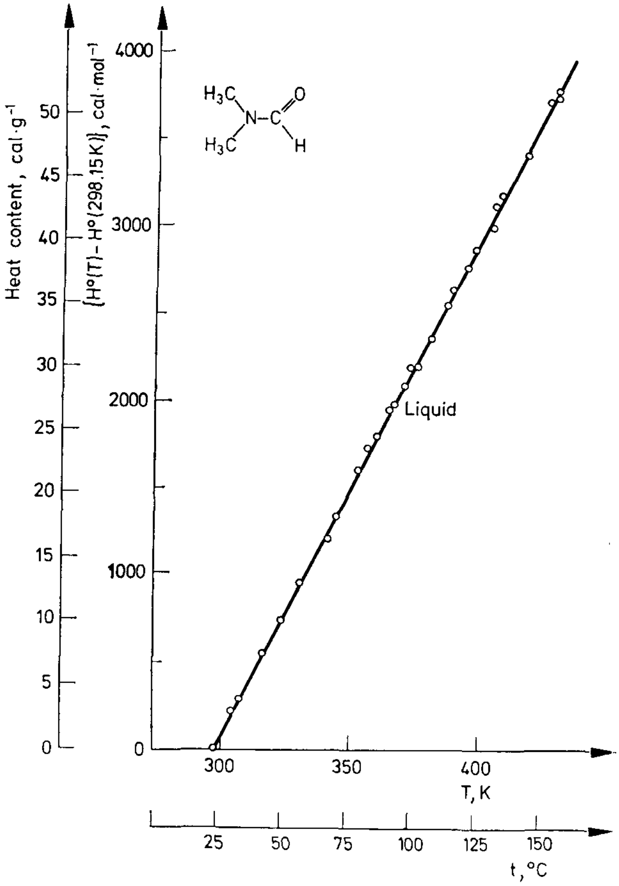


Fig. 1. Experimental and calculated relative enthalpies of N,N-dimethyl formamide *vs.* temperature

The values of the relative enthalpy (both experimental and calculated) are plotted in Fig. 1; the values of the thermodynamic functions are tabulated in Table 2.

4-nitro-1-chlorobenzene

Solid state: 298.15–354.65 K

$$\{H^\circ(T) - H^\circ(298.15\text{ K})\} = -44548.751 + 239.067\,(T/K) - 300.618 \cdot 10^{-3}\,(T/K)^2 \text{ cal} \cdot \text{mole}^{-1} \qquad (9)$$

Standard deviation = ± 1.372 cal. mole^{-1}, that is ± 0.08 per cent. $C_p^0 =$

$$= 239.067 - 601.236 \cdot 10^{-3}\,(T/K) \text{ cal} \cdot \text{mole}^{-1} \cdot \text{K}^{-1} \qquad (10)$$

Table 2

Values of thermodynamic functions for N,N-dimethyl formamide

T	$\{H^\circ(T)-H^\circ(298.15\ \mathrm{K})\}$	C_p	$\{S^\circ(T)-S^\circ(298.15\ \mathrm{K})\}$
K	cal. mole^{-1}	cal. mole^{-1}.K^{-1}	
298.15	0.0	28.8	0.0
300	64.078	28.8	0.178
310	352.139	28.8	1.123
320	640.199	28.8	2.037
330	928.260	28.8	2.924
340	1216.321	28.8	3.784
350	1504.382	28.8	4.619
360	1792.443	28.8	5.431
370	2080.504	28.8	6.220
380	2368.564	28.8	6.988
390	2656.625	28.8	7.736
400	2944.686	28.8	8.467
410	3232.747	28.8	9.178
420	3520.807	28.8	9.872
430	3808.868	28.8	10.550

$$\{S^\circ(T) - S^\circ(298.15\ \mathrm{K})\} = -1183.091 + 550.571 \log (T/K) - 601.236 \cdot 10^{-3} (T/K)\ \mathrm{cal} \cdot \mathrm{mole}^{-1} \cdot \mathrm{K}^{-1} \quad (11)$$

Liquid state: 354.65 – 466.85 K

$$\{H^\circ(T) - H^\circ(298.15\ \mathrm{K})\} = -15085.862 + 57.351 (T/K)\ \mathrm{cal} \cdot \mathrm{mole}^{-1} \quad (12)$$

Standard deviation = ± 101.072 cal · mole^{-1}, that is ± 1.16 per cent.

$$C_p^\circ = 57.351\ \mathrm{cal} \cdot \mathrm{mole}^{-1} \cdot \mathrm{K}^{-1} \quad (13)$$

$$\{S^\circ(T) - S^\circ(298.15\ \mathrm{K})\} = -326.821 + 132.079 \log (T/K)\ \mathrm{cal} \cdot \mathrm{mole}^{-1} \cdot \mathrm{K}^{-1} \quad (14)$$

