

Organic Compounds Possessing the Plastic Crystalline Phase: Calculation of Their Fusion Enthalpies

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Abstract

For the first time, for different organic and inorganic compounds possessing the plastic crystalline phase, a new semiempirical equation describing dependence of their fusion enthalpies on such physico-chemical quantities as normal melting temperature, surface tension, molar volume and critical molar volume is received on the base of the principle of corresponding states and the energy equipartition theorem. Moreover, the proposed equation allows one to take into account the particularities of one-particle molecular rotation in the plastic crystalline phase.

Keywords

Fusion Enthalpies Calculation, Organic Compounds, Inorganic Compounds, Plastic Crystalline Phases

1. Introduction

Many organic and inorganic compounds with globular molecules form so-called plastic crystals near their melting temperatures [1]. The definition of “globular” implies that either the molecules (or atoms) of these compounds have high symmetry (2,2-dimethylpropane, CH₄, SF₆, Kr, Xe) or when molecular rotation around one of the molecular axes of symmetry leads to some figure of rotation whose shape is close spherical (for instance, cyclopentane, cyclohexane, 2,2,3-trimethylbutane, PH₃, HCl). In addition, near the melting temperature, the plastic-crystalline phase of plastic crystals is characterized by orientational disorder in the direction of the axes of rotation of the molecules that form it, while long-range order is still preserved in the time-averaged location of the centers of mass of its

molecules [2]. Thus, the nature of the movement of molecules in plastic crystals is similar to the movement of molecules in liquids: their molecules oscillate around equilibrium positions due to interaction with neighboring molecules, and also rotate, however, maintaining the long-range order of their mutual arrangement, as in ordinary crystals.

It should be noted here that the characteristic of rotation of molecules in the plastic crystalline phase is determined primarily by the absolute temperature T of this phase, as well as the magnitude of the energy barriers caused by intermolecular interactions between neighboring particles [3]. If the temperature T is sufficiently high and the above energy barriers are small enough, then practically free rotation of the molecules of the plastic phase (around any of the three possible rotation axes for each molecule) takes place. The presence of the such free rotations leads to the lower values of the fusion enthalpies for the solid chemical compounds, existing in their plastic crystalline phase, than for compounds which do not have the given phase (see the work [3]). As the examples of the plastic-crystalline chemical compounds whose molecules have practically free rotation near their melting points, we can cite adamantane [4], octafluorocyclobutane [5], camphor [6]. However, a more common case of molecular motion in the plastic phase is the situation when the magnitude of the energy barriers that must be overcome to realize free rotation slightly exceeds the time-averaged value of thermal kinetic energy for each rotational degree of freedom of any molecules of the plastic phase under consideration. In this case, the molecules of the plastic phase under consideration undergo librational movements, which, due to fluctuations in kinetic energy caused by intermolecular interactions, can lead to their sudden spatial reorientation (molecular tumbling) and, accordingly, to their orientational disorder. So, for example, a study of the plastic crystalline phase of sulfur hexafluoride (see [7]) has shown that the average one-particle isotropic librational angle is equal to 14° . Obviously, the closer the absolute temperature T of the plastic phase is to the melting temperature of the compound under study, the more often such jumps (tumbings) occur. Upon reaching the appropriate melting temperature, these molecular jumps transform into free one-particle rotations in the bulk of the corresponding liquid phase. So, for instance, for tetramethylsilane, cyclohexane, cyclopentane, and 2,3-dimethylpropane, the values of the energy barriers (required for molecular tumbling in their plastic crystalline phases) are equal to 30.36, 9.63, 4.19 and 3.68 kJ/mol respectively [8]-[10].

Here it is to be noted that most often plastic crystals have cubic crystalline structures [11]. Also the plastic crystalline phase can appear in the case when non-globular or elongated molecules possess degrees of rotational freedom about a preferred axis. Then the free rotation around this axis may be excited in crystals while still retaining three-dimensional positional order. Such structures are called "hexagonal plastic crystals". For example, the such situation takes place for near melting solid phases of nitrogen and hydrogen (see [12] [13]). One can say that plastic crystals possess weak intermolecular interactions and are liquid-like. So,

the surface layer of the solid phase of hydrogen possesses the clear-cut quasi-liquid nature, when the molecules of this layer can take part in their translational motion, which realizes in the form of their molecular jumps [14].

Thus, taking into account the circumstances mentioned above, such as the proximity of the plastic crystalline phase of chemical compounds to their liquid one (considered at their corresponding melting points) and the small values of their fusion enthalpies ΔH , the aim of the present work is to find an equation relating ΔH to the physicochemical quantities of the liquid phase of these compounds, which arises as a result of the melting of their plastic-crystalline phase.

