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# THE CARVOXIME SYSTEM.

## IV. HEAT CAPACITIES AND ENTHALPIES OF MELTING OF *dl*-CARVOXIME, *l*-CARVOXIME AND STANDARD n-HEPTANE

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### ABSTRACT

Heat capacities between 160 and 385 K and enthalpies of melting of *dl*-carvoxime and *l*-carvoxime were determined by adiabatic calorimetry. The performance of the apparatus was checked on standard n-heptane. The enthalpy of melting values are *dl*-carvoxime, 22.70 ± 0.06; *l*-carvoxime, 17.02 ± 0.02; n-heptane, 14.059 ± 0.010 kJ mol$^{-1}$.

### INTRODUCTION

The present paper reports on the results of measurement by adiabatic calorimetry of the heat capacities and the enthalpies of melting of *dl*-carvoxime, *l*-carvoxime and standard n-heptane. It is the fourth account of our investigation which aims at a better understanding of the relations between structure and thermodynamic properties of the solid solutions formed by *laevo*-rotatory and *dextro*-rotatory carvoxime ($C_{10}H_{15}NO$).

The results of the crystal structure determinations of *dl*- and *l*-carvoxime, which have been reported in Part I[1] and Part II[2], respectively, give rise to a model in which the two types of lattice sites named D and L are occupied in the following manner:

in *l*-carvoxime both D- and L-sites are occupied by *l*-molecules;

in *dl*-carvoxime the D-sites are occupied by *d*-molecules and the L-sites by *l*-molecules;

for compositions between *l* and *dl* all L-sites are occupied by *l*-molecules, the remaining *l*-molecules and the *d*-molecules being distributed over the D-sites; etc.

Enthalpies of melting of lower accuracy have also been reported in Part III[3], in which an account is given of DSC experiments and of phase diagram calculations.

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The DSC experiments also revealed the presence of another, *metastable*, series of solid solutions, and showed for *dl*-carvoxime the ability to assume several solid forms.

## EXPERIMENTAL

### *Materials*

As starting materials we used commercial, technically pure, samples of *d*-carvone and *l*-carvone. These substances are present in naturally occurring essential oils; e.g., *d*-carvone in caraway oil and *l*-carvone in oil of spearmint. *l*-Carvoxime was prepared from *l*-carvone and *dl*-carvoxime from a 1 : 1 mixture of *d*- and *l*-carvone.

Solutions of carvone and hydroxylamine hydrochloride in methanol were joined and left at room temperature. After three days the reaction mixture was poured into four times its volume of water upon which carvoxime separated. The crude material was recrystallized from methanol. Final purification took place by the rapid zone refining technique described by Bollen et al.[4]; loads of 4 $cm^3$ having a speed of 6 cm $h^{-1}$ passed through 20 zones.

### *Apparatus*

The adiabatic calorimeter we used (indication number II) has been described previously[5]. It consists of a 9 $cm^3$ sample container surrounded in vacuo by two temperature–controlled shields. For experiments in the lower temperature range the vacuum can is immersed in liquid nitrogen: for experiments above room temperature the can is immersed in granular ice. A new three-lead 100 $\Omega$ platinum resistance thermometer (indication number 5) with improved calibration has been applied because of breakage of the previous one. This thermometer was calibrated *in situ* against our laboratory standard, a four-lead 25 $\Omega$ platinum resistance thermometer calibrated on IPTS-68 at the Kamerlingh Onnes Laboratory at Leyden. The performance check of the apparatus on n-heptane[5] was repeated on the same standard sample obtained from the National Bureau of Standards at Washington. Calorimetric results for n-heptane, including standard samples, have been surveyed by Stull[6] and Huffman[7]. The sample container was filled in air. Before tightening the screw cap, which presses a closure sheath into the sharp edge of the container aperture, the air was pumped off. In the case of n-heptane a teflon sheath was used. This impeded experiments between 230 and 310 K, since teflon shows an anomalous heat capacity in that region[8]. Therefore, in the experiments on the carvoximes, the teflon sheath was replaced by a golden one. Before the experiments were started, the carvoxime samples were melted, quenched and annealed for some hours at about 5 K below the melting temperature. Annealing was also done before each new series of runs.