The processing of information supplied by the discontinuity in the relative temperature enthalpy variation (due to melting of the substance) yielded the following results:

$$T_M = 354.65\ \mathrm{K}$$

H_M:
graphical = 2836.026 cal · mole^{-1}
calculated = 2827.937 cal · mole^{-1}
average = 2831.981 cal · mole^{-1}

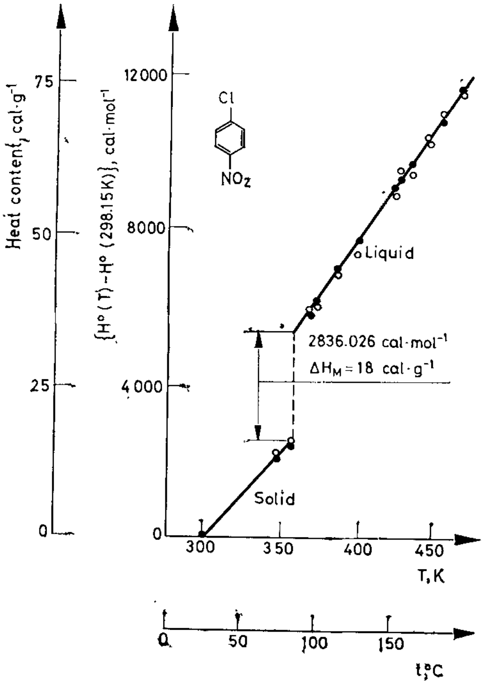


Fig. 2. Experimental and calculated relative enthalpies of 4-nitro-1-chlorobenzene *vs.* temperature

Equations (9–14) were employed in tabulation of the main thermodynamic functions (Table 3); plots were drawn of the temperature variation of the experimental relative enthalpy in comparison with the calculated curve (Fig. 2).

Sodium p-nitrophenoxide

Solid state: 309.15 – 393.15 K

$$\{H^\circ(T) - H^\circ(298.15\ \mathrm{K})\} = -26985.871 + 109.407\,(T/K) - 64.658 \cdot 10^{-3}\,(T/K)^2\ \mathrm{cal \cdot mole^{-1}} \qquad (15)$$

Standard deviation = ± 58.239 cal · mole^{-1}, that is ± 1.31 per cent.

$$C_p^\circ = 109.407 - 0.129\,(T/K)\,\mathrm{cal \cdot mole^{-1} \cdot K^{-1}} \qquad (16)$$

$$\{S^\circ(T) - S^\circ(298.15\ \mathrm{K})\} = -585.007 + 251.964 \log (T/K) - 0.129\,(T/K)\ \mathrm{cal \cdot mole^{-1} \cdot K^{-1}} \qquad (17)$$

Table 3

Values of thermodynamic functions for 4-nitro-1-chlorobenzene

T	$\{H^\circ(T)-H^\circ(298.15\ \text{K})\}$	C_p°	$\{S^\circ(T)-S^\circ(198.15\ \text{K})\}$
K	cal. mole^{-1}	cal. mole^{-1}. K^{-1}	
298.15	0.0	59.808	0.0
300	115.729	58.606	0.368
310	672.629	52.684	2.196
320	1169.406	46.671	3.776
330	1606.059	40.659	5.120
340	1982.588	34.647	6.248
350	2298.994	28.634	7.167
360	5560.498	57.351	11.761
370	6134.008	57.351	12.384
380	6707.518	57.351	13.914
390	7281.028	57.351	15.404
400	7854.538	57.351	16.856
410	8428.048	57.351	18.273
420	9001.558	57.351	19.655
430	9575.068	57.351	21.005
440	10148.578	57.351	22.323
450	10722.088	57.351	23.612
460	11295.598	57.351	24.873
470	11896.108	57.351	26.107

The values of the relative enthalpy (both experimental and calculated) are plotted in Fig. 3; the values of the thermodynamic functions are tabulated in Table 4.

Table 4

Values of thermodynamic functions for sodium p-nitrophenoxide*

T	$\{H^\circ(T)-H^\circ(298.15\ \text{K})\}$	C_p°	$\{S^\circ(T)-S^\circ(298.15\ \text{K})\}$
K	cal. mole^{-1}	cal. mole^{-1}. K^{-1}	
310	716.665	69.417	2.736
320	1403.390	68.127	4.921
330	2077.183	66.837	6.997
340	2738.044	65.547	8.975
350	3385.974	64.257	10.857
360	4020.972	62.967	12.648
370	4643.039	61.677	14.357
380	5252.174	60.387	15.985
390	5848.377	59.097	17.537

* The tabulated values of the thermodynamic functions are given for the compound $O_2N \cdot C_6H_4 \cdot ONa \cdot 2H_2O$ ($M \cdot W = 161.091$), which is stable between 309.15 and 393.15 K (36–120°)

