Lecture 22: 12.02.05 The Boltzmann Factor and Partition Function; Thermal Behavior of the Einstein Solid

Today:

Reading: Engel and Reid 31.5, 32.1, 32.2, 33.1-33.3

Supplementary Reading: Engel and Reid 33.4-33.5

Last time

Two postulates form the basis of statistical mechanics

1. When U, V, and N are fixed, each allowed microstate is equally probable.
2. The ensemble average of a thermodynamic property is equivalent to the time-averaged macroscopic value of the property measured for the real system.

The microscopic definition of entropy

- Ludwig Boltzmann's ansatz:

$$S = k_b \ln W = -k_b \sum_{j=1}^{W} p_j \ln p_j \qquad \text{indistinguishable particles (most common case)}$$

$$S = k_b \ln \Omega \qquad \text{distinguishable particles}$$

- It is extensive like the entropy
- Increases with U, like entropy
- Obeys the third law, like entropy

The first postulate satisfies the second law

- Just as the second law dictates the equilibrium *macrostate* in classical thermodynamics, the second law dictates what *microstates* the system will reside in at equilibrium:

What next? the problem of probabilities…

- The ensemble of a statistical mechanical system contains all thermodynamic information of the system
- All thermodynamic properties of a system can be calculated from the probabilities of the ensemble:

$$U = <E> = \sum_{j=1}^{W} p_j E_j$$

- The central problem of statistical mechanics is to determine the probabilities of microstate occupation:

  o …as in classical thermodynamics, we apply the second law: find the set of probabilities that maximize the entropy of the system.

The Boltzmann factor and Partition function

- We started our discussion of statistical mechanics by looking at fixed (U, V, N) isolated systems. Now, we turn to the experimentally more interesting case of systems with fixed *temperature*. The ensemble for fixed (*T, V,* and *N*) includes all possible microstates for the solid that have the same temperature; it is called the ***canonical ensemble*** ('canonical' because it is used so often to model real systems).

- ***Recall that for systems with constant (T,V,N), the second law is satisfied when the Helmholtz free energy (F = U - TS) is a minimum***.

    - To determine the equilibrium probability p_j for each individual state *j*, we simply calculate what values of p_j (for each possible state j) minimize the Helmholtz free energy *F,* subject to the constraint that the p_j's act like a probability and sum to 1:

- We want to calculate the minimum in *F* with respect to p_j for all possible states *j*:

- To satisfy the constraint that the p_j sum to 1, we use the method of Lagrange multipliers. We minimize *F* with the constraint included:

o☐ We define the summation in the denominator as the ***partition function Q.*** The importance of this sum will soon be apparent (for now, at least it simplifies our notation!).

