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Boiling point of tetrahalomethanes

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Abstract

The plot of the boiling points of tetrahalomethanes versus the number of electrons in a molecule shows that the change in the boiling point on replacing one halogen atom with another is constant regardless of the molecular structure. A comparison of the same plot for noble gas molecules shows that the contribution of each halogen atom in a molecule to the intermolecular interaction is comparable with that of the nearest noble gas atom. This suggests that the whole intermolecular potential of tetrahalomethanes is dominated by noble gas-type dispersion interactions. The effects of molecular and liquid structures, and polar interactions seem to be negligible.

Keywords: Boiling point; Tetrahalomethanes; Noble gas molecules; Intermolecular potential; Dispersion interactions; Polar interactions

1. Introduction

It is well known that there is a strong correlation between the boiling point and the molecular structure. Anderson [1,2] derived a useful equation for the estimation of the boiling point of haloalkanes using Kinney's original work [3]. Shigaki et al. [4] developed a more sophisticated equation. These studies are based on the idea that the same atomic group contributes the same amount towards the boiling point. Situations are often encountered where a knowledge of the approximate boiling points of a wide variety of substances is required. In such circumstances it is time-saving to use empirical equations of this kind. In order to extend the equation to broad classes of substances, a study focusing on how the molecular properties affect the boiling point could give important information.

On the basis of the London formula for dispersion interaction [5], Myers [6] showed that the boiling points of spherical, cylindrical and flat molecules follow different equations. Recently, Van der Puy [7] reported a boiling point estimation method for perfluoroalkanes using a similar method. These studies focused on non-polar molecules, and hence could avoid complications due to polar interactions.

In the present paper, the relation between tetrahalomethanes and noble gases is shown via the plot of the boiling point versus the number of electrons in a molecule. The contribution of a halogen atom to the boiling point is comparable to that of the corresponding noble gas atom, regardless of whether the molecule has a permanent dipole or not. An explanation for this behavior is given on the basis of a theoretical approach for the dispersion interaction.

2. Molecular properties of tetrahalomethanes

Molecular data for tetrahalomethanes are listed in Table 1, as well as those for noble gas molecules. The entropy of evaporation ΔS was calculated from the relations $\Delta S = \Delta H / T_b$, where ΔH and T_b are the enthalpy of evaporation and the boiling point, respectively. The permanent dipole moment D is also listed in Table 1 for the later discussion of polar interactions. The refractive index n_D at the sodium D line wavelength and the density ρ are also listed in the table for later reference.

In Fig. 1, the boiling point is plotted a a function of the number of electrons in a molecule. A similar plot can be obtained by choosing the molecular weight as the abscissa. The number of electrons has been chosen because the electronic structure is directly responsible for most physicochemical properties of molecules and their assembly. Fig. 1 illustrates that the change in the boiling point on replacing a certain halogen atom by another one is constant regardless to the molecular structure. The boiling points of noble gas molecules are also plotted in the same figure. The change from Ne to Ar results in an elevation of 60 K, which closely corresponds to the 55 K increase in the boiling point of $CBr_mCl_nF_{4-m-n}$ with unit increase of n. Similar behavior is observed for all halogen pairs, i.e., Cl–Br replacement results

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Table 1
The molecular constants of tetrahalomethanes [a]