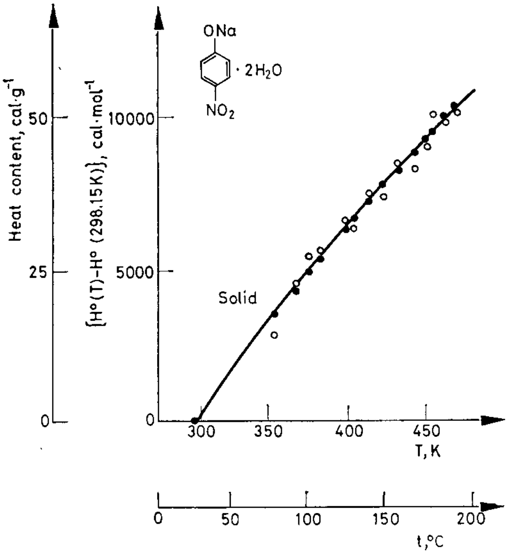


Fig. 3. Experimental and calculated relative enthalpies of sodium p-nitrophenoxide *vs.* temperature

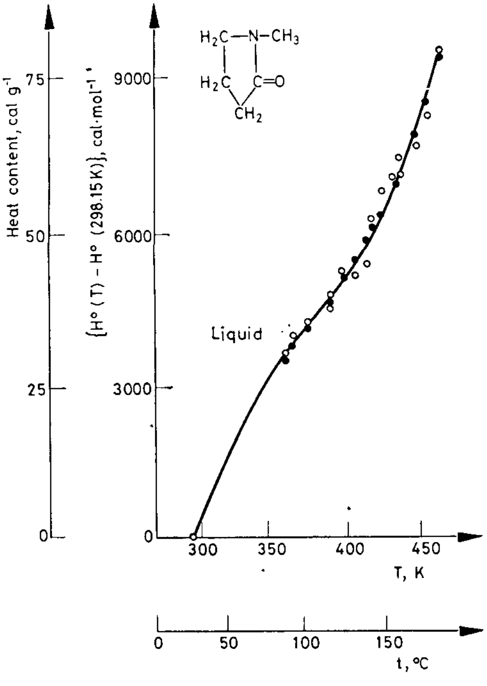


Fig. 4. Experimental and calculated relative enthalpies of 1-methyl-2-pyrrolidone *vs.* temperature

1-methyl-2-pyrrolidone

Liquid state: 298.15 – 461.15 K

$$\{H^\circ(T) - H^\circ(298.15\ \mathrm{K})\} = -137677.592 + 1070.703\,(T/K) - \\ - 2782.975 \cdot 10^{-3}\,(T/K)^2 + 2483.702 \cdot 10^{-6}\,(T/K)^3\ \mathrm{cal \cdot mole^{-1}} \qquad (18)$$

Standard deviation = ± 73.722 cal · mole^{-1} that is ± 0.98 per cent.

$$C_p^\circ = 1070.703 - 5565.950 \cdot 10^{-3}\,(T/K) + 7451.106 \cdot 10^{-6}\,(T/K)^2 \\ \mathrm{cal \cdot mole^{-1} \cdot K^{-1}} \qquad (19)$$

$$\{S^\circ(T) - S^\circ(298.15\ \mathrm{K})\} = -4773.208 + 2465.829 \log(T/K) - \\ - 5565.950 \cdot 10^{-3}(T/K) + 3725.551 \cdot 10^{-6}\,(T/K)^2\ \mathrm{cal \cdot mole^{-1} \cdot K^{-1}} \qquad (20)$$

Equations (18–20) were employed in tabulation of the main thermodynamic functions (Table 5); plots were drawn of the temperature variation of the experimental relative enthalpy in comparison with the calculated curve (Fig. 4).

Table 5

Values of thermodynamic functions for 1-methyl-2-pyrrolidone

T	$\{H^\circ(T)-H^\circ(298.15\ \mathrm{K})\}$	C_p°	$\{S^\circ(T)-S^\circ(198.15\ \mathrm{K})\}$
K	cal. mole^{-1}	cal. mole^{-1}. K^{-1}	
298.15	0.0	73.566	0.0
300	125.512	71.517	0.461
310	788.407	61.309	2.641
320	1356.675	52.592	4.456
330	1845.219	45.364	5.956
340	2268.941	39.627	7.239
350	2642.743	35.381	8.331
360	2981.528	32.624	9.280
370	3300.198	31.357	10.160
380	3613.654	31.581	10.997
390	3936.799	33.295	11.838
400	4284.536	36.499	12.735
410	4671.766	41.194	13.686
420	5113.392	47.379	14.766
430	5624.315	55.054	15.974
440	6219.439	64.219	17.336
450	6913.665	74.874	18.901
460	7721.896	87.020	20.692
470	8695.033	100.656	22.711

4,4'-dinitrodiphenyl ether

Solid state: 298.15 – 418.15 K

$$\{H^\circ(T) - H^\circ(298.15\ \mathrm{K})\} = -236277.596 + 1953.612\ (T/K) - 5468.053 \cdot 10^{-3}\ (T/K)^2 + 5279.140 \cdot 10^{-6}\ (T/K)^3\ \mathrm{cal \cdot mole^{-1}} \quad (21)$$

Standard deviation = ± 63.886 cal · mole^{-1}, that is ± 0.85 per cent.