p (E)
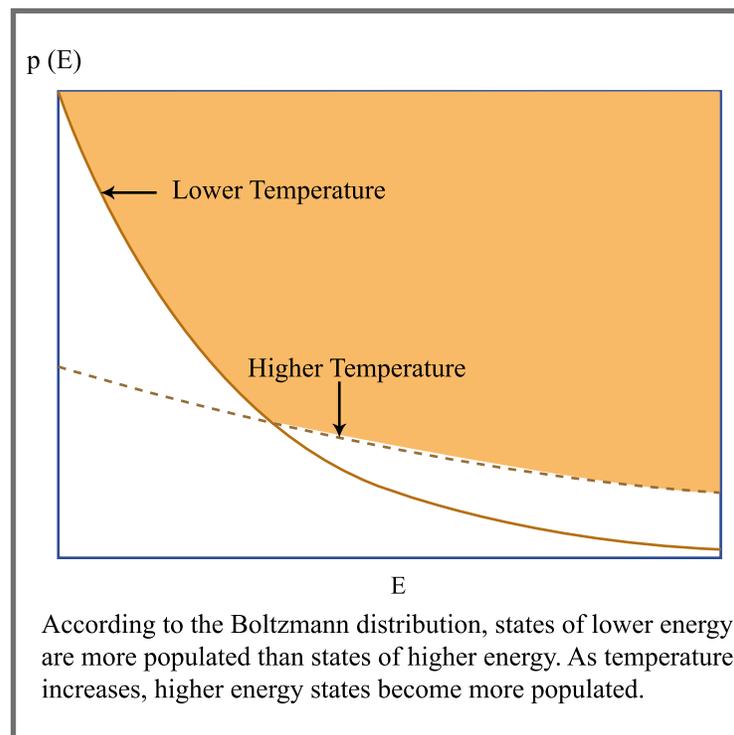
Lower Temperature

Higher Temperature

E

According to the Boltzmann distribution, states of lower energy are more populated than states of higher energy. As temperature increases, higher energy states become more populated.

Figure by MIT OCW.

o   The quantity *exp(-E$_i$/kT)* is known as the **Boltzmann factor**: it is the 'thermal weighting factor' that determines how many atoms access a given state of energy ε_i. The Boltzmann factor indicates that states with high energies will not be accessible at low temperature, but may occur with a high frequency in the ensemble at high temperature.

All thermodynamic quantities can be calculated from the partition function

- The Boltzmann factor and partition function are the two most important quantities for making statistical mechanical calculations. *If we have a model for a material for which we can calculate the partition function, we know everything there is to know about the thermodynamics of that model*.

- All thermodynamic quantities of interest can be derived using the partition function. Using the convenient dummy variable *β = 1/k$_b$T*, some examples are:

$$U = <E> = -\frac{\partial \ln Q}{\partial \beta} = kT^2 \frac{\partial \ln Q}{\partial T}$$

$$S = k \ln Q + kT \frac{\partial \ln Q}{\partial T}$$

$$F = U - TS = <E> - TS = -k_b T \ln Q$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = kT \left(\frac{\partial \ln Q}{\partial V}\right)_{T,N}$$

The partition function of molecules/atoms vs. multi-molecular systems

- It is often straightforward to develop models at the molecular level for allowed energies/states (this is what we are doing in the bonding half of 3.012 right now), and to even write the partition function for individual molecules. But how do we handle the case when we have a mole of atoms in a system and we want to determine Q? It is not possible to enumerate all the possible states by hand (or by computer for that matter, today).

    - We use a lower-case q to denote the partition function for an individual atom/molecule in our system:

    - One way to deal with systems comprised of N_{Av} molecules is to assume the molecules/atoms are independent. If each the N molecules is independent, the microstate of one molecule is not dependent on the microstate of its neighbors: the wave functions are independent, and the total energy of the system is simply the sum of the energy eigenvalues for each individual atom:

    - If we then look at the total partition function for the multi-molecular system, we have:

    - If the atoms/molecules are indistinguishable, then we must add a term to correct for indistinguishable states:

- This equation gives us a simple route to making calculations for macroscopic systems from molecular level-detailed models.

The Einstein Solid

- Now that we have the formula for the probabilities in a system at constant temperature, we can start making some predictions for our Einstein solid harmonic oscillator model.

The complete partition function for the Einstein solid[2]

- Recall that in the Einstein solid, the atoms are assumed to vibrate in a harmonic potential. The energy of this confined oscillation is quantized:

$$E_n = \left(n + \frac{1}{2}\right)h\nu$$

- We performed microcanonical calculations (fixed *E,V,N*) for a very imaginary 3-atom, 1D-oscillating solid. If we take the more realistic case of allowing each atom to oscillate in *X*, *Y*, and *Z* space, we have 3 quantized energies:

