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Polymorphism of 2-Methyl-2-chloropropane and 2,2-Dimethylpropane (Neopentane): Thermodynamic Evidence for a High-Pressure Orientationally Disordered Rhombohedral Phase through Topological *p*−*T* Diagrams

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The trimorphism of $(CH_3)_3CCl$, a member of the $(CH_3)_{4-n}CCl_n$ series, is reexamined as a function of the temperature and pressure. Its topological $p-T$ diagram is constructed resorting to the available thermodynamic and crystallographic data for the four observed crystalline solids and the data extrapolated from binary phase diagrams sharing compounds of this series. The p,T coordinates of the five stable triple points are calculated together with the slopes of the two-phase equilibrium curves. Through these results, the uncharacterized phase IV (a high-pressure orientationally disordered stable phase) is shown to coincide with the rhombohedral phase (R) which is the orientationally disordered stable phase for the members with $n = 2$, 3, and 4 at ordinary pressure. In addition, the existence of a isomorphous high-pressure R phase is postulated for the first member [neopentane, $(CH_3)_4C$] of the series.

1. Introduction

The molecules in the series of methylchloromethane derivatives, $(CH_3)_{4-n}CCl_n$ ($0 \leq n \leq 4$), have tetrahedral geometry around the central C-atom and possess globular (or nearly spherical) shapes that can form crystals of rather high symmetry in which molecules are orientationally disordered because of rotational freedom, even if the translational orientation is maintained. Such crystals, called plastic crystals, are often referred to as an orientationally disordered crystalline (ODIC) state.[1]

For the compounds corresponding to $n = 0$ and 1 (2,2-dimethylpropane and 2-methyl-2-chloropropane, respectively), only one face-centered cubic (FCC) ODIC phase is observed.[2−5]

As far as the remaining compounds ($n = 2$, 3, and 4) are concerned, dimorphism occurs in the ODIC state.[2,6−8] They crystallize into a rhombohedral (R) phase, which is the stable crystalline phase, or into a cubic (C) phase [FCC for $n = 3$ and 4, and simple cubic for $n = 2$], which is metastable with respect to the former and behaves monotropically at ordinary pressure. On cooling the liquid, phase C crystallizes first and transforms into phase R on further cooling, whereas melting is observed at a temperature lower than that for phase R upon heating phase C.

Local order in the liquid state of all compounds of this series was recently modeled through molecular dynamic simulation.[9] It was found that scattering functions $S(k)$ calculated from random orientations account better for the experimental $S(k)$ functions of compounds for which $n = 0$ and 1, whereas the experimental $S(k)$ functions for the other compounds ($2 \leq n \leq 4$) were well described using particular orientational configurations. The stable ODIC phase for these compounds ($2 \leq n \leq 4$) is the R phase in which disorder may be related to particular orientations because of a decrease in symmetry with respect to the cubic phase in which disorder results from random orientations.

On the basis of this information, we hypothesized that 2,2-dimethylpropane and 2-methyl-2-chloropropane might also exhibit dimorphism in the ODIC state, i.e., crystallize as the R phase. Although it should be metastable at ordinary pressure, the R phase may become a stable phase either by increasing the pressure or by modifying the molecular neighboring (e.g., through mixing with homologous compounds). In this article, thermodynamic and structural data on unary and binary diagrams are used to draw topological $p-T$ diagrams to check for this hypothesis.

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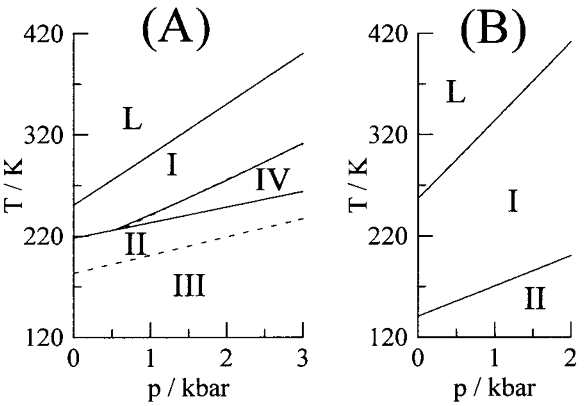

Figure 1. Experimental $p-T$ phase diagrams of (A) $(CH_3)_3CCl$[12] and (B) $(CH_3)_4C$.[17]

2. Data on the Polymorphism of 2-Methyl-2-chloropropane [$(CH_3)_3CCl$] and 2,2-Dimethylpropane [$C(CH_3)_4$]

2.1. Data on $p-T$ Diagrams of Pure Compounds. *2.1.a. 2-Methyl-2-chloropropane.* Three phases of 2-methyl-2-chloropropane have been characterized at ordinary pressure. Phase III, the low-temperature ordered phase (monoclinic, space group $P2_1/m$, $Z = 2$, $V/Z = 141.1$ Å^3 at $T = 132.2$ K) transforms on heating into phase II (tetragonal, $P4/nmm$, $Z = 2$, $V/Z = 152.2$ Å^3 at $T = 213.2$ K), which in turn transforms into phase I, a FCC ODIC phase ($Z = 4$, $V/Z = 161.5$ Å^3 at $T = 223.2$ K) on further heating. Phase I eventually melts at 247.8 K.

