

The System Carbon-Tetrachloride+ Neopentane: A Complete Thermodynamic Analysis

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An experimental reinterpretation together with a thermodynamic analysis of the two-component system (CCl₄) + (C(CH₃)₄) has been performed. The 35-year-old specific heat diagrams obtained by adiabatic calorimetry have been revised in order to remove the inconsistencies of the tentative experimental phase diagram. The fact that the two components of the system do not have the same ODIC form was ignored 30 years ago and, at present, it has been considered. From a thermodynamic point of view the two-component system is a very nice example of crossed isodimorphism: two ODIC+ liquid loops crossing each other give rise to a three-phase equilibrium. The thermodynamic information of the excess magnitudes is wide enough to perform a complete and realistic thermodynamic analysis. Likewise, the excess thermodynamic magnitudes in the ODIC states have been well explained by means of the quasi-subregular solution model including a compensation law. © 2000 Academic Press

Key Words: carbon tetrachloride; neopentane; plastic crystals; thermodynamic analysis; crossed isodimorphism; enthalpy-entropy compensation.

1. INTRODUCTION

Some time ago, the system carbon-tetrachloride (CCl₄) + neopentane (C(CH₃)₄) gained a certain interest. This was mainly due to the fact that the pure components have simple nonpolar molecules very close in shape and size. As a consequence, it was considered as a good thermodynamic test for some theories about solution thermodynamics (1–5), most of them being devoted to explaining the properties of the liquid mixtures by means of assuming more or less regular structure in the liquid state. It is well known that certain kinds of solid state like plastic crystalline state, also referred to as orientationally disordered crystalline (ODIC)

state, have many features in common with the liquid state like disorder and isotropy and, in particular, a real lattice structure. It follows that measurements of the excess functions of solid solutions of this kind of solid state should permit, in some instances, a better test for these existing theories of mixtures than is presently possible with the liquid state.

According to these facts, Westrum and co-workers studied exhaustively several mixtures between neopentane and carbon-tetrachloride from a thermodynamic point of view and even they proposed an experimental two-component system (6, 7). In fact, they considered this system because they thought it forms a continuous series of solutions in the ODIC mixed state. Nowadays, the interesting polymorphic behavior of carbon-tetrachloride (8–10) and the polymorphism of neopentane are well known (9, 11–14). On the basis of these studies it is presently known that the stable ODIC state of CCl₄ is rhombohedral (R) and the stable ODIC state of C(CH₃)₄ is face-centred cubic (C_F). Hence, the impossibility of forming a continuous series of orientationally disordered solid solutions is obvious, and therefore, likewise the incompatibility of the experimental two-component system proposed by Chang and Westrum (7); see Fig. 1. This experimental system was tentatively constructed on the basis of heat capacity versus temperature diagrams, determined by adiabatic calorimetry. In reality the tentative nature of the experimental system is limited to its mid-range on the temperature scale, which is the range around 200 K. In addition to the fact, which has been ignored, that the two components of the system do not have the same ODIC form, other circumstances must be considered. First of all, it is important to realize that in the published paper (7), which appeared in 1970, the existence of the R form of CCl₄ was known by Chang and Westrum and no further reinterpretation of this fact was made. Moreover, the previous two-phase region [C_{F1} + C_{F2}] (see Fig. 1) is not thermodynamically reproducible with the mixing properties published in a previous paper (6).

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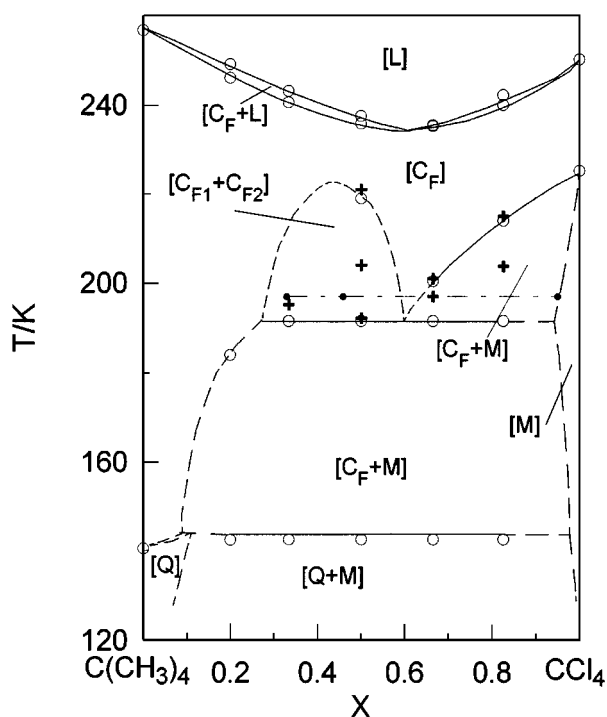


FIG. 1. Original experimental (○) two-component system CCl₄ + C(CH₃)₄ reported by Chang and Westrum (7). The names of the phases correspond also to the original work. The symbols (+) correspond to some reinterpreted experimental values from specific heat diagrams. The symbol (●) and the dot-dashed line correspond to a new reinterpretation of the temperature-composition of the three-phase equilibrium line.