$$C_p^\circ = 1953.612 - 10.963\ (T/K) + 15.837 \cdot 10^{-3}\ (T/K)^2\ \mathrm{cal \cdot mole^{-1} \cdot K^{-1}} \quad (22)$$

$$\{S^\circ(T) - S^\circ(298.15\ \mathrm{K})\} = -8576.211 + 4499.168\ \log\ (T/K) - 10.936\ (T/K) + 7.918 \cdot 10^{-3}\ (T/K)^2\ \mathrm{cal \cdot mole^{-1} \cdot K^{-1}} \quad (23)$$

Liquid state: 418.15 – 491.07 K

$$\{H^\circ(T) - H^\circ(298.15\ \mathrm{K})\} = -346223.200 + 1496.401\ (T/K) - 1524.068 \cdot 10^{-3}\ (T/K)\ \mathrm{cal \cdot mole^{-1}} \quad (24)$$

Standard deviation = ± 220.266 cal · mole^{-1}, that is ± 1.18 per cent.

Table 6

Values of thermodynamic functions for 4,4'-dinitrodiphenyl ether

T	$\{H^\circ(T)-H^\circ(298.15\ \mathrm{K})\}$	C_p°	$\{S^\circ(T)-S^\circ(198.15\ \mathrm{K})\}$
K	cal. mole^{-1}	cal. mole^{-1}. K^{-1}	
298.15	0.0	100.848	0.0
300	218.014	98.142	0.588
310	1133.090	85.387	3.595
320	1936.476	75.801	6.163
330	2659.846	69.381	8.378
340	3334.876	66.129	10.423
350	3993.239	66.044	12.342
360	4666.611	69.127	14.225
370	5386.666	75.377	16.206
380	6185.081	84.795	18.331
390	7093.528	97.379	20.691
400	8143.684	113.132	23.374
410	9367.222	132.051	36.381
420	13419.625	216.241	141.466
430	15429.906	185.761	146 206
440	17133.675	155.281	150.119
450	18533.480	124.801	153.274
460	19628.471	94.321	155.706
470	20418.649	63.841	157.413
480	20904.013	33.361	158.432
490	21084.563	2.881	158.830

4,4'-diaminodiphenyl ether

Solid state: 298.15 – 465.45 K

$$C_p^\circ = 1496.401 - 3.048\,(T/K)\,\text{cal} \cdot \text{mole}^{-1} \cdot \text{K}^{-1} \tag{25}$$

$$\{S^\circ(T) - S^\circ(298.15\ \text{K})\} = -\,7618.647 + 3446.211\log(T/K) - 3.048\,(T/K)\,\text{cal} \cdot \text{mole}^{-1} \cdot \text{K}^{-1} \tag{26}$$

The discontinuity in the temperature variation of the relative enthalpy is due to the solid-liquid transition and may be employed in evaluation of the parameters of this transition. The graphical method, as well as Eqs (21) and (24), yields:

$T_M = 418.15$ K

$$H_M \quad \begin{array}{ll} \text{graphical} & = 2419.953\ \text{cal} \cdot \text{mole}^{-1} \\ \text{calculated} & = 2499.846\ \text{cal} \cdot \text{mole}^{-1} \\ \text{average} & = 2459.899\ \text{cal} \cdot \text{mole}^{-1} \end{array}$$

As in the previous cases, the values of the thermodynamic functions are tabulated (Table 6) and the temperature variation of the relative enthalpy (both experimental and calculated) is plotted (Fig. 5).

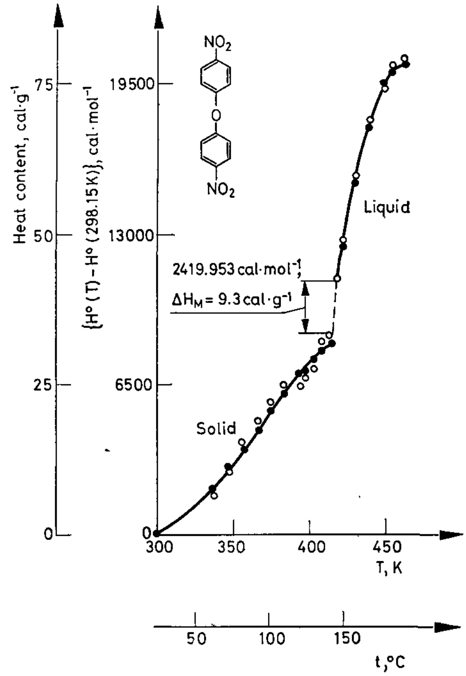


Fig. 5. Experimental and calculated relative enthalpies of 4,4'-dinitrodiphenyl ether *vs.* temperature

$$\{H^\circ(T) - H^\circ(298.15\ \mathrm{K})\} = -13357.951 + 22.367\ (T/K) + 75.250 \cdot 10^{-3}\ (T/K)^2\ \mathrm{cal \cdot mole^{-1}} \qquad (27)$$