$$E_{n_x} = \left(n_x + \frac{1}{2}\right)h\nu$$

$$E_{n_y} = \left(n_y + \frac{1}{2}\right)h\nu$$
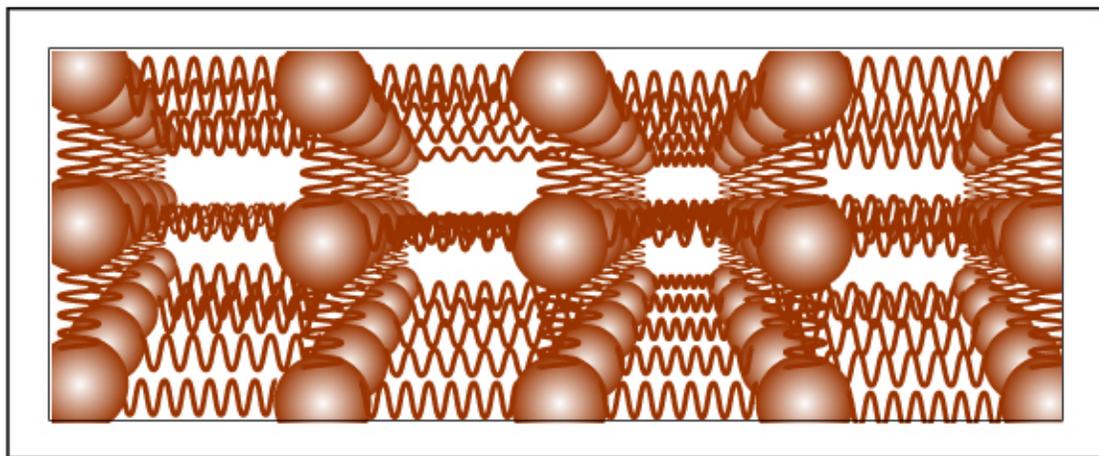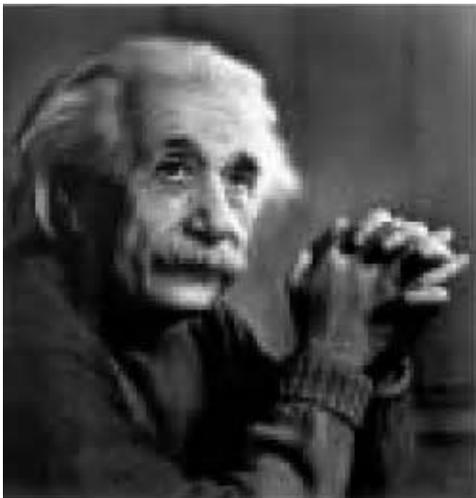
$$E_{n_z} = \left(n_z + \frac{1}{2}\right)h\nu$$

Figure by MIT OCW.

- The total energy in one microstate (characterized by one set of values n_x, n_y, n_z) for one atom of the solid is:

- It follows that the molecular partition function for one atom of the solid is:

- Since the vibration in each of the 3 directions is equivalent (i.e. $E_{n_x}(n_x = 1) = E_{n_y}(n_y = 1) = E_{n_z}(n_z = 1) = E_{n=1}$), the three sums in Q_{atom} are the same. We can therefore write:

- We showed above that the partition function for a system of *N* non-interacting distinguishable atoms or molecules is given by $Q = (q_{atom})^N$. Thus, for the partition function of the entire Einstein solid, we have:

- The infinite sum looks messy, but we can simplify this partition function. To shorten the following notation, let's use $\beta = 1/kT$:

- Using the approximation $\dfrac{1}{1-x} = \sum\limits_{n=0}^{\infty} x^n$ (for $x^2 < 1$), we can obtain:

- Finally, substituting, we arrive at the simplified total partition function for the Einstein solid:

$$Q = \left[\frac{e^{\frac{\beta h\nu}{2}}}{e^{\beta h\nu} - 1} \right]^{3N} = \left[\frac{e^{\frac{h\nu}{2kT}}}{e^{\frac{h\nu}{kT}} - 1} \right]^{3N}$$

Thermodynamic properties of the Einstein solid[2,4]