Second, a recent work on mixed crystalline samples carried out by van der Linde (15) has led to new insights about the interpretation of specific heat diagrams obtained by adiabatic calorimetry. For these reasons we decided to use Chang and Westrum's original and carefully specific heat diagrams and their enthalpy increment data to remove the inconsistencies from the mid-range of the original, tentative phase diagram.

The aim of the present work is then twofold: on the one hand, to perform a reinterpretation of the specific heat diagrams to obtain a remodeled experimental two-component system, obviously, taking into account the knowledge of the two different ODIC states. On the other hand, to establish thermodynamic compatibility of the two-component system CCl₄ + C(CH₃)₄ with regard to the new experimental reinterpretation. Likewise, the thermodynamic mixing properties of the orientationally disordered mixed crystals in terms of the enthalpy-entropy compensation theory will also be obtained.

The paper is organized as follows. In Section 2 we present the available experimental information and perform a detailed reinterpretation of Chang and Westrum's original specific heat diagrams, pointing out the modifications on the original two-component system proposed by these authors. In Section 3, a complete thermodynamic analysis is

carried out. Finally, in Section 4 a general discussion in terms of the enthalpy-entropy compensation theory is performed.

2. EXPERIMENTAL INFORMATION

2.1. Pure Component Data and Phase Diagram

In relation to the CCl₄ pure component, when cooled from the liquid state, an orientationally disordered face-centered cubic (C_F) is formed and upon further cooling transforms either to an orientationally disordered rhombohedral form (R) or to an ordered monoclinic form (M). In contrast, warming the monoclinic solid induces, at first, a transformation to a rhombohedral phase and finally to the liquid state. As demonstrated by Rudman *et al.* (8-10), the rhombohedral ODIC is the most stable form. The ODIC face-centered cubic is a metastable form, which is only present when cooling the sample from liquid state (monotropic form).

As far as the C(CH₃)₄ pure component is concerned, there exist two stable forms in the solid state: a low-temperature ordered form the symmetry of which (tetragonal (11-13) or hexagonal (9)) has not yet been settled (hereinafter referred as Q), and a high-temperature ODIC form displaying a C_F structure.

Taking into account the polymorphism of the pure component data a brief summary of the available thermal information is gathered in Table 1.

With regard to the phase diagram data, five compositions (C(CH₃)₄)_{1-x}(CCl₄)_x (X = 0.2, 0.334, 0.501, 0.666, and 0.826) were studied by Chang and Westrum using an adiabatic calorimeter (7). These authors considered the *equilibrium method* to ensure thermal equilibrium in the transition regions. In such a way, by means of heat capacity measurements, not only the transition temperature but also the enthalpy increment of each solid-solid transition and fusion were accurately determined. It is important to point out that all heat capacity measurements were made from the ordered solid to the liquid state. Thus, the measurements are a good representation of the various phase transitions between stable forms but we believe that a new interpretation must be done in light of the van der Linde study.

To start with, for the invariant three-phase [C_F + R + M] equilibrium the following specifications have been made. For the temperature of the invariant equilibrium we propose the value of 197.0 K; it is the mean of Chang and Westrum's value of 203.8 K for the X = 0.826 sample (see Fig. 1 of Ref. 7) and our own readings for three other compositions: (X = 0.334; T = 195.2 K), (X = 0.501; T = 192.2 K), and (X = 0.666; T = 197.0 K). The compositions of the coexisting phases were derived from the enthalpy increment data by means of the Tamann's method, (C_F, X = 0.33; R, X = 0.46; M, X = 0.95). Next, the temperatures, read from the specific heat diagrams, at which the

