

Molar heat capacity measurement of CaHCl and CaHBr

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Abstract. Molar heat capacities of two hydride ion conductors, namely, CaHCl and CaHBr, were measured by differential scanning calorimetry. The measured molar heat capacity data of these compounds as a function of temperature is given by the following expressions:

$$C_p < \text{CaHCl} > (\text{J K}^{-1} \text{ mol}^{-1}) = 57.806 + 16.420 \times 10^{-3} \cdot T - 1.006 \times 10^6 \cdot T^{-2} \quad (308\text{--}748 \text{ K})$$
$$C_p < \text{CaHBr} > (\text{J K}^{-1} \text{ mol}^{-1}) = 56.534 + 44.880 \times 10^{-3} \cdot T - 1.481 \times 10^6 \cdot T^{-2} \quad (323\text{--}713 \text{ K})$$

From the above expressions, molar enthalpy increments, entropies and Gibbs energy functions of these compounds were derived and reported.

Keywords. Liquid sodium; hydrogen sensor; hydride ion conducting electrolyte; molar heat capacity; differential scanning calorimetry.

1. Introduction

Fast breeder reactors use liquid sodium as the heat transfer medium in both primary and secondary coolant circuits because of its favorable physical, chemical and nuclear properties.¹ At the steam generator module, liquid sodium and water are separated by ferritic tubes of 3 to 4 mm wall thickness for heat transfer. All possible care is taken to avoid direct contact between water and sodium as in the event of any micro-crack in the ferritic tubes, the high-temperature and high-pressure steam can leak into liquid sodium. As the reaction between sodium and water is highly exothermic, and the reaction products hydrogen and sodium hydroxide are explosive and caustic, respectively, would cause further damage. Hence, it should be detected at its inception stage for quick remedial action. It is a safety requirement for online monitoring hydrogen and oxygen concentration in liquid sodium to avoid this type of accidental condition.¹

A hydrogen sensor has been developed in the authors' laboratory to detect hydrogen concentration at ppb levels in liquid sodium. It is essentially a solid electrolyte based electrochemical concentration cell

for online monitoring of the concentration of hydrogen in liquid sodium. A mixture of alkaline earth hydrides along with alkaline earth halides is employed as the electrolyte for this purpose.²⁻⁴ CaCl₂-CaH₂³ and CaBr₂-CaH₂⁵ pseudo-binary systems were identified as thermodynamically stable systems for the development of such an electrolyte. In these systems, the compounds CaHCl and CaHBr are the hydride ion conductors. It is important to determine the thermodynamic data of these compounds. This paper reports the measurement of molar heat capacity data of CaHCl and CaHBr for the temperature range 308–748 K by using a differential scanning calorimeter.

2. Experimental

2.1 Preparation and characterization of samples

Most of the chemicals used in this work are air and moisture sensitive and hence were handled in argon atmosphere glove boxes. High purity inert atmosphere is maintained in the glove boxes using a liquid sodium tray which getters trace levels of oxygen and moisture (<1 ppm). CaHCl was prepared by heating a stoichiometric mixture of Ca and

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CaCl_2 in the hydrogen atmosphere. CaCl_2 (AR grade, M/s. ABCR, Germany) was purified by heating above its melting point and by bubbling argon gas saturated with HCl vapor in the molten salt. The experimental setup is shown schematically in Figure 1. Details of the purification procedure are described elsewhere.⁶ Commercial grade argon gas (>99.99%, Bhoruka Gases, India) was bubbled in HCl solution (37% solution, E. Merck, India) and subsequently through of P_2O_5 (>98%, RFCL India Pvt. Ltd., India) and CaCl_2 (>97%, Himedia Laboratories Pvt. Ltd., India) powders packed 'U' tube columns to remove the moisture. The dry HCl-argon gas mixture was bubbled in the molten CaCl_2 for 30 min. The outlet gas was then passed through several stages of CaCl_2 and P_2O_5 packed columns. These columns were provided at the outlet to eliminate the possibility of ingress of air/moisture through back suction. Finally, the gas was let out by passing through a NaOH (>97%, E. Merck, India) scrubber. The process was continued for another 30 min, with pure argon gas to remove any trace levels of HCl present in the melt. The quartz vessel assembly containing the crucible with purified salt was placed inside the transfer port of the argon atmosphere sodium glove box (oxygen and moisture content <1 ppm) with a flow of argon maintained through the vessel. During this transfer, the quartz vessel was at high temperature ($\sim 400^\circ\text{C}$). Argon flow through the vessel is then disconnected, and the

