Assignment 4 solutions

Question 1:

For $^{11}B^{16}O$, $\nu = 1885.69\ cm^{-1}$ and $B = 1.7820\ cm^{-1}$.

Question 2:

The lowest energy excited state lies $23833.7\ cm^{-1}$ above the ground state. At 1000 K, $kT = 695\ cm^{-1}$. Since the energy of the first excited state is much higher than kT in the range of temperatures considered in this assignment, it is reasonable to ignore the electronically excited states.

Question 3:

For ^{11}B, $m = 11.009\,305\,5$ u. For ^{16}O, $m = 15.994\,914\,622\,1$ u. The mass of the molecule is therefore 27.004 220 1 u.

Question 4:

Translational partition function:

$$> mBO := 27.0042201 \frac{[[\frac{g}{mol}]]}{6.0221367e23[[mol^{-1}]]}$$

$$mBO := \frac{4.484159269\ 10^{-26} [[\frac{kg}{mol}]]}{[[\frac{1}{mol}]]} \quad (1)$$

$$> k := 1.380658e{-}23 [[\frac{J}{K}]]$$

$$k := 1.380658\ 10^{-23} [[\frac{m^2\,kg}{s^2\,K}]] \quad (2)$$

$$> V := 0.4[[L]]$$

$$V := 0.4\ [[L]] \quad (3)$$

$$> h := 6.6260755e{-}34[[J \cdot s]]$$

$$h := 6.6260755\ 10^{-34} [[\frac{m^2\,kg}{s}]] \quad (4)$$

$$> qT := T \rightarrow \frac{(2 \cdot \pi \cdot mBO \cdot k \cdot T)^{\frac{3}{2}} \cdot V}{h^3}$$

(5)

$$qT := T \rightarrow \frac{2\sqrt{2}\,(\pi\, mBO\, k\, T)^{3/2}\, V}{h^3} \tag{5}$$

> $simplify(qT(1000[[K]]))$

$$3.335887288\ 10^{29} \tag{6}$$

Rotational partition function:

> $B := 1.7820[[cm^{-1}]]$

$$B := 1.7820 \left[\left[\frac{1}{cm}\right]\right] \tag{7}$$

> $\sigma := 1$

$$\sigma := 1 \tag{8}$$

> $c := 2.99792458e8\left[\left[\frac{m}{s}\right]\right]$

$$c := 2.99792458\ 10^{8} \left[\left[\frac{m}{s}\right]\right] \tag{9}$$

> $qR := T \rightarrow \frac{k \cdot T}{\sigma \cdot h \cdot c \cdot B}$

$$qR := T \rightarrow \frac{k\, T}{\sigma\, h\, c\, B} \tag{10}$$

> $simplify(qR(1000[[K]]))$

$