TABLE 1
Thermal Parameters of the Pure Components (Temperatures T and Enthalpy Changes ΔH)

| $C(CH_3)_4$ | $T_{Q \rightarrow F}$ (K) | $\Delta H_{Q \rightarrow F}$ ($J \cdot mol^{-1}$) | $T_{F \rightarrow L}$ (K) | $\Delta H_{F \rightarrow L}$ ($J \cdot mol^{-1}$) | | | References |
|-------------|---------------------------|-----------------------------------------------------|-------------------------------|---------------------------------------------------------|---------------------------|-----------------------------------------------------|------------|
| | 140.5 | | 256.8 | 3093.0 | | | (7) |
| | 140.0 | 2570.7 ± 1.3 | 254.2 | 3190.0 ± 1.3 | | | (9) |
| | 130.2 | | 253.5 | | | | (11) |
| | 140.5 | 2630 | 256.8 | 3090 | | | (14) |
| | 140.0 | 2570 | 256.5 | 3250 | | | (16) |
| | 139.0 | 2560 | 253.8 | 3240 | | | (17) |
| CCl_4 | $T_{M \rightarrow R}$ (K) | $\Delta H_{M \rightarrow R}$ ($J \cdot mol^{-1}$) | $T_{F \rightarrow L}$ (m) (K) | $\Delta H_{F \rightarrow L}$ (m) ($J \cdot mol^{-1}$) | $T_{R \rightarrow L}$ (K) | $\Delta H_{R \rightarrow L}$ ($J \cdot mol^{-1}$) | |
| | 225.5 | | | | 250.3 | | (18) |
| | 225.35 ± 0.5 | 4581 ± 13 | | | 250.3 | 2515 ± 8 | (19) |
| | 226.6 ± 1.0 | 4477 ± 180 | 244.8 ± 1.0 | 1753 ± 180 | 247.8 ± 2.0 | 2494 ± 200 | (10) |
| | | | 245.7 ± 0.1 | 1848 ± 2 | 250.28 ± 0.10 | 2558 ± 4 | (20) |
| | | | | 1787 ± 5 | | 2530 ± 12 | (21) |
| | 225.7 ± 0.1 | 4631 ± 20 | 246.00 ± 0.01 | 1830 ± 70 | 250.53 ± 0.01 | 2562 ± 6 | (22) |

Note. Q, M, R, and C_F are the tetragonal (or hexagonal), monoclinic, rhombohedral, and face-centred cubic forms; L is the liquid state.

transition to C_F or R is complete, are ($X = 0.200$; $T = 184$ K), ($X = 0.666$; $T = 201$ K), and ($X = 0.826$; $T = 214$ K). The most interesting specific heat diagram, that is to say in the present context, is the one for $X = 0.501$, because it completely and clearly reveals the transition from R to C_F . The [$C_F + R$] two-phase region is entered at 204 K and left at 221 K. The heat effect of the transition, read from the elevation in the specific heat diagram, is about $0.5 \text{ kJ} \cdot \text{mol}^{-1}$ (the value is in agreement with the distance between the two heat-of-melting curves in Fig. 3, for $X = 0.5$). The experimental modifications for the two-component system are shown in Fig. 1, together with Chang and Westrum's original proposition.

2.2. Available Thermodynamic Mixing Properties

Several authors have exhaustively studied the excess properties of the liquid state. Mathot and Desmyter in 1953 (23), by means of vapor pressure measurements, determined the excess Gibbs energy. A few years later, Englert-Chwoles in 1955 (24), using an adiabatic and an isothermal calorimeter, reported the excess enthalpy and entropy. More recently, Harsted and Thomsen in 1974 (25), by means of an isothermal calorimeter, obtained the excess enthalpy. From these data, the liquid state can be considered as regular ($S^{E,L} \approx 0$); that is to say, the excess enthalpy is the same as the excess Gibbs energy. The values of Mathot and Desmyter are not much far away from those reported by Englert-Chwoles; see Fig. 2a. The data have been fitted in a two-parameter form of a Redlich-Kister polynomial

$$G^{E,L}(X) = X(1 - X)[1247 - 39(1 - 2X)] \text{ J} \cdot \text{mol}^{-1}. \quad [1]$$

The values of the excess enthalpy function derived by Chang and Westrum (6) for the ODIC mixed state are wholly questionable. They were derived assuming complete miscibility in the ODIC mixed state. These values are shown in

