THERMODYNAMIC STUDIES OF 1,1-DICYCLOHEXYLDODECANE, 1,1-DIPHENYLDODECANE, AND 1-PHENYL-1-CYCLOHEXYLDODECANE AT LOW TEMPERATURES

1960

SovietRxiv

Abstract

Full Text

CHEMISTRY

K. A. KARASHARLI and P. G. STRELKOV

THERMODYNAMIC STUDIES OF 1,1-DICYCLOHEXYLDODEC 1,1-DIPHENYLDODECANE, AND 1-PHENYL-1-CYCLOHEXYLDODECANE AT LOW TEMPERATURES

(Presented by Academician V. A. Kargin, December 10, 1959)

The aim of the present investigation was to determine the thermodynamic quantities under standard conditions for dicyclohexyldodecane, diphenyldodecane, and 1-phenyl-1-cyclohexyldodecane. All three substances had first been purified by a chromatographic method*. Dicyclohexyldodecane and diphenyldodecane were further purified by the zone-melting method ([1]). The purity was assessed in the calorimeter from the depression of the melting point, analogously to ([2]). The apparatus, procedure, and order of measuring c_p have been described earlier ([3]).

The heat capacity of the empty calorimeter in the range from 12 to 320°K was measured at 47 points; that of dicyclohexyldodecane at 69, diphenyldodecane at 90, and 1-phenyl-1-cyclohexyldodecane at 67 points.

The experimental values of the heat capacities were graphically smoothed and tabulated at equal temperature intervals (Table 1). The deviation of the experimental heat-capacity values from the smoothed curve does not exceed 0.15%. Over the entire range of measurements no deterioration of heat exchange was observed that would indicate sorption by the substance of the helium present in the calorimeter as the heat-exchange gas.

Table 1

Smoothed values of the heat capacities $c_p \left(\frac{\text{cal}}{\text{deg} \cdot \text{mole}}\right)$

Temp., °K	$C_{24}H_{34}$	$C_{24}H_{40}$	$C_{24}H_{46}$	Temp., °K	$C_{24}H_{34}$	$C_{24}H_{40}$	$C_{24}H_{46}$
10	1.561	1.490	1.38	191* solid 2	76.51	–	–
20	8.606	7.460	6.12	200	80.011	83.92	84.90
30	15.244	14.24	13.8	225	89.69	93.89	93.7
40	21.079	20.71	20.3	250	98.318	104.54	103.13

Temp., °K	$C_{24}H_{34}$	$C_{24}H_{40}$	$C_{24}H_{46}$	Temp., °K	$C_{24}H_{34}$	$C_{24}H_{40}$	$C_{24}H_{46}$
50	26.549	26.70	25.95	275	107.537	122.67	116.98
75	38.510	39.56	39.27	275.84* solid	–	123.00	–
100	49.086	49.05	49.95	275.84* liquid	–	143.00	–
125	56.526	57.23	58.5	281.4* solid	109.842	–	–
150	65.015	65.45	67.00	281.4* liquid	139.308	–	–
175	75.854	74.25	75.85	300	142.153	146.40	136.20
191* solid 1	82.71	–	–				

* Extrapolation.

In view of the presence of impurities in the samples, melting begins at lower temperatures and affects the heat-capacity curves for 20-30° up to the triple point. Therefore, in order to obtain the heat capacity of the solid phase in this region, the additional effective heat capacity, determined by the formula

$$\Delta c_i = H_{\text{melt}} \frac{T^* - T^s}{(T^s - T_i)^2},$$

was subtracted from the smoothed heat-capacity values,

* The substances were synthesized at the Institute of Petrochemical Synthesis, Academy of Sciences of the USSR, by A. A. Petrov and co-workers (^{4}).

where Δc_i is the effective increase in heat capacity caused by melting of impurities; T^* is the triple-point temperature; T^s is the melting temperature of the substance; T_i is the temperature at which the additional effective heat capacity is calculated; H_{m} is the heat of fusion.

In view of the fact that the heat capacity of dicyclohexyldodecane and 1-phenyl-1-cyclohexyldodecane in the temperature range from 13° K and above does not obey the limiting Debye law ($c = aT^3$), extrapolation to 0° K was carried out graphically. This is entirely permissible, especially since, according to our estimate, the absolute error in the entropy value, taking into account the insufficient purity of the preparation at 298.16° K (0.3-0.4 entropy units), is greater than the entropy value at 15° K (0.2 entropy units). Apparently, for these substances the limiting law is manifested at lower temperatures.

For diphenyldodecane, in the temperature range from 13 to 16° K the dependence of heat capacity on temperature becomes cubic: $c_p = 1.43 \cdot 10^{-3} T^3$. For this substance, in the temperature range 181-199° K, a peak in the heat-capacity curve was found, probably due to a phase transition associated with a change in the crystal structure (Fig. 1). The integral heat of the phase transition is:

$$H_{\text{trans}} = 460.7 \pm 1\ \frac{\text{cal}}{\text{mol}}.$$

Fig. 1

The standard values of entropy and enthalpy were obtained by numerical integration of the curves $c(T)$ and $\frac{c_p}{T}(T)$. The values of the thermodynamic quantities for all three substances are given in Table 2.

Table 2

Thermodynamic quantities under standard conditions

Name of substance	Formula	$H_{298.16} - H_0$, cal/mol	$S^\circ_{298.16}$, cal/deg·mol	H_m, cal/mol	S_m, cal/deg·mol	T_m, °K	$c^\circ_{p298.16}$, cal/deg·mol	Purity, mol %
Dicyclohexyldodecane (s.)	$C_{24}H_{46}$	19519± 50	130.42± 0.4	1058± 50	35.20± 0.15	300.58± 0.02	134.46	98.2
1-Phenyl-1-cyclohexyldodecane (l.)	$C_{24}H_{40}$	30166± 80	166.33± 0.6	8406± 50	30.51± 0.15	275.84± 0.02	146.06	97.6
Diphenyldodecane (l.)	$C_{24}H_{34}$	28672± 80	163.70± 0.6	9284± 50	33.00± 0.15	281.40± 0.02	141.934	99.01

All-Union Scientific-Research Institute of Physicotechnical and Radiotechnical Measurements

Received
9 XII 1959

CITED LITERATURE

1. F. W. Schwab, E. J. Wichers, J. Res. Nat. Bur. Stand., **32**, 253 (1944).

2. W. J. Taylor, F. D. Rossini, J. Res. Nat. Bur. Stand., **32**, 197 (1944).

3. P. G. Strelkov, E. S. Itskevich et al., ZhFKh, **28**, 459 (1954).

4. O. R. Sergienko, L. N. Kvitkovskii, A. A. Tsedilina, A. A. Petrov, DAN **120**, No. 3, 541 (1958).