An additional intermediate phase (between phase II and phase I) was reported.[10] Nevertheless, the existence of the additional phase was discarded by recent synchrotron radiation experiments having shown that it corresponds to pretransitional effects associated to hindered molecular tumbling.[4]

Phase changes as a function of temperature and pressure were investigated in the 220−320 K and 0.1−300 MPa ranges.[11−13] Besides phases I, II, and III, a fourth phase (phase IV) was disclosed at higher pressures (see Figure 1A). Dielectric studies showed that this fourth phase is orientationally disordered.[13]

The vaporization enthalpy was 27.55 kJ·mol^{-1} at 324 K.[14] Data for the liquid−vapor equilibrium curve ($l-v$) were obtained in the 295−320 K[15] and 254−324 K[16] ranges, and both sets were consistent. They were fitted to equation $p\ (\mathrm{bar}) = 41530.7 \exp(-3443.27/T)$ (square reliability factor $r^2 = 0.9998$), from which $\Delta_l^vH = 28.63$ kJ·mol^{-1} was calculated, in fair agreement with the experimental value.[14]

Available thermodynamic data on phase changes are compiled in Table 1.

2.1.b. 2,2-Dimethylpropane. Two solid phases of 2,2-dimethylpropane have been reported: a low-temperature ordered phase II, whose symmetry, tetragonal ($a = 11.2$ Å, $c = 11.5$ Å at 123.2 K)[3] or hexagonal ($a = 11.30$ Å, $c = 8.81$ Å, $Z = 12$ at 118.2 K)[2], has still to be ascertained, and a high-temperature FCC ODIC phase I ($V/Z = 172$ Å^3 at $T = 233.2$ K)[2].

Table 1. Thermodynamic Parameters of the Phase Transitions for the $(CH_3)_3CCl$ and $(CH_3)_4C$ Compounds

compound	transition	T (K)	ΔH (kJ·mol^{-1})	ΔV (cm^3·mol^{-1})	dP/dT (bar·K^{-1})
$(CH_3)_3CCl$	I−l	248.1[5,19]	1.76[5,19]	4.6[5,21]	17.54[13]
	II−I	219.8[5,19]	5.75[5,19]	4.4[5,21]	58.80[13]
	III−II	183.6[5,19]	2.08[5,19]	1.8[5,21]	55.55[13]
$(CH_3)_4C$	I−l	256.5[2,23]	3.35[2,23]		14.97[17]
	II−I	140.5[2,23]	2.62[2,23]		37.78[17]

The $p-T$ diagram for equilibria involving condensed phases (Figure 1B) was investigated up to 2000 bar in the 130−400 K range.[17]

From vapor pressure data reported,[18] the p(bar) versus T(K) values for the $l-v$ curve were fitted to equation $p(\mathrm{bar}) = 76391.5 \exp(-3170.15/T)$ ($r^2 = 0.9998$), from which $\Delta_l^vH = 26.36$ kJ·mol^{-1} was calculated.

Available thermodynamic data on phase changes are compiled in Table 1.

3. Data Extrapolated from Binary Phase Diagrams at Ordinary Pressure

Solid phases that potentially exist in one-component systems may not be produced experimentally. However, phases that crystallize as binary alloys may be a clue to their ability to form as pure phases. Thus, thermodynamic and structural properties of such elusive one-component phases may be extrapolated from those of binary solid solutions.