Standard deviation = ± 122.312 cal · mole^{-1}, that is ± 1.34 per cent.

$$C_p^\circ = 22.367 + 0.150\,(T/K)\,\mathrm{cal \cdot mole^{-1} \cdot K^{-1}} \qquad (28)$$

$$\{S^\circ(T) - S^\circ(298.15\,\mathrm{K})\} = -172.183 + 51.511 \log(T/K) + 0.150\,(T/K)\ \mathrm{cal \cdot mole^{-1} \cdot K^{-1}} \qquad (29)$$

Liquid state: 465.45 – 502.15 K

$$\{H^\circ(T) - H^\circ(298.15\,\mathrm{K})\} = -2037422.958 + 8247.119\ (T/K) - 8243.881 \cdot 10^{-3}\ (T/K)^2\ \mathrm{cal \cdot mole^{-1}} \qquad (30)$$

Standard deviation = ± 109.661 cal · mole^{-1}, that is ± 0.56 per cent.

$$C_p^\circ = 8247.119 - 1.648\,(T/K)\,\mathrm{cal \cdot mole^{-1} \cdot K^{-1}} \qquad (31)$$

Table 7

Values of thermodynamic functions for 4,4'-diaminodiphenyl ether

T	$\{H^\circ(T)-H^\circ(298.15\ \mathrm{K})\}$	C_p°	$\{S^\circ(T)-S^\circ(298.15\ \mathrm{K})\}$
K	cal. mole^{-1}	cal. mole^{-1}. K^{-1}	
298.15	0.0	67.089	0.0
300	124.649	67.367	0.415
310	807.344	68.867	2.649
320	1505.089	70.367	4.860
330	2217.884	71.867	7.048
340	2945.729	73.367	9.216
350	3688.624	74.867	11.364
360	4466.569	76.367	13.494
370	5219.564	77.867	15.607
380	6007.609	79.367	17.704
390	6810.704	80.867	19.785
400	7628.849	82.367	21.851
410	8462.044	83.067	23.903
420	9310.289	85.367	25.943
430	10173.584	86.867	27.970
440	11051.929	88.367	29.984
450	11945.324	89.867	31.986
460	12853.769	91.367	33.978
470	17649.659	7472.559	3471.160
480	21803.979	7456.079	3628.277
490	24309.524	7439.599	3781.976
500	25166.292	7423.119	3932.065

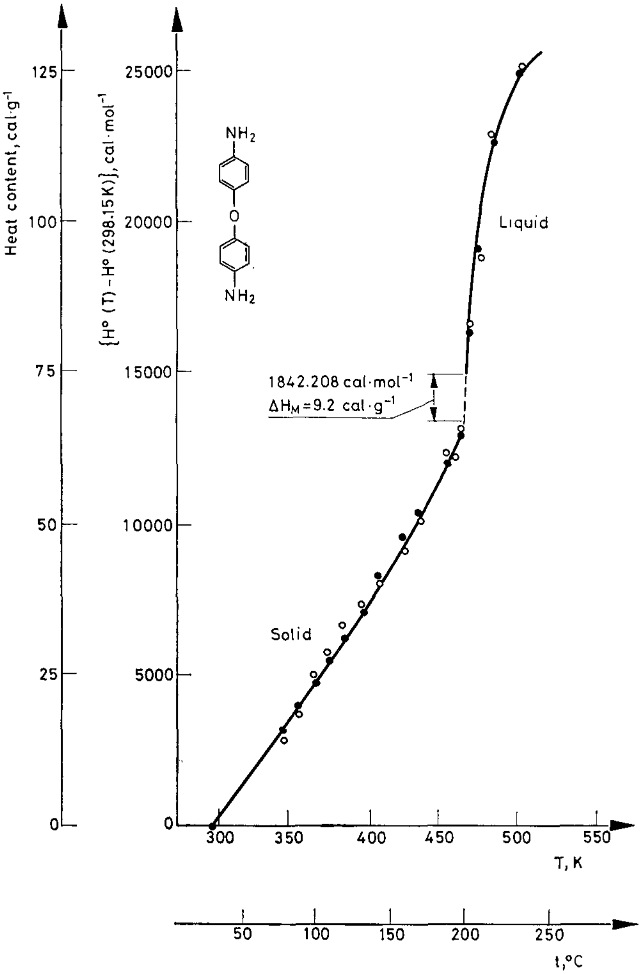


Fig. 6. Experimental and calculated relative enthalpies of 4,4'-diaminodiphenyl ether *vs.* temperature

$$\{S^\circ(T) - S^\circ(298.15\ \mathrm{K})\} = -46505.782 + 18993.115 \log (T/K) - 1.648 (T/K)\ \mathrm{cal \cdot mole^{-1} \cdot K^{-1}}. \quad (32)$$

The processing of information supplied by the discontinuity in the relative enthalpy variation (due to melting of the substance) yielded the following results:

$T_M = 465.45$ K

$$H_M: \quad \begin{array}{ll} \text{graphical} & = 1842.208 \text{ cal} \cdot \text{mloe}^{-1} \\ \text{calculated} & = 1858.474 \text{ cal} \cdot \text{mole}^{-1} \\ \text{average} & = 1850.341 \text{ cal} \cdot \text{mole}^{-1} \end{array}$$

Equations (27–32) were employed in tabulation (Table 7) of the main thermodynamic functions; plots were drawn of the temperature variation of the experimental relative enthalpy in comparison with the calculated curve (Fig. 6).

