McQuarrie 5–3

Set kinetic energy equal to total energy.

$$\frac{3}{2}kT = \frac{h^2}{8m\underset{\uparrow \atop a=1\,cm}{a^2}}\underbrace{(n_x^2+n_y^2+n_z^2)}_{3n^2}$$

$$n = \left(\frac{3}{2}kT\,\frac{8ma^2}{3h^2}\right)^{1/2} = 7.94\times10^7 \simeq 8\times10^7$$

The classical correspondence limit states that the results of quantum mechanics approach those of classical mechanics as quantum numbers get large. Here the quantum number is quite large, which adds justification for the replacement of the sum with an integral in calculation of the translational partition function.

McQuarrie 5-15 $m = 83.798$ amu $\quad 1\,\text{amu} = 1.6605\times10^{-27}$ kg

$$q_{trans} = \left(\frac{2\pi m k T}{h^2}\right)^{3/2} V = 7.42\times10^{32}\ m^{-3}\,V$$

$$q_{elec} \cong \omega_{e1} + \omega_{e2} e^{-\beta\Delta\varepsilon_{12}} + \omega_{e3} e^{-\beta\Delta\varepsilon_{13}} + \cdots$$

Omit q_{nucl} (will ultimately cancel ~~out~~ out for chemical transformation)

From NIST database, for Kr

consider just these three

$4s^2 4p^6$	^1S	$J = 0$	$E = 0.0\ cm^{-1}$
$4s^2 4p^5 (^2P^\circ_{3/2}) 5s$	$^2[3/2]^\circ$	$J = 2$	$\Delta\varepsilon_{12}$ 79,971.7417 cm^{-1}
		1	80,916.7670 cm^{-1} $\Delta\varepsilon_{13}$
$4s^2 4p^5 (^2P^\circ_{1/2}) 5s$	$^2[1/2]^\circ$	$J = 0$	85,191.6166 cm^{-1}
		1	85,846.7056 cm^{-1}

$\vdots$

$$q_{elec} \cong 1 + 5e^{-\beta\Delta\varepsilon_{12}} + 3e^{-\Delta\varepsilon_{13}}$$ Note: $\omega = 2J+1$

$\Delta\varepsilon_{12} = 1.5844\times10^{-18}$ J $\quad \Delta\varepsilon_{13} = 1.6032\times10^{-18}$ J $\quad \Delta\varepsilon_{14} = 1.6878\times10^{-18}$ J

$$q_{elec} = 1 + 2.87\times10^{-167} + 1.82\times10^{-169}$$

Obviously for Kr, the excited state contributions are negligible $\Longrightarrow q_{elec} \cong 1$

$Q = \frac{q^N}{N!}$ $\quad N = N_A$

volume of 1 mol of ideal gas in m^3 at 1 atm, 25°C

$A = -kT\ln Q = -RT\ln q + RT(\ln N_A - 1)$

$= RT(-\ln(7.42\times10^{32}) - \ln(0.0224) + \ln(6.022\times10^{23}) - 1)$

$= RT(-75.7 + 6.032 + 54.8 - 1) = -136\ J$

$E = kT^2\frac{d\ln Q}{dT} = RT^2\frac{d\ln q}{dT} = RT^2\left[\frac{d\ln q_{trans}}{dT} + \underbrace{\frac{d\ln \overset{\approx 1}{q_{ele}}}{dT}}_{0}\right]$

$= RT^2\frac{d}{dT}\ln\left(\frac{2\pi mkT}{h^2}\right)^{3/2} = \frac{3}{2}RT^2\left(\frac{h^2}{2\pi mkT}\right)\left(\frac{2\pi mk}{h^2}\right)$

$= \frac{3}{2}RT = 3.72\ kJ$

$C_v = \frac{dE}{dT} = \frac{3}{2}R = 12.5\ JK^{-1}$

$\mu = -kT\left(\frac{d\ln Q}{dN}\right)_{V,T} = -kT\frac{d}{dN}(N\ln q - N\ln N + N) = -kT\ln\left(\frac{q}{N}\right)$

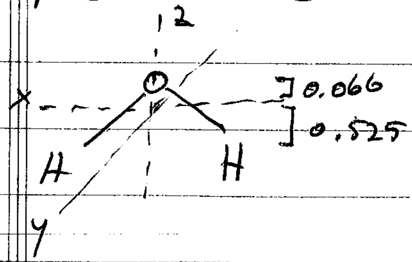
$= -kT\ln\left(\frac{7.42\times10^{32}}{6.022\times10^{23}}\cdot0.0224\right) = -6.13\times10^{20}\ J$