3.a. 2-Methyl-2-chloropropane. Two binary diagrams involving 2-methyl-2-chloropropane [$(CH_3)_3CCl$] and either carbon tetrachloride (CCl_4) or 1,1,1-trichloroethane [$(CH_3)CCl_3$] have been investigated as a function of temperature at ordinary pressure in the whole composition range.[19,20] Both diagrams exhibit extended ranges of FCC and R solid solutions (see Figure 2A,B). Thus, both phase diagrams were interpreted as a result of two interfering loops, [FCC + liquid] and [R + liquid], based on the well-known crossed isodimorphism. Extrapolating the [R + liquid] loops to pure $(CH_3)_3CCl$ allowed the melting temperature for its metastable R phase to be determined at 233.5 K in both cases. Similarly, the associated enthalpy of fusion, Δ_R^lH was found to be 2.6 kJ·mol^{-1}. The specific volumes $(V/Z)_R$ for pure $(CH_3)_3CCl$ at 231.2 and 237.2 K (159.5 Å^3 and 159.9 Å^3, respectively) were determined by extrapolating the isothermal V/Z values of the R solid solutions of both diagrams as a function of composition. Assuming a linear relationship between $(V/Z)_R$ and temperature, a value of 159.7 Å^3 was found for pure $(CH_3)_3CCl$ at 233.5 K, i.e., the melting temperature of phase R. Thus, a volume change of 5.64 cm^3·mol^{-1} upon melting of the R phase was calculated by using the density values of the

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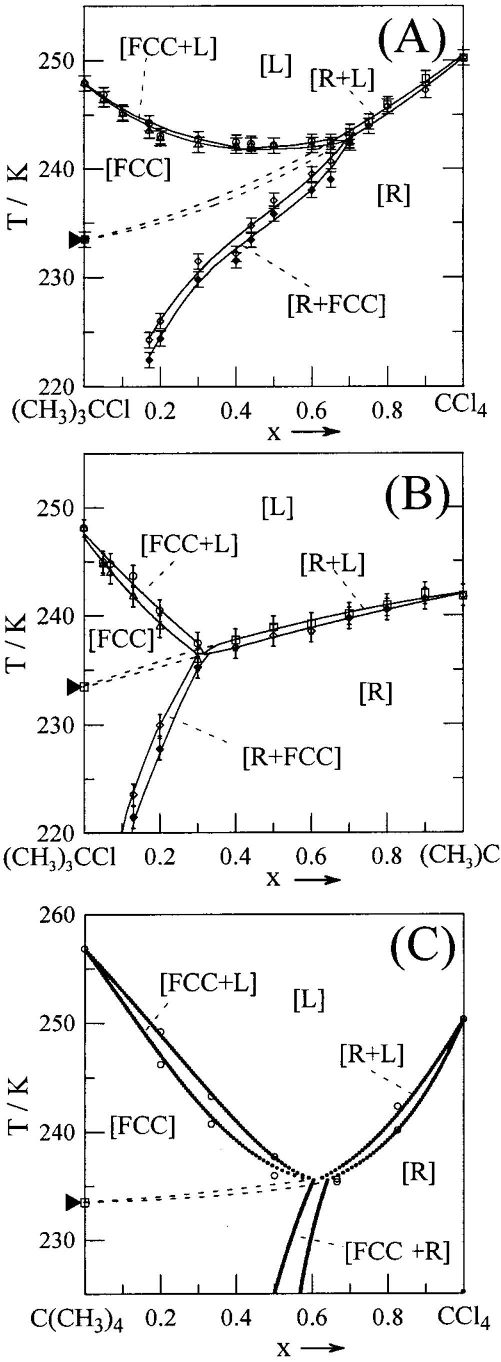

Figure 2. Melting phase diagrams of binary systems: (A) $(CH_3)_3CCl + CCl_4$[19]; (B) $(CH_3)_3CCl + CH_3CCl_3$[20]; (C) $(CH_3)_4C + CCl_4$.[24]

liquid phase given in the literature as a function of temperature.[21]

3.b. 2,2-Dimethylpropane. The $(CH_3)_4C-CCl_4$ phase diagram was interpreted first in terms of a continuous solid solution in the ODIC state.[22,23] Because it was shown[2] that the structures of the ODIC phases of pure components are different (FCC and R, respectively), the diagram has recently been reexamined and interpreted in terms of crossed isodimorphism.[24] As a result, melting of the metastable R phase of $(CH_3)_4C$ was found to occur at 220.0 K with an enthalpy change of 2.4 kJ·mol^{-1}. Nevertheless, data on density or molecular volume as a function of composition still require quantitative structural information on the R phase of $(CH_3)_4C$ to be extrapolated.

4. Topological $p-T$ Diagrams

The stability hierarchy of S_i polymorphs of a pure compound, and the thermodynamic conditions of their existence, can be determined through a topological representation of the corresponding $p-T$ diagram.

General rules for constructing such diagrams have been published.[25-27] By and large, they are as follow:

(i) The melting triple points S_i-l-v are located on a unique $l-v$ curve so that their metastability degree increases as T (S_i-l-v) decreases.

