modes can be considered independent simple harmonic oscillators.[14] When this is the case, each vibrational mode has its own partition function and

$$Z_v = \prod_{p=1}^{P} Z_{v,p} = \prod_{p=1}^{P} \frac{e^{-\theta_{v,p}/2T}}{\left(1 - e^{-\theta_{v,p}/T}\right)}$$

Values of $\theta_{v,p}$ for a number of polyatomic gases are listed in Table IIIC-2.[15] These data permit the determination of the vibrational contribution to the properties of polyatomic gases. Since the total vibrational partition function is the product of the separate mode partition functions, the total vibrational properties are the sum of the contribution of the separate modes. Thus, the results of Exer. 13 can be applied to each mode separately, see Table IIIC-1.

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[14]As the amplitude of vibration increases several factors combine to distort the assumption of the independent, simple harmonic vibrational model. The potential well is not parabolic at higher energy levels, Fig. IIIC-2. Coupling between vibrational modes will occur and at high vibrational amplitudes the oscillation in molecular moment will cause rotation vibration coupling.

[15]The number of modes of a given frequency are designated by their number in parentheses, $\theta_{v,p}(2)$, etc., in Table IIIC-2.

Ans. 12. The levels of interest are the 1st ($\ell = 0$), the 2nd ($\ell = 1$) and the 10th ($\ell = 9$). At $T = 0.1\ \theta_v$

$$\rho_v(0) = (1 - e^{-10})(e^{-10})^0 = 0.99995, \quad \rho_v(1) = (1 - e^{-10})(e^{-10})^1 = 4.54 \cdot 10^{-5}$$

and

$$\rho_v(9) = 8.19 \cdot 10^{-40}.$$

Similarly, at $T = \theta_v$: $\rho_v(0) = 0.632$, $\rho_v(1) = 0.233$, $\rho_v(9) = 2.87 \cdot 10^{-5}$

and at $T = 10\ \theta_v$: $\rho_v(0) = 0.0861$, $\rho_v(1) = 0.0779$, $\rho_v(9) = 0.0387$

Ans. 13.

$$\bar{u}_v = \bar{R}T^2 \left\{ \frac{\partial}{\partial T} \ln\left[\frac{e^{-\theta_v/2T}}{\left(1-e^{-\theta_v/T}\right)}\right] \right\}_{\bar{v}} = \bar{R}T^2 \frac{d}{dT}\left[-\frac{\theta_v}{2T} - \ln\left(1-e^{-\theta_v/T}\right)\right]$$

$$= \bar{R}T^2\left[+\frac{\theta_v}{2T^2} - \frac{-(\theta_v/T^2)e^{-\theta_v/T}}{\left(1-e^{-\theta_v/T}\right)}\right] = \bar{R}\ \theta_v\left[\frac{1}{2} + \frac{1}{\left(e^{\theta_v/T} - 1\right)}\right]$$

$$\bar{c}_{v,v} = \left(\frac{\partial \bar{u}_v}{\partial T}\right)_v = \frac{\partial}{\partial T}\left\{\bar{R}\ \theta_v\left[\frac{1}{2} + \frac{1}{\left(e^{\theta_v/T} - 1\right)}\right]\right\}_{\bar{v}} = \bar{R}\theta_v\left[\frac{(\theta_v/T^2)e^{\theta_v/T}}{\left(e^{\theta_v/T} - 1\right)^2}\right] = \frac{\bar{R}(\theta_v/T)^2\ e^{\theta_v/T}}{\left(e^{\theta_v/T} - 1\right)^2}$$

$$\bar{s}_v = \frac{\bar{u}_v}{T} + R\ln Z_v = \bar{R}\left(\frac{\theta_v}{T}\right)\left[\frac{1}{2} + \frac{1}{\left(e^{\theta_v/T} - 1\right)}\right] + \bar{R}\ln\left[\frac{e^{-\theta_v/2T}}{\left(1-e^{-\theta_v/T}\right)}\right] = \bar{R}\left[\left(\frac{\theta_v}{T}\right)\frac{1}{\left(e^{\theta_v/T} - 1\right)} - \ln\left(1-e^{-\theta_v/T}\right)\right]$$