2. Theory

In order to find the sought equation for the quantity ΔH let us consider a system consisting of a mole of some chemical compound having a plastic crystalline phase. We shall also assume that, firstly, this phase is at its melting point; and, secondly, that the process of its melting is incomplete. In this case the system will contain both: its solid phase and its liquid one along with the interface between these two phases. Further, it was shown in the work [15] that for different liquids considered at their normal freezing points, their liquid phase contains the so-called “hot” (excited) molecules. Unlike the other molecules of the considered near-freezing liquid phase these “hot” molecules can move throughout the entire volume of the given phase. At the same time (see [15]) any of these “hot” molecules is situated and moves within some its spherical cavity (cage), whose radius is proportional to the quantity V_c (where V_c is the critical volume of the chemical compound under study. It was also shown in [15] that for one mole of any non-associated near-freezing liquid the total number N of such “hot” molecules can be defined by means of the following equations:

$$N = \xi N_A \quad (1)$$

where N_A is Avogadro's number, and the coefficient of proportionality ξ is defined as:

$$\xi = \exp(-g\sigma V^{2/3}/T) \quad (2)$$

In Equation (2) σ is surface tension of a liquid, V and T are, respectively, its molar volume and its freezing point, and ξ is the constant, whose numerical value is equal to 9.35×10^6 ($J^{-1} \cdot K \cdot mol^{2/3}$). The constant ξ does not depend on T or on the nature of the liquid phase [15].

It is to be noted here that the presence of these “hot” moving molecules in the above-mentioned cavities is the first (and the main) difference between the melt of the plastic crystalline phase and the corresponding solid plastic crystalline phase. The second difference is connected with the fact, that the considered “hot” molecules (unlike the molecules of the solid plastic crystalline phase) take part in their translational and free rotational motions within the limits of their one-particle spherical cavities. In their turn, all the molecules of the solid plastic crystalline phase take part only in their vibrational and librational motions. Nevertheless,

their librations can be accompanied with the corresponding (jump-like) one-particle reorientations, creating the orientational disorder, which is characteristic for the plastic crystalline phase.

Thus, bearing in mind all the above-mentioned, we shall consider that the process of the melting of the investigated plastic crystalline phase is being realized on the interface between the solid and liquid phases and is reduced to the appearance on this surface the above considered “hot” molecules. Then the newly formed “hot” molecules along with those molecules of this interface (which have kept their vibrational and librational motions) pass into the liquid phase. It is clear that the formation of any of these “hot” molecules requires both the conditions: the overcoming of the potential energy barriers, describing its three-dimensional vibrations (and librations) and the formation in the liquid phase (near the interface) the mentioned spherical cavities which will contain the “hot” molecules under study. Further, we shall consider only the liquid phase of the studied two-phases melting system. Obviously, during the process of the melting, the amount of the liquid phase will increase. Let, further, some number dN_i of the molecules have passed from the above-considered interface into the liquid phase. We can write the number dN_i as:

$$dN_i = dN_{1i} + dN_{2i} \quad (3)$$

Here dN_{1i} are dN_{2i} are, respectively, the number of the passed “hot” molecules and that of the vibrating ones (which have kept their vibrational motion by passing from the solid phase to the liquid one). Now we can write the following expression for the enthalpy changing dH_i which accompanies the above molecular passing of the number dN_i molecules:

$$dH_i = TdS_i + VdP + \mu_1 dN_{1i} + \mu_2 dN_{2i}. \quad (4)$$

In Equation (4) dS_i is the change (the differential) of the entropy of the considered liquid phase which is caused by the passing of the above dN_i molecules from the solid phase to the liquid one. The quantity V is the volume of the liquid phase under study; and P is the external (normal) atmospheric pressure ($P = \text{const} = 0.1 \text{ MPa}$). As P is constant, so the second term in Equation (4) is equal to zero. The chemical potentials μ_1 and μ_2 are, respectively, the one-particle chemical potentials of the “hot” molecules and the vibrating (see above) ones.

Since the one-particle chemical potential is equal to a certain amount of energy that must be spent in order to add one new molecule of a chemical compound to the system under study, we shall further consider the values of μ separately for “hot” and vibrating molecules which abandon the interface between the two phases and enter the liquid phase. Besides, the character of molecular motion of the vibrating molecules is not changed by the above passing, so, hereafter, we shall suppose that their transition into the considered liquid phase does not require any energy consumption; and therefore, the quantity μ_2 is equal to zero. Thus, we can rewrite Equation (4) in the form:

$$dH_i = TdS_i + \mu_1 dN_{1i}. \quad (5)$$

Considering that all the solid phase is transformed into the liquid one (the melting process is over) and bearing in mind that enthalpy and entropy are additive quantities, we can do the summation over the index i for all the quantities dH_i . Since the volume concentration of the “hot” molecules in the studied liquid phase remains constant, therefore we consider that the quantity μ_1 remains also constant. Then, for the total sum of all dH_i the following equation holds:

$$\Delta H = T\Delta S + \mu_1 N. \quad (6)$$

In Equation (6) ΔH and ΔS are, respectively, the molar fusion enthalpy and the molar fusion entropy which accompany the melting of the compound under study. Here we have also taken into account that the sum of dN_{li} equals to N , where the number N is being defined by means of Equations (1) and (2).

Now, we have to find the quantity μ_1 for the “hot” molecules which appear in the liquid phase during the investigated melting process. For this purpose, let us firstly define the average one-particle energy which is required for the formation in the liquid phase (near the interface) of the above mentioned one-particle spherical cavity. It was shown in the work [16] that the following equation holds for the radius R of this cavity:

$$R = (3V_c/4\pi N_A)^{1/3}. \quad (7)$$

In Equation (7) V_c is the molar critical volume of the chemical compound under study.