## METHOD

The raw calorimetric data are corrected for constant energy-leak, for short time energy-leak due to momentary deviations of shield control and for differing contributions of teflon and golden closure sheaths using published data[8, 9]. Molar heat capacities at saturation pressure $C_{sat}$ are found by

$$C_{sat} = \frac{(\Delta E)_{corr} - \int_{T_1}^{T_2} C_{cont}(T)\,\mathrm{d}T}{(T_2 - T_1)\,m} \qquad (1)$$

where $(\Delta E)_{corr}$ is the corrected energy input, $C_{cont}(T)$ is the fitted heat capacity polynomial function of the empty sample container, $T_1$ and $T_2$ are the equilibrium temperatures at begin and end of the input, $m$ is the number of moles. Neglecting corrections for saturation pressure and vapour volume[10], the numerator of (1) divided by $m$ can be approximated by the molar enthalpy increment $\Delta H$. Furthermore, curvature corrections[11] are negligible outside the melting range, so eqn (1) gives $C_{sat}(T_m)$ with $T_m = (T_1 + T_2)/2$. These values are tabulated, while for the melting ranges enthalpy increments are listed.

The enthalpy of melting is calculated as the total excess enthalpy increment over the entire temperature interval where melting takes place. The initial temperature $T^{start}_{melting}$ of the premelting (the onset of melting effects which increase the heat capacity of the solid phase) is taken as the temperature from which the experimental heat capacities start to deviate more than two times their standard deviation from the fitted heat capacity function. This function is found by an iterative procedure of least-squares fitting the experimental points to the polynome $C_{fit} = \sum_{i=0}^{n} c_i T^i$ where $n$ stands for the number of significant parameters. In each step experimental points that deviate more than two times their standard deviation from the fit are rejected. It is clear but acceptable that $T^{start}_{melting}$ still depends on the experimental precision. The

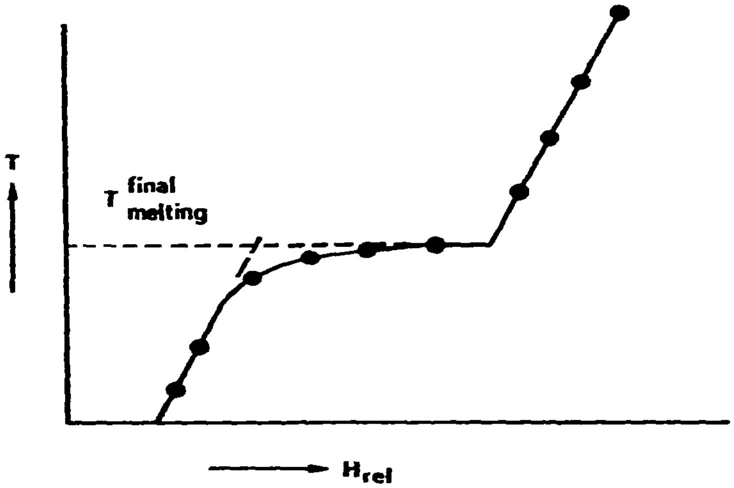

Fig. 1. Melting curve.

resulting function is called the normal heat capacity of the solid. The end of the melting range $T^{\text{final}}_{\text{melting}}$ is read from a plot of measured equilibrium temperatures against relative molar enthalpy (see Fig. 1). The enthalpy of melting at the final melting temperature is then calculated from a series of inputs between $T_1'$ and $T_2'$ that spans the entire melting range, as follows

$$\Delta H_{\text{melting}} = [(H_{\text{rel}})_{T_2'} - (H_{\text{rel}})_{T_1'}] - \left[\int_{T_1'}^{T^{\text{final}}_{\text{melting}}} C_{\text{fit}}(\text{solid})\mathrm{d}T + \int_{T^{\text{final}}_{\text{melting}}}^{T_2'} C_{\text{fit}}(\text{liquid})\mathrm{d}T\right] \quad (2)$$