(ii) Each triple point is the crossing point of three two-phase equilibrium curves, in such a way that their metastable extensions alternate with their more stable counterparts.[28]

(iii) For a pure compound involving n polymorphs, the number of triple points, C, in the $p-T$ diagram is given by equation[29]

$$C = \frac{(n+2)!}{3!(n+2-3)!}$$

Therefore, 10 and 20 triple points are to be located (although they cannot all be stable) in trimorphism and tetramorphism, respectively.

(iv) Data from calorimetric measurements, performed on samples in sealed pans within which a dead volume remains, are related to triple points involving the vapor phase rather than to normal transition points.

(v) The stability hierarchy is related to vapor pressure inequalities following the Ostwald rule (the lower the vapor pressure the more stable the phase). Thus, topological $p-T$ diagrams allow the sublimation curves to be located with respect to each other, and consequently, vapor pressure inequalities, as a function of temperature, to be obtained.

Such topological $p-T$ diagrams may be scaled by combining data from high-pressure experiments on condensed phases with data obtained at “ordinary” pressure and involving the vapor phase, namely data from differential scanning calorimetry and vapor pressure measurements. The two-phase equilibria concerning just condensed phases may be described by straight lines ($p_{\alpha\beta} = A_{\alpha\beta}T + B_{\alpha\beta}$) assuming $\Delta_\alpha{}^\beta S$ and $\Delta_\alpha{}^\beta V$ to be constant, and those involving the vapor phase by equation $p_{\alpha v} = A_{\alpha v}\exp(-\Delta_\alpha{}^v H/RT)$.

4.a. $p-T$ Diagram of 2-Methyl-2-chloropropane. The existence of the three known polymorphs of 2-meth-

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Table 2. Triple Points Corresponding to the Trimorphism of $(CH_3)_3CCl$ Compound

triple points	T (K)	P (bar)
I l v	248.1	$39.0 \cdot 10^{-3}$
I II v	219.8	$5.85 \cdot 10^{-3}$
II III v	183.6	$0.12 \cdot 10^{-3}$
I II III	835.4	36210.2
II l v	225.8	$9.92 \cdot 10^{-3}$
I III v	208.9	$2.45 \cdot 10^{-3}$
I II l	207.8	−707.4
II III l	82.62	−5608.9
III l v	215.1	$4.63 \cdot 10^{-3}$
I III l	191.9	−986.1

Table 3. Additional Triple Points Involving the Rhombohedral Phase of the $(CH_3)_3CCl$ Compound

triple points	T (K)	P (bar)
I II R	228.6	519.1
II III R	319.7	7562.1
R l v	233.5	$16.4 \cdot 10^{-3}$
II R v	221.9	$7.06 \cdot 10^{-3}$
I III R	209.0	9.47
III R v	208.9	$2.55 \cdot 10^{-3}$
I R v	208.7	$2.41 \cdot 10^{-3}$
II R l	217.9	−312.0
III R l	198.8	−693.3
I R l	127.9	−2107.7

Table 4. Parameters for the Equations of the Two-Phase Equilibrium Curves Involving the Vapor Phase (v) and the Condensed Phases of the $(CH_3)_3CCl$ Compound

$P_{\alpha v} = A_{\alpha v} \exp(\Delta^{\alpha}{}_{v}H/RT)$

$\alpha - v$	$A_{\alpha v}$ (bar)	$\Delta^{\alpha}{}_{v}H$ ($J \cdot mol^{-1}$)
$l-v$	41530.7	28629
I$-v$	97475.2	30389
II$-v$	2266351.5	36139
III$-v$	8852746.6	38219
R$-v$	160945.4	31259

$P_{\alpha\beta} = A_{\alpha\beta}T + B_{\alpha\beta}$

$\alpha - \beta$	$A_{\alpha\beta}$ ($bar \cdot K^{-1}$)	$B_{\alpha\beta}$ (bar)
I−II	58.8235	−12929.4
I$-l$	17.5439	−4352.6
II$-l$	39.1642	−8844.7
III−II	55.5550	−10199.0
III−I	57.7964	−12071.4
III$-l$	42.4766	−9136.9
R$-l$	19.9705	−4663.1
R−I	26.0012	−5425.4
II−R	77.3316	−17160.8
III−R	68.6168	−14333.0

