Thermodynamic and Structural Properties of Molten CsCl as Obtained by Computer Simulation

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CsCl was computer simulated using the Monte Carlo (MC) method on the basis of interionic pair potentials. Calculations were carried out at constant pressure (1 atm) and at different temperatures covering the liquid phase. The thermodynamic and structural properties thus obtained were in good agreement with the corresponding experimental values when available.

A discussion of these properties in relation to those of CsBr and CsI was also carried out. Finally the polarization energy of CsCl along with those of CsBr and CsI, was compared with the results that can be obtained using simpler models recently proposed.

In previous work the structures of molten CsBr [1] and CsI [2] were computer simulated by the MC method on NPT ensembles at $P = 1$ atm. In order to obtain a more complete view of the properties of caesium halides, in the present work molten CsCl at $T = 1573$ (b.p.), 1173 and 919 (m.p.) K was studied. For comparison solid CsCl, at the m.p., was also simulated. The procedure of the computations and the methods for reducing the computer time were described previously [1]. The polarization energy of the system was computed separately, apart from the MC loop; to evaluate this energy, different methods which were recently proposed in literature have been used and compared.

Calculations

The interionic pair potential is assumed as:

$$\varphi_{ij}(r) = z_i z_j r^{-1} - c_{ij} r^{-6} + a_{ij} \exp(-b r) \qquad (1)$$

where r is the distance between ions i and j having charge z_i and z_j, c_{ij} is the van der Waals coefficient, a_{ij} and b are the parameters of the repulsive term which were previously calculated [3]. The values of these constants were: $|z_i z_j| = 2.3067 \cdot 10^{-11}$ erg Å; $a_{++} + a_{--} = 0.846 \cdot 10^{-8}$, $a_{+-} = 0.110 \cdot 10^{-8}$ erg, $b = 2.54$ Å^{-1} (see Ref. [3]); $c_{--} = 0.986 \cdot 10^{-10}$, $c_{+-} = 0.164 \cdot 10^{-9}$, $c_{++} = 0.512 \cdot 10^{-9}$ erg Å^6 (see Ref. [4]). On the basis of the Huggins model with Fumi-Tosi data [5] a ratio $a_{--}/a_{++} = 1/4$ was assumed. Within the MC chain the repulsive term was expressed as the inverse power function:

$$^{\mathrm{R}}\varphi_{ij} = a_{ij} r^{-b} . \qquad (2)$$

While equilibrating the system this function was periodically tested against the exponential one so that the difference in the total repulsive energy did not exceed 0.5%.

The repulsive potentials proposed by Spears [6] yielded, as in the case of CsBr, a strongly relaxed structure. These potentials were thus neglected.

The model and the computer programs used were the same as in [1].

Results

a) Thermodynamic Properties

The results obtained for the molar volume V, the internal energy U, and the coulomb $^{\mathrm{C}}E$, repulsive $^{\mathrm{R}}E$, van der Waals $^{\mathrm{W}}E$ and polarization $^{\mathrm{P}}E$ energies for the liquid at the examined temperatures and for the solid at the melting point are summarized in Table 1. The experimental values reported for the volumes are those by Johnson et al. [7] (solid) and by Yaffe and van Artsdalen [8] (liquid). The value at the boiling point was obtained by extrapolation. The agreement between V_{calc} and V_{exp} is always good except for the solid at the m.p. (-10%).

The values of U_{calc} were deduced from the mean configurational energy E by:

$$U = E + 3\,R\,T . \qquad (3)$$

The corresponding U_{exp} can be evaluated on the basis of the crystal energy of the solid at 298 K along with the molar heat capacity and the transition and fusion enthalpies [9]. In the previous study of CsBr and CsI, the U_{298}'s were taken from Cubicciotti's work [10]: the values thus obtained for the liquid deviated by about 3% from the calculated ones. Recently, Ladd [11] has reported data for U_{298}