## RESULTS

TABLE I

EXPERIMENTAL HEAT CAPACITIES OF n-HEPTANE AT SATURATION PRESSURE

Sample mass, 3.6182 g; molecular weight, 100.21; $T_m$ is the mean temperature of the interval $\Delta T$.

| $T_m(K)$[a] | $\Delta T(K)$ | $C_{\text{sat}}$ $(J\ mol^{-1}K^{-1})$ | $T_m(K)$[a] | $\Delta T(K)$ | $C_{\text{sat}}$ $(J\ mol^{-1}K^{-1})$ |
|---|---|---|---|---|---|
| *Run 1* | | | 190.9183 | 14.7180 | 201.65 |
| 160.7166 | 5.1168 | 128.85 | 204.5388 | 12.4780 | 201.08 |
| 166.7247 | 6.8841 | 133.34 | 216.2056 | 10.8191 | 202.09 |
| 172.7270 | 5.0247 | 137.85 | 226.4117 | 9.5618 | 203.64 |
| 178.0741 | 5.6630 | 145.20[b] | 236.2793 | 10.1523 | 206.05 |
| | | | 247.3031 | 11.8729 | 208.18 |
| | melting | | 257.3594 | 8.2137 | 211.15 |
| 187.0123 | 6.2630 | 202.37 | | | |
| 197.6049 | 12.1899 | 201.26 | *Run 4* | | |
| 209.9769 | 12.5496 | 201.55 | 242.2811 | 12.7824 | 207.09 |
| 222.5223 | 12.5204 | 203.28 | 254.8504 | 12.2891 | 210.22 |
| 234.9884 | 12.3635 | 205.90 | 267.2742 | 12.5213 | 214.29 |
| 247.2198 | 12.0674 | 208.67 | 324.2534 | 12.9126 | 235.04 |
| 259.6621 | 12.7622 | 212.15 | 341.9995 | 22.5360 | 241.87 |
| 327.2243 | 13.1064 | 236.05 | 354.6370 | 2.6622 | 247.08 |
| 340.3171 | 13.0284 | 241.09 | | | |
| 350.7446 | 7.7907 | 245.57 | *Run 5* | | |
| | | | 182.0947 | 6.1491 | 203.41[c] |
| *Run 2* | | | 201.4470 | 14.3243 | 201.10 |
| 313.1541 | 5.1130 | 229.91 | 214.8482 | 12.4442 | 201.66 |
| 317.7409 | 4.0038 | 232.89 | 226.4345 | 10.7022 | 203.43 |
| | | | 238.0541 | 12.4830 | 206.07 |
| *Run 3* | | | 250.6654 | 12.6994 | 208.86 |
| 157.3697 | 11.0991 | 125.94 | 263.4733 | 12.8726 | 212.68 |
| 167.1499 | 8.4372 | 133.41 | 316.8711 | 12.9550 | 232.22 |
| 173.4941 | 4.2290 | 138.49 | 330.0261 | 13.2328 | 236.67 |
| | | | 341.8836 | 10.4065 | 241.18 |
| | melting | | 352.0516 | 9.8651 | 245.75 |

[a] The number of digits of the temperature only has significance on a relative scale.

[b] This value falls in the premelting region.

[c] Supercooled liquid.