Then the internal surface area Q of the cavity will be $4\pi R^2$. As it was also shown in the work [16] the energy E required for the formation of such cavity is proportional to the given area Q and the quantity σ of the surface tension of the studied liquid phase. Thus, we can write the following equation for E :

$$E = \chi\sigma Q. \quad (8)$$

Further, basing on the results received in the works [15]-[17], in the present work we shall consider that the coefficient of proportionality χ between E and the product $\sigma \times Q$ does not depend on T and is constant for different near-freezing liquids. Now, using Equation (7), we can write the expression for E as:

$$E = \chi(36\pi)^{1/3} (N_A)^{-2/3} \sigma V_c^{2/3} = \varphi\sigma V_c^{2/3}. \quad (9)$$

In Equation (9) the coefficient of proportionality φ ($\varphi = \chi(36\pi)^{1/3} (N_A)^{-2/3}$) does depend on T and is constant for various near freezing liquids. However, the value of E defined by means of Equation (9) presents only some part of the total energy which is required for entering of one separate molecule from the solid phase into the liquid one. Really, for any considered molecule some additional one-particle energy is required for the overcoming of the potential energy barriers which are connected with its three oscillatory motions and one librational movement.

In the present work we shall suppose that all these motions are harmonic, *i.e.* the total energy of any of them can be described by means of the two corresponding quadratic terms. In this case (see [18]) the average one-particle kinetic energy

for any of the above-mentioned motions will be numerically equal to the corresponding potential well. Further, basing on the energy equipartition theorem, one can suppose (see [18] [19]) that for any of the given motions its kinetic energy equals to kT (where k is Boltzmann's constant, and T is the melting temperature). Therefore, for any of the molecules of the solid phase, the one-particle energy value required for the overcoming of all its potential energy barriers (in order to make it free and put it into its cavity) will be $4 kT$. However, there are a number of cases, when the value of the given one-particle energy is less than $4 kT$. First of all, it is about the melting of the solid plastic phase of the inert gases. Since the molecules of these gases are monatomic, so we can consider only their vibrational motions because their librational motion is absent. So, for these chemical compounds the above-mentioned one-particle energy value will be equal to $3 kT$. The similar situation takes place for the high-temperature melting of the chemical compounds, whose molecules have the practically free rotation in their solid plastic phase. For instance, it occurs for the melting of such compounds as adamantane or camphor (see the Introduction). Therefore, for the such compounds the above-mentioned one-particle energy value is also $3 kT$. Thus, hereafter, we shall consider that for any molecule passing from the solid phase into the liquid one, the thermal energy spent for this process is associated with overcoming four or three of its energy barriers and is equal to $4 kT$ or $3 kT$, respectively.

Further, using Equation (9), we can write the expression for μ_1 in the following final form:

$$\mu_1 = nkT + \varphi\sigma V_c^{2/3}. \quad (10)$$

In Equation (10) the number n is the coefficient at kT which may be equal to 3 or 4; it is the total number of overcome one-particle potential energy barriers related to one-particle vibrational and librational motions.

Here we have to clarify some details connected with involving of two boundary solid molecular layers into the corresponding liquid phase. Let the first of the above two layers coincide with the interface between two phases, and the second one be the corresponding solid neighboring layer. Obviously, there is some density gradient whose direction is normal to the interface and whose magnitude changes in time. Now we shall consider motion of the molecules in the second solid layer. If the density change of the first surface layer is small enough to affect one-particle vibrational movements in the second layer and at the same time it is sufficient to transform one of the one-particle librational modes into the corresponding free rotation of molecules belonging to this second layer, then these molecules will have also free rotation. That's why the number n for the molecules that initially did not have free rotation is equal to four.

Now we have to define the quantity ΔS entering Equation (6). It can be done basing on the following reasons. First of all, it should be noted that for the studied liquid system, *i.e.* one mole of some chemical compound at its freezing point, not all N_A molecules belong to the above near-freezing liquid phase. Really, it was shown in the works [20] [21] that the molecular layers situated near the surface of

the given liquid form the so-called quasi-crystalline phase. This phase contains only vibrating molecules [20]-[22]. The thickness of this phase equals to zero at the corresponding critical temperature of the studied compound. At the same time, the thickness of the considered phase reaches its maximum when T goes to the normal freezing point of the compound.

Further we can note that the real liquid phase includes only some number N_L molecules (but not all the N_A ones). Hereafter, basing on the principle of the corresponding states, we shall suppose that the number N_L equals to $\varkappa N_A$, where the coefficient \varkappa does not depend on the nature of a liquid. Thus, among the above N_L molecules there are the number $\xi \varkappa N_A$ of the “hot” molecules (see Equations (1) and (2)) and the number $(\varkappa N_A - \xi \varkappa N_A)$ of the vibrating ones.