vessel was transferred inside the glove box after the usual evacuation steps. The salt was carefully separated from the quartz crucible inside the glove box and was stored inside a vessel, equipped with KF-coupling closure, as secondary containment. The purity of the prepared salt was ascertained from its melting point. About 20 mg of the sample was taken inside a thin walled 15 mm long iron crucible of 3 mm diameter and hermetically sealed using a pulsed arc welding unit in the glove box. The melting point was determined using the DTA equipment, SETSYS 16-18 Evolution (M/s. Setaram, France). Prior to the measurement, temperature calibration of DTA was carried out by measuring the melting points of high purity metal standards.

The purified CaCl_2 was mixed with the stoichiometric amount of calcium metal (99.5% pure, Johnson Matthey, Germany) and heated in a hydrogen atmosphere at 750°C for 120 h. The schematic of the experimental assembly is shown in Figure 2. A one end closed pure iron thimble with a thin-walled portion at the bottom welded to a stainless steel pipe, which in turn is welded to a knife-edged flange was used to hold Ca, CaCl_2 mixture and closed at the top. It was then placed over a knife-edged flanged stainless steel vessel with provision for flowing hydrogen gas and sealed using a copper gasket. The hydrogen gas diffused through the thin iron membrane. The calcium metal was first converted to CaH_2 in situ and reacted with CaCl_2 to produce CaHCl .

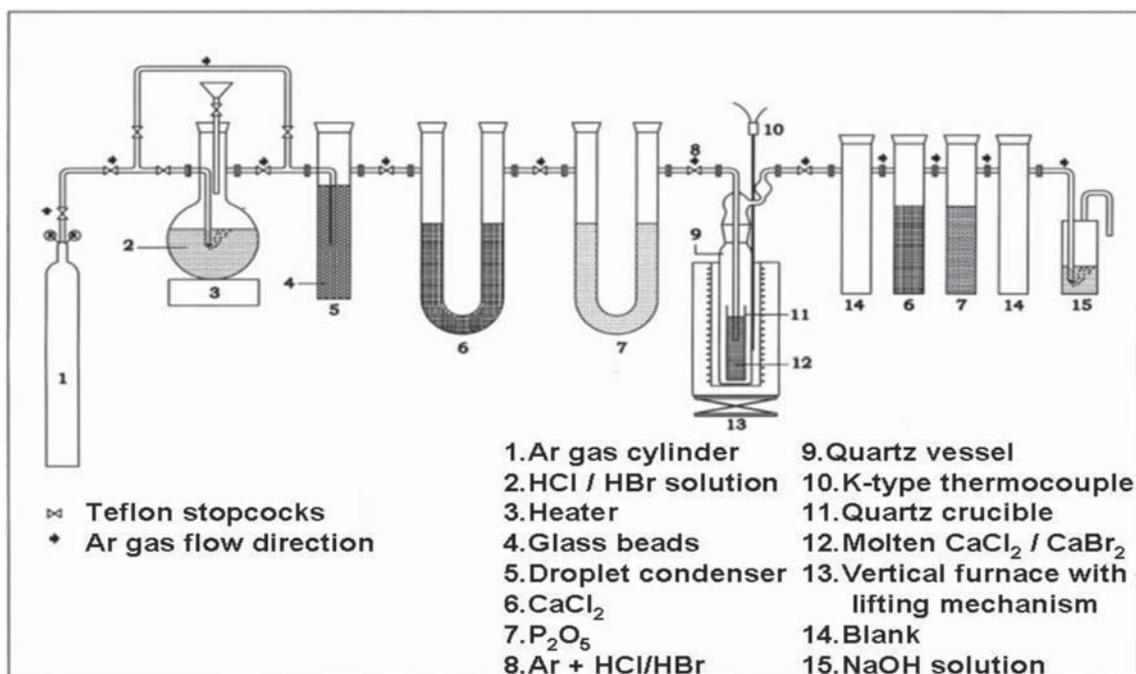


Figure 1. Schematic diagram of the salt purification setup.