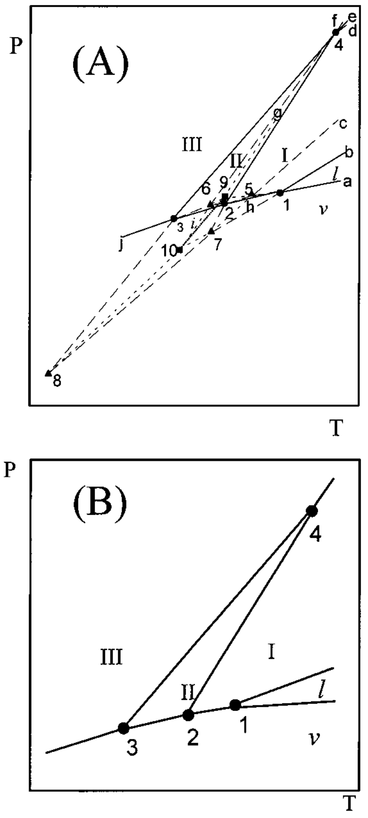

Figure 3. (A) $p-T$ diagram of trimorphism for $(CH_3)_3CCl$. Triple points: Stable points (●): I l v (1), I II v (2), II III v (3), I II III (4); metastable points (▲): II l v (5), I III v (6), I II l (7), II III l (8); supermetastable points (■): III l v (9), I III l (10). Equilibrium curves: $l-v$ (a), I$-l$ (b), II$-l$ (c), II−III (d), I−III (e), I−II (f), III$-l$ (g), I$-v$ (h), II$-v$ (i), III$-v$ (j). (B) Stable topological $p-T$ phase diagram of trimorphism for $(CH_3)_3CCl$.

yl-2-chloropropane may be accounted for by a $p-T$ diagram involving 10 triple points whose coordinates are gathered in Table 2.

They have been determined by means of the equations for the two-phase equilibria (Table 4) calculated according to a procedure already applied to construct the adamantane $p-T$ diagram[30]:

- Starting from the equation for the $l-v$ curve, equations for the S_i-v equilibria (i = I, II, and III) were calculated assuming $p_{lv} = p_{Si-v}$ at triple point S_i-l-v and $\Delta_i{}^vH = \Delta_i{}^lH + \Delta_l{}^vH$. This procedure was also applied to the sublimation curves that meet at $Si-Sj-v$ triple points assuming $\Delta_i{}^vH = \Delta_i{}^jH + \Delta_j{}^vH$.
- As far as the equilibria involving only condensed phases are concerned, the slopes of the linear equations for I$-l$, I−II, and II−III have been taken from literature, and the slopes for the II$-l$, I−III, and III$-l$ equilibria have been determined from the coordinates of the triple points they go through.

The resulting $p-T$ diagram for this trimorphism is given in Figure 3A (all equilibria), B (only stable equilibria).

Now, because the R phase was foreseen to be a polymorph of $(CH_3)_3CCl$, a $p-T$ diagram accounting for this tetramorphism has to be constructed. This entails 10 supplementary triple points (Table 3) to be located in the former $p-T$ diagram.

A sublimation enthalpy of 31.259 $kJ \cdot mol^{-1}$ for the R phase is determined from $\Delta_R{}^vH = \Delta_R{}^lH + \Delta_l{}^vH$. This value is incorporated into the equation ($p_{Rv} = A_{Rv}$(exp $-31259/RT$) of the R$-v$ equilibrium and constant A_{Rv} determined by equalizing the pressures of the R$-v$ and $l-v$ equilibria at triple point R$-l-v$ (233.5 K). Applying the same procedure to the R$-v$ and I$-v$, the R$-v$ and II$-v$, and the R$-v$ and III$-v$ equilibrium curves, the coordinates of the I−R$-v$, II−R$-v$, and III−R$-v$ triple points can be calculated, respectively. The equation of the R$-l$ melting curve is determined from the Clapeyron equation, then the coordinates of the I−R$-l$ triple point are found at the crossing point of the R$-l$ and I$-l$ curves. The linear equation for the I−R equilibrium is obtained from the coordinates of triples points I−R$-v$ and I−R$-l$. Crossings of I−R and I−III, and I−R and I−II lead to the coordinates of triple points I−III−R and I−II−R, respectively. The coordinates of the I−II−R and II−R$-v$ triple points provide us with the linear equation