Bis-(4-aminophenyl)methane

Solid state: 298.15 – 363.65 K

$$\{H^\circ(T) - H^\circ(298.15 \text{ K})\} = 87977.615 - 606.019\,(T/K) + 1042.900 \cdot 10^{-3}\,(T/K)^2 \text{ cal} \cdot \text{mole}^{-1} \qquad (33)$$

Standard deviation = ± 101.56 cal · mole^{-1}, that is ± 2.09 per cent.

$$C_p^\circ = -606.019 + 2.086\,(T/K) \text{ cal} \cdot \text{mole}^{-1} \cdot \text{K}^{-1} \qquad (34)$$

Table 8

Values of calculated thermodynamic functions for bis-(4-aminophenyl)-methane

T	$\{H^\circ(T)-H^\circ(298.15\text{ K})\}$	C_p°	$\{S^\circ(T)-S^\circ(298.15\text{ K})\}$
K	cal. mole^{-1}	cal. mole^{-1}. K^{-1}	
298.15	0.0	15.922	0.0
300	32.915	19.781	0.104
310	334.415	40.641	1.089
320	844.495	61.501	2.703
330	1563.155	82.361	4.917
340	2490.395	103.321	7.675
350	3626.315	124.081	10.964
360	4970.615	144.941	14.755
370	8457.171	114.338	25.786
380	9590.719	112.978	28.817
390	10710.596	111.618	31.735
400	11816.792	110.258	34.546
410	12909.308	108.898	37.251
420	13988.143	107.538	39.862
430	15053.297	106.178	42.377
440	16104.771	104.818	44.802
450	17142.564	103.458	47.143
460	18166.677	102.098	49.404
470	19177.109	100.738	51.568

$$\{S^\circ(T) - S^\circ(298.15\text{ K})\} = 2831.526 - 1395.662 \log (T/K) + 2.086 (T/K) \text{ cal} \cdot \text{mole}^{-1} \cdot \text{K}^{-1} \quad (35)$$

Liquid state: 363.75 – 469.15 K

$$\{H^\circ(T) - H^\circ(298.15\text{ K})\} = -43101.928 + 164.658 (T/K) - 68.403 \cdot 10^{-3} (T/K)^2 \text{ cal} \cdot \text{mole}^{-1} \quad (36)$$

Standard deviation = ± 158.623 cal · mole^{-1}, that is ± 0.99 per cent.

$$C_p^\circ = .164.658 - 0.136 (T/K) \text{ cal} \cdot \text{mole}^{-1} \cdot \text{K}^{-1} \quad (37)$$

$$\{S^\circ(T) - S^\circ(298.15\text{ K})\} = -897.773 + 379.207 \log (T/K) - 0.136 (T/K) \text{ cal} \cdot \text{mole}^{-1} \cdot \text{K}^{-1} \quad (38)$$

The processing of information supplied by the discontinuity in the relative enthalpy temperature variation (due to melting of the substance) yielded the following results:

T_M = 363.65 – 363.75 K

H_M graphical = 2180.970 cal · mole^{-1}
calculated = 2228.459 cal · mole^{-1}
average = 2204.714 cal.mole^{-1}

Equations (33 – 38) were employed in tabulation (Table 8) of the main thermodynamic functions; plots were drawn of the temperature variation of the experimental relative enthalpy in comparison with the calculated curve (Fig. 7).

Bis(4-maleic acidimide, phenyl)methane

Solid state: 298.15 – 429.65 K

$$\{H^\circ(T) - H^\circ(298.15\text{ K})\} = 11513.390 - 105.667 (T/K) + 224.541 \cdot 10^{-3} (T/K^2) \text{ cal} \cdot \text{mole}^{-1} \quad (39)$$

Standard deviation = ± 31.864 cal · mole^{-1}, that is ± 2.078 per cent.

$$C_p^\circ = 0.449 (T/K) - 105.667 \text{ cal} \cdot \text{mole}^{-1} \cdot \text{K}^{-1} \quad (40)$$

$$\{S^\circ(T) - S^\circ(298.15\text{ K})\} = 468.262 + 0.449 (T/K) - 243.351 \log (T/K) \text{ cal} \cdot \text{mole}^{-1} \cdot \text{K}^{-1} \quad (41)$$

Liquid state: 432.05 – 571.15 K

$$H^\circ(T) - H^\circ(298.15\text{ K}) = 510.750 + 31.524 (T/K) - 11.463 \cdot 10^{-3} (T/K)^2 \text{ cal} \cdot \text{mole}^{-1} \quad (42)$$

Standard deviation = ± 45.730 cal · mole^{-1}, that is ± 0.31 per cent.

