

Pressure Dependence of the Melting of RbHSO_4

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The temperature and enthalpy of melting have been studied in the range up to 0.55 GPa by means of differential scanning calorimetry. In the range below a triple point at $(498 \pm 5) \text{ K}$ and $(0.27 \pm 0.02) \text{ GPa}$ the results can be expressed by means of linear relations: $T = 476 + 80 p$, and $\Delta H = 22.4 - 29.8 p$, where the corresponding units are K, kJ/mol and GPa. Above the triple point the correlation between pressure and temperature corresponds to Simon's equation, $p = 0.27 + 1.57 \times 10^{-3} (T - 498)^{1.28}$, and the enthalpy of melting decreases linearly with the pressure: $\Delta H = 9.50 - 10.65 (p - 0.28)$. Comparison is made with a recent study by Sinitsyn et al.

As a part of our extended program concerning phase transitions of some alkali metal hydrogen salts [1–6], we have determined the pressure dependence of the melting point of RbHSO_4 up to about 0.55 GPa. We intended to wait with a report until we had completed high-pressure studies of other phase transitions of RbHSO_4 in the same way as we did for CsHSO_4 [4]. However, a recently published paper on the p – T phase diagram of RbHSO_4 [7] prompted us to present our results concerning the melting curve now and to make comparisons between the two studies.

DSC Study of Melting and Solidification

The experiments were performed in the same way as described previously [4]. Figure 1 shows the melting point of RbHSO_4 as a function of hydrostatic pressure together with the corresponding solidification temperatures, which usually lie some 10–20 degrees below the melting points. There is a clear tendency that this hysteresis decreases at higher pressures. Two pressure regions can be distinguished. In the range below

0.27 GPa the correlation with pressure is linear for melting as well as for solidification, while it is non-linear above 0.27 GPa, and there is also a change of slope at 0.27 GPa. The linear part of the melting curve is represented by the equation:

$$T (\text{K}) = 476 + 80.1 p (\text{GPa}). \quad (1)$$

In this range there is also a linear correlation for the enthalpy of melting, see Fig. 2:

$$\Delta H (\text{kJ/mol}) = 22.4 - 29.8 p (\text{GPa}). \quad (2)$$

The measured enthalpy is significantly lower when the melt solidifies, being about 14.5 kJ/mol at normal pressure. A similar difference between the enthalpies of melting and solidification has been observed for other salts of the same family, such as CsHSO_4 [4]. Making use of the Clausius-Clapeyron equation, the following relation is derived for the pressure dependence of the volume change:

$$\Delta V (\text{cm}^3/\text{mol}) = 3.7 - 5.3 p (\text{GPa}). \quad (3)$$

There is an evident discontinuity for the enthalpy of melting at about 0.27 GPa, see Fig. 2, and the DCS traces tended to split into two peaks in a region just above this pressure. These observations are taken as evidence that there is a triple point at $0.27 \pm 0.02 \text{ GPa}$ and $498 \pm 5 \text{ K}$; compare the discussion below of the proton conducting phase found by Sinitsyn et al. [7].

It is obvious that the melting curve in the non-linear region can be described by Simon's equation, i.e. there is a similarity with the melting curve of CsHSO_4 [4]. An equation based on five points would be

$$p (\text{GPa}) = 0.27 + 1.57 \times 10^{-3} (T - 498)^{1.28}. \quad (4)$$

In this range the enthalpy of melting can be expressed by a linear relation:

$$\Delta H = 9.50 - 10.65 (p - 0.28). \quad (5)$$

Discussion

There is good agreement between our results and [7] in two aspects. Thus, the melting point at normal pressure is 476 K according to both studies. Furthermore, the proposed triple point lies at $0.27 \pm 0.02 \text{ GPa}$ and $498 \pm 5 \text{ K}$ according to our measurements, and at $0.28 \pm 0.02 \text{ GPa}$ and $495 \pm 8 \text{ K}$ according to [7]. How-

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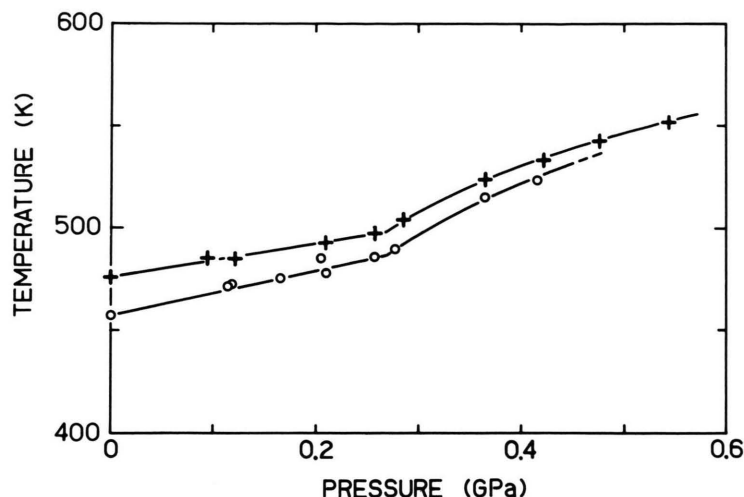


Fig. 1. Temperatures of melting (+) and solidification (o) of rubidium hydrogen sulphate. There are several indications that there is a triple point at 498 K and 0.27 GPa.