- Now that we have the partition function, it is straightforward to determine thermodynamic quantities for the Einstein solid. First, let's derive the internal energy:
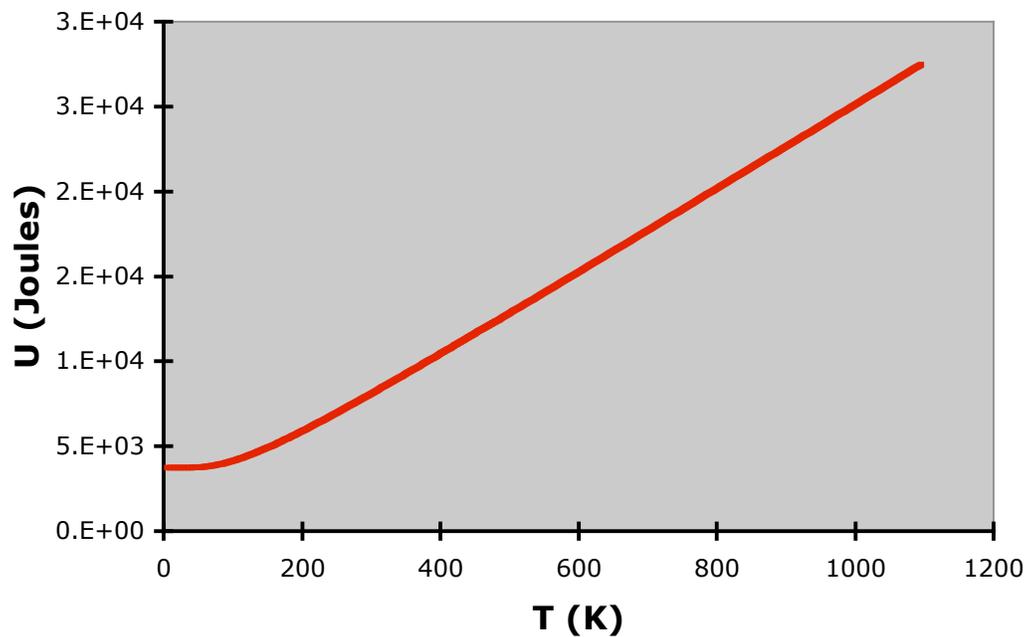
- This result is a general property of quantum mechanical degrees of freedom where the energy of excitations is linear with the quantum number (remember here, the energy of the oscillator is $E = h\nu(n + 1/2)$). ***Any such degree of freedom contributes k_bT to the total energy of each molecule.***

- Using the internal energy, we can calculate the heat capacity of the Einstein solid:

- Since $\beta = 1/kT$:

- Thus we can write the derivative *dU/dT* in the more convenient form:

- We introduce the 'Einstein temperature':

- Plugging Θ into the expression for heat capacity we have:

- This result states that the heat capacity of different materials depends only a characteristic temperature related to the vibrations allowed in the crystal. The Einstein solid heat capacity is plotted below as calculated for Diamond, compared to the experimentally measured heat capacity- and we see quite good agreement over a broad range of temperatures.

Experimental values of the heat capacity of diamond (●) compared with values calculated by the Einstein model (———), using the characteristic temperature $\theta_{vibration}$ = hv/k = 1320K. Vibrations are frozen out at low temperatures.
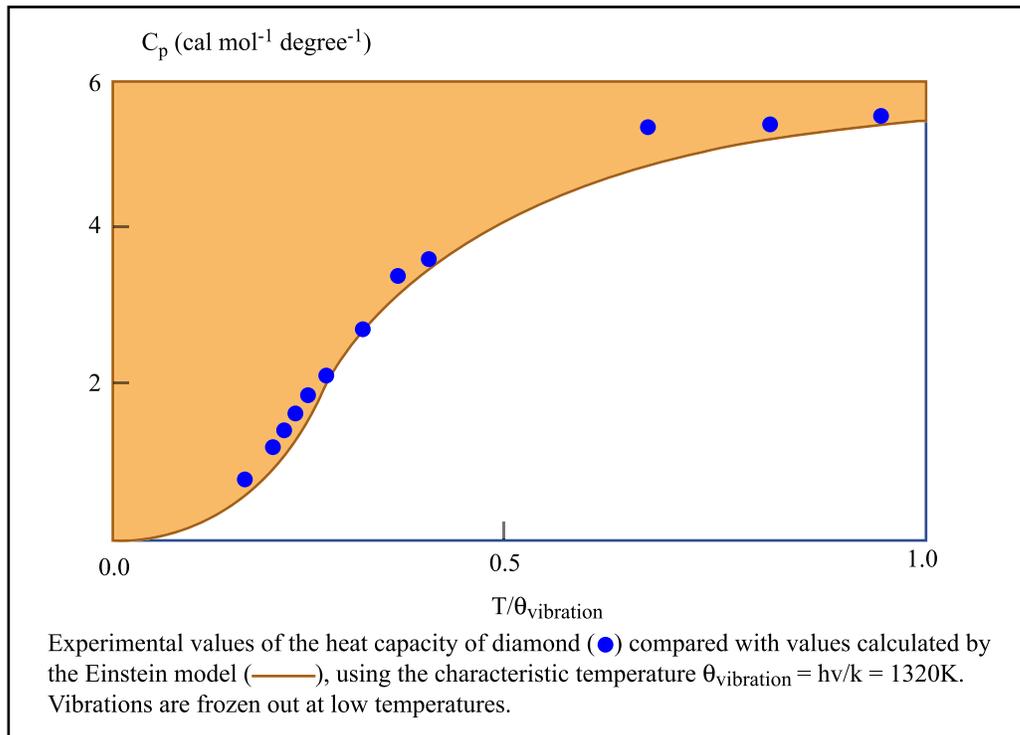
Figure by MIT OCW.