Nevertheless, the spatial positions for all the NL molecules remain practically the same as they were in the corresponding solid phase. Even for the above considered “hot” molecules their time-average positions remain in the centers of their molecular cavities (cages). Here it is to be noted, that the results of the work [23] indicate that the maximum possible displacements, describing one-particle jumps of the “hot” molecules within their cavities are essentially less than average intermolecular distances. Further, as it was found in [24], the molecular structure of any liquid phase (taken near its normal freezing point) can be considered as some lattice system, which is constructed from the two sub-lattices: the first is formed by the vibrating molecules, and the second includes the above “hot” ones. Moreover, the vibrating molecules are being transformed into the new “hot” ones after passing of some impulse from the former “hot” molecules, which, obviously, become the newly formed vibrating ones (see [24]). It means that we can suppose that there is some movement of one-particle molecular cavities (whose number equals ξN_L or $\xi \varkappa N_A$ and any of these cavities is occupied only by one molecule) involving all the NL molecules. In the other words, the given cavities may be considered as some quasi-particles, which can move through the studied bulk liquid phase. Then the new microstates of the investigated liquid system will arise due to the movement of these cavities among the N_L knots of the two above mentioned sub-lattices.

Now we can write the following expression for the thermodynamic probability W , describing the macro-state of the system:

$$W = \prod [N_L - i + 1] = \prod [\varkappa N_A - i + 1]. \quad (11)$$

Here the symbol Π denotes the product of the corresponding multipliers, whose index i changes from 1 up to $\xi \varkappa N_A$. Using Equation (1), Equation (11) can be also rewritten in the following form:

$$W = N_L! / (N_L - \xi \varkappa N_A)! = (\varkappa N_A)! / (\varkappa N_A - \xi \varkappa N_A)! \quad (12)$$

Here the symbol “!” means the corresponding factorial. Now, considering that in the solid state there are none of the above-considered one-particle cavities, including the “hot” molecules, and using the well-known Boltzmann’s entropy formula ($S = k \ln W$) we can write the following equation for the quantity ΔS :

$$\Delta S = S_L - S_S = S_L = k \ln \left[\frac{(z N_A)!}{(z N_A - \xi z N_A)!} \right] \quad (13)$$

In Equation (13) S_L and S_S are, respectively, the entropy values connected with distribution of the above one-particle cavities in the liquid and solid phases of the system under study. Further, using Stirling's formula, one can easily show that:

$$\Delta S = k \xi z N_A \ln(z N_A / e) = \xi z R \ln(z N_A / e). \quad (14)$$

Here the product of the constants k and N_A is denoted as R (R is the universal gas constant), and e is the base of the natural logarithm. Denoting $z R \ln(z N_A / e)$ as δ , we receive the simple final expression for ΔS :

$$\Delta S = \delta \xi. \quad (15)$$

In Equation (15) the coefficient of proportionality δ does not depend on temperature and is constant for various near-freezing liquids.

Now, uniting Equations (6), (10), (15) and bearing in mind that $N = \xi \cdot N_A$ (see Equation (1)), we can write for the quantity ΔH the following final equation:

$$\Delta H = \xi \left(nRT + \psi \sigma V_c^{2/3} + \delta T \right). \quad (16)$$

Here the quantity ξ is defined by means of Equation (2) and the constant ψ (which does not depend on T and on the chemical nature of the melting plastic crystalline phase under study) equals to $\varphi \cdot N_A$.

3. Results and Discussion

The practical usage of Equation (16) requires the numerical values of the constants ψ and δ . In order to determine their values, the six chemical compounds presented in **Table 1** were considered at their normal freezing points T . The values of V_∞ , V_c , and σ for these compounds were taken from [25]-[32].

Table 1. To the definition of the constants ψ and δ in Equation (16).

No	Compound:	n	$T(K)$	$V \times 10^6$ (m ³ /mol)	$V_c \times 10^6$ (m ³ /mol)	$\sigma \times 10^3$ (N/m)	ΔH (kJ/mol)	
							Exp.	Calc.
1	Argon	3	83.78	27.97	75.26	13.39	1.178	1.173
2	Nitrogen	3	63.15	32.20	89.47	11.15	0.723	0.722
3	Hexafluoroethane	4	173.15	81.8	224	14.06	2.69	2.69
4	Arsine	4	157.15	43.69	128	32.20	1.1962	1.1962
5	2-Chloro-2-methylpropane	4	247.15	116.0	295	24.82	2.01	2.02
6	Tetramethylsilane	4	165.92	113.9	361	23.59	0.705	0.711

It should be noted that the compounds given in **Table 1** were chosen for the following reasons: firstly, they are well studied experimentally and, secondly, they have various chemical structures, which differ significantly. A part of them belongs to organic compounds, another one is presented by inorganic substances.

For nitrogen the number n equals to 3. It follows from the experimental fact that for the high-temperature β -phase of solid nitrogen (near its melting point) the reorientation motion of its molecules becomes practically free (see [33]).