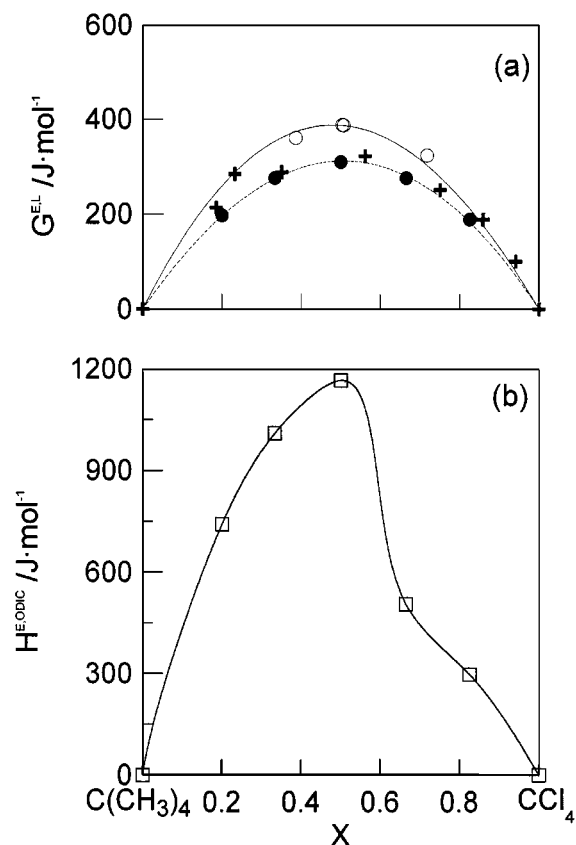


FIG. 2. Excess properties of the liquid state (a) and ODIC state (b). +, Ref. (23); ●, Ref. (24); ○, Ref. (25); □, Ref. (6).

Fig. 2b, where a discontinuity between $X = 0.5$ and $X = 0.7$ mole fractions can be clearly observed. Obviously, at present we know that this discontinuity must be due to the existence of a phase separation region between both stable disordered forms: R and C_F .

3. THERMODYNAMIC ANALYSIS

3.1. Theoretical Background

In a thermodynamic analysis of a two-component system $A + B$ under isobaric conditions, each possible form of the mixture has associated a molar Gibbs energy function. From this function, all thermodynamic information of that form can be derived. Likewise, it is well known that the equilibrium condition of a system at fixed X and T under isobaric conditions occurs when the total Gibbs energy reaches its lowest value. Thus, when at a given T two Gibbs energy curves characterizing two different forms intersect, there will be a pair of coexisting forms.

Let us assume a mixture between components A and B in a form α . The Gibbs energy is a temperature- and composition-dependent function that can be written as

$$G^\alpha(X, T) = (1 - X)\mu_A^{*\alpha}(T) + X\mu_B^{*\alpha}(T) + RT$$

$$[(1 - X)\ln(1 - X) + X\ln X] + G^{E,\alpha}(X, T), \quad [2]$$

where X represents the mole fraction of B , $\mu_A^{*\alpha}(T)$ and $\mu_B^{*\alpha}(T)$ are the Gibbs energies of pure components A and B respectively, R is the gas constant, and $G^{E,\alpha}(T, X)$ is the excess Gibbs energy that accounts for the deviation of the mixture in form α from the ideal mixing behavior. The knowledge of the above expression for each form is generally not available, particularly because $\mu_A^{*\alpha}(T)$, $\mu_B^{*\alpha}(T)$, and $G^{E,\alpha}(T, X)$ are habitually unknown. However, in order to determine and to analyze a two-phase equilibrium region between two arbitrary forms α and β in a two-component phase diagram, a simplified treatment, named Equal-Gibbs Curve (EGC) method (26), can be made. In such a way, the difference between the Gibbs energies of α and β forms can be written as

$$\Delta G^{\alpha-\beta}(X, T) = G^\beta(X, T) - G^\alpha(X, T) = (1 - X)\Delta\mu_A^*(T) + X\Delta\mu_B^*(T) + \Delta G^E(X, T), \quad [3]$$

where for $i = A$ or B , $\Delta\mu_i^*(T) \approx \Delta H_i^* - T\Delta S_i^*$ (ΔH_i^* and ΔS_i^* are the enthalpy and entropy changes in the transition of the pure components A and B) and $\Delta G^E(T, X)$ is the excess Gibbs energy difference between both forms. Equation [3] is equal to 0 when both G curves are equal. This takes place for each X at different temperatures, named EGC temperatures or more simply EGC curve ($T_{EGC}(X)$).

Taking into account the above considerations it is easy to prove that

$$T_{EGC}(X) = \frac{(1 - X)\Delta H_A^* + X\Delta H_B^*}{(1 - X)\Delta S_A^* + X\Delta S_B^*} + \frac{\Delta G_{EGC}^E(X)}{(1 - X)\Delta S_A^* + X\Delta S_B^*}. \quad [4]$$

The first term on the right side of Eq. [4] is denoted by T_{zero} and is named zero line, being pure component dependent. However, the second term on the right side of Eq. [4] depends on the excess Gibbs energy difference along the EGC curve. Obviously the zero line can be obtained numerically from pure component data. Nevertheless, the true $T_{EGC}(X)$ is unknown. The EGC method requires some experimental data of the α - β region to realize an iterative procedure in which one obtains a reasonable EGC curve and in addition to the $\Delta G_{EGC}^E(X)$. This procedure can be automatically made by means of the WINIFIT program (27), which is a modification, in a Windows version, of the well-known LIQFIT program (28).

