[redacted]

1.8. Convert the total energy E into quanta, each of energy $h\nu$. Let R be the number of these quanta; clearly, $R = E/h\nu$. Now follow the argument developed on page 70 of the text, whereby the number Ω for this problem turns out to be

$$(R+N-1)!/R!(N-1)! . \tag{1}$$

For $N >> 1$, expression (1) gives

$$\ell n\,\Omega \approx (R+N)\ \ell n(R+N) - R\ \ell n\, R - N\ \ell n\, N .$$

The expression for T now follows straightforwardly; we get

$$\frac{1}{T} = k\left(\frac{\partial\,\ell n\,\Omega}{\partial E}\right)_N = \frac{k}{h\nu}\left(\frac{\partial\,\ell n\,\Omega}{\partial R}\right)_N = \frac{k}{h\nu}\,\ell n\left(\frac{R+N}{R}\right) = \frac{k}{h\nu}\,\ell n\left(1+\frac{Nh\nu}{E}\right),$$

so that

$$T = \frac{h\nu}{k}\Big/\ell n\left(1+\frac{Nh\nu}{E}\right).$$

For $E >> Nh\nu$, we recover the classical result: $T = E/Nk$.

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3.18: $\langle(\Delta\epsilon)^3\rangle = \langle(\epsilon^3 - 3\epsilon^2\langle\epsilon\rangle + 3\epsilon\langle\epsilon\rangle^2 - \langle\epsilon\rangle^3\rangle$

$$\langle(\Delta\epsilon)^3\rangle = \langle\epsilon^3\rangle - 3\langle\epsilon\rangle\langle\epsilon^2\rangle + 2\langle\epsilon\rangle^3$$

now $\langle\epsilon\rangle = U = \frac{Tr(He^{-\beta H})}{Z = Tr(e^{-\beta H})}$ ① (1)

$$\frac{\partial U}{\partial\beta} = -T^2 k\frac{\partial U}{\partial T} = -kT^2 C_V$$

also $\frac{\partial U}{\partial\beta} \stackrel{①}{=} \frac{-Tr(H^2 e^{-\beta H})}{Z} + \frac{[Tr(He^{-\beta H})]^2}{Z^2} = -\langle\epsilon^2\rangle + \langle\epsilon\rangle^2$

result: $+kT^2 C_V = +\langle\epsilon^2\rangle - \langle\epsilon\rangle^2 = \langle(\Delta\epsilon)^2\rangle$ ②

$$= \frac{Tr\,\epsilon^2 e^{-\beta\epsilon}}{Tr\,e^{-\beta\epsilon}} - \left(\frac{Tr\,\epsilon e^{-\beta\epsilon}}{Tr\,e^{-\beta\epsilon}}\right)^2$$

$\frac{\partial}{\partial\beta}(2)$: $\frac{\partial}{\partial\beta}$ L.H.S $= -kT^2\frac{\partial}{\partial T}(kT^2 C_V) = -k^2 T^4\frac{\partial C_V}{\partial T} - 2k^2T^3 C_V$

$-\frac{\partial^2 U}{\partial\beta^2} = \frac{\partial}{\partial\beta}$ R.H.S of (2) $= -\frac{Tr(H^3 e^{-\beta H})}{Tr\,e^{-\beta H}} + \frac{Tr(H^2 e^{-\beta H})\,Tr(He^{-\beta H})}{(Tr\,e^{-\beta H})^2}$

$$-2\langle\epsilon\rangle\left\{-\langle\epsilon^2\rangle + \langle\epsilon\rangle^2\right\} =$$

$$= -\langle\epsilon^3\rangle + 3\langle\epsilon^2\rangle\langle\epsilon\rangle - 2\langle\epsilon\rangle^3 = -\langle(\Delta\epsilon)^3\rangle$$

$$\Rightarrow \langle(\Delta\epsilon)^3\rangle = k^2T^4\frac{\partial C_V}{\partial T} + 2k^2T^3 C_V \quad \text{Q.E.D.}$$

for ideal gas: $U = \frac{3}{2}NkT$; $C_V = \frac{3}{2}Nk$, $\frac{\partial C_V}{\partial T} = 0$

$$\Rightarrow \langle(\Delta\epsilon)^2\rangle = kT^2 C_V = \frac{3}{2}Nk^2T^2 \Rightarrow \left\langle\left(\frac{\Delta\epsilon}{U}\right)^2\right\rangle = \frac{\frac{3}{2}Nk^2T^2}{(\frac{3}{2}NkT)^2} = \frac{2}{3N} \checkmark$$

$$\left\langle\left(\frac{\Delta\epsilon}{U}\right)^3\right\rangle = \frac{2k^2T^3\,\frac{3}{2}Nk}{(\frac{3}{2}NkT)^3} = \frac{8}{9N^2} \checkmark \quad \text{Q.E.D.}$$

