Free electrons contribute to the properties of all conductors. Our development of free electron properties, however, has been limited to materials in which the number of free electrons is fixed. This is true for the metallic conductors and of course for non-conductors which have no free electrons. In semiconductors the number of free electrons varies with temperature and eqns. IIID-21 and 22 are inadequate to describe their properties. The manner of this variation is discussed qualitatively in Unit IIIE in terms of its significance to transport properties. Although free electrons make only marginal contributions to "thermostatic" properties, they are of primary importance to transport and transport properties.

Thus far we have considered only elemental solids that have lattice points occupied by atoms. These elements include the metals, rare gases, and the transition elements (see Unit ICS). In these solids the only vibrational modes are those associated with oscillation of the atoms with respect to the bonds that join them. Since each atom is fixed by the same bonds, the single characteristic temperature of the Debye model is reasonably successful in predicting the vibrational energy of these lattices. This characteristic is shared by the compound crystal formed of ionic molecules— the sodium chloride structure, see Fig. ICS-6. Each atom in this structure is also fixed in position by identical bonds. Thus a single Debye temperature is sufficient to model these crystals as well. It is, however, necessary to account for the fact that there are three modes of vibration per atom or $2 \cdot 3 = 6$ modes per molecule. The Debye cutoff frequency is determined by the total number of lattice vibration modes. Thus for *ionic molecular solids* formed in the *sodium chloride structure* the *Debye temperature* is related to the sound speed by

$$\theta_D = \frac{hc_s}{k}\left(\frac{6N_A}{4\bar{v}}\right)^{1/3} \qquad \text{(IIID-24a)}$$

The phonon contribution to the internal energy and specific heat of these insulating crystals becomes

$$\bar{u}_{phn}(T,\ \theta_D) = 6\bar{R}T\ D(x_D) \qquad \bar{c}_{v,phn} = 6\bar{R}\left[4D(x_D) - \frac{3x_D}{(e^{x_D}-1)}\right] \qquad \text{(IIID-25,26)}$$

Exercise 18. What is the specific heat of table salt (NaCl) at STP? What will be the high temperature limit value of $\bar{c}_v$ and at what temperature will it be achieved?

Exercise 19. The sound speed and density of potassium chloride are reported to be 2430 m/s and 1.99 g/cm^3. Determine the Debye temperature of this crystal and estimate its specific heat at room temperature.

An examination of eqn. IIID-25 or the answer to Exer. 18 reveals that the classical limit, $T \gg \theta_D$, lattice specific heat of a sodium chloride structure solid is $6\bar{R}$. (Recall that the limit is $3\bar{R}$ in atomic lattice point elements.) This result can be generalized to all molecular and atomic solids. Each atom in a solid has three degrees of