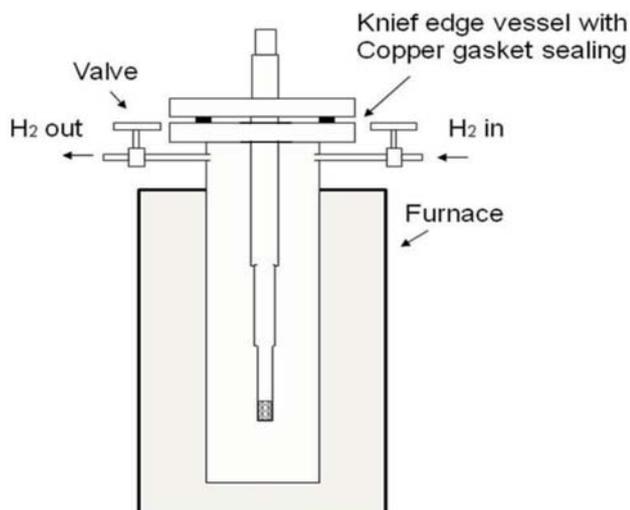
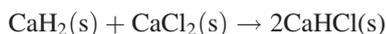
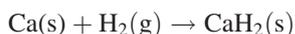


Figure 2. Arrangement used for the preparation of CaHCl.



CaHBr was also prepared by adopting a similar procedure followed for CaHCl preparation using purified CaBr₂. CaBr₂ was prepared by the reaction of CaCO₃ (>99.95%, M/s. Alfa Aesar, USA) with distilled HBr (47% solution, M/s. E. Merk, India). The CaBr₂ solution was heated over a hot plate and dried under flowing argon gas. It was then purified by heating it above its melting point in a quartz crucible placed in a quartz vessel in a stream of dry argon gas containing HBr.

The compounds prepared were analyzed by XRD (M/s Inel, France) using Cu K_α radiation. The XRD patterns of CaHCl and CaHBr were matched with the JCPDS files 04-08-3390 and 04-08-3393, respectively.⁷ These samples were pelletized, sintered and used for heat capacity measurements. To verify the performance of DSC, the molar heat capacity of ThO₂ was also determined. For this, ThO₂ powder (99.9% pure, Indian Rare Earths Ltd., India) was also pelletized, sintered at 1500 °C for 6 h and used.

2.2 Differential scanning calorimetry

The molar heat capacity of CaHCl and CaHBr were measured employing a differential scanning calorimeter (Model No. DSC827e, Mettler Toledo, Switzerland). Temperature calibration was carried out using high pure indium and zinc (0.99998 mass fraction purity, M/s. Impag AG, Switzerland) metals. The standard uncertainty in the measurement of temperature was determined to be ±0.4 K. The sintered pellets of CaHCl and CaHBr were sealed in 40 μl Al-pans.

The quantity of samples used varied from 25 to 40 mg. The samples were taken out of the glove box moment before loading into the instrument. DSC measurements were carried out in the temperature range of 308–748 K using 10 K min⁻¹ heating rate with 1% H₂-Ar gas mixture as a purge gas with a flow rate of 50 mL min⁻¹. A three-segment heating program was used in these measurements. The first segment was an isothermal segment for 5 min; the second segment was a heating segment with a heating rate of 10 K min⁻¹, and the final segment was an isothermal segment for 5 min. A more detailed experimental procedure is described elsewhere.⁸ A sapphire disc was used as the standard during heat capacity measurements. The proper functioning of the calorimeter was checked by the measurement of the molar heat capacity of ThO₂. Two pellets for each sample were studied, and an average of at least six reproducible measurements at each temperature from each sample pellet is reported. After the measurements, the samples were weighed and analyzed by XRD to ensure phase purity. The observed mass losses were less than 0.02% showing an insignificant loss due to vaporization.

