they generate phonons.[26] Thus like atomic lattices the external vibrational modes of a molecular lattice point crystal can be modeled with satisfactory accuracy using a single Debye cutoff temperature and the Debye continuum model.[28]

From the preceding discussion we conclude that the properties of molecular lattice point crystals can be treated as a linear superposition of an Einstein function for each of the separate internal modes and a Debye continuum for the collective external modes. The procedures required to complete such an evaluation are presented in Appendix A, which includes application to both ice and dry ice. But some general trends can be recognized without detailed study. The internal mode characteristic temperatures, $\theta_{v,p}$ see Table IIIC-2, are often high enough that the optical modes are unexcited at ordinary temperatures (frequently up to the melting point of the solid). The Debye temperature can be determined from sound speed data. Often it is low enough that the acoustical modes are fully excited at ordinary temperatures. Under these conditions ($\theta_D < T << \theta_{v,p}$) the specific heats of linear and nonlinear molecular crystals respectively are $\bar{c}_{v,l} \simeq 5\bar{R}$ and $\bar{c}_{v,n\ell} \simeq 6\bar{R}$. A much more quantitative perception of these principles can be gained by studying Appendix A.

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[28]The Debye model ignored the detailed motions of the atomic lattice. It accounted for the spring stiffness through the effect of sound speed on the cutoff temperature (or cutoff temperatures, if the longitudinal and transverse waves are treated separately). Improved results can be achieved if a model is used that accounts for the natural frequencies of the spring mass complex constituting the lattice. This can be done in terms of a modified frequency spectrum, $g_{phn}(\nu)$. In most cases the improvement in results is not warranted by the increased difficulty of calculation, see Ref. 6.

Ans. 18. From Table IIID-1, $\theta_D = 281$ K and $x_D = \theta_D/T = 281$ K/300 K = 0.937. Thus using Table IIID-2, $D(x_D) = 0.693$. So

$$\bar{c}_{v,phn}(300\ \text{K}) = 6\bar{R}\left[4 \cdot 0.693 - \frac{3 \cdot 0.937}{(e^{0.937}-1)}\right] = 5.76\ \bar{R} = 47.9\ \text{J/(g mol K)}$$

The classical limit is established at approximately $x_D = 0.5$ or $T = 2 \cdot 281$ K = 562 K. The limiting value is $\bar{c}_{v,phn} = 6\bar{R}$.

Ans. 19. $M_K = 39.10$ and $M_{Cl} = 35.45$, thus $M_{KCl} = 74.55$ kg/(kg mol)

$$\theta_D = \left(\frac{6\ N_A\rho}{4\pi M}\right)^{1/3} \frac{hc_s}{k} = \left[\frac{6 \cdot 6.023 \cdot 10^{26}/(\text{kg mol}) \cdot 1.99 \cdot 10^3\ \text{kg/m}^3}{4\pi \cdot 74.55\ \text{kg/(kg mol)}}\right]^{1/3}$$

$$\cdot \frac{6.625 \cdot 10^{-34}\ \text{Js/part} \cdot 2430\ \text{m/s}}{1.380 \cdot 10^{-23}\ \text{J/(part K)}} = 230\ \text{K}$$

Thus at room temperature, $x_D = 230$ K/300 K = 0.767 and $D(x_D) = 0.745$. Finally

$$\bar{c}_{v,phn}(300\ \text{K}) = 6\bar{R}\ 4 \cdot 0.745 - \frac{3 \cdot 0.767}{(e^{0.767}-1)} = 5.90\ \bar{R} = 49.1\ \text{J/(g mol K)}$$