- In particular, at high temperatures, we see the limiting behavior of the heat capacity is $C_V = 3R$, correctly predicting the limiting value of C_v observed experimentally for many solids

- At low temperatures, the agreement with actual data is not as good:

- Experimentally, C_V is found to approach zero much more quickly for most materials, as approximately $C_V \sim T^3$ as T approaches 0.

A better model: The Debye solid

- The Einstein model makes the simplification of assuming the atoms of the solid vibrate at a single, unique frequency:
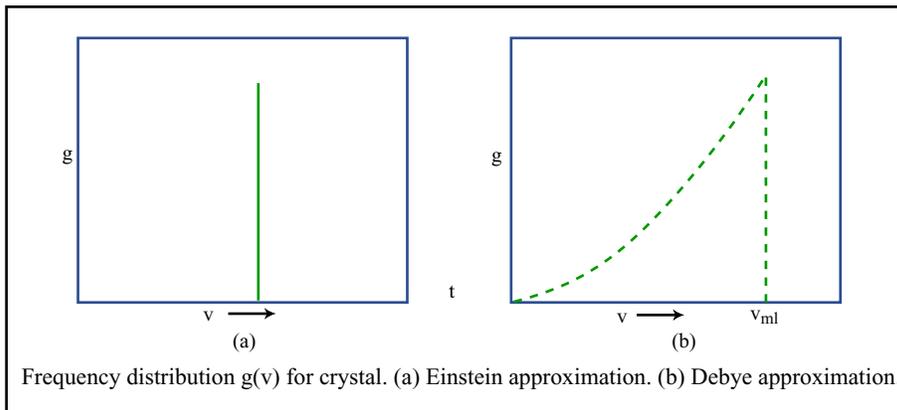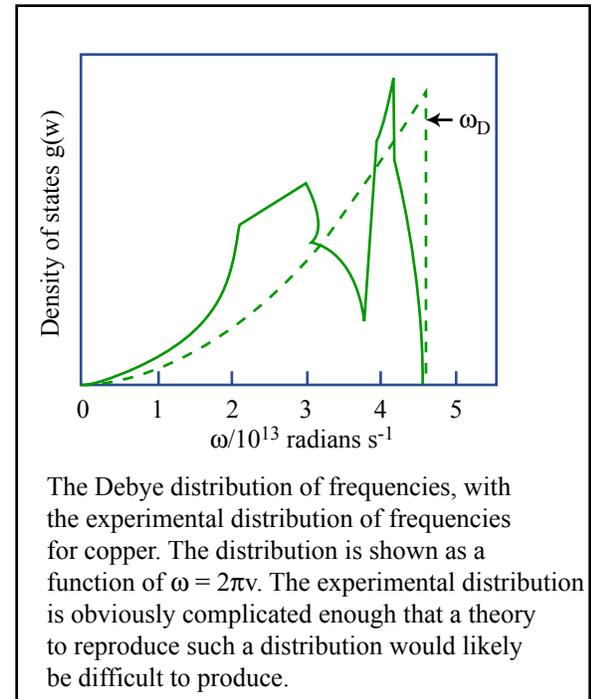

Frequency distribution g(v) for crystal. (a) Einstein approximation. (b) Debye approximation.