[redacted]

2.4. The rigid rotator is a model for a diatomic molecule whose internuclear distance r may be regarded as fixed. The orientation of the molecule in space may be denoted by the angles θ and φ, the conjugate variables being $p_\theta = mr^2\dot{\theta}$ and $p_\varphi = mr^2 \sin^2\theta\dot{\varphi}$. The energy of rotation is given by

$$E = \frac{1}{2}m(r\dot{\theta})^2 + \frac{1}{2}m(r\sin\theta\dot{\varphi})^2 = \frac{p_\theta^2}{2mr^2} + \frac{p_\varphi^2}{2mr^2\sin^2\theta} = \frac{M^2}{2I},$$

where $I = mr^2$ and $M^2 = p_\theta^2 + \left(p_\varphi^2 / \sin^2\theta\right)$.

The "volume" of the relevant region of the phase space is given by the integral $\int dp_\theta dp_\varphi d\theta\, d\varphi$, where the region of integration is constrained by the value of M. A little reflection shows that in the sub-space of p_θ and p_φ we are restricted by an elliptical boundary with semi-axes M and $M\sin\theta$, the enclosed area being $\pi M^2 \sin\theta$. The "volume" of the relevant region, therefore, is

$$\int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi}(\pi M^2\sin\theta)d\theta\, d\varphi = 4\pi^2 M^2 .$$

$$\left(\frac{\partial P}{\partial T}\right)_\mu = \frac{5}{2T}P - \frac{\mu}{kT^2}P = \left[\frac{5}{2} - \ell n\left\{\frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{3/2}\right\}\right]\frac{Nk}{V}$$

which, by eqn. (1.5.1a), is precisely equal to S/V.

[redacted]

2.8. We write $V_{3N} = AR^{3N}$, so that $dV_{3N} = A \cdot 3NR^{3N-1} dR$. At the same time, we have

$$\int_0^\infty \cdots \int_0^\infty e^{-\sum_{i=1}^{N} r_i} \prod_{i=1}^{N} r_i^2 dr_i = \prod_{i=1}^{N} \int_0^\infty e^{-r_i} r_i^2 dr_i = 2^N . \qquad (1)$$

The integral on the left may be written as

$$\int_0^\infty e^{-R} (4\pi)^{-N} dV_{3N} = \int_0^\infty e^{-R} (4\pi)^{-N} A \cdot 3NR^{3N-1} dR = (4\pi)^{-N} A \cdot 3N\, \Gamma(3N) . \qquad (2)$$

Equating (1) and (2), we get: $A = (8\pi)^N / (3N)!$, which yields the desired result for V_{3N}.

The "volume" of the relevant region of the phase space is given by

$$\int \prod_{i=1}^{3N} dq_i dp_i = V^N \int \prod_{i=1}^{N} (4\pi p_i^2 dp_i) = V^N (8\pi E^3 / c^3)^N / (3N)! ,$$

so that

$$\Sigma(N, V, E) = V^N (8\pi E^3 / h^3 c^3)^N / (3N)! ,$$

which is a function of N and VE^3. An *isentropic* process then implies that $VE^3 = const.$

The temperature of the system is given by

$$\frac{1}{T} = \left(\frac{\partial (k \ln \Sigma)}{\partial E} \right)_{N,V} = \frac{3Nk}{E}, \quad \text{i.e.} \quad E = 3NkT .$$

The equation for the isentropic process then becomes $VT^3 = const.$, i.e. $T \propto V^{-1/3}$; this implies that $\gamma = 4/3$. The rest of the thermodynamics follows straightforwardly. See also Problems 1.7 and 3.15.