3. Results and Discussion

3.1 Molar heat capacities of ThO₂

The molar heat capacity of ThO₂ was measured in the temperatures 333–753 K and shown in Figure 3. The relative standard deviations of the measurements are within 3%. The measured molar heat capacity values of ThO₂ as a function of temperature were fitted to the following polynomial expression:

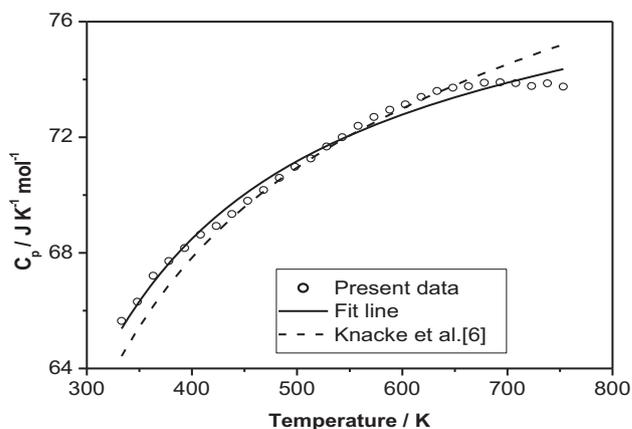


Figure 3. Molar heat Capacity of ThO₂.

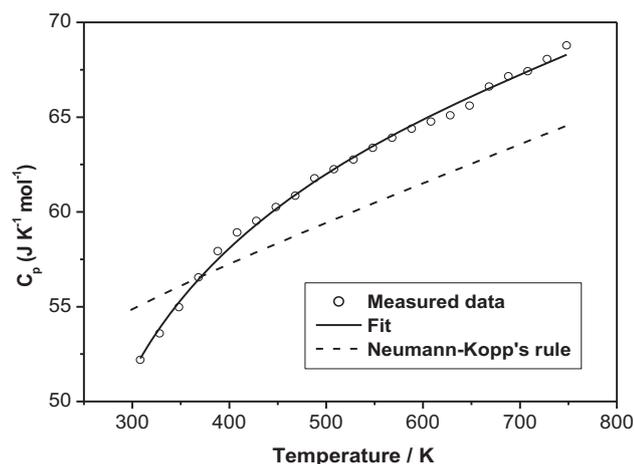


Figure 4. Molar heat capacity of CaHCl.

$$C_p < \text{ThO}_2 > \text{ (J K}^{-1}\text{mol}^{-1}\text{)}$$

$$= 73.671 + 3.360 \times 10^{-3} \cdot T - 1.044$$

$$\times 10^6 \cdot T^{-2} (333-753 \text{ K}) \quad (1)$$

The standard error of the fit is $\pm 0.29 \text{ J K}^{-1} \text{ mol}^{-1}$. The fitted polynomial curve is shown in Figure 3. The molar heat capacity data of ThO_2 from the compilations of Knacke *et al.*⁹ are also shown in Figure 3. The present data are in good agreement with the data reported by Knacke *et al.*⁹ and it is within $\pm 2.0\%$.