Figure by MIT OCW.

The Debye distribution of frequencies, with the experimental distribution of frequencies for copper. The distribution is shown as a function of $\omega = 2\pi v$. The experimental distribution is obviously complicated enough that a theory to reproduce such a distribution would likely be difficult to produce.

Figure by MIT OCW.

- 'g' in Figure 5-4 above from Hill is the distribution of vibrational frequencies present in the crystal. In the Einstein model, only one vibrational frequency is assumed for all atoms in the crystal. However, atoms sitting on different lattice sites may have difference accessible vibrational frequencies- which depend on what neighbors they 'feel' around them- this is seen in the complex distribution of vibrational frequencies shown in Figure 22.8 from Mortimer for a real sample of copper. The Debye model approximates the true frequency distribution by assuming the distribution shown in Figure 5-4(b): a distribution that is continuous up to some frequency cut-off (v_m). The Debye expression for heat capacity becomes:

$$C_V = k_b \int_0^\infty \frac{\left(\dfrac{hv}{k_bT}\right)^2 e^{\frac{hv}{k_bT}}}{\left(e^{\frac{hv}{kT}} - 1\right)^2} g(v)dv$$

- This approximation leads to a heat capacity behavior near zero Kelvin which better captures experimentally-observed behavior:

$$T \rightarrow 0, \ C_V \rightarrow \frac{12 N k_b \pi^4}{5} \left(\frac{T}{\theta_D} \right)^3$$

$$\text{where } \theta_D \equiv \left(\frac{h \nu_m}{k_b} \right) = \text{Debye temperature}$$

▪ The Debye model performs quite well for predicting the thermal behavior of many solid materials:
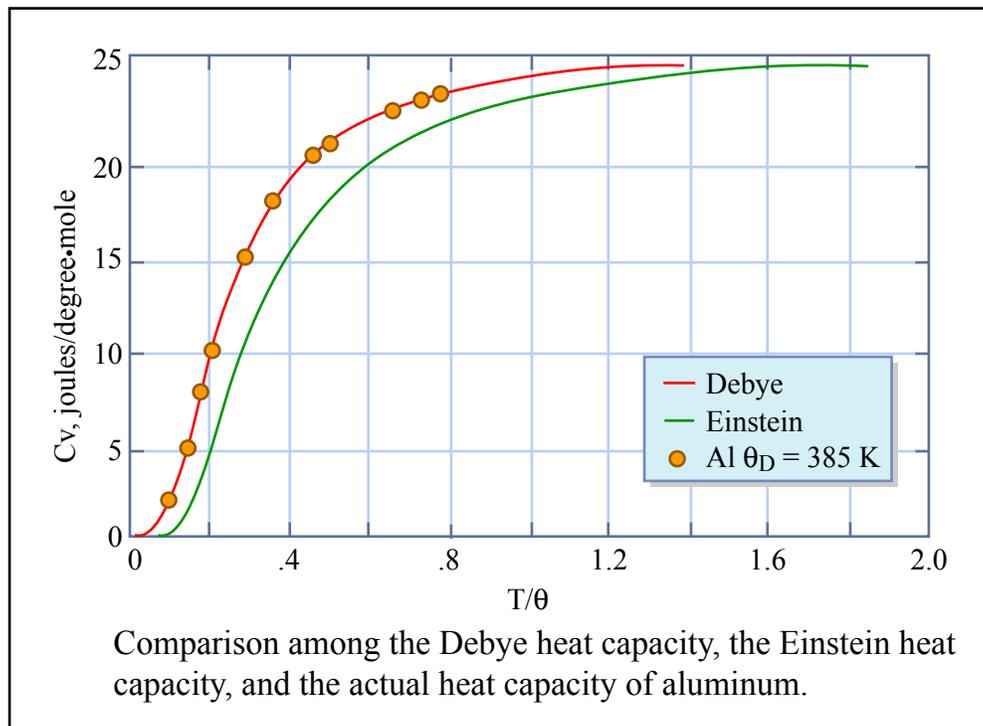

Comparison among the Debye heat capacity, the Einstein heat capacity, and the actual heat capacity of aluminum.