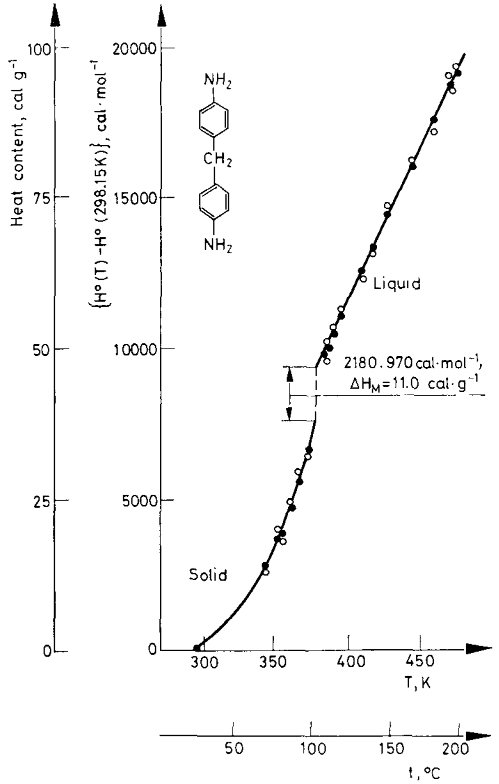


Fig. 7. Experimental and calculated relative enthalpies of bis-(4-aminophenyl)-methane *vs.* temperature

$$C_p^\circ = 31.524 - 22.926 \cdot 10^{-3}\,(T/K)\,\text{cal} \cdot \text{mole}^{-1} \cdot \text{K}^{-1} \tag{43}$$

$$\{S^\circ(T) - S^\circ(298.15\ \text{K})\} = -172.807 - 22.926 \cdot 10^{-3}\ (T/K) + 72.600 \log\ (T/K)\,\text{cal} \cdot \text{mole}^{-1} \cdot \text{K}^{-1} \tag{44}$$

The discontinuity in the relative enthalpy temperature variation (due to the solid–liquid transition) was employed in evaluation of the parameters of melting. The graphical method, as well as Eqs (39) and (42), yields:

T_M = 429.65 – 432.05 K

H_M: graphical = 4336.4 cal · mole^{-1}
calculated = 4375.342 cal · mole^{-1}
average = 4355.871 cal · mole^{-1}

As in the previous cases, the values of the thermodynamic functions are tabulated (Table 9) and the temperature variation of the relative enthalpy (both experimental and calculated) is plotted (Fig. 8).

Table 9

Values of calculated thermodynamic functions for bis-(4-maleic acidimide-phenyl)-methane

T	$\{H°(T)-H°(298.15\ K)\}$	C_p°	$\{S°(T)-S°(298.15\ K)\}$
K	cal. mole^{-1}	cal. mole^{-1}. K^{-1}	
298.15	0.0	28.227	0.0
300	21.980	29.057	0.176
310	335.010	33.548	1.202
320	692.948	38.039	2.337
330	1095.795	42.530	3.577
340	1543.549	47.020	4.911
350	2036.212	51.511	6.339
360	2573.783	56.002	7.853
370	3156.263	60.493	9.448
380	3783.650	64.984	11.121
390	4455.946	69.475	12.867
400	5173.150	73.965	14.681
410	5935.262	78.456	16.563
420	6742.282	82.547	18.506
430	11946.561	21.665	8.524
440	12162.073	21.436	9.020
450	12375.292	21.207	9.499
460	12586.219	20.978	9.963
470	12794.853	20.748	10.412
480	13001.195	20.519	10.846
490	13205.244	20.290	11.268
500	13407.000	20.061	11.675
510	13606.464	19.831	12.070
520	13805.635	19.602	12.453
530	13998.513	19.373	12.825
540	14191.099	19.144	13.184
550	14381.392	18.915	13.534
560	14569.393	18.685	13.873
570	14755.101	18.456	14.201

Conclusions

The data obtained for the studied compounds allowed calculation of thermodynamic functions which characterize the individual substance; likewise, calculations could be made of the thermal effects of some reactions whose reactants are the substances studied in this work.

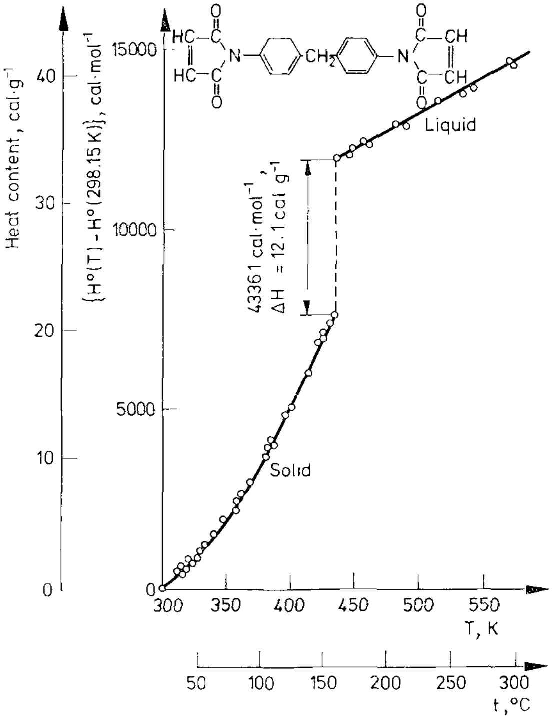


Fig. 8. Experimental and calculated relative enthalpies of bis-(4-maleic acidimide-phenyl)-methane *vs.* temperature