Molecule	T_b (K)	n_D	ρ (g cm^{-3})	ΔH (kJ mol^{-1})	ΔS [b] (J mol^{-1} K^{-1})	D (debye)
CF_4	145.2			12.61	86.86	0.0
$CClF_3$	191.7			16.43	85.72	0.46
CCl_2F_2	243.4			20.45	84.01	0.51
CCl_3F	296.8	1.3838 (17 °C)	1.4995 (15 °C)	25.29	85.22	0.49
CCl_4	349.9	1.4574 (25 °C)	1.58445 (25 °C)	30.04	85.85	0.0
$CBrF_3$	216					0.65
$CBrClF_2$	269.9					
$CBrCl_2F$	326	1.4304 (20 °C)	1.93 (20 °C)			
$CBrCl_3$	376.9	1.5061 (20 °C)	2.012 (20 °C)			0.21
CBr_2F_2	296.1	1.4016 (15 °C)	2.31 (15 °C)			0.66
CBr_2ClF	353.5	1.4750 (20 °C)	2.3172 (20 °C)			
CBr_2Cl_2	408.2	1.5499 (25 °C)	2.40 (25 °C)			0.25
CBr_3F	381	1.5260 (20 °C)	2.76 (20 °C)			0.58
CBr_3Cl	432.2					0.2
CBr_4	463.2					0.0
CF_3I	251	1.3710 (−29.8 °C)	2.3608 (−32.5 °C)			1.0
$CClF_2I$	306					
CCl_2FI	362	1.5100 (20 °C)	2.3153 (20 °C)			
CCl_3I	414	1.5856 (20 °C)	2.3640 (20 °C)			
CF_2I_2	353					
Ne	27.3 [c]			1.796 [d]	65.79	
Ar	87.5 [c]			6.487 [d]	74.14	
Kr	120.9 [c]			9.016 [d]	74.57	
Xe	166.1 [c]			12.640 [d]	76.10	

[a] All data for tetrahalomethanes are from Ref. [8].
[b] Calculated from T_b and ΔH.
[c] Ref. [9].
[d] Ref. [10].

in a change in the boiling point which is as great as the boiling point difference between Ar and Kr, etc.

The entropy of evaporation data give almost the same value for all compounds for which data are available, whereas the data for the permanent dipole vary from molecule to molecule depending on the molecular structure.

3. Discussion

3.1. Overview of the boiling point behavior

The plot in Fig. 1 suggests that the intermolecular interaction in liquid tetrahalomethanes is likely to be explained on the same basis as noble gas liquids, because the contribution of a single halogen atom to the boiling point is closely related to that of the corresponding noble gas atom. This implies that dispersion interaction dominates over intermolecular interaction in tetrahalomethanes, as it does for noble gas atoms. This is surprising because, in terms of their molecular structure, it is possible for tetrahalomethanes to have other types of interaction. The permanent dipole of tetrahalomethanes can cause polar interactions. Moreover, the environment of halogen atoms can be different from that of noble gas atoms because of the steric effects of the molecules. It will be shown below that these effects can be negligible.

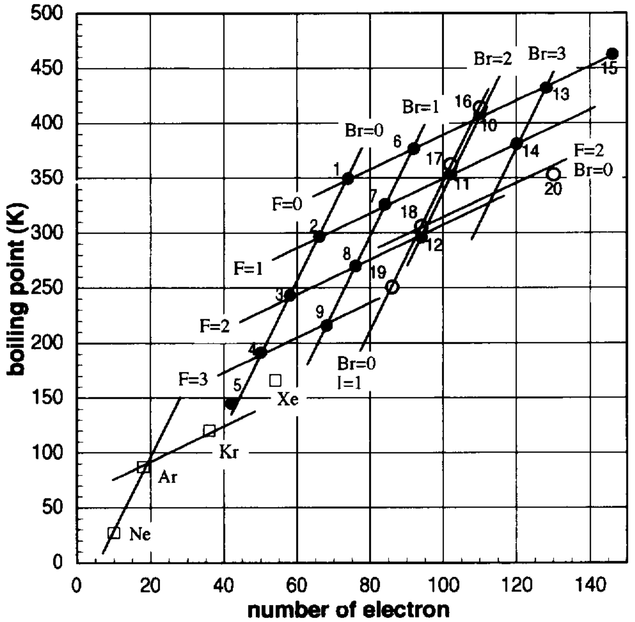

Fig. 1. Boiling points of tetrahalomethanes and noble gases plotted as a function of the total number of electrons in a molecule: ●, molecules containing no iodine; ○, molecules containing iodine; □, noble gases. The numbers on each plot indicate the following molecules: 1, CCl_4; 2, CCl_3F; 3, CCl_2F_2; 4, $CClF_3$; 5, CF_4; 6, $CBrCl_3$; 7, $CBrCl_2F$; 8, $CBrClF_2$; 9, $CBrF_3$; 10, CBr_2Cl_2; 11, CBr_2ClF; 12, CBr_2F_2; 13, CBr_3Cl; 14, CBr_3F; 15, CBr_4; 16, CCl_3I; 17, CCl_2FI; 18, $CClF_2I$; 19, CF_3I; 20, CF_2I_2.