Figure by MIT OCW.

Examination of heat capacities of different materials

- If heat capacities correlate with molecular degrees of freedom in a material, we might expect materials that have similar degrees of freedom to have similar heat capacities. This is in fact seen for many materials. Consider first a comparison of the heat capacity in 3 different crystalline non-metals:[2]
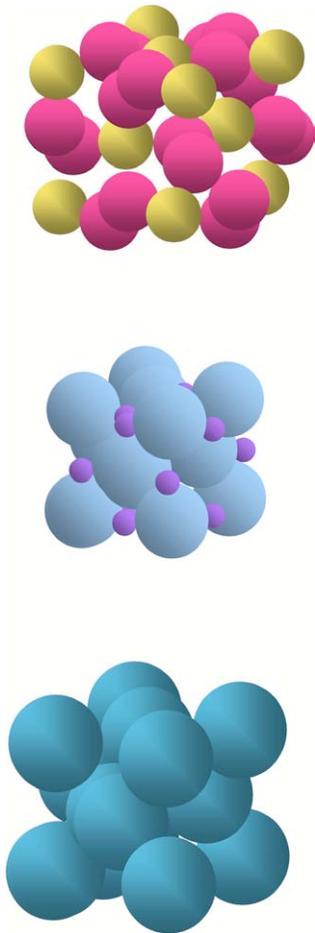
Cp, J/ mol•K
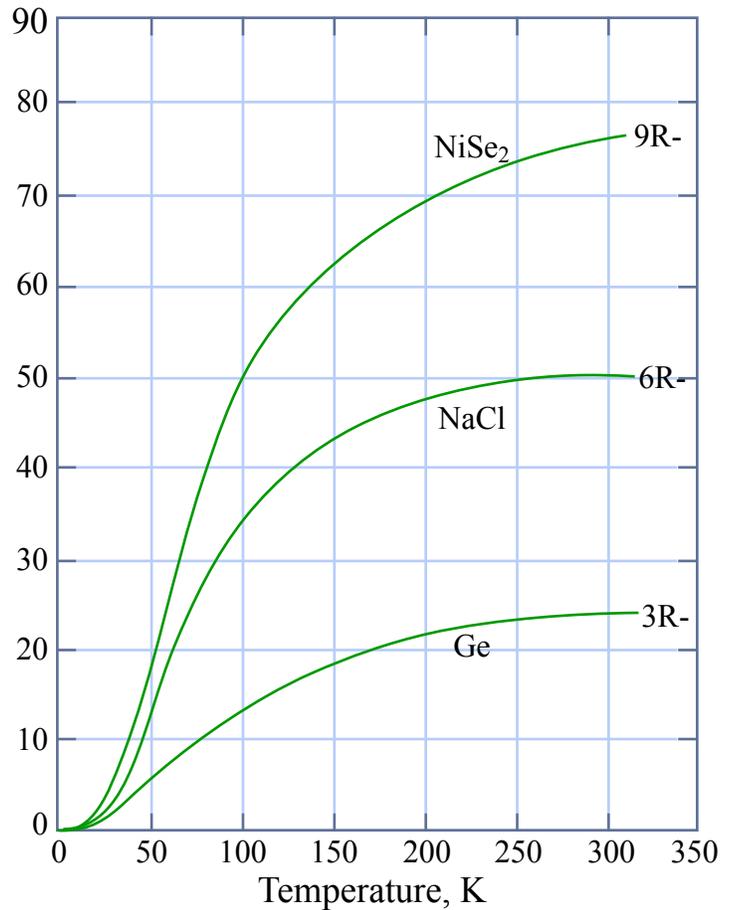
Molar heat capacity at constant pressure of three crystalline nonmetals.