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	at 1573 K (b.p.)	at 1178 K	liquid at 919 (m.p.)	solid at 919 (m.p.)
V_{calc}	78.4	66.0	60.2	48.3
V_{exp}	(80.4)*	67.0	60.3	54.2
U_{calc}	−135.6	−142.7	−147.2	−151.7
U_{exp}	−133.2	−141.0	−145.7	−150.7
${}^{\text{C}}E$	−159.5	−164.5	−167.5	−172.0
${}^{\text{R}}E$	27.6	29.7	31.0	32.9
${}^{\text{W}}E$	−13.1	−14.9	−16.2	−18.1
${}^{\text{P}}E$	−4.6	−3.9	−3.2	−2.3

Table 1. Thermodynamic properties of CsCl. The volumes are in cm^3 mole^{-1}, the energies in kcal mole^{-1} (* extrapolated value).

Table 2. Crystal energies of caesium halides in kcal mole^{-1}.

	Ref. 10	Ref. 11
CsCl	$U_{298} = -155.9$	−160.0
CsBr	$U_{298} = -151.1$	−153.4
CsI	$U_{298} = -143.7$	−145.3

the absolute values of which are by about 2 − 3% larger than those proposed by Cubicciotti. Table 2 reports these data. The U_{exp} values reported in Table 1 were calculated using Ladd's results: the deviations between U_{exp} and U_{calc} amount in this case to about 1%. Using Cubicciotti's value the difference would be about 4%: also in the case of CsBr and CsI the agreement between U_{calc} and U_{exp} largely improves by using the U_{298} values proposed by Ladd.

The heat of fusion deducible from Table 1 is 4.5 while the experimental one is 4.96[9] kcal mole^{-1}. The calculated heat capacity is 18 − 20 e.u. while literature reports a value varying from 17.8 to 20.6 in the same temperature range.

As regards the other quantities reported in Table 1 it should be noted that in the liquid at the m.p. the coulomb, repulsive and van der Waals energies are in the ratio:

$$100 : 18.5 : 9.7 .$$

The corresponding ratios for CsBr are:

$$100 : 19.9 : 11.7$$

and for CsI

$$100 : 21.4 : 13.5 .$$

b) Radial Distribution Functions

Figure 1 reports the RDF's of molten CsCl at 1573 and 919 K. The functions were obtained on the basis of the histograms of the ionic pair distances and are thus resolved into: RDF of like ions $g_{\text{l}}(r)$ $[=\frac{1}{2}(g_{--}+g_{++})]$, of unlike ions $g_{\text{u}}(r)$ $(=g_{+-})$ and of all ions $g_{\text{tot}}(r)$ $[\frac{1}{2}(g_{\text{u}}+g_{\text{l}})]$.

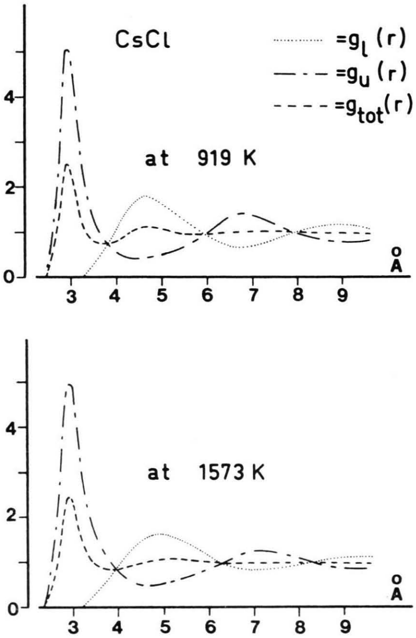

Fig. 1. Radial distribution functions of molten CsCl at the melting point (919 K) and at the boiling point (1573 K) for like ions (g_{l}), for unlike ions (g_{u}) and for all ions (g_{tot}).

Table 3 reports, as most significant features, the distance of minimum approach (d), the abscissa of the maximum of the main peak ($r^{\max}$) and that of the minimum following the main peak ($r^{\min}$) of the function $g(r)$ along with the coordination number (n). For like ions only the mean function $g_{\text{l}}(r)$ is reported since the two components g_{--} and g_{++} are very similar. The "penetration" of like ions into the first coordination sphere is significant: for liquid CsCl at m.p. there are 0.1 like ions on a total coordination of 3.6, at the b.p. there are 0.2 like ions on 3.2 total ions. Other features are similar to those of cases previously discussed.