3.2. The Odic Solid + Liquid Equilibria

The ODIC solid + liquid equilibria of the $CCl_4 + C(CH_3)_4$ system is an example of crossed isodimorphism. This means the existence of two ODIC solid + liquid loops crossing each other, giving rise to a eutectic (or peritectic) three-phase equilibrium: one of the loops involving the $[C_F + L]$ equilibrium and the other the $[R + L]$ equilibrium.

3.2.1. The $[C_F + L]$ equilibrium. In such an equilibrium the C_F -metastable melting point of CCl_4 is experimentally well known. In Table 1, we show the most noticeable values of the melting temperature and the heat of fusion. In this thermodynamic analysis we preferred the values of Arentsen and van Miltenburg (20), which were determined with care by means of an adiabatic calorimeter. The data concerning the C_F -stable melting point of $C(CH_3)_4$ are also consigned in Table 1. For the analysis we choose the values of Chang and Westrum (7). In addition, three experimental values of the liquidus curve and the excess Gibbs energy of the liquid state are known, Eq. [1]. The EGC method via the WINIFIT program provides the excess Gibbs energy of the C_F -ODIC state. The result for the excess Gibbs energy of the C_F form at the mean temperature ($T_m = T_{EGC}(X = 0.5)$) of the $[C_F + L]$ equilibrium is given by a two-parameter form of a Redlich-Kister polynomial:

$$G^{E,F}(X, T_m = 237 \text{ K}) = X(1 - X)[1849 - 48(1 - 2X)]\text{J}\cdot\text{mol}^{-1}. \quad [5]$$

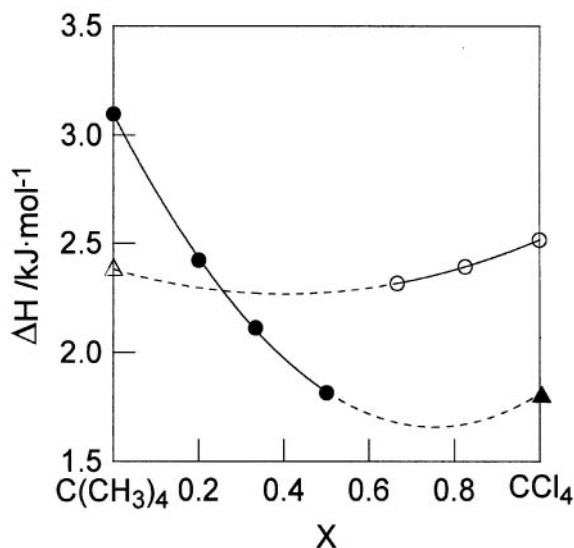


FIG. 3. Enthalpy of melting as a function of the composition for the two ODIC mixed states (●, C_F) and (○, R), reported by Chang and Westrum (7). The symbols (△) and (▲) are the extrapolated metastable enthalpy of melting for $C(CH_3)_4$ and CCl_4 , respectively.

3.2.2. *The [R + L] equilibrium.* Unlike the [C_F + L] equilibrium, the rhombohedral metastable transition temperature and heat of fusion of the $C(CH_3)_4$ are unknown. Thus, the first step of the analysis consisted in the estimation of these two metastable values.

As far as the R-metastable heat of fusion of the $C(CH_3)_4$ is concerned, information on the enthalpy of melting as a function of mole fraction is available, see Fig. 3. By extrapolating the values corresponding to the [R + L] equilibrium at $X = 0$, the enthalpy of melting of pure $C(CH_3)_4$ in its metastable state can be roughly read. We obtained a value of about $2350 \text{ J}\cdot\text{mol}^{-1}$. In a same way, from Fig. 3, the enthalpy of melting of pure CCl_4 in its metastable C_F state can also be read. The value is about $1800 \text{ J}\cdot\text{mol}^{-1}$. Let us remember that the experimental reported value in Table 1 is ranged between 1753 and $1848 \text{ J}\cdot\text{mol}^{-1}$. This proves the validity of the method, and then the obtained metastable enthalpy of melting of pure $C(CH_3)_4$ is probably not far away from the real value.

