vibrational freedom and the classical limit energy of each vibrational degree of freedom is $2 \cdot (kT/2)$. Thus the *classical limit vibrational specific heat of all pure substance solids* is $\bar{c}_v = 3n_a\bar{R}$, where n_a is the number of atoms per molecule. However, more detailed consideration of solids whose lattice points are occupied by molecules requires that we differentiate between the intramolecular vibrations that affect the crystal as a whole, *the acoustical modes*, and the vibrations that occur within the molecule, *the optical modes*.[25]

Optical Modes. The molecules that occupy the lattice points of a solid have associated *internal* vibrational modes which number $3n_a - 5$ in linear molecules and $3n_a - 6$ in nonlinear molecules (see Unit IIIC, Sect. IIIC). In general these modes are initiated at relatively high temperatures, see Table IIIC-2, and occur at a relatively fixed frequency.[26] The property contributions of these modes can be predicted in the same manner as that for internal vibration of a gas molecule.[27]

Acoustical Modes. Molecular lattice points vibrate both linearly and torsionally with respect to the forces that bind them one to another in the lattice. Vibration of any individual molecule in one of these modes will induce vibration in its other modes and those of its neighbors. Thus the external vibrational modes (five per molecule in linear molecules, six per molecule in nonlinear molecules) are not fixed to any particular lattice point nor do they occur at any single frequency. These modes belong to the lattice as a whole—

[25]Covalent molecules form molecular lattice point crystals. These include the homonuclear diatomic molecule crystals formed by the oxidizing elements, e.g., N_2, O_2, Cl_2.

[26]The internal modes are called the optical modes because their excitation frequencies are sufficiently high that an incident photon is much more likely to be absorbed by excitation of an internal mode vibration than by lattice vibration. The external modes are called the acoustical modes because they are much more likely to absorb an incident phonon, sound wave, than are the high frequency internal modes.

[27]Table IIIC-1 gives a summary of the relationships needed to determine the property contributions of an internal vibrational mode. They were applied to the three modes of vibration of an atomic lattice under the Einstein model for the properties of solids. Application to the internal modes of a molecular lattice is considered in Appendix A.

Ans. 17. If state (a) is within the T^3 region, then T_a is easily determined from the condition

$$\bar{c}_{v,el} = \frac{\pi^2}{2}\bar{R}\frac{T_a}{\theta_F} = \bar{c}_{v,phn} = \frac{12}{5}\pi^4\bar{R}\left(\frac{T_a}{\theta_D}\right)^3 \quad \text{or} \quad T_a = \left[\frac{5(215\ K)^3}{24\pi^2 \cdot 6.35 \cdot 10^4 K}\right]^{\frac{1}{2}} = 1.82\ K$$

Since $T_a/\theta_D < 1/12$, our initial assumption is justified.

Similarly if state (b) is at sufficiently high temperatures $T > \theta_D$, then $\bar{c}_{v,phn} = 3\bar{R}$ and T_b can be determined from the condition.

$$\bar{c}_{v,el} = \frac{\pi^2}{2}\bar{R}\frac{T_b}{\theta_F} = \bar{c}_{v,phn} = 3\bar{R} \quad \text{or} \quad T_b = \frac{6}{2}\theta_F = \frac{6}{\pi^2} \cdot 6.35 \cdot 10^4 K = 3.86 \cdot 10^4 K$$

Since $T_b >> \Theta_D$, this assumption is also justified.