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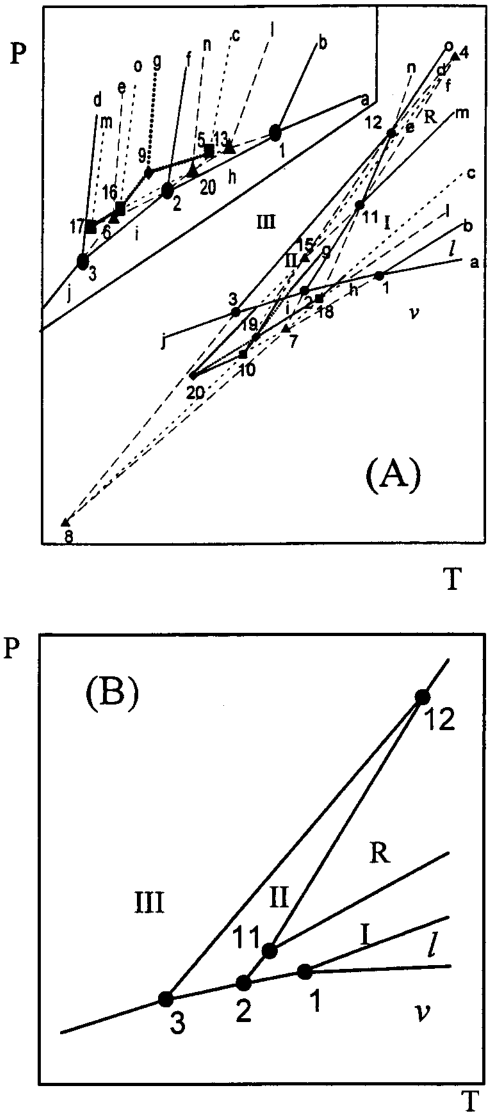

Figure 4. (A) $p-T$ diagram of tetramorphism for $(CH_3)_3CCl$. Triple points: Stable points (●): I l v (1), I II v (2), II III v (3), I II R (11), II III R (12); metastable points (▲): I II III (4), I III v (6), I II l (7), II III l (8), R l v (13), II R v (14), I III R (15); supermetastable points (■): II l v (5), I III l (10), III R v (16), I R v (17), II R l (18); hypermetastable points (◆): III l v (9), III R l (19), I R l (20). Equilibrium curves: $l-v$ (a), I$-l$ (b), II$-l$ (c), II−III (d), I−III (e), I−II (f), III$-l$ (g), I$-v$ (h), II$-v$ (i), III$-v$ (j), R$-v$ (k), R$-l$ (l), R−I (m), R−II (n), R−III (o). The inset enlarges the temperature−pressure domain between triple points 1 and 3. (B) Stable topological $p-T$ phase diagram of tetramorphism for $(CH_3)_3CCl$.

of the II−R equilibrium. The II−R−l and III−R−l triple points are located through curves II−R and R−l and curves III−l and R−l, respectively.

The coordinates of the 10 supplementary triple points and the equations for the two-phase equilibrium curves involving phase R are given in Tables 2−4.

The $p-T$ diagram for this tetramorphism is shown in Figure 4A (all equilibria), B (stable equilibria).

The diagram in Figure 4B, where it is shown that phase R is stable under high pressure, is virtually the same as that given in Figure 1A, which results from previous works[12,13] that experimentally revealed the existence of a fourth phase (phase IV) stable under high pressure. Moreover, the coordinates calculated for the I−II−R triple point (228.6 K, 519 bar) are close to the experimental values for I−II−IV (232 K −≈750 bar[12] or 227 K −≈500 bar,[13] values read from figures), and the slope calculated for the I−R equilibrium (26.0 bar·K^{-1}) is very close to those previously obtained experimentally (27.5[12] or 26.2 bar·K^{-1} [13]).

It follows that the hypothetical R phase and the experimental phase IV of $(CH_3)_3CCl$ are one and the same. In addition, by incorporating the experimental entropy change $\Delta_{IV}{}^{I}S = 4.2$ J·K^{-1}·mol^{-1} [12] and the slope of the I−R equilibrium curve into the Clapeyron equation, a volume change value of 1.62 cm^3·mol^{-1} is obtained, which falls within the experimental values (1.5−1.8 cm^3·mol^{-1}).[13]

Table 5. Triple Points Corresponding to the Dimorphism of the $(CH_3)_4C$ Compound

triple points	T (K)	P (bar)
I l v	256.5	0.328
II l v	187.3	$3.42 \cdot 10^{-3}$
I II v	140.5	$3.45 \cdot 10^{-3}$
I II l	64.28	−2878.0

Table 6. Parameters for the Equations of the Two-Phase Equilibrium Curves Involving the Vapor Phase (v) and the Condensed Phases of the $(CH_3)_4C$ Compound

$P_{\alpha v} = A_{\alpha v} \exp(-\Delta H_{\alpha v}/RT)$

$\alpha-v$	$A_{\alpha v}$ (bar)	$\Delta H_{\alpha v}$ (J·mol^{-1})
$l-v$	76391.5	26358
I$-v$	350647.8	29608
II$-v$	3325657.0	32236
R$-v$	276052.7	28708