Further, the numerical values of the constants ψ and δ were defined by means of the multiple regression analysis applied to the data set of **Table 1**. The found values of ψ and δ are equal to 7.7035×10^7 (J/mol) and 8.6087 (J/[mol·K]), respectively. The results of the usage of Eq. (16) with the above found values of ψ and δ are presents in **Table 2** for the large number of various organic and inorganic compounds. The experimental values of V_o , V , σ needed for these calculations were taken from the works [13] [15] [27]-[32] [34]-[53]. The comparison of the values ΔH calculated by means of Equation (16) and the corresponding experimental ones [13] [15] [27]-[32] [34]-[53] shows that this equation describes the fusion enthalpies of all the studied compounds adequately. Here it should be noted that the numbers n equal to 3 for the following cases. Firstly, for the compounds, whose molecules rotate practically free within their high-temperature solid plastic phases considered near their normal melting points (see the Introduction) and, secondly, for the mono-atomic inert gases. The rest compounds of **Table 2** have $n = 4$. The only exception is hydrogen, which has $n = 2$. It is due to the mentioned in the Introduction fact that the solid phase of hydrogen (which is near the interface between its solid and liquid phases) can be considered as some quasi-liquid phase [14]. The molecules, belonging to this phase, have both the types of their molecular motion, namely, the free rotation and the one-dimensional molecular jumps. It means, that for any of these molecules one of its three vibrational potential barriers has been overcome. Thus, for hydrogen the number n is equal to two.

Table 2. To the calculation of ΔH by means of Equation (16).

No	Compound:	n	$T(K)$	$V \times 10^6$ (m ³ /mol)	$V_c \times 10^6$ (m ³ /mol)	$\sigma \times 10^3$ (N/m)	ΔH (kJ/mol)		
							Exp.	Calc.	LOOCV
1	Adamantane	3	541	166.8	458	9.41	13.80	13.72	12.95
2	(d,l)-Camphor	3	451.6	183.9	503	19.38	6.79	6.72	6.66
3	Norbornene	3	315.15	120.3	314.4	22.13	3.54	3.73	3.73
4	Octafluorocyclobutane	3	231.75	116.0	325	16.49	2.77	2.83	2.84
5	2-Methyl-2-butanol	3	261.15	105.5	319	28.15	2.24	2.22	2.02
6	Acetylene	4	192.15	42.08	113.2	19.11	3.760	3.730	3.68
7	Methane	4	90.67	35.6	99.5	17.78	0.939	0.926	0.938
8	Camphene	4	317.6	161.8	482	25.57	2.7	2.7	2.8
9	2,2,3-Trimethylbutane	4	248.57	137.2	398	22.27	2.20	2.12	2.16
10	2,2-Dimethylpropane	4	256.58	114.4	307	15.11	4.370	4.382	4.349

Continued

11	Cyclobutane	4	182.4	71.5	210	30.0	1.090	1.117	1.154
12	Cyclopentane	4	179.7	80.2	260	37.0	0.57	0.53	0.55
13	Cyclohexane	4	279.4	106.4	308	27.23	2.73	2.75	2.79
14	Cycloheptane	4	265.15	116.7	390	30.5	1.88	1.81	1.86
15	Carbon monoxide	4	68.13	32.7	92.17	12.45	0.8386	0.8381	0.8440
16	Helium	3	1.76	27.53	57.53	0.317	0.021	0.021	0.020
17	Neon	3	24.55	16.17	41.8	5.68	0.339	0.339	0.336
18	Krypton	3	115.78	34.13	92.3	16.10	1.634	1.634	1.624
19	Xenon	3	161.35	44.28	119.4	18.7	2.29	2.29	2.28
20	Radon	3	202.15	50.45	139	23.0	2.7	2.7	2.69
21	Hydrogen chloride	4	158.97	28.5	87.6	32.1	1.993	1.981	2.000
22	Hydrogen bromide	4	185.15	36.3	100	29.42	2.408	2.478	2.489
23	Hydrogen iodide	4	222.50	48.2	130.0	29.9	2.873	2.883	2.894
24	Hydrogen sulfide	4	187.61	34.8	99.7	32.4	2.3781	2.3650	2.3804
25	Hydrogen selenide	4	207.43	39.6	115	33.38	2.5167	2.5708	2.5932
26	Phosphine	4	139.41	41.7	113.3	28.1	1.13	1.13	1.15
27	Sulfur hexafluoride	4	222.65	79.0	200.4	11.67	5.02	5.03	4.91
28	Rhenium hexafluoride	4	291.65	86.7	230	22.48	4.60	4.56	4.54
29	Hydrogen	2	13.96	26.11	63.8	3.02	0.117	0.117	0.123

The values of ΔH calculated by means of Equation (16) are given in **Table 2** along with the values of ΔH obtained by the so-called “Leave-one-out” Cross-Validation Scheme (LOOCV). The given statistical method consists in consequent removal of one of the studied compounds from the regression analysis and the following calculation of the predicted quantity for the removed compound. It can be seen that the values of the fusion enthalpies in the last two columns of **Table 2** are very close to each other and to the corresponding experimental ones.

It should be noted that the mechanism described above for the occurrence of one-particle free rotation at the interface in the presence of a density gradient normal to it can occur not only for molecular, but also for ionic crystals. So, for example, as the temperature increases, free rotation of ions can appear both in single-crystalline samples at the boundaries between ionic layers [54] and in polycrystalline samples [55] on the outer boundary surface of polycrystals (see [56], [57]). That is, in principle, an equation similar to Equation (16) can also hold for ionic plastic crystals.