Table 3. RDF features of molten CsCl (all distances in Å) (* of which 0.2 are like ions; ** of which 0.1 are like ions).

	at 1573 K	at 919 K
d_u	2.36	2.46
r_u^{max}	2.95	2.95
r_u^{min}	4.6	4.4
n_u	3.9	4.2
d_l	3.16	3.30
r_l^{max}	4.9	4.6
r_l^{min}	7.1	6.8
n_l	11.1	12.4
r_{tot}^{max}	2.95	2.95
r_{tot}^{min}	3.8	3.75
n_{tot}	3.2 *	3.6 **

Table 4. Comparison of the ^{P}E values as obtained by different methods, for molten caesium halides at the m.p. All values are in kcal mole^{-1}. Figures in brackets are cut distances in Å.

	CsCl	CsBr	CsI
^{P}E (no cut)	−3.2	−3.4	−3.2
^{P}E (cut at r_{tot}^{min})	−3.05 (3.75)	−3.3 (3.9)	−3.0 (4.10)
^{P}E with Eq. (5)	−9.8 (3.63)	−12.4 (3.84)	−10.0 (4.14)
^{P}E with Eq. (4)	−40.8 (3.63)	−48.6 (3.84)	−38.0 (4.14)

Levy et al.[12] reported, on the basis of X-ray diffraction studies, a first shell with 4.6 neighbors centered at 3.53 Å and a second shell of 7.1 neighbors centered at 4.87 Å.

c) Polarization Energy

The polarization energy ^{P}E has been evaluated, apart from the MC loop, on a single configuration every 5000 of the generated ones. The ionic polarizabilities used were:

$$\alpha_{Cs^+} = 2.94; \quad \alpha_{Cl^-} = 3.05 \text{ Å}^3$$

which are the averages of many values reported in the literature[13]. The method used to compute ^{P}E, fully described in Ref.[14], is based on the evaluation of the electrostatic field acting on each ion, as a result of the action of all other ions. The values obtained for CsCl are reported in Table 1.

Recently Michielsen and Woodcock[15] suggested that "the polarization energy consists almost entirely of contributions from the shortest distances between positive and negative ions". Following this suggestion, the electric field on each ion was also calculated assuming that only the first coordination sphere is responsible. In other words each ion was considered as interacting only with the ions within a distance less than or equal to r_{tot}^{min}. These calculations were carried out also for CsBr and CsI and showed that the approximation is good: an underestimation of about 5 − 10% is obtained. It was also observed that cuts at longer distances gave overestimation of ^{P}E. The obtained results are reported in Table 4.

To further discuss the problem, Rittner's equation, which gives the polarization energy for a two body system[16]:

$$^{P}\varphi_{ij} = -e^2(\alpha_+ + \alpha_-)/2\,r^4 \tag{4}$$

was taken into consideration.

This relation, which cannot be directly used for these ensembles with many body interactions, was semiempirically modified[15] to obtain the ^{P}E of the system on the basis of an effective pair potential: calculations are limited to the unlike ions up to a distance $r = 1.25\,r_0$ (r_0 = equilibrium distance of the ion pair in the gas phase). Beyond this distance the energy is zero. The proposed equation is:

$$^{P}\varphi_{ij} = -e^2\,\frac{\alpha_+ + \alpha_-}{2\,r^4}\left(1.5 - 1.2\,\frac{r}{r_0}\right). \tag{5}$$

Table 4 reports the results obtained for the caesium halides with Eq. (5) along with those given by the direct application of Eq. (4) within the same distance $1.25\,r_0$.

As expected, Eq. (4) gives erroneous predictions. The results are largely improved by Eq. (5), but they are not yet fully reliable. Even on a semiempirical basis, it is difficult to accept Eq. (5) since, according to this equation, the polarization energy of a system with a symmetrical charge distribution is not zero.

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