As far as the R-metastable melting temperature of pure $C(CH_3)_4$ is concerned, information on two experimental values of the liquidus curve of the [R + L] equilibrium together with the estimated metastable heat of fusion are available. The WINIFIT program enables us to realize a great number of trial and error calculations. The assessed value is chosen to be 220 K , and the excess Gibbs energy at the mean temperature of the equilibrium in a two-parameter form of a Redlich-Kister polynomial is

$$G^{E,R}(X, T_m = 230 \text{ K}) = X(1 - X) [1303 - 488(1 - 2X)] \text{ J}\cdot\text{mol}^{-1}. \quad [6]$$

3.3. The Ordered Solid + ODIC Solid Equilibria

The ordered solid forms of pure $C(CH_3)_4$ (Q) and pure CCl_4 (M) are obviously not isostructural. Likewise the experimental data of the two-component system seem to show the existence of limited miscibility in the Q form as well as the possibility of formation of monoclinic mixed crystals. Accordingly, the concept of crossed isodimorphism was also applied. To do so, two simple equilibria [R + M] and [C_F + Q] were considered. The information on the stable parts is rather limited, particularly for the [C_F + Q] equilibrium. For this reason, the present analysis was an exercise in finding the better accordance between the experimental and the calculated phase diagram. To start with, the metastable transition temperatures of pure $C(CH_3)_4$ and pure CCl_4 in M and Q forms, respectively, were found, via the WINIFIT program, as a result of a great number of trial and error calculations. The chosen values were 81 and 173 K , respectively. As an arbitrary choice, the entropy of transition of each metastable form was taken to be the same as that of each stable form. It is important to point out that the results of the analysis were not modified by minor changes in the metastable parameters. The obtained excess Gibbs energy values of the Q and M forms are rather arbitrary. In particular the better accordance was obtained when miscibility in the monoclinic solid state was virtually negligible. There is no reason to think that the miscibility in M state exists. In fact, the miscibility in the ordered solid state for other systems between ODIC crystals is known to be negligible (29–32). Taking into account the above considerations, the chosen excess Gibbs energies for the Q and M forms expressed in a Redlich-Kister polynomials are

$$G^{E,Q}(X, T_m) = X(1 - X)3045 \text{ J}\cdot\text{mol}^{-1} \quad [7]$$

$$G^{E,M}(X, T_m) = X(1 - X)[4658 - 2642(1 - 2X)] \text{ J}\cdot\text{mol}^{-1}. \quad [8]$$

4. DISCUSSION

4.1. Thermodynamic Mixing Properties in the ODIC State

In Section 3, the excess Gibbs energies of the C_F -ODIC and R-ODIC states have been determined at a defined temperature, named mean temperature of the corresponding equilibria [C_F + L] and [R + L] respectively. It would be desirable to dispose of the temperature dependence for each excess Gibbs energy. A simple way to take into account this dependence is to adopt a quasi-subregular solution model that has proven successful in other cases (31, 33–35). In such a model, the excess Gibbs energy can be written as

$$G^{E,ODIC}(X, T) = X(1 - X)A_1 \left[1 - \frac{T}{T_c} \right] [1 + A_2(1 - 2X)], \quad [9]$$

where $G^{\text{E,ODIC}}$ depends on parameters A_1 , A_2 , and T_c . A_1 and A_2 account for the magnitude and the asymmetry of this function, respectively. The T_c parameter, named compensation temperature or characteristic temperature, is defined as the ratio between excess enthalpy and excess entropy. T_c represents the temperature at which there exists compensation between excess enthalpy and excess entropy, i.e., $H^{\text{E}} = T_c S^{\text{E}}$ and, therefore, the excess Gibbs energy becomes zero. According to this model, the excess enthalpy and excess entropy are temperature independent and can be written as

$$H^{\text{E,ODIC}}(X) = X(1 - X)A_1[1 + A_2(1 - 2X)] \quad [10]$$

$$S^{\text{E,ODIC}}(X) = X(1 - X)\frac{A_1}{T_c}[1 + A_2(1 - 2X)]. \quad [11]$$

In terms of the enthalpy–entropy compensation theory (36), in its simpler formulation, i.e., temperature-independent, excess enthalpy and entropy, the compensation temperature T_c is the same for an ensemble of similar systems, called *class* of systems. In contrast, the parameters A_1 and A_2 describe each particular system of the class. A class of 7 similar systems in their C_{F} -mixed ODIC state between neopentane-like compounds has been recently proposed, with the uniform compensation temperature being about 630 K (37). Similar findings for other classes of systems, like the alkane family (18 systems, $T_c = 320$ K) in their rotator RI form (38), the common-ion alkali halide family (13 systems, $T_c = 2565$ K) in their solid form (39), and the p-dihalobenzene family (10 systems, $T_c = 500$ K) in their solid form (33), have been reported.