TABLE 2

FITTED HEAT CAPACITIES AND THEIR STANDARD DEVIATIONS OF n-HEPTANE AT SATURATION PRESSURE

| *T(K)* | $C_{\rm fit}$ *(J mol$^{-1}$K$^{-1}$)* | | $C_{\rm S.B.S.}$[a] *(J mol$^{-1}$K$^{-1}$)* |
|---|---|---|---|
| | solid | | |
| 160 | 128.09 | ± 0.10 | 129.03 |
| 165 | 131.93 | 0.07 | 132.46 |
| 170 | 135.77 | 0.08 | 136.03 |
| 175 | 139.62 | 0.12 | 139.82 |
| 180 | 143.46[b] | 0.16 | 145.13 |
| 182.7 | 145.53[b] | 0.19 | (148.58 at 182.56 K) |
| | liquid | | |
| 182.7 | 203.06[b] | 0.21 | (203.15 at 182.56 K) |
| 190 | 201.91 | 0.13 | 201.86 |
| 200 | 201.27 | 0.11 | 201.31 |
| 210 | 201.54 | 0.11 | 201.68 |
| 220 | 202.59 | 0.10 | 202.74 |
| 230 | 204.27 | 0.08 | 204.36 |
| 240 | 206.48 | 0.08 | 206.47 |
| 250 | 209.09 | 0.09 | 208.93 |
| 260 | 212.03 | 0.11 | 211.73 |
| 270 | 215.22 | 0.12 | 214.81 |
| 280 | 218.58 | 0.13 | 218.23 |
| 290 | 222.09 | 0.13 | 221.75 |
| 300 | 225.69 | 0.12 | 225.44 |
| 310 | 229.37 | 0.12 | 229.27 |
| 320 | 233.13 | 0.12 | 233.25 |
| 330 | 236.98 | 0.11 | 237.38 |
| 340 | 240.93 | 0.10 | 241.67 |
| 350 | 245.04 | 0.14 | 246.09 |

[a] Douglas et al.[12]. [b] Extrapolated.

TABLE 3

ENTHALPY CHANGES IN THE MELTING RANGE OF n-HEPTANE

Sample mass, 3.6182 g; molecular weight, 100.21; $\Delta H_{\rm excess}$ is the experimental enthalpy increment $\Delta H$ minus $\Delta H_{\rm norm}$, the integrated normal heat capacity.

| *Temp. interval*[a] | $\Delta H$ *(J mol$^{-1}$)* | $\Delta H_{\rm norm}$ *(J mol$^{-1}$)* | $\Delta H_{\rm excess}$ *(J mol$^{-1}$)* |
|---|---|---|---|
| *Run 1*[b] | | | |
| 175.2426–180.9056 K | 822 | 804 | 18 |
| 180.9108–182.7148 K | 12010 | 261 | 11749 |
| 182.7148–183.8731 K | 2531 | 234 | 2297 |
| | | | + 14064 |
| *Run 3* | | | |
| 175.6215–182.6853 K | 4781 | 1009 | 3772 |
| 182.6853–182.6938 K | 7997 | 1 | 7996 |
| 182.6938–182.6925 K | 1408 | 0 | 1408 |
| 182.6925–182.6955 K | 717 | 0 | 717 |
| 182.6955–183.8738 K | 398 | 237 | 161 |
| | | | + 14054 |

[a] The number of digits of the temperatures only has significance on a relative scale. Equilibrium temperatures in the melting range may be determined within 0.01 K.

[b] Run numbers correspond to those of Table 1.

### *Standard n-heptane*

The experimental heat capacities are listed in Table 1. The melting range covered 176 to 182.7 K. The fitted heat capacity functions, summarized in Table 2, have two and five significant parameters, respectively (see Table 6). The third column of Table 2 contains smoothed values of the N.B.S.[12]. Agreement exists within 0.7% for the solid and 0.2% for the liquid phase below 340 K. The fitted functions have been extrapolated to calculate excess enthalpies for inputs in the melting range (see Table 3). The temperatures in the last section of the melting curve scattered between 182.69 and 182.72 K: the N.B.S. value[12] for the triple point of the pure substance is 182.56 K.