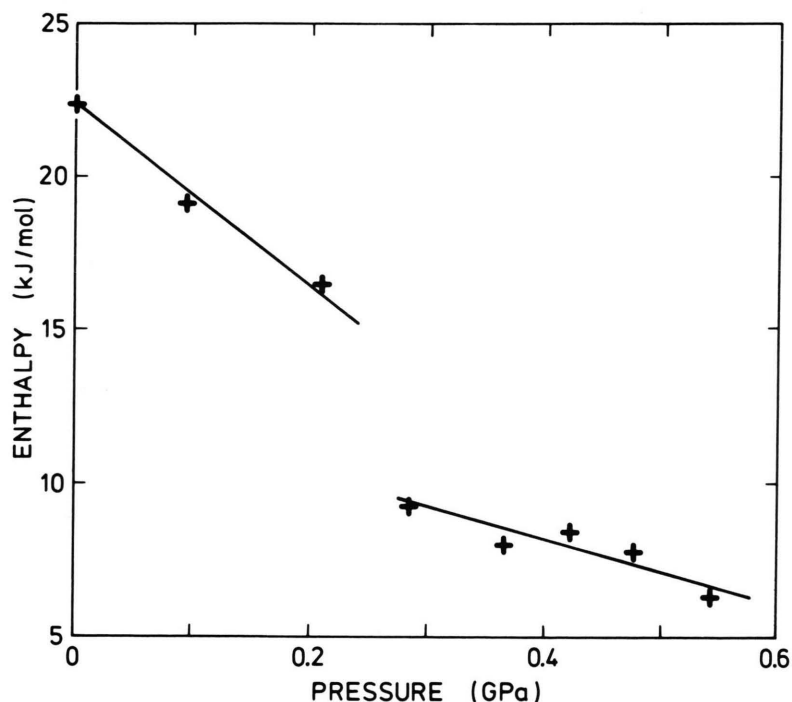


Fig. 2. Enthalpy of melting for rubidium hydrogen sulphate.

ever, there are discrepancies between the two studies concerning three other properties of the solid-liquid transition.

First, Sinitsyn et al. [7] claim that the melting temperature is a quadratic function of pressure for the range up to the triple point, see (1) of [7]. This is indeed an uncommon behaviour, since the correlation between melting temperature and pressure can mostly

be described by Simon's equation [8], where, instead, the slope dT/dp is a decreasing function of pressure. An extended review covering about 200 substances [9] has confirmed the generality of Simon's equation, with the exception of systems where the melting temperature has a maximum, and ^3He in the vicinity of 0 K, where the melting curve is concave to the pressure axis, i.e. similar to (1) and Fig. 1 of [7]. However, if one

considers the rather large scattering of the points shown in their figure, it is not evident that the proposed quadratic correlation has a strong experimental support.

Secondly, as remarked by Sinitsyn et al. [7], a consequence of their equation (1) is that the volume change ΔV is nil at zero pressure, i.e. that the coexisting liquid and solid phases should have the same specific volume. Again, this is a rather unusual result, which is in clear contradiction with our results as represented by (3). A volume change at normal pressure of $3.7 \text{ cm}^3/\text{mol}$ for RbHSO_4 seems reasonable in comparison with the $7.2 \text{ cm}^3/\text{mol}$ of CsHSO_4 [4].

A third discrepancy concerns the range above the triple point, where Sinitsyn et al. [7] report a linear temperature-pressure relation with $dT/dp = 200 \text{ K/GPa}$, while we suggest a non-linear relation according to Simon's equation. In our case the initial slope is of the order of 270 K/GPa , while dT/dp is about 100 K/GPa at 0.55 GPa . It appears from Fig. 1 of [7] as if they terminated their study of the melting curve at about 0.4 GPa .

Sinitsyn et al. [7] based their study of the p - T phase diagram on conductivity measurements, and they report that a phase called IV has a high proton conductivity. The paraelectric phase (space group $P2_1/c$), which exists over a wide temperature range at normal pressure is called I, while III denotes a high pressure phase. In addition to the triple point (I-IV-L) at 495 K and 0.28 GPa , there is also one (I-III-IV) at 466 K and 0.60 GPa . Extrapolations of (2) and (5) to 0.27 GPa

give $\Delta H(\text{I, L}) = 14.4 \text{ kJ/mole}$ and $\Delta H(\text{IV, L}) = 9.6 \text{ kJ/mole}$. Thus $\Delta H(\text{I, IV}) = 4.8 \text{ kJ/mole}$. The accuracy is of course moderate for this calculated transition enthalpy. It can be compared with the enthalpy of the corresponding transition to the proton-conducting phase of CsHSO_4 , which is 5.1 kJ/mole at 0.27 GPa [4].

Concerning the solid-solid transition lines determined by Sinitsyn et al. [7], there are at least qualitative similarities with the paraelectric-superionic transition of RbHSeO_4 . Thus, their $dT/dp = -80 \pm 15 \text{ K/GPa}$ for the I-IV transition and $18 \pm 7 \text{ K/GPa}$ for the III-IV one, can be compared with our results for RbHSeO_4 [5], namely -36 K/GPa below 0.4 GPa and 74 K/GPa at higher pressures, and also with the -20 K/GPa reported by Poprawski and Dziedzic for the range up to 0.3 GPa [10].

In contrast to the negative slope of the paraelectric-superionic transition of the two rubidium salts, the corresponding dT/dp is slightly positive for CsHSO_4 and very close to zero for CsHSeO_4 [5]. Thus, regarding the temperature gradients dT/dp , there is more similarity between two salts if they have the cation in common, than if this is the case for the anion.

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