The dispersion interaction between two atoms was originally formulated by London [5]. The formula successfully describes the interaction between noble gas atoms. However, it is not clear that the theory is applicable to tetrahalomethanes. The following points should be examined before concluding that a noble gas-type dispersion interaction determines the boiling point of tetrahalomethanes. (1) Is the boiling point accounted for only by the intermolecular interaction? (2) Is it possible to describe the dispersion interaction between polyatomic molecules by considering a molecule as a unit? If not, can the molecular interaction be interpreted by the summation of interactions between atoms in the neighboring molecules? Is the method consistent with the boiling point behavior of tetrahalomethanes? (3) From the viewpoint of atom–atom interactions, it is possible to describe theoretically the interaction between different halogen atoms. Is the boiling point behavior consistent with this theoretical estimation of the dispersion interaction? (4) Is the effect of polar interactions upon the boiling point negligible?

3.2. Trouton's rule

It is well known that the latent heat, or enthalpy of evaporation ΔH, divided by the boiling point T_b, i.e. the entropy of evaporation ΔS, is constant for non-associable liquids (Trouton's rule). Table 1 shows that this rule applies to the tetrahalomethane system, i.e., ΔS values calculated from ΔH and T_b are almost the same for all the tetrahalomethanes for which data are available. The fact that ΔS is independent of the molecular structure means that ΔH is proportional to T_b. Hence the boiling point can be used as a measure of the intermolecular interaction.

Although noble gas entropies are about 15% smaller than those of tetrahalomethanes, the difference is not so large as to affect the plot given below.

3.3. Myers' plot

Myers has derived the relation between the boiling point and molecular volume for molecules of different shapes [6]. The starting point for the derivation is the London formula [5] for the dispersion energy between two atoms, i.e.

$$E=\frac{3I\alpha^2}{4r^6} \qquad (1)$$

where I, r and α are the ionization potential, interatomic distance and polarizability, respectively. For spherical molecules [6]

$$T_b^{1/2} \propto R_m I^{1/2}/V_b \qquad (2)$$

where T_b, R_m, I and V_b are the normal boiling point, the molar polarizability, the ionization energy and the molar volume at the boiling point, respectively. The quantity R_m is calculated from n_D (refractive index at sodium D line) by the Lorentz–Lorentz relation and V_b may be obtained from ρ (density).

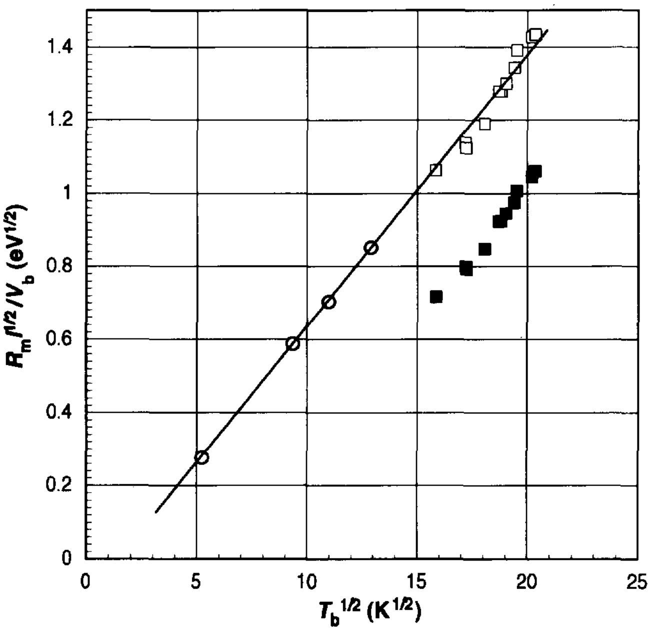

Fig. 2. The plot of Myers' equation for spherical molecules: ■, tetrahalomethanes; O, noble gases; □, tetrahalomethanes after subtracting a 'dead volume' from the molecular volume.