Figure by MIT OCW.

- o Thus in these structurally-related crystals, the heat capacity per N_{Av} atoms is very similar, ~3R, or 25 J/mole K. We will show later in the term that this plateau value can be predicted by treating the atoms in the solid as a collection of harmonic oscillators.
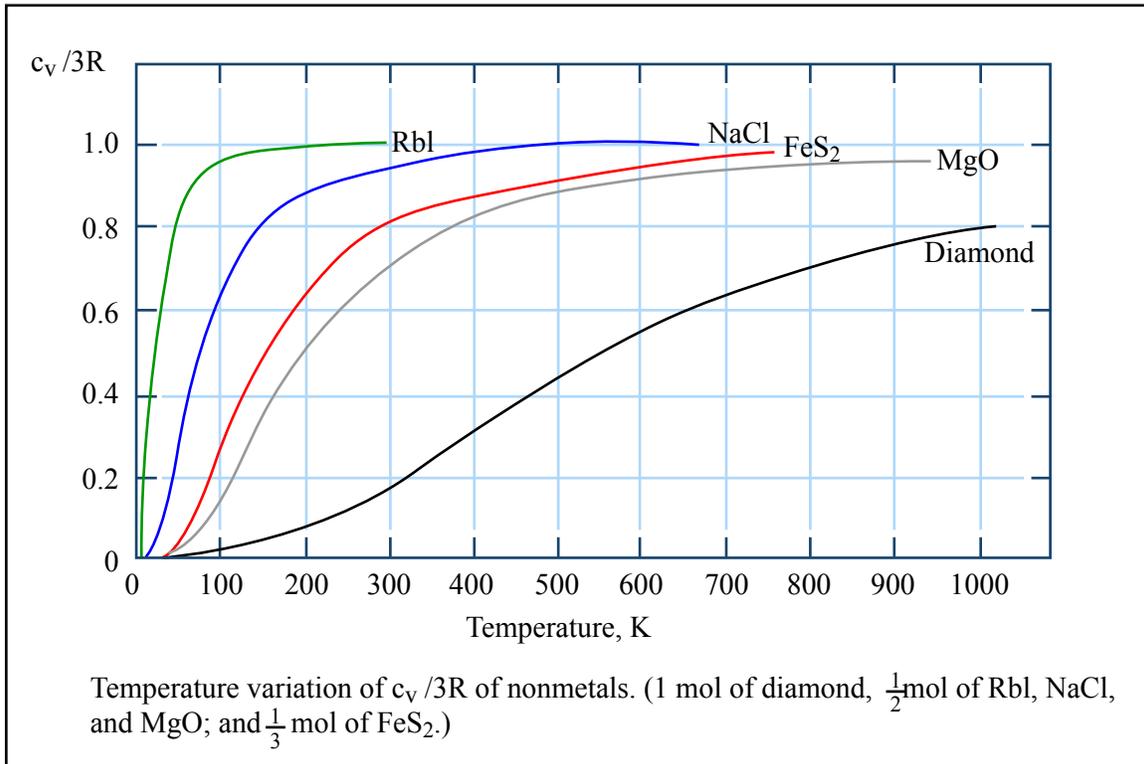
Temperature variation of $c_v/3R$ of nonmetals. (1 mol of diamond, $\frac{1}{2}$mol of Rbl, NaCl, and MgO; and $\frac{1}{3}$ mol of FeS$_2$.)

Figure by MIT OCW.

References

1.   Dill, K. & Bromberg, S. *Molecular Driving Forces* (New York, 2003).
2.   Cima, M. (2002).
3.   Chabay, R. & Sherwood, B. *Matter & Interactions*.
4.   Hill, T. L. *An Introduction to Statistical Thermodynamics* (Dover Publications, Inc., New York, 1986).
5.   Mortimer, R. G. *Physical Chemistry* (Academic Press, New York, 2000).
6.   Gaskell, D. R. *Introduction to Metallurgical Thermodynamics* (Hemisphere, New York, 1981).