Of all the modes to be considered, only vibration is commonly encountered near its characteristic temperature ($T \sim \theta_v$). In fact, for polyatomic gases it is uncommon for at least one vibrational mode not to be in such a region. In addition, vibration is the first mode whose properties can be analytically determined at all temperatures. (Translational and rotational consideration was limited to high temperatures, and nuclear spin to low temperatures.) A more thorough study of these modes would reveal that the general behaviors of all internal modes are very similar. Thus, a study of the relationship between the low, high, and intermediate temperature properties of a vibrational mode will improve our perception of properties in general. Fig. IIIC-3 presents a graphical representation of the $c_{v(v,p)}$ as a function of dimensionless vibrational temperature, T/θ_v. (The function plotted appears in Table IIIC-1 and Ans. 13.) At low temperatures $c_{v,v} \Rightarrow 0$. As $T \Rightarrow \theta_v$, $c_{v,v}$ increases sharply approaching the limit $2(\bar{R}/2)$ as $T >> \theta_v$. Except for the multiple of $(\bar{R}/2)$ in the high-temperature limit, these are general characteristics of all modes. We summarize:

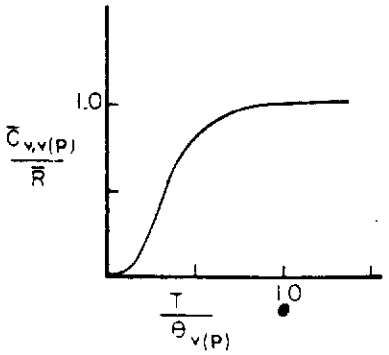

Fig. IIIC-3. Vibrational Specific Heat

Low-Temperature Limit, $T << \theta$. In this limit a mode is said to be unexcited. Its particles condense into the lowest accessible levels.[16] An internal mode's particles condense into the lowest "ground" level, $p_{p,1} \Rightarrow 1$. Thus, the spacing between the first and second level is very important to the distribution. This is the quantum limit. Such modes contribute no more than a constant to properties. The constant is zero for the specific heat.

High-Temperature Limit, $T >> \theta$. In this limit a mode is said to be fully excited. The particles are distributed broadly over many levels. The spacing between levels is negligible in comparison to the average energy of the particles. Thus, energy can be considered continuous. This is the Newtonian or classical limit of the mode. The energy contribution of modes is a constant multiple of $\bar{R}T/2$ and its specific heat contribution is a constant multiple of $\bar{R}/2$.[17]

[16]The low-temperature limit of the external (translational) mode is complicated by the consequences of particle symmetry. Bosons condense into the lowest level in a manner similar to that discussed above. But Fermions are limited to no more than a single particle per state. Thus they will crowd into the lowest available empty states. The distinction between these two distinct low-temperature "degenerate" conditions causes their low-temperature behavior to be quite different. Unit IIID treats free electron behavior in metals. This is an illustration of degenerate Fermion behavior.

[17]The fact that the classical limit contribution to the energy is a multiple of $kT/2 (k \equiv \bar{R}/N_A)$ per particle is called the *equipartition of energy* principle. It requires that the discrete energy spectrum approach a continuum (the high temperature limit) and that the energy be expressible in a quadratic form (Ref. 4, pg. 72). These characteristics are shared by the translational, rotational, and vibrational modes.

Ans. 14. $P_{\ell,CO_2} = 3 \cdot 3 - 5 = 4$, $P_{n\ell,H_2O} = 3 \cdot 3 - 6 = 3$, $P_{n\ell,NH_3} = 3 \cdot 4 - 6 = 6$, $P_{n\ell,C_6H_6} = 3 \cdot 12 - 6 = 30$.