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RÉSUMÉ — On donne les valeurs des fonctions thermodynamiques des 8 composés organiques suivants, en conditions non réactionnelles, dans l'intervalle de températures 298.15—550 K: diméthylformamide $CHO \cdot N(CH_3)_2$, *p*-nitrochlorobenzène $Cl \cdot C_6H_4 \cdot NO_2$, *p*-nitrophénoxysodium $NO_2 \cdot C_6H_4 \cdot ONa$, N-méthylpyrrolidone $CH_3 \cdot N \cdot CO \cdot CH_2 \cdot CH_2$, CH_2 dinitrodiphényl-4,4' éther $(NO_2 \cdot C_6H_4)_2O$, diaminodiphényl-4,4' méthane $(NH_2 \cdot C_6H_4)_2CH_2$, 4-4' bis maléinimide diphénylméthane $(C_6H_4 \cdot N \cdot CO \cdot CH : CH \cdot CO)_2CH_2$.

L'enthalpie relative a été obtenue à partir de données calorimétriques fournies par un calorimètre à chute. La chaleur spécifique et l'entropie relative sont des fonction dérivées de la précédente. Les équations donnant la variation de l'enthalpie relative en fonction de la température sont obtenues par traitement des données calorimétriques sur ordinateur par la méthode des moindres carrés. Les paramètres des transitions solide-liquide ont été déterminés à partir de la discontinuité de la variation de l'enthalpie relative avec la température.

ZUSAMENFASSUNG — Die Werte der thermodynamischen Funktionen folgender 8 organischer Verbindungen werden unter nicht-reagierenden Bedingungen im Temperaturbereich von 298.15 bis 550 K angegeben: Dimethylformamid, $CHO \cdot N(CH_3)_2$; *p*-Nitrochlorbenzol, $Cl \cdot C_6H_4NO_2$; Natrium-*p*-Nitrophenoxid, $NO_2 \cdot C_6H_4ONa$; N-Methylpyrrolidon, $CH_3 \cdot N \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH_2$; 4-4'-Dinitrodiphenyläther, $(NO_2 \cdot C_6H_4)_2O$; 4-4'-Diaminodiphenyläther, $(NH_2C_6H_4)_2O$; 4—4'-Diaminodiphenylmethan, $(NH_2 \cdot C_6H_4)_2CH_2$; 4-4'-bis-Maleinimid-Diphenylmethan, $(C_6H_4 \cdot N \cdot CO \cdot CH : CH \cdot CO)_2CH_2$.

Die relative Enthalpie wird aus kalorimetrischen Daten der Temperaturgefällekalorimetrie erhalten. Die Wärmekapazität und die relative Entropie sind Funktionen der erwähnten Werte. Die Gleichungen der Temperaturänderung der relativen Enthalpie wurden mittels Computerverarbeitung der kalorimetrischen Daten, mit der Methode der kleinsten Quadrate erhalten. Die Parameter der fest-flüssig Übergänge wurden an Hand der Diskontinuität der Temperaturänderung der relativen Enthalpie bestimmt.

Резюме — Приведены значения термодинамических функций, определенных в области температур 298,15—550 К и в нереакционных условиях, для следующих органических соединений: диметилформамид — $CHO \cdot N(CH_3)_2$; п-нитрохлорбензол — $Cl \cdot C_6H_4 \cdot NO_2$. п-нитрофенолят натрия—$NO_2 \cdot C_6H_4 \cdot ONa$; N-метилпирролидон—$CH_3 \cdot N \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH_2$; 4,4'-динитродифенилэфир — $(NO_2 . C_6H_4)_2O$; 4,4'-диаминодифенилэфир — $(NH_2 . C_6H_4)_2O$; 4,4'-диаминодифенилметан — $(NH_2 . C_6H_4)_2CH_2$; 4,4'-бис-малеинимиддифенилметан — $(C_6H_4 . N . CO . CH{:}CH . CO)_2CH_2$. Относительная энтальпия получена из калориметрических данных с помощью капельного калориметра. Теплоемкость и относительная энтропия являются функциями, выведенными из предыдущего. Уравнения температурного изменения относительной энтальпии были получены обработкой калориметрических данных на компьютере по методу наименьших квадратов. Параметры переходов типа твердое тело-жидкость были определены посредством разрыва температурного изменения относительной энтальпии.