$S = k\ln Q + \frac{E}{T} = -\frac{A}{T} + \frac{E}{T} = 12.9\ JK^{-1}$

$A = -136\ J \quad E = 3.72\ kJ \quad C_v = 12.5\ JK^{-1} \quad S = 12.9\ JK^{-1}$

$\mu = -6.13\times10^{20}\ J$

1. McQuarrie 8-1.



$16x = 2(0.96 \cos 52^\circ - x)$

$x = 0.066$ Å

$I_z = 2(0.96 \sin 52^\circ)^2 = 1.14$ units $= \text{Å}^2 m_H$

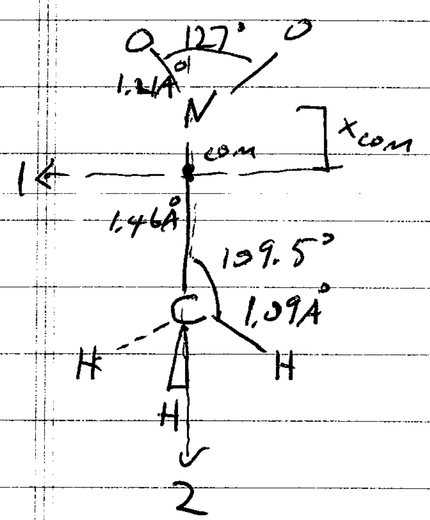
$I_x = 16(0.066)^2 + 2(0.525)^2 = 0.624$

$I_y = 16(0.066)^2 + 2\left[(0.525)^2 + \left(\frac{1.5}{2}\right)^2\right] = 1.746$

$$\Theta_r = \frac{h^2}{8\pi^2 I k}$$

		Table 8-1	
$\Theta_{r_x} = \frac{h^2}{8\pi^2 I_x k}$	$= 39.1K$	$40.1K$	Agreement good.
$\Theta_{r_y} = \frac{h^2}{8\pi^2 I_y k}$	$= 13.9K$	$13.4K$	
$\Theta_{r_z} = \frac{h^2}{8\pi^2 I_z k}$	$= 21.3K$	$20.9K$	

McQuarrie 8-14.



$$x_{com} = \frac{1}{61}\left(-32 r_{NO}\cos(63.5) + 12 r_{NC} + 3\left(r_{CH}\cos(180-190.5) + r_{NC}\right)\right)$$
$$= 0.094\text{Å}$$

$$I_2 = \frac{1}{N_A}\cdot 32\left(r_{NO}\sin 63.5°\right)^2 + 3\left(r_{CH}\sin 70.5\right)^2$$
$$= 67.5\times 10^{-47}\ kg\text{-}m^2$$

$$N_A I_1 = I_1^{(O_2)} + I_3^{(H_3)} + 0.094^2\cdot 14 + (1.46-0.094)^2\cdot 12$$
$$N_A I_1^{(O_2)} = 32\left(0.094 + (1.21\cos 63.5°\right)^2$$
$$N_A I_1^{(H_3)} = 3\left[(1.46-0.094) + 1.09\cos 70.5\right]^2 + \frac{1}{2} r_{HH}^2$$
$$r_{HH} = r_{CH}\sin\left(\frac{109.5°}{2}\right)$$

$$I_1 = 74.0\times 10^{-47}\ kg\cdot m^2$$
$$I_\perp = I_1 + 32\left(r_{NO}\sin 63.5°\right)^2/N_A = 136\times 10^{-47}\ kg\ m^2$$

$$S^\circ_{298} = S^\circ_{tr} + S^\circ_{rot} + S^\circ_{vib}$$

$$S^\circ_{tr} = \frac{5}{2}R + R\ln\left(\left[\frac{2\pi MkT}{h^2}\right]^{3/2}\frac{V^{id}}{N_A}\right)$$ where V^{id} is volume of ideal gas at 298K + 1 atm
$$= 38.1\ eu$$

$$S^\circ_{rot} = 2R + R\ln\left[\sqrt{\pi}\,(I_1 I_2 I_\perp)^{1/2}\left(\frac{8\pi^2 kT}{h^2}\right)^{3/2}\cdot\sqrt{\pi}\left(\frac{8\pi^2 kT}{h^2}\right)^{1/2}\frac{I_{int}}{6}\right]$$
$11.86\times 10^{-47}\ kg\ m^2$

sym. no. for internal rotation
$$= 25.5\ eu$$

$$S^\circ_{vib} = R\sum_v\left[\frac{e^{-\Theta_v/T}\ \frac{\Theta_v}{T}}{1-e^{-\Theta_v/T}} - \ln(1-e^{-\Theta_v/T})\right] = 1.85\ eu$$

$S^\circ_{298} = 65.4\ eu$ ($S^\circ_{298} = 61.2$ eu from Table ~~8~~ 1-36)