TABLE 4

EXPERIMENTAL HEAT CAPACITIES OF *dl*- AND *l*-CARVOXIME AT SATURATION PRESSURE

Molecular weight: 165.23. $T_m$ is the mean temperature of the interval $\Delta T$.

| $T_m(K)^a$ | $\Delta T(K)$ | $C_{sat}$ $(J\ mol^{-1}K^{-1})$ | $T_m(K)^a$ | $\Delta T(K)$ | $C_{sat}$ $(J\ mol^{-1}K^{-1})$ |
|---|---|---|---|---|---|
| *dl*-carvoxime, sample mass 3.1532 g | | | | | |
| *Run 1* | | | | | |
| 369.1931 | 5.9186 | 420.00$^b$ | 266.6264 | 13.1651 | 228.72 |
| 374.6949 | 4.8663 | 374.58 | 279.9342 | 13.3890 | 239.41 |
| | | | 294.9880 | 16.5600 | 253.71 |
| *Run 2* | | | 310.0171 | 13.3977 | 263.86 |
| 211.2776 | 12.6684 | 183.11 | 308.3455 | 13.2987 | 262.79 |
| 221.6465 | 8.0159 | 192.00 | melting, including exothermic effect | | |
| 234.5003 | 12.8384 | 203.01 | | | |
| 247.3799 | 12.8747 | 213.48 | 371.3731 | 7.7562 | 372.78 |
| 260.0906 | 12.5008 | 223.72 | 380.0227 | 9.4822 | 378.27 |
| 277.4011 | 22.0634 | 238.06 | | | |
| 294.8522 | 12.6390 | 253.95 | *Run 4* | | |
| 318.3768 | 26.5937 | 271.13 | 184.5099 | 13.3482 | 162.10 |
| 334.8480 | 6.2649 | 283.76 | 197.5563 | 12.7146 | 172.42 |
| 341.3309 | 6.6494 | 290.92 | 210.0922 | 12.3201 | 182.57 |
| 348.0058 | 6.6048 | 300.86$^c$ | 222.7306 | 12.8954 | 192.96 |
| | | | 235.5752 | 12.7464 | 204.05 |
| | melting | | 249.2342 | 14.5156 | 215.28 |
| 370.6550 | 7.6371 | 372.66 | 262.8526 | 12.6708 | 226.23 |
| 378.3387 | 7.6986 | 378.04 | 277.4031 | 13.0876 | 240.94$^b$ |
| 386.1979 | 7.9777 | 382.29 | 290.5966 | 13.2228 | 250.54 |
| | | | 305.9681 | 17.4339 | 263.00 |
| *Run 3* | | | 320.8007 | 11.9662 | 274.26 |
| 158.8483 | 13.1012 | 142.49 | 333.5860 | 13.4888 | 285.45 |
| 179.5954 | 12.2323 | 158.89 | | | |
| 190.9574 | 10.4644 | 167.87 | | melting | |
| 202.2368 | 12.0755 | 177.04 | 366.3762 | 2.3201 | 370.30 |
| 214.5116 | 12.4457 | 186.64 | 371.3161 | 7.5180 | 373.64 |
| 229.4003 | 17.2782 | 199.31 | 379.0788 | 7.9622 | 378.05 |
| 241.6054 | 13.0406 | 209.35 | 386.7848 | 7.4024 | 382.52 |
| 254.0835 | 11.8718 | 218.47 | | | |

(Continued on p. 331)