4. Conclusion

The following conclusions can be drawn. Equation (16) allows one to perform the adequate calculation of the fusion enthalpy for various organic and inorganic compounds possessing the high-temperature plastic crystalline phase. The obtained equation may also be used to determine the possibility of free one-particle molecular rotations in the plastic crystalline phase for other substances with the same crystalline phase. In addition, our preliminary results indicate that the functional dependence similar to Equation (16) can hold also for organic compounds whose high-temperature crystalline phases differ from the plastic one.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

- [1] Das, S., Mondal, A. and Reddy, C.M. (2020) Harnessing Molecular Rotations in Plastic Crystals: A Holistic View for Crystal Engineering of Adaptive Soft Materials. *Chemical Society Reviews*, **49**, 8878-8896. <https://doi.org/10.1039/d0cs00475h>
- [2] Timmermans, J. (1961) Plastic Crystals: A Historical Review. *Journal of Physics and Chemistry of Solids*, **18**, 1-8. [https://doi.org/10.1016/0022-3697\(61\)90076-2](https://doi.org/10.1016/0022-3697(61)90076-2)
- [3] Rao, C.N.R. (1985) Molecular Motion in Plastic Crystals. *Proceedings of the Indian Academy of Sciences*, **94**, 181-199. <https://doi.org/10.1007/bf02841265>
- [4] Windsor, C.G., Saunderson, D.H., Sherwood, J.N., Taylor, D. and Pawley, G.S. (1978) Lattice Dynamics of Adamantane in the Disordered Phase. *Journal of Physics C: Solid State Physics*, **11**, 1741-1759. <https://doi.org/10.1088/0022-3719/11/9/013>
- [5] Szcześniak, E. and Brookeman, J.R. (1983) N.M.R. Study of Solid Perfluorocyclobutane. *Molecular Physics*, **48**, 1221-1228. <https://doi.org/10.1080/00268978300100871>
- [6] Rossiter, V. (1972) The Relative Permittivity Transition in Solid Camphor. *Journal of Physics C: Solid State Physics*, **5**, 1969-1975. <https://doi.org/10.1088/0022-3719/5/15/011>
- [7] Hohlwein, D. (1981) Numerical Structure Factor Calculation of Orientationally Disordered Molecules. *Acta Crystallographica Section A*, **37**, 899-903. <https://doi.org/10.1107/s0567739481001927>
- [8] Steenbergen, C. and de Graaf, L.A. (1979) Neutron Scattering Studies of the Solid Tetramethyl Compounds of Silicon, Germanium and Tin. *Physica B+C*, **96**, 15-26. [https://doi.org/10.1016/0378-4363\(79\)90096-2](https://doi.org/10.1016/0378-4363(79)90096-2)
- [9] de Graaf, L.A. (1969) Study of Molecular Motions in Cyclohexane and Cyclopentane by Cold-Neutron Scattering. *Physica*, **40**, 497-516. [https://doi.org/10.1016/0031-8914\(69\)90199-2](https://doi.org/10.1016/0031-8914(69)90199-2)
- [10] Lechner, R.E., Rowe, J.M., Sköld, K. and Rush, J.J. (1969) Study of Molecular Reorientation in Solid Neopentane by Quasielastic Neutron Scattering. *Chemical Physics Letters*, **4**, 444-448. [https://doi.org/10.1016/0009-2614\(69\)85008-6](https://doi.org/10.1016/0009-2614(69)85008-6)
- [11] Demus, D. (2001) Calamitic Liquid Crystals. In: Jürgen Buschow, K.H., Cahn, R.W., et al., Eds., *Encyclopedia of Materials: Science and Technology*, Elsevier, 880-887. <https://doi.org/10.1016/b0-08-043152-6/00168-6>
- [12] Scott, T.A. (1976) Solid and Liquid Nitrogen. *Physics Reports*, **27**, 89-157.