3.2 Molar heat capacities of CaHCl

The measured molar heat capacity data of CaHCl are shown in Figure 4 and given in Table 1. The relative standard deviations of the measurements are within 3%. The measured data of CaHCl were fitted to the following expression using the least-squares method:

$$C_p < \text{CaHCl} > \text{ (J K}^{-1}\text{mol}^{-1}\text{)}$$

$$= 57.806 + 16.420 \times 10^{-3} \cdot T - 1.006$$

$$\times 10^6 \cdot T^{-2} (308-748 \text{ K}) \quad (2)$$

The standard error of the fit is $\pm 0.27 \text{ J K}^{-1} \text{ mol}^{-1}$. The fitted curve is also shown in Figure 4. These data on the molar heat capacity of CaHCl are reported for the first time. The measured molar heat capacity of CaHCl is compared with the data computed by Neumann-Kopp's rule¹⁰ using molar heat capacity data of CaH_2 and CaCl_2 ⁹ in Figure 4. The discussion on the observed deviations is given in Sect. 3.4. No data are available in the literature for the S_{298}^0 value of CaHCl and it was estimated from $S_{298.15}^0$ values of CaCl_2 and CaH_2 , which were $108.370 \text{ J K}^{-1} \text{ mol}^{-1}$ and $41.999 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively.⁹ The $C_{p, 298.15\text{K}}$ value of CaHCl determined from the fit was 6.2% lower than the value estimated by invoking Neumann-Kopp's rule and using the corresponding values from the literature⁹ for CaCl_2 ($72.64 \text{ J K}^{-1} \text{ mol}^{-1}$) and CaH_2 ($37.00 \text{ J K}^{-1} \text{ mol}^{-1}$). Assuming that the $S_{298.15}^0$ value of CaHCl will also be 6.2% lower than the value derived from Neumann-Kopp's rule, it was deduced to be $71.3 \text{ J K}^{-1} \text{ mol}^{-1}$. Using this value for $S_{298.15}^0$ and expression (2) for the molar heat capacity, the molar enthalpy increments, entropies and Gibbs energy functions of CaHCl were computed and are given in Table 1 along with the measured and fitted molar heat capacity values.

3.3 Molar heat capacities of CaHBr

The measured molar heat capacity data of CaHBr is shown in Figure 5. The observed relative standard

Table 1. Thermodynamic functions of CaHCl.

T (K)	$C_p \text{ (J K}^{-1} \text{ mol}^{-1}\text{)}$		$(H_T^0 - H_{298.15}^0)$ (J mol ⁻¹)	$S_T^0 \text{ (J K}^{-1} \text{ mol}^{-1}\text{)}$	$-(G_T^0 - H_{298.15}^0)/T \text{ (J K}^{-1} \text{ mol}^{-1}\text{)}$
	Measured	Fit			
298.15	–	51.4	0	71.3	71.3
308	52.2	52.3	511	73.0	71.4
348	55.0	55.2	2663	79.6	71.9
388	57.9	57.5	4919	85.7	73.1
428	59.5	59.3	7257	91.5	74.5
468	60.8	60.9	9662	96.8	76.2
508	62.2	62.2	12126	101.9	78.0
548	63.4	63.5	14640	106.7	79.9
588	64.4	64.6	17201	111.2	81.9
628	65.1	65.6	19803	115.4	83.9
668	66.6	66.5	22445	119.5	85.9
708	67.4	67.4	25124	123.4	87.9
748	68.8	68.3	27839	127.1	89.9

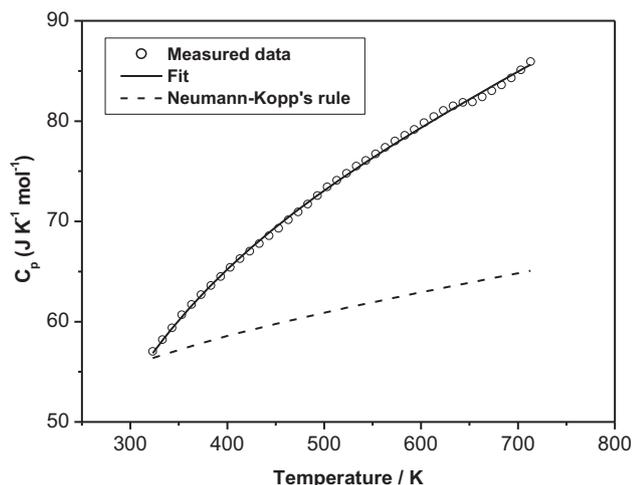


Figure 5. Molar heat capacity of CaHBr.