TABLE 4 *(continued)*

| $T_m(K)^a$ | $\Delta T(K)$ | $C_{sat}$ ($J\ mol^{-1}K^{-1}$) | $T_m(K)^a$ | $\Delta T(K)$ | $C_{sat}$ ($J\ mol^{-1}K^{-1}$) |
|---|---|---|---|---|---|
| *l*-carvoxime, sample mass 3.4646 g | | | | | |
| | | | *Run 3* | | |
| *Run 1* | | | 304.2788 | 14.0066 | 261.05 |
| 197.2622 | 13.1482 | 175.92 | 315.2535 | 7.8862 | 270.05 |
| 210.1182 | 12.5339 | 185.52 | | melting | |
| 222.6727 | 12.5347 | 195.40 | | | |
| 235.2204 | 12.5048 | 205.85 | 348.5756 | 2.4177 | 360.86 |
| 247.6974 | 12.3838 | 215.01 | | | |
| 258.4973 | 12.6958 | 222.88 | *Run 4* | | |
| 271.2432 | 12.6974 | 232.57$^{b}$ | 312.2651 | 14.1952 | 267.90 |
| 284.0582 | 12.8622 | 243.65 | 311.1445 | 14.8901 | 267.42 |
| 295.4083 | 9.7651 | 253.72 | | melting | |
| *Run 2* | | | 345.3001 | 5.1816 | 357.33$^{d}$ |
| 195.1130 | 13.0778 | 174.76 | 353.1888 | 10.5631 | 363.97 |
| 208.5371 | 13.7475 | 185.27 | 364.4236 | 11.8417 | 371.90 |
| 221.8947 | 12.9239 | 195.96 | 375.1543 | 9.5427 | 379.45 |
| 234.8605 | 12.9621 | 206.24$^{b}$ | | | |
| 247.8557 | 12.9802 | 215.80 | *Run 5* | | |
| 260.9240 | 13.0988 | 225.51 | | melting | |
| 271.5383 | 14.7279 | 234.16 | | | |
| 287.3200 | 16.7651 | 246.66 | 351.6249 | 7.8735 | 362.73 |
| 302.3300 | 13.1510 | 258.33 | 359.5307 | 7.8876 | 368.81 |
| 314.3231 | 10.6944 | 268.46 | 367.4510 | 7.9051 | 373.43 |
| 322.5845 | 5.7690 | 276.62$^{c}$ | 374.0755 | 5.3085 | 378.18 |
| 328.2360 | 5.4760 | 286.99$^{c}$ | 379.4157 | 5.3278 | 381.20 |
| 333.6869 | 5.3718 | 301.19$^{c}$ | 384.7778 | 5.3441 | 385.48 |

[a] The number of digits only has significance on a relative scale.

[b] Rejected because this value deviates more than two times the standard deviation from the fit.

[c] This value falls in the premelting region.

[d] Supercooled liquid after heat loss overnight.

Therefore, absolute temperatures are estimated to have a maximal systematic error of +0.2 K. The enthalpy of quasi-isothermal melting at 182.7 K was found as 14059 ± 10 J mol$^{-1}$ from two runs, which corresponds to the literature within 0.3% or better:

| | | |
|---|---|---|
| $\Delta H_{melting}$ (J mol$^{-1}$) | 14059 ± 10 | this work |
| | 14023 ± 14 | N.B.S.[12] |
| | 14047 ± 17 | Stull[6] |
| | 14037 ± 8 | Huffman et al.[7]. |

### *dl- and l-carvoxime*

Experimental heat capacities and fitted results are given in Tables 4 and 5 for both *dl*- and *l*-carvoxime. The inputs in the melting ranges, defined above, are collected in Table 7. The melting ranges are 345 to 365.1 K for *dl*-carvoxime and 320 to 346.5 K for *l*-carvoxime. $\Delta H_{norm}$ was calculated from the fitted functions of which the parameters are given in Table 6.