- [https://doi.org/10.1016/0370-1573\(76\)90032-6](https://doi.org/10.1016/0370-1573(76)90032-6)
- [13] Emsley, J. (1991) *The Elements*. Clarendon Press.
- [14] Maruyama, M., Bienfait, M., Liu, F.C., Liu, Y.M., Vilches, O.E. and Rieutord, F. (1993) Quasi-Liquid Molecular Layer at Solid Hydrogen Surfaces. *Surface Science*, **283**, 333-337. [https://doi.org/10.1016/0039-6028\(93\)90999-z](https://doi.org/10.1016/0039-6028(93)90999-z)
- [15] Gorbachev, M.Y. (2009) Semi-Empirical Relation between Freezing Point and Critical Point Properties of a Wide Variety of Molecular Liquids. *Physics and Chemistry of Liquids*, **47**, 188-194. <https://doi.org/10.1080/00319100701810222>
- [16] Gorbachev, M.Y. (1999) Influence of Some Physico-Chemical Characteristics of Non-Associated Liquids on Sound Velocity Therein. *Journal de Chimie Physique et de Physico-Chimie Biologique*, **96**, 923-933. <https://doi.org/10.1051/jcp:1999179>
- [17] Gorbachev, M.Y. (2003) Viscosity of Near-Boiling Nonassociated Liquids: Dependence on Surface Tension, Molecular Mass and Intramolecular Conformational Transitions. *Physics and Chemistry of Liquids*, **41**, 263-270. <https://doi.org/10.1080/0031910031000082057>
- [18] Moelwyn-Hughes, E.A. (1961) *Physical Chemistry*. Pergamon Press.
- [19] Gorbachev, M.Y. (2006) Thermal Kinetic Energy of Liquids with Conformationally Rigid Molecules. *Physics and Chemistry of Liquids*, **44**, 145-152. <https://doi.org/10.1080/00319100500424134>
- [20] Gorbachev, M.Y. (2001) Dependence of Surface Tension of Near-Boiling Non-Associated Liquids on Their Molar Volume and Some Critical Constants. *Physics and Chemistry of Liquids*, **39**, 315-325. <https://doi.org/10.1080/00319100108031665>
- [21] Gorbachev, M.Y. and Dimoglo, A.S. (2013) New Semiempirical Equation Describing Evaporation and Condensation in Nonassociated Liquids. *Journal of Chemistry*, **2013**, Article ID: 964091. <https://doi.org/10.1155/2013/964091>
- [22] Tong, J., de Bruyn, N., Alieva, A., Legge, E.J., Boyes, M., Song, X., *et al.* (2024) Crystallization of Molecular Layers Produced under Confinement onto a Surface. *Nature Communications*, **15**, Article No. 2015. <https://doi.org/10.1038/s41467-024-45900-0>
- [23] Dimitrov, V.I. (2006) Theory of Fluidity of Liquids, Glass Transition, and Melting. *Journal of Non-Crystalline Solids*, **352**, 216-231. <https://doi.org/10.1016/j.jnoncrysol.2005.11.026>
- [24] Peluso, F. (2023) How Does Heat Propagate in Liquids? *Liquids*, **3**, 92-117. <https://doi.org/10.3390/liquids3010009>
- [25] Cachadiña, I., Mulero, A. and Tian, J. (2015) Surface Tension of Refrigerants—Selection of Data and Recommended Correlations. *Journal of Physical and Chemical Reference Data*, **44**, Article 023104. <https://doi.org/10.1063/1.4921749>
- [26] Harada, M., Atake, T. and Chihara, H. (1977) Thermodynamic Properties of Polymorphic Phases of Tetramethylsilane. *The Journal of Chemical Thermodynamics*, **9**, 523-534. [https://doi.org/10.1016/0021-9614\(77\)90156-2](https://doi.org/10.1016/0021-9614(77)90156-2)
- [27] Dean, J.A. (1987) *Handbook of Organic Chemistry*. McGraw-Hill Book Company.
- [28] Morachevsky, A.G. and Sladkov, I.B. (1996) *Physicochemical Properties of Molecular Inorganic Compounds*.
- [29] Acree, W. and Chickos, J.S. (2016) Phase Transition Enthalpy Measurements of Organic and Organometallic Compounds. Sublimation, Vaporization and Fusion Enthalpies from 1880 to 2015. Part 1. C1–C10. *Journal of Physical and Chemical Reference Data*, **45**, Article 033101. <https://doi.org/10.1063/1.4948363>
- [30] Sprow, F.B. and Prausnitz, J.M. (1966) *Surface Tensions of Simple Liquids*.

- Transactions of the Faraday Society*, **62**, Article 1097.
<https://doi.org/10.1039/tf9666201097>
- [31] Bogdanov, S.N., Ivanov, O.P. and Kupriianova, A.V. (1976) Refrigeration Technology.
- [32] Yaws, C.L. (2008) Thermophysical Properties of Chemicals and Hydrocarbons. William Andrew Inc.
- [33] Pursky, O.I. (2015) Molecular Rotation and Volume Dependence of the Thermal Conductivity in Liquid N₂. *Journal of Physical Studies*, **19**, 3602-3605.
<https://doi.org/10.30970/jps.19.3602>
- [34] Dean, J.A. (1999) Lange's Handbook of Chemistry. McGraw-Hill Book Company.
- [35] Nikolsky, B.P. (1963) Chemist's Handbook.
- [36] Jasper, J.J. (1972) The Surface Tension of Pure Liquid Compounds. *Journal of Physical and Chemical Reference Data*, **1**, 841-1010. <https://doi.org/10.1063/1.3253106>
- [37] Mulero, A. and Cachadiña, I. (2014) Recommended Correlations for the Surface Tension of Several Fluids Included in the REFPROP Program. *Journal of Physical and Chemical Reference Data*, **43**, Article ID: 023104. <https://doi.org/10.1063/1.4878755>
- [38] Hyeon-Deuk, K. and Ando, K. (2015) Communication: Dynamical and Structural Analyses of Solid Hydrogen under Vapor Pressure. *The Journal of Chemical Physics*, **143**, Article ID: 171102. <https://doi.org/10.1063/1.4935509>
- [39] Poling, B.E., Prausnitz, J.M. and O'Connell, J.P. (2001) The Properties of Gases and Liquids. McGraw-Hill.
- [40] Gharagheizi, F., Eslamimanesh, A., Tirandazi, B., Mohammadi, A.H. and Richon, D. (2011) Handling a Very Large Data Set for Determination of Surface Tension of Chemical Compounds Using Quantitative Structure-Property Relationship Strategy. *Chemical Engineering Science*, **66**, 4991-5023.
<https://doi.org/10.1016/j.ces.2011.06.052>
- [41] Vogt, G.J. and Pitzer, K.S. (1976) Entropy and Heat Capacity of Methane; Spin-Species Conversion. *The Journal of Chemical Thermodynamics*, **8**, 1011-1031.
[https://doi.org/10.1016/0021-9614\(76\)90133-6](https://doi.org/10.1016/0021-9614(76)90133-6)
- [42] Leadbetter, A.J. and Thomas, H.E. (1965) Density and Surface Tension of Liquid Xenon and Theory of Corresponding States for the Inert Gases. *Transactions of the Faraday Society*, **61**, 10. <https://doi.org/10.1039/tf9656100010>
- [43] Singh, A.N., Dyre, J.C. and Pedersen, U.R. (2021) Solid-Liquid Coexistence of Neon, Argon, Krypton, and Xenon Studied by Simulations. *The Journal of Chemical Physics*, **154**, Article 134501. <https://doi.org/10.1063/5.0045398>
- [44] Marcus, Y. (2016) Solubility Parameters of Permanent Gases. *Journal of Chemistry*, **2016**, 1-18. <https://doi.org/10.1155/2016/4701919>
- [45] Tong, B., Tan, Z. and Wang, S. (2008) Low Temperature Heat Capacities and Thermodynamic Properties of 2-Methyl-2-Butanol. *Chinese Journal of Chemistry*, **26**, 1561-1566. <https://doi.org/10.1002/cjoc.200890282>
- [46] Rietveld, I.B., Barrio, M., Veglio, N., Espeau, P., Tamarit, J.L. and Céolin, R. (2010) Temperature and Composition-Dependent Properties of the Two-Component System D- and L-Camphor at 'ordinary' Pressure. *Thermochimica Acta*, **511**, 43-50.
<https://doi.org/10.1016/j.tca.2010.07.023>
- [47] Donnelly, R.J. and Barenghi, C.F. (1998) The Observed Properties of Liquid Helium at the Saturated Vapor Pressure. *Journal of Physical and Chemical Reference Data*, **27**, 1217-1274. <https://doi.org/10.1063/1.556028>