In Fig. 2, $R_m I^{1/2}/V_b$ is plotted against $T_b^{1/2}$. Two lines are observed, one of which is from noble gas molecules and the other is from tetrahalomethanes. This is also observed in Myers' original work, where noble gas molecules and tetrahydrides lie on the same line while tetrahalides lie on a different line. This means that the theory is not capable of providing a universal description for the interaction of spherical molecules. However, the deviation of the plot of tetrahalomethanes from the noble gas molecules in Fig. 2 can be corrected if the molecular volume is scaled by subtracting a certain amount of 'dead volume'. It is plausible that the 'dead volume' is due to the central part of a molecule which would not contribute to the intermolecular potential [11]. This implies that Eq. (1) is not a good approximation if the whole molecule is taken as an interaction unit. It seem rather better to formulate the intermolecular interaction as the summation of the interaction between atoms composing the molecule.

3.4. Viewpoint from atom–atom interaction

Calculation of the total interaction energy requires the number of interaction pairs in the system, which is related to the coordination number. Estimation of the coordination number in the liquid state is quite difficult since, in general, it is different from the crystalline state. An orientational variation in the molecular interaction also exists in a series of tetrahalomethanes, i.e., 'tail-to-tail' interaction gives a potential energy different from the 'head-to-tail' interaction. This supports the viewpoint that the dispersion interaction should be explained by the interaction between atoms.

The following consideration clarifies this argument. By analogy with Eq. (1), the dispersion energy between two

Table 2
The atomic constants of halogen and noble gas atoms

Atom	van der Waals radius [a], $r_{ii}/2$ (nm)	Atomic polarization [b], α_i (cm^3 mol^{-1})	Ionization energy [c], I_i (eV)	Dispersion energy, $E_{ii}=3I_i\alpha_i^2/4r_{ii}^6$ (eV)
F	0.147	0.557	17.4	0.017
Cl	0.175	2.18	13.0	0.070
Br	0.185	3.05	11.8	0.089
I	0.198	5.35	10.5	0.161
Ne	0.154	0.3956	21.6	0.008
Ar	0.188	1.6411	15.8	0.031
Kr	0.202	2.4844	14.0	0.041
Xe	0.216	4.044	12.1	0.063

[a] Ref. [13].
[b] Ref. [9].
[c] Ref. [14].

molecules is usually described by taking the whole molecule as a unit of the interaction as follows:

$$E=\frac{3I}{4r^6}\alpha_{\mathrm{mol}}^2=\frac{3I}{4r^6}\sum_i^{\mathrm{all}}\sum_j^{\mathrm{all}}\alpha_i\alpha_j \qquad (3)$$

where r is the intermolecular distance and α_{mol} and α_i are the molecular and atomic polarizabilities, respectively. In deriving this equation, the approximation that the molecular polarizability is close to the summation of the atomic polarizabilities is employed. On the other hand, the dispersion interaction between two atoms, i and j, may be written [5]:

$$E_{ij}=\frac{3}{2r_{ij}^6}\frac{I_iI_j}{I_i+I_j}\alpha_i\alpha_j \qquad (4)$$

where r_{ij} is the distance between atoms i and j, and I_i is the ionization potential of atom i. Since the intermolecular interaction E' is the summation of the interaction between the atoms in the molecules,

$$E'=\sum_{ij}E_{ij}=\frac{3}{2}\sum_{ij}\frac{1}{r_{ij}^6}\frac{I_iI_j}{I_i+I_j}\alpha_i\alpha_j \qquad (5)$$