TABLE 5

FITTED HEAT CAPACITIES AND THEIR STANDARD DEVIATIONS OF *dl*-CARVOXIME AND *l*-CARVOXIME AT SATURATION PRESSURE

| $T(K)$ | *dl*-carvoxime $C_p$ (J mol$^{-1}$K$^{-1}$) | | *l*-carvoxime $C_p$ (J mol$^{-1}$K$^{-1}$) | | $T(K)$ | *dl*-carvoxime $C_p$ (J mol$^{-1}$K$^{-1}$) | | *l*-carvoxime $C_p$ (J mol$^{-1}$K$^{-1}$) | |
|---|---|---|---|---|---|---|---|---|---|
| | solid | | solid | | | | | | |
| 160 | 142.16 | ± 0.30 | 148.98$^a$ | ± 0.82 | 310 | 264.93 | ± 0.21 | 265.55 | ± 0.21 |
| 170 | 150.34 | 0.28 | 156.23$^a$ | 0.65 | 320 | 273.12 | 0.23 | 273.91 | 0.29 |
| 180 | 158.53 | 0.25 | 163.55$^a$ | 0.50 | 330 | 281.30 | 0.25 | 282.35$^a$ | 0.41 |
| 190 | 166.71 | 0.23 | 170.96 | 0.37 | 340 | 289.49 | 0.27 | 290.86$^a$ | 0.54 |
| 200 | 174.90 | 0.21 | 178.43 | 0.27 | 346.5 | | | 296.44$^a$ | 0.64 |
| 210 | 183.08 | 0.19 | 185.98 | 0.21 | | | | liquid | |
| 220 | 191.27 | 0.17 | 193.60 | 0.18 | 346.5 | | | 359.15 | 0.26 |
| 230 | 199.45 | 0.16 | 201.30 | 0.18 | 350 | 297.67$^a$ | 0.30 | 361.57 | 0.23 |
| 240 | 207.64 | 0.14 | 209.07 | 0.19 | 360 | 305.86$^a$ | 0.32 | 368.48 | 0.17 |
| 250 | 215.82 | 0.14 | 216.92 | 0.20 | 365.1 | 310.03$^a$ | 0.34 | | |
| 260 | 224.01 | 0.14 | 224.84 | 0.20 | | liquid | | | |
| 270 | 232.19 | 0.14 | 232.83 | 0.19 | 365.1 | 369.36$^a$ | 0.26 | | |
| 280 | 240.38 | 0.15 | 240.90 | 0.17 | 370 | 372.35 | 0.18 | 375.39 | 0.17 |
| 290 | 248.56 | 0.17 | 249.04 | 0.16 | 375 | 375.41 | 0.13 | 378.84 | 0.21 |
| 300 | 256.75 | 0.19 | 257.26 | 0.17 | 380 | 378.46 | 0.14 | 382.30 | 0.25 |
| | | | | | 385 | 381.51 | 0.21 | 385.76 | 0.30 |

$^a$ *Extrapolated.*

TABLE 6

PARAMETERS $c_i$ OF THE HEAT CAPACITY FUNCTION $C_{p} = \sum_{i=0}^{n} c_i T^i$ OF n-HEPTANE, *dl*-CARVOXIME AND *l*-CARVOXIME

| | *Solid* | *Liquid* |
|---|---|---|
| n-heptane | $c_0 = 5.152$ J mol$^{-1}$K$^{-1}$ | $c_0 = 6.92261 \cdot 10^2$ J mol$^{-1}$K$^{-1}$ |
| | $c_1 = 7.6836 \cdot 10^{-1}$ J mol$^{-1}$K$^{-2}$ | $c_1 = -6.89116$ J mol$^{-1}$K$^{-2}$ |
| | | $c_2 = 3.456259 \cdot 10^{-2}$ J mol$^{-1}$K$^{-3}$ |
| | | $c_3 = -7.38839 \cdot 10^{-5}$ J mol$^{-1}$K$^{-4}$ |
| | | $c_4 = 5.98774 \cdot 10^{-8}$ J mol$^{-1}$K$^{-5}$ |
| *dl*-carvoxime | $c_0 = 1.1196 \cdot 10$ J mol$^{-1}$K$^{-1}$ | $c_0 = 1.46322 \cdot 10^2$ J mol$^{-1}$K$^{-1}$ |
| | $c_1 = 8.1851 \cdot 10^{-1}$ J mol$^{-1}$K$^{-2}$ | $c_1 = 6.1089 \cdot 10^{-1}$ J mol$^{-1}$K$^{-2}$ |
| *l*-carvoxime | $c_0 = 4.3016 \cdot 10$ J mol$^{-1}$K$^{-1}$ | $c_0 = 1.19653 \cdot 10^2$ J mol$^{-1}$K$^{-1}$ |
| | $c_1 = 6.0294 \cdot 10^{-1}$ J mol$^{-1}$K$^{-2}$ | $c_1 = 6.9118 \cdot 10^{-1}$ J mol$^{-1}$K$^{-2}$ |
| | $c_2 = 3.7068 \cdot 10^{-4}$ J mol$^{-1}$K$^{-3}$ | |