deviations of the measurements are in the range of 1–3%. The measured data were fitted to the following expression using the least-squares method:

$$C_p < \text{CaHBr} > \left(\text{J K}^{-1} \text{mol}^{-1} \right) = 56.534 + 44.880 \times 10^{-3} \cdot T - 1.481 \times 10^6 \cdot T^{-2} (323-713 \text{ K}) \quad (3)$$

The standard error of the fit is $\pm 0.26 \text{ J K}^{-1} \text{mol}^{-1}$. The least squares fitted curve is also shown in Figure 5. There is no heat capacity data reported in the literature for CaHBr, and the present data are reported for the first time. S_{298}^0 value of CaHBr was estimated as in the case of CaHCl. The experimental C_p , 298.15K value of CaHBr determined from the fit was 3.9% lower than the value estimated by Neumann–Kopp’s rule using the corresponding values from the literature⁹ for CaH₂ (37.00 J K⁻¹ mol⁻¹) and CaBr₂ (73.92 J K⁻¹ mol⁻¹). Assuming that the $S_{298.15}^0$

value of CaHBr will also be 3.9% lower than the value derived from Neumann–Kopp’s rule, it was deduced to be 82.5 J K⁻¹ mol⁻¹ from $S_{298.15}^0$ values of CaH₂ and CaBr₂, viz., 41.999 J K⁻¹ mol⁻¹ and 129.704 J K⁻¹ mol⁻¹, respectively.⁹ Using this value for $S_{298.15}^0$ and expression (3) for the molar heat capacity, the molar enthalpy increments, entropies and Gibbs energy functions of CaHBr were computed and are given in Table 2 along with the measured and fitted molar heat capacity values.

3.4 Deviations of C_p from Neumann–Kopp’s rule

Neumann–Kopp’s rule (NKR) is an additive rule wherein an estimate of molar heat capacities of a compound is arrived by the stoichiometric addition of molar heat capacities of the individual component compounds, mostly applied to oxides. Leitner *et al.*¹⁰ have described the possible cause for the deviations of measured heat capacity and that obtained by NKR for mixed oxides. In this study, it is attempted for CaHCl and CaHBr. A good estimate is obtained whenever the crystal structures of the products and reactants are the same or with minimum distortions. Further, the deviation can be due to the difference in the molar volumes of the products and the reactants. As seen from Figure 4, the measured molar heat capacities of CaHCl were lower than the NKR values below $\sim 370 \text{ K}$ and higher above this temperature. In the case of CaHBr (Figure 5), the measured molar heat capacities of CaHBr were higher than the NKR values for the entire temperature range. The crystal structures of CaH₂ (orthorhombic), CaBr₂ (tetragonal) CaCl₂ (orthorhombic) CaHBr (Tetragonal) and CaHCl (Tetragonal) are not the same. Hence, the bonding environment, bonding type and coordination numbers are

Table 2. Thermodynamic functions of CaHBr.

T (K)	C_p (J K ⁻¹ mol ⁻¹)		$(H_T^0 - H_{298.15}^0)$ (J mol ⁻¹)	S_T^0 (J K ⁻¹ mol ⁻¹)	$-(G_T^0 - H_{298.15}^0)/T$ (J K ⁻¹ mol ⁻¹)
	Measured	Fit			
298.15	–	53.3	0	82.5	82.5
323	57.0	56.8	1369	86.9	82.7
353	60.7	60.5	3131	92.1	83.3
393	64.5	64.6	5634	98.8	84.5
433	67.8	68.1	8289	105.3	86.1
473	70.9	71.1	11074	111.4	88.0
513	74.1	73.9	13977	117.3	90.1
553	76.7	76.5	16986	123.0	92.2
593	79.2	78.9	20095	128.4	94.5
633	81.5	81.2	23299	133.6	96.8
673	83.0	83.5	26594	138.7	99.1
713	85.9	85.6	29976	143.5	101.5

Table 3. Comparison of unit cell volumes of ternary compounds (V_{TC}) and calculated unit cell volumes using unit cell volumes of binary compounds (V_{BC}).