As for the two-component system $\text{CCl}_4 + \text{C}(\text{CH}_3)_4$, their C_{F} -mixed ODIC state might be included into the class of the neopentane-like compounds. In order to verify such an assumption, the T_c value must be calculated. In practice, A_1 , A_2 , and T_c values can be derived from excess Gibbs energy data for a given temperature (T_m for instance) in combination with data of experimental excess enthalpy. In Section 2.2 we pointed out the existence of excess enthalpy data for the ODIC state, although they are totally questionable. We have recalculated these values taking into account the necessary existence of a demixing region between C_{F} - and R-ODIC forms. The calculation was made as an approximation, assuming that $\Delta H^{\text{E}} \approx \Delta H_m - \Delta H_{\text{mm}}$, where ΔH_m is the enthalpy of melting and ΔH_{mm} is the enthalpy change of the ideal mechanical mixture ($\Delta H_{\text{mm}} = (1 - X)\Delta H_A + X\Delta H_B$; in a mixture $A_{1-X}B_X$). In such a calculation we have considered the metastable enthalpy of melting of each pure component. The recalculated values are shown in Fig. 4, together with the estimated error bars. It is important to point out that the error bars for the data of the R mixed state are estimated to be greater than those of the C_{F} -mixed

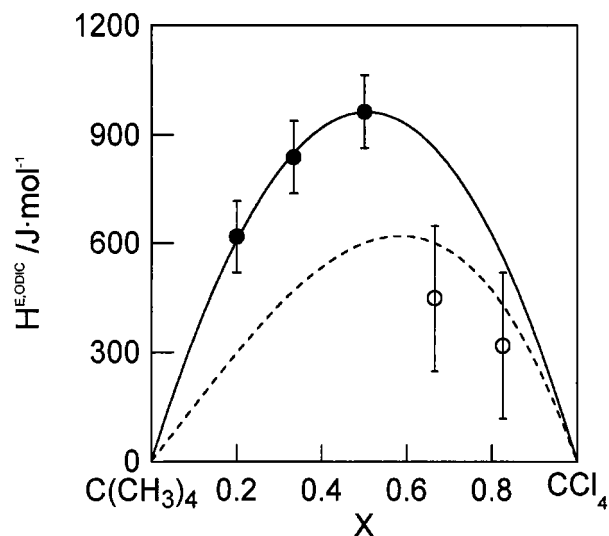


FIG. 4. Calculated values of the excess enthalpy for the ODIC mixed states (\bullet , C_{F}) and (\circ , R). The solid and dashed lines are calculated following the quasi-subregular solution model.

state due to the incertitude for the enthalpy of melting of the metastable R form of $\text{C}(\text{CH}_3)_4$. For the C_{F} -ODIC state, the equimolar excess enthalpy is $964 \text{ J}\cdot\text{mol}^{-1}$. The value of the equimolar excess Gibbs energy read from Eq.[5] is $462 \text{ J}\cdot\text{mol}^{-1}$. The calculated excess entropy is $2.115 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, and thus, the compensation temperature calculated from these values is 456 K, certainly too far away from 630 K. It is essential to realize that in the two-component systems included in the class mentioned above, the intermolecular interactions by hydrogen bonds play an important role in the ODIC mixed state. Nevertheless, in the system $\text{CCl}_4 + \text{C}(\text{CH}_3)_4$ the intermolecular interactions by hydrogen bonds are completely absent, and possibly this is the cause of such a disagreement. Therefore, it would be reasonable to assume that the C_{F} -mixed ODIC state of the $\text{CCl}_4 + \text{C}(\text{CH}_3)_4$ is out of this class. Parameters A_1 and A_2 (gathered in Table 2) were deduced from Eqs. [5] and [9]. They provide, through Eq. [10], the excess enthalpy represented by a solid line in Fig. 4. The excellent agreement between the curve and the experimental values is a good indication of the validity of the performed analysis.

With regard to the R-ODIC state of the two-component system dealt with in this work, the available excess enthalpy

TABLE 2
Parameters A_1 , A_2 , and T_c (See Eq. [9], for both C_{F} - and R-Mixed States

| | A_1 (J mol^{-1}) | A_2 | T_c (K) |
|----------------|-------------------------------|------------------|-----------|
| C_{F} | 3950 ± 416 | -0.11 ± 0.02 | 456 |
| R | 2675 ± 479 | -0.26 ± 0.21 | 503 |

data do not permit an accurated determination of the compensation temperature T_c . Nevertheless, at present, we dispose of excess thermodynamic data of the certainly related $C(CH_3)Cl_3 + CCl_4$ two-component system in its R-ODIC mixed state (40) for which the compensation temperature is determined to be 503 K. In addition, there are not too many differences in the intermolecular interactions with regard to the $CCl_4 + C(CH_3)_4$ two-component system. As a consequence, the same class, i.e., the same compensation temperature of 503 K for both systems in their R-ODIC mixed state, can be probably assumed. It is well worth noting that this result is close to the T_c value of the C_F -mixed crystals ($T_c = 456$ K), proving that in fact, C_F - and R-mixed crystals are not far away from a thermodynamic point of view. Following the same procedure as mentioned above, the parameters A_1 and A_2 , also consigned in Table 2, can be deduced from Eq. [6]. The corresponding excess enthalpy, taking into account Eq. [10], is represented by a dashed line in Fig. 4. The satisfactory agreement between the experimental data and the calculated curve reinforce the coherence of the followed assumptions.