Preliminary experiments showed that melting of the material results in a lowering of the melting temperature in the subsequent run. For both samples the total decrease was about 0.2 K which amounts to a solid insoluble contamination of about 0.4 mol %. The triple point temperatures of pure *dl*- and *l*-carvoxime are therefore reported as 365.1 ± 0.2 K and 346.5 ± 0.2 K, while two complete melting runs for each substance

TABLE 7

ENTHALPY CHANGES IN THE MELTING RANGES OF *dl*- AND *l*-CARVOXIME

Molecular weight: 165.23. $\Delta H_{excess}$ is the experimental enthalpy increment $\Delta H$ minus $\Delta H_{norm}$, the integrated normal heat capacity.

| *Temp. interval*[a] | $\Delta H$ ($J\ mol^{-1}$) | $\Delta H_{norm}$ ($J\ mol^{-1}$) | $\Delta H_{excess}$ ($J\ mol^{-1}$) |
|---|---|---|---|
| *dl*-carvoxime, sample mass 3.1532 g | | | |
| *Run 2*[b] | | | |
| 350.2521–364.7182 K | 11147 | 4395 | 6752 |
| 364.7182–366.8193 K | 16724 | 748 | 15976 |
| | | | ÷ 22728 |
| *Run 3* | | | |
| 315.0196–328.8200 K | 3760 | 3791 | − 31 |
| 328.8200–342.2037 K | 3588 | 3826 | −238 |
| 342.2037–367.4651 K | 29476 | 7754 | 21722 |
| | | | ÷ 21453[c] |
| *Run 4* | | | |
| 337.5607–364.8812 K | 24685 | 8160 | 16525 |
| 264.8812–365.2161 K | 6253 | 105 | 6148 |
| | | | ÷ 22673 |
| *l*-carvoxime, sample mass 3.4646 g | | | |
| *Run 2*[b] | | | |
| 319.7000–325.4690 K | 1596 | 1593 | 3 |
| 325.4980–330.9740 K | 1572 | 1538 | 34 |
| 331.0010–336.3728 K | 1618 | 1534 | 84 |
| *Run 3* | | | |
| 319.2125–347.3435 K | 25083 | 8074 | 17009 |
| *Run 4* | | | |
| 318.6164–346.0185 K | 17410 | 7791 | 9619 |
| 346.0185–346.2633 K | 5384 | 73 | 5311 |
| 346.2633–347.3234 K | 2462 | 366 | 2096 |
| | | | ÷ 17026 |
| *Run 5* | | | |
| 339.3538–347.6699 K | 18677 | 2517 | 16160 |

[a] The number of digits of the temperatures only has significance on a relative scale. Equilibrium temperatures in the melting range may be determined within 0.01 K.

[b] Run numbers correspond to those of Table 4.

[c] During this run an exothermic effect was observed.

lead to enthalpy of melting values of 22701 ± 60 and 17018 ± 20 J mol$^{-1}$, respectively (see Table 7). In run 3 on *dl*-carvoxime a gradual exothermic effect occurred in the melting range. The heat capacity of the solid measured in that run did not deviate. Exothermic effects were also observed in DSC experiments[3] along with the occurrence of several solid forms. The results by adiabatic calorimetry and those by DSC[3] agree within experimental uncertainties.

| | $T(K)$ | $\Delta H(kJ\,mol^{-1})$ | |
|---|---|---|---|
| *dl*-carvoxime | 365.1 ± 0.2 | 22.70 ± 0.06 | adiab. cal. |
| | 364.9 ± 0.1 | 22.2 ± 0.4 | DSC |
| *l*-carvoxime | 346.5 ± 0.2 | 17.02 ± 0.02 | adiab. cal. |
| | 346.1 ± 0.2 | 17.2 ± 0.4 | DSC |

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