Example A1. The speed of sound in solid water is reported as 3200 m/s. Predict the specific heat at constant volume for ice just below the melting point.

The vibrational characteristic temperatures are listed in Table IIIC-2: 2294 K, 5262 K, 5404 K. The Debye temperature is determined from eqn. IIID-A4b.

The required specific volume can be obtained from Table IC-3: $v = v_s(0.01°C) = 1.0908$ cm^3/g. Thus

$$\theta_D = \left(\frac{3N_A}{4\pi vM}\right)^{1/3} \cdot \frac{hc_s}{k} = \left[\frac{3 \cdot 6.023 \cdot 10^{23}/(g\,mol)}{4\pi \cdot 1.0908\ cm^3/g \cdot 18.02\ g/(g\,mol)}\right]^{1/3}$$

$$\cdot \frac{6.625 \cdot 10^{-34} Js/part \cdot 3.2 \cdot 10^5 cm/s}{1.38 \cdot 10^{-23} J/(part\ K)} = 298\ K$$

Thus, at $T = 0.01°C = 273$ K, $x_{D,n\ell} = 298$ K/273 K = 1.09. $D(x_{D,n\ell}) = 0.653$ and

$$\frac{\bar{c}_{v,n\ell}}{\bar{R}} = 6\left[4 \cdot 0.653 - \frac{3 \cdot 1.09}{(e^{1.09}-1)}\right] = 5.73$$

And $x_{v,1} = 2294$ K/273 K = 8.40, $x_{v,2} = 19.3$ and $x_{v,3} = 19.8$

$$\frac{\bar{c}_{v,1}}{\bar{R}} = (8.4)^2 \frac{e^{8.4}}{(e^{8.4}-1)^2} = 0.0159, \quad \frac{\bar{c}_{v,2}}{\bar{R}} = 1.55 \cdot 10^{-6}, \quad \frac{\bar{c}_{v,3}}{\bar{R}} = 9.87 \cdot 10^{-7}$$

Finally, $\bar{c}_{v,n\ell} = (5.73 + 0.0159 + 0 + 0) \cdot 8.314\ J/(g\,mol\,K) = 47.8\ J/(g\,mol\,K)$

Exercise A1. The speed of sound in solid carbon dioxide (dry ice) is low enough that the acoustical waves of dry ice are fully excited at the temperature level of its normal sublimation point, -78°C. Predict the specific heat at constant volume of dry ice at its normal sublimation point. (Answer on page 30.)