An empirical estimation of the compensation temperature based on a large variety of mixtures: molecular, ionic, and metallic, can also be made, taking into account the equation

$$T_c = (4.00 + 0.16) \frac{T_{m_A} T_{m_B}}{T_{m_A} + T_{m_B}}, \quad [12]$$

in which T_{m_A} and T_{m_B} are the melting temperatures of the first and second pure components in the mixture (41). Let us be clear that for all the mixtures involved in Eq. [12], isomorphism was supposed to exist. It must be mentioned this is not the case for the system presented in this paper, so the empirical Eq. [12], must be used carefully. In particular, we have two different forms and two possible different compensation temperatures, and thus, the empirical Eq. [12] could be applied taking into account the stable and metastable melting temperatures. The values of 502 and 468 K have been obtained for both C_F - and R-mixed ODIC, respectively. These values not only are close to those calculated above but they are also close themselves. Moreover, it must be emphasised that for both ODIC mixed states, C_F and R, the compensation temperature is above the corresponding mean temperature, so they are located in the ordinary region of the $\log T_c - \log T_m$ representation (37).

4.2. The Calculated Phase Diagram

The results consigned in Table 2 together with Eqs. [7] and [8] have been used to calculate the complete phase diagram $C(CH_3)_4 + CCl_4$. This calculation has been performed by means of the ProPhase program (42). This calculation, together with the reinterpreted experimental

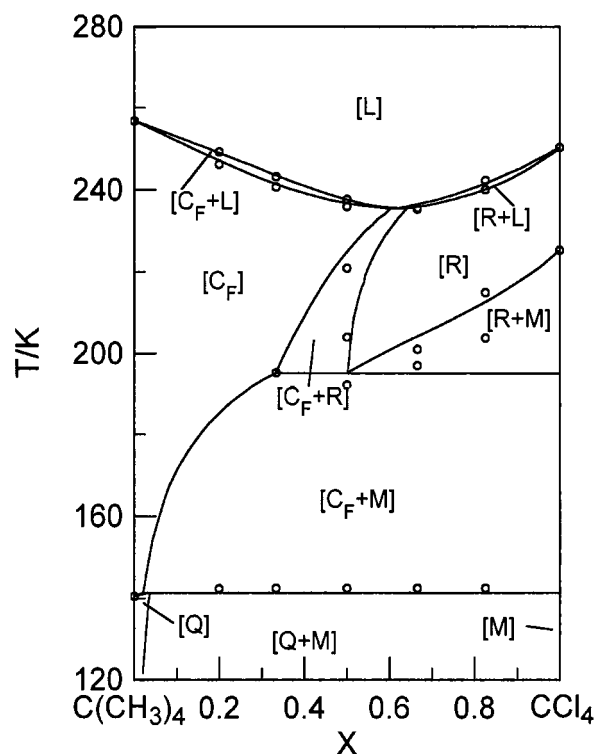


FIG. 5. Calculated phase diagram (solid line) and reinterpreted experimental temperature-composition data (○) (7).

temperature-composition data provided by Chang and Westrum (7), is shown in Fig. 5. As can be seen, the experimental data are quite well reproduced.

A comparison between the calculated and experimental values for the three-phase equilibria of the system is given in Table 3.

Finally, we point out two principal features of the two-component system dealt with in this work:

- This system is an excellent test for the isodimorphism concept for performing thermodynamic analysis in systems

TABLE 3
Experimental (E) and Calculated (C) Temperatures and Mole Fractions (X_M , X_N , X_P) Characterizing the Three-Phase Equilibria for the Two-Component System

| Invariant | T (K) | X_M | X_N | X_P |
|-------------|---------|---------------|---------------|-------------|
| Peritectoid | | | | |
| E | 142.5 | ≈ 0.1 | ≈ 0.1 | ≈ 1 |
| C | 141.2 | 0.02 | 0.03 | 1 |
| Eutectoid | | | | |
| E | 197.0 | 0.33 | 0.46 | 0.95 |
| C | 197.0 | 0.33 | 0.50 | 1 |
| Eutectic | | | | |
| E | — | — | — | — |
| C | 234.8 | 0.60 | 0.61 | 0.64 |

like this. In particular, the existence of experimental mixing properties and experimental data on metastable transitions is a less-common fact.

● The quasi-subregular solution model including a compensation law accounts for the excess thermodynamic properties. In particular, there exists a quite good agreement between the model excess enthalpy and the experimental one.

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