$P_{\alpha\beta} = A_{\alpha\beta} T + B_{\alpha\beta}$

$\alpha-\beta$	$A_{\alpha\beta}$ (bar·K^{-1})	$B_{\alpha\beta}$ (bar)
I−II	37.759	−5305.1
I$-l$	14.974	−3840.5
II$-l$	23.387	−4381.3
R$-l$	11.760	−2587.2
R−II	47.711	−8134.6
R−I	−29.796	13349.9

4.b. $p-T$ Diagram of 2,2-Dimethylpropane (Neopentane). The dimorphism of $(CH_3)_4C$ entails four triple points to be located in its $p-T$ diagram. The I$-l-v$ triple point corresponds to the melting point of the high-temperature FCC phase (phase I), and the I−II$-v$ triple point (which is also a stable triple point) corresponds to the I−II transition point. The two remaining triple points (II$-l-v$ and I−II$-l$) are metastable. They are located at the crossing points of the II$-v$ and $l-v$ curves and of the I−II and II$-l$ curves, respectively. Because curves I$-l$ and II$-l$ diverge as p increases, the metastable I−II$-l$ triple point has to be located in the low-pressure region of the $p-T$ diagram.

The coordinates for the four triple points and the equations for the two-phase equilibrium curves are compiled in Tables 5and 6, respectively. The topological $p-T$ diagram for this dimorphism is shown in Figure 5A.

Now assuming that the R phase potentially exists for pure $(CH_3)_4C$, as suggested by the thermodynamic analysis of the $(CH_3)_4C-CCl_4$ binary system, the previous $p-T$ diagram has to be completed, given that the R$-l-v$ triple point (220 K) should lie between the II$-l-v$ and I$-l-v$ triple points on the $l-v$ curve.

Because crystallographic data on phase R are lacking, the Clapeyron equation cannot be used to calculate the slope of the metastable R$-l$ curve. Nevertheless, keep