- [48] Vybyvanets, V.I., Kosukhin, A.V., Cherenkov, A.V. and Shilkin, G.S. (2016) Production and Investigation into Properties of High-Pure Rhenium Fluorides. *IOP Conference Series: Materials Science and Engineering*, **112**, Article 012042. <https://doi.org/10.1088/1757-899x/112/1/012042>
- [49] Montaña, D., Bandrés, I., Ballesteros, L.M., Lafuente, C. and Royo, F.M. (2011) Study of the Surface Tensions of Binary Mixtures of Isomeric Chlorobutanes with Methyl Tert-Butyl Ether. *Journal of Solution Chemistry*, **40**, 1173-1186. <https://doi.org/10.1007/s10953-011-9717-z>
- [50] Lebedev, B., Smirnova, N., Kiparisova, Y. and Makovetsky, K. (1992) Thermodynamics of Norbornene, of Its Polymerization Process and of Polynorbornene from 0 to 400 K at Standard Pressure. *Die Makromolekulare Chemie*, **193**, 1399-1411. <https://doi.org/10.1002/macp.1992.021930616>
- [51] Rathjens, G.W. and Gwinn, W.D. (1953) Heat Capacities and Entropy of Cyclobutane. *Journal of the American Chemical Society*, **75**, 5629-5633. <https://doi.org/10.1021/ja01118a047>
- [52] Aston, J.G., Fink, H.L., Tooke, J.W. and Cines, M.R. (1947) Melting Point Calorimeter for Purity Determinations. *Analytical Chemistry*, **19**, 218-221. <https://doi.org/10.1021/ac60004a002>
- [53] Rabinovich, V.A. and Khavin, Z.Ja. (1978) Kratkiy Himicheskiy Spravochnik. Khimija. <https://archive.org/details/kratkiy-himich-spravochnik-1978/mode/2up>
- [54] Hannachi, N., Elwej, R., Roisnel, T. and Hlel, F. (2023) Effect of Changing Anion on the Crystalline Structure, Crystal Structure, Hirschfeld Surface, IR and NMR Spectroscopy of Organic Salts and Hybrid Compounds: $C_6H_4(NH_3)_2Cl_2$ (I), β - $[C_6H_{10}N_2]_2ZnCl_4$ (II), Respectively. *Open Journal of Inorganic Chemistry*, **13**, 1-24.
- [55] Oh, M., Yoon, Y., Moon, D. and Jang, E. (2021) Effect of Improving the Slip Properties of the Organic Materials on the Inorganic Filler in Heat Dissipated Pad. *Materials Sciences and Applications*, **12**, 595-602. <https://doi.org/10.4236/msa.2021.1212039>
- [56] Nishikawa, K., Fujii, K., Yamada, T., Yoshizawa-Fujita, M. and Matsumoto, K. (2022) Free Ionic Rotators on Crystal Lattice Points—Structures of Ionic Plastic Crystals. *Chemical Physics Letters*, **803**, Article 139771. <https://doi.org/10.1016/j.cplett.2022.139771>
- [57] Heuer, A.H. (2008) Oxygen and Aluminum Diffusion in α - Al_2O_3 : How Much Do We Really Understand? *Journal of the European Ceramic Society*, **28**, 1495-1507. <https://doi.org/10.1016/j.jeurceramsoc.2007.12.020>