Eqs. (3) and (5) are closely related. However, the distance is more properly defined by Eq. (5) because it is averaged out in Eq. (3). The distance r_{ij} largely depends on the position of the atom to be taken as a partner and, hence, on the liquid structure. Information regarding the effect of the liquid structure disappears in Eq. (3). This may explain why tetrahalomethanes do not lie on the same line as noble gas molecules unless a 'dead volume' is subtracted. This 'dead volume' may arise from the averaging process for the set of r_{ij} into r in Eq. (3). The above argument is in agreement with the success of the atom–atom potential method [12] for the estimation of the molecular interaction in solid state.

3.5. Interaction between different halogen atoms

If we assume that halogen atoms are randomly distributed in the liquid where no specific halogen–halogen pair is preferred, and also that the number of the interaction pairs is the same for all the tetrahalomethanes, the fact that the $CX_nY_{4-m-n}Z_m$ (X,Y,Z = halogen) molecules lie on the straight line defined by $CX_{4-m}Z_m$ and $CY_{4-m}Z_m$ (Fig. 1) indicates that the interaction between different atoms is the arithmetic mean of the interactions between the same atoms, i.e.,

$$E_{ij}\approx\frac{E_{ii}+E_{jj}}{2} \qquad (6)$$

It can be shown that Eq. (6) may be obtained via a simple calculation. Assuming that mechanisms other than dispersion interaction are negligible, and using Eq. (4), we obtain the relation among E_{ii}, E_{jj} and E_{ij}:

$$E_{ij}=\sqrt{E_{ii}E_{jj}} \qquad (7)$$

using the theorem that the arithmetic mean is close to the geometric mean when two quantities are comparable, i.e., $(I_i+I_j)/2=(I_iI_j)^{1/2}$ and $r_{ij}=(r_{ii}+r_{jj})/2=(r_{ii}r_{jj})^{1/2}$. Values of E_{ii} for halogen atoms are listed in Table 2. The values increase from F to I, the difference between F and I being 9.5-times. This means that the difference between the geometric and arithmetic means is at most 41%. Since the relative abundance of this specific interaction pair in all the interaction pairs is less than half, the contribution of this deviation from the linearity becomes much smaller than 41%, and hence E_{ij} in Eq. (6) would be a good approximation to that in Eq. (4). In Fig. 1 the effects of a replacement of F with I could not be examined because of the lack of data for iodides. If we exclude I from this consideration, the largest difference occurs between F and Br with 27% between the geometric and arithmetic means. In conclusion, the linear relation among the boiling points of $CX_{4-m}Z_m$, $CY_{4-m}Z_m$ and partially substituted tetrahalomethanes, $CX_nY_{4-m-n}Z_m$ shown in Fig. 1 is consistent with the theory of dispersion interaction.

Randomization of molecular orientations in the liquid state is important. In the solid state molecules are in a highly ordered state and they do not have the freedom to change their orientation. The lack of thermal averaging results in the preferred interaction pair of halogen atoms in each molecule and in the number of interaction pairs characteristic to each molecule. As a result, the melting points of molecular solids are strongly dependent on the crystal structure, and do not show the good correlation found with the boiling points.

3.6. Polar interactions

The boiling point data are well explained neglecting polar interactions. Assuming a molecular spacing of 6 Å and dipole moments of 0.5 D (see Table 1), the largest dipole–dipole interaction is 1.7 kJ mol^{-1}. If we assume, for example, a coordination number of six, the interaction becomes 5.1 kJ mol^{-1} which is not negligible compared with the enthalpy of evaporation listed in Table 1. However, it should be noted that it is comparable to the thermal energies ($RT_{298}=2.5$ kJ mol^{-1}). The thermal average of the dipole–dipole interaction is much smaller, especially at the boiling point. This may explain why there is no differentiation between molecules with and without permanent dipoles in the plot of boiling point versus the electron number.

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