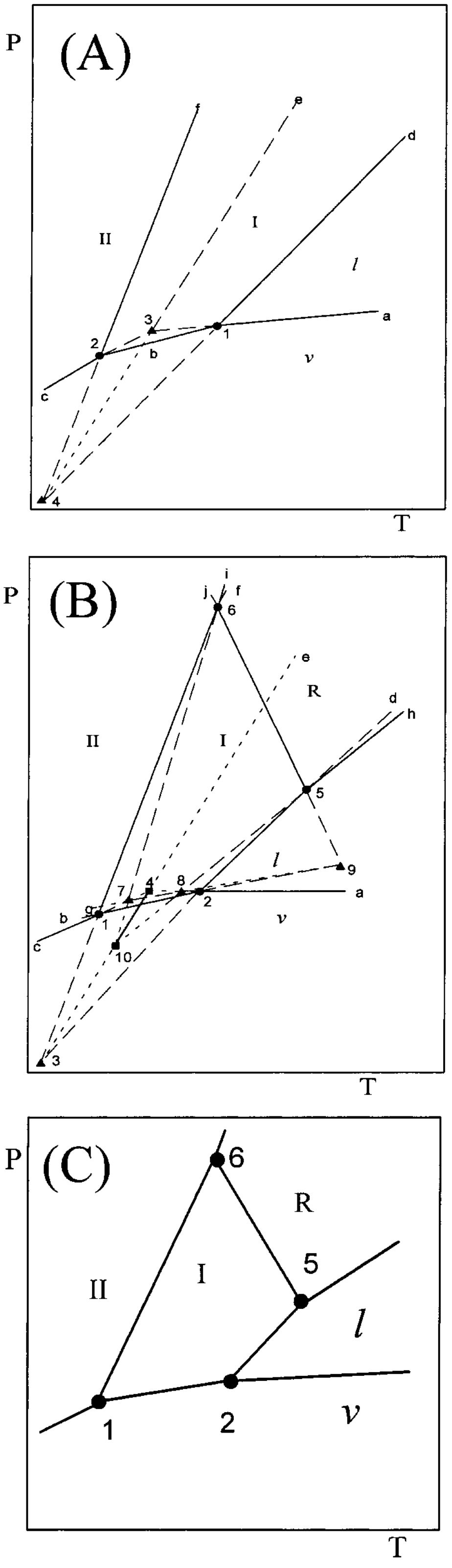

Figure 5. (A) $p-T$ diagram of dimorphism for $(CH_3)_4C$. Triple points: Stable points (●): I II v (1), I L v (2); metastable points (▲): II I l (3), II l v (4). Equilibrium curves: $l-v$ (a), I$-v$ (b), II$-v$ (c), I$-l$ (d), II$-l$ (e), II$-$I (f). **(B)** $p-T$ diagram of trimorphism for $(CH_3)_4C$. Triple points: Stable points (●): I II v (1), I l v (2), I R l (5), I II R (6); metastable points (▲): II I l (3), II R v (7), R l v (8), I R v (9); supermetastable points (■): II l v (4), R II l (10). Equilibrium curves: $l-v$ (a), I$-v$ (b), II$-v$ (c), I$-l$ (d), II$-l$ (e), II$-$I (f), R$-v$ (g), R$-l$ (h), R$-$II (i), R$-$I (j). **(C)** Stable topological $p-T$ phase diagram of trimorphism for $(CH_3)_4C$.

Table 7. Additional Triple Points Involving the Rhombohedral (R) Phase of the $(CH_3)_4C$ Compound

triple points	T (K)	P (bar)
R l v	220.0	$42.1 \cdot 10^{-3}$
R I v	452.6	134.1075
R II v	170.5	$44.2 \cdot 10^{-3}$
R I l	390.0	19998.8
R II l	154.3	-772.5
R I II	277.2	5090.6

in mind that the $p-T$ diagram of $(CH_3)_4C$ was investigated up to about 2000 bar and that no hint for the existence of a third (high-pressure) phase was observed. Then, if the R phase really exists, the I$-$R$-l$ triple point should fall at a pressure larger than 2000 bar. This corresponds to $T = 390$ K on the I$-l$ curve. It follows that the slope of the R$-l$ curve should be 11.76 bar·K^{-1} at most. Incorporating $\Delta_R{}^lH = 2350$ J·mol^{-1} and $T_{R-l} = 220$ K into the Clapeyron equation, a volume variation of 9.08 cm^3·mol^{-1} upon melting of phase R is calculated. Taking $V_l(220\ \text{K}) = 108.0$ cm^3·mol^{-1}, this leads to $V_R(220\ \text{K}) = 98.95$ cm^3·mol^{-1} (164.23 Å^3 per molecule) and to a packing coefficient $\eta = 0.589$, close to the values (0.59$-$0.61) found for the R phases of the $(CH_3)_{4-n}CCl_n$ ($1 \leq n \leq 4$) compounds. If this were true, the R$-l$ equilibrium should become stable at high pressure and a stable high-pressure phase region for phase R should exist, as illustrated in Figure 5B (all equilibria), C (stable equilibria). This postulated trimorphism entails additional triple points and two-phase equilibrium curves whose coordinates and equations are compiled in Tables 7 and 6, respectively.

5. Conclusions

The polymorphism of two members of the $(CH_3)_{4-n}CCl_n$ ($0 \leq n \leq 4$) series of methylchloromethane derivatives, 2,2-dimethylpropane [neopentane, $(CH_3)_4C$] and 2-methyl-2-chloropropane [$(CH_3)_3CCl$], has been studied as a function of the pressure and the temperature.

As far as $(CH_3)_3CCl$ is concerned, three solid phases (trimorphism) at ordinary pressure have been gathered into a topological $p-T$ diagram. The existence of an orientationally disordered rhombohedral phase R, which is known to exist for the other members of the series, has been located in the $p-T$ diagram by means of a complete set of experimental data emanating from the thermodynamic analysis of some two-component systems. Taking this fourth phase R into account results in the first description ever to be reported for a tetramorphism through a topological $p-T$ diagram. In addition, this demonstrates that the phase in question corresponds to a stability domain at high pressure (from 519.1 bar) and high temperature (from 228.6 K) which undoubtedly agrees with the one previously reported for phase IV in the experimental $p-T$ diagram.

Although the polymorphism of $(CH_3)_4C$ has been described as a dimorphism, the existence of phase R for all the members of the methylchloromethane series has been assumed. The stability domain of phase R in the $p-T$ plane has been predicted by means of partial thermodynamic information (melting temperature and enthalpy change) obtained from the $(CH_3)_4C-CCl_4$ binary system. On the basis of the experimental $p-T$ phase diagram, we have hypothesized that the possible stability domain should be located at pressures higher than 2000 bar and temperatures higher than 390 K. This assumption provides reasonable values for the packing coefficient (and then for the molar volume) for the postulated metastable phase R at ordinary pressure. Although many works have been devoted to seizing the thermodynamics and the dynamics of the experimentally available phase I of neopentane by means of molecular dynamics,[31−38] the existence of an orientationally disordered rombohedral phase R was not inferred from this method. In this line of reasoning the present work can stimulate molecular dynamics studies on such a phase, for which, in addition, suitable thermodynamic properties are given here.

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