<u>Problem 49.20 RHK)</u>

We have to show that (a) *the molar internal energy* E_{int} *of a solid can be written, according to Einstein's theory of heat capacities, as*

$$E_{\text{int}} = 3RT_E \left(\frac{1}{e^x - 1} \right),$$

in which $x = T_E / T$, where T_E *is the Einstein temperature* $h\nu/k$. (b) *We have to verify that* E_{int} *approaches its classical value of* $3RT$ as $T \to \infty$.

<u>Solution:</u>

(a)

According to the Einstein's theory of atomic oscillations, an oscillator with characteristic frequency ν at temperature T will have an average energy

$$\frac{h\nu}{\exp(h\nu/kT) - 1} .$$

As a molecule can oscillate in three independent directions, the total vibrational energy of a mole, N_A, of molecules at temperature T will therefore be

$$E_{\text{int}} = 3N_A \times \frac{h\nu}{\exp\left(h\nu/kT\right)-1} \ ,$$

$$= 3R \times \frac{h\nu/k}{\exp\left(h\nu/kT\right)-1}.$$

We have used that the gas constant R and Avogadro number N_A are related through the Boltzmann constant k as $R = N_A k$.

Einstein temperature is defined as

$T_E = h\nu/k$.

Therefore,

$$E_{\text{int}} = \frac{3RT_E}{\exp\left(T_E/T\right)-1} = \frac{3RT_E}{e^x-1},$$

where we have substituted x for T_E/T .

(b)

As

$T \to \infty$ $\lim_{T\to\infty} x = T_E/T \to 0.$

Also,

$\lim_{x\to 0}\left(e^x-1\right) \to x,$

$\therefore$ as $T \to \infty$:$E_{\text{int}} = 3RT$