Compounds	Structure	Cell volume (\AA^3)	No. of formula unit (Z)	Unit cell volume/formula unit (\AA^3)		Volume change
				V_{TC}	V_{BC}	
CaHCl	Tetragonal	101.75	2	50.88	$\frac{1}{2}$ (CaH ₂ + CaCl ₂), 59.91	17.75%
CaHBr	Tetragonal	117.75	2	58.88	$\frac{1}{2}$ (CaH ₂ + CaBr ₂), 68.80	16.85%
CaH ₂	Orthorhombic	143.77	4	35.94	–	–
CaCl ₂	Orthorhombic	167.73	2	83.87	–	–
CaBr ₂	Tetragonal	203.32	2	101.66	–	–

*Unit cell volumes were taken from JCPDS files 04-08-3390, 04-08-3393, 00-31-0266, 00-24-0223 and 01-71-5406 respectively for CaHCl, CaHBr, CaH₂, CaCl₂ and CaBr₂.

also not the same in the product and the starting compounds. All these could be the contributing factors for the difference in the measured and estimated molar heat capacity values.

Molar heat capacity (C_p) can be regarded as a contribution due to the lattice vibrations (C_{ph}) (phonons), lattice dilations (C_{dil}) and other factors (C_{others}) such as due to electrons involved in conduction, excitation of localized electrons and vacancy formation, etc. This can be expressed as,

$$C_p = C_{ph} + C_{dil} + C_{others} \quad (4)$$

For pure ionic crystals like CaHCl and CaHBr, the contributions due to excitations of localized and conduction electrons are expected to be less. But contributions from vacancies of calcium V_{Ca}''' and hydrogen V_H^* could not be ruled out. Harmonic and anharmonic vibrations contribute to the phonon vibrations. C_{dil} , is given by the following expression:

$$C_{dil} = C_p - C_v = TV\alpha^2/\beta \quad (5)$$

wherein the C_v is the molar heat capacity at constant volume, V is the molar volume, α is the isobaric volume expansion, β is the isothermal compressibility. At low temperatures, harmonic phonon vibrations are dominating but, at high temperatures, the dilatation and an-harmonic correction terms dominate. The harmonic part becomes equal to Dulong–Petit law limiting value of $3NR$, where N is the number of atoms per formula unit and R is the universal gas constant.

$$C_p = C_{har} + C_{anh} + C_{dil} \\ = 3NR + C_{anh} + TV\alpha^2/\beta \quad (6)$$

Hence the deviation from NKR is mainly due to anharmonic contributions and dilation terms. Leitner *et al.*¹⁰ have indicated that the contributions due to anharmonicity is significant only at 1000 K or above.

Thus the deviations from the NKR are attributed to the dilution term C_{dil} , in the measurement range of interest. The difference in molar volumes of compounds, their temperature coefficients of expansions, and compressibility factors as given by the following expression will affect the C_{dil} values.

$$\Delta C_{dil}/T = V_{AB}(\alpha_{AB}^2/\beta_{AB}) - x_A V_A(\alpha_A^2/\beta_A) \\ - x_B V_B(\alpha_B^2/\beta_B) \quad (7)$$

where AB represents the ternary compound formed from the constituent binary compounds A and B.

The crystal structure and unit cell volume per formula unit for both binary compounds and ternary compounds are given in Table 3. The volume change due to the formation of ternary compound from the corresponding binary compounds is also listed. It can be seen that the ternary compound formation was accompanied by a reduction in the cell volume. However, to calculate contributing terms, it is necessary to have data on α and β parameters which are not available in the literature.

4. Conclusions

The molar heat capacity measurements were carried out for CaHCl and CaHBr using DSC and the corresponding estimated thermodynamic functions of the two compounds were determined. The high-temperature molar heat capacity data of CaHCl and CaHBr are reported for the first time.

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