3.012 FØ5

SOLUTIONS TO THERMO/STAT. MECH. PRACTICE PROBLEMS

E&R P31.12

$$q = e^{-0/T} + e^{-100/T} + e^{-200/T}$$

$$= 1 + e^{-100/T} + e^{-200/T}$$

$$T = 50\text{K}: \quad p_0 = \frac{e^{-0/T}}{q} = \frac{1}{\underbrace{1 + e^{-100/50} + e^{-200/50}}_{1.15}} = 0.867$$

$$p_1 = \frac{e^{-100/T}}{q} = 0.118$$

$$p_2 = \frac{e^{-200/T}}{q} = 0.016$$

$T = 500\text{K}$: $q = 2.49$

$\therefore p_0 = 0.40$

$p_1 = 0.329$

$p_2 = 0.269$

$T = 5000\text{K}$: $q = 1 + 0.98 + 0.96 = 2.94$

$\therefore p_0 = 0.340$

$p_1 = 0.333$

$p_2 = 0.327$

E&R P31.13 AS DISCUSSED IN THE TEXT, 6000 cm^{-1} IS THE $\Delta\tilde{\nu}$ WAVE NUMBER FOR THE ENERGY LEVEL SPACING, RELATED TO ΔE BY:

$$\Delta E = hc\Delta\tilde{\nu} = (6.626\times10^{-34}\ \text{J}\cdot\text{s})(3\times10^{10}\ \text{cm}\cdot\text{s}^{-1})(6000\ \text{cm}^{-1})$$

$$= 1.19\times10^{-19}\ \text{J}$$

WE ARE TOLD THAT 8 TIMES AS MANY MOLECULES ARE FOUND IN THE GROUND STATE AS THE EXCITED STATE:

$$\therefore \frac{p_0}{p_1} = 8 \qquad \frac{p_0}{p_1} = \frac{\left(\frac{e^{-E_0/kT}}{q}\right)}{\left(\frac{e^{-E_1/kT}}{q}\right)} = \frac{e^{-E_0/kT}}{e^{-E_1/kT}} = e^{\Delta E/kT}$$

$\Delta E \equiv E_1 - E_0$

$$e^{\Delta E/kT} = e^{(1.19\times10^{-19}\,J)/kT} = 8 \longrightarrow \frac{8619}{T} = \ln 8$$

$$\therefore \boxed{T = 4145\ K}$$

E+R 31.19

$$\frac{p_0}{p_1} = 5 \longrightarrow \frac{e^{-E_0/kT}}{e^{-E_1/kT}} = e^{\Delta E/kT} = 5$$

$$\frac{94{,}157}{T} = \ln 5 \qquad \therefore \boxed{T = 58.5\times10^{3}\ K}$$

E+R 31.20

$$E_1 = hc\tilde{\nu} = (2.41\times10^{-21}\ J)$$

121.1 cm^{-1}

$$\left(\begin{array}{c}\text{PROBABILITY TO}\\ \text{OCCUPY } \underline{\text{EITHER}} \text{ EXCITED}\\ \text{STATE AT } T=100K\end{array}\right) = 2p_1 = 2\left(\frac{e^{-E_1/kT}}{q}\right) = \underline{0.148}$$

2 IDENTICAL ENERGY LEVELS AT 121.1 cm^{-1}

$$q = e^{-0/kT} + e^{-0/kT} + e^{-\varepsilon_1/kT} + e^{-\varepsilon_1/kT}$$

$$= 2 + 2e^{-\varepsilon_1/kT} = 2 + 2e^{-174.6/T} = 2.35$$

@ 500K : $p(T=500K) = 2p_1 = \underline{0.414}$

$$q = 3.41$$

@ 2000K : $p(T=2000K) = 2p_1 = \underline{0.478}$

$$q = 3.83$$

$U = \frac{NkT}{2}$ $C_V = \frac{Nk}{2}$

$\boxed{\text{EVR P33.3}}$

$$\varepsilon_m = \alpha m^2$$

$$q = \sum_{m=0}^{\infty} e^{-\alpha m^2/kT} = \sum_{m=0}^{\infty} \left(e^{-\alpha/kT}\right)^{m^2} \qquad Q = q^N$$

$$U = kT^2 \frac{\partial \ln Q}{\partial T} = \frac{NkT}{2}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{Nk}{2}$$

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(a) $q = e^{-(-D)/kT} + e^{-(-D)/kT} + e^{-0/kT}$

$= 2e^{D/kT} + 1$

(b) $U = kT^2 \dfrac{\partial \ln q}{\partial T} = kT^2 \left(\dfrac{-\frac{2D}{kT^2} e^{D/kT}}{(1+2e^{D/kT})} \right) = \dfrac{-2D e^{D/kT}}{(1+2e^{D/kT})}$

(c) $U(T\to\infty) = \dfrac{-2D}{1+2} = -\frac{2}{3}D$

(d) $U(T\to 0) = -D$

(e) $\dfrac{p_3}{(p_1+p_2)} = \dfrac{e^{-0/kT}}{2e^{D/kT}} = \frac{1}{2}e^{-D/kT}$

(f) $S = -k_b \sum_{j=1}^{3} p_j \ln p_j \qquad q(T\to\infty) = 3$

$= -k_b\, 3\left[\frac{1}{q}\ln\frac{1}{q}\right] = -k_b \ln\left(\frac{1}{3}\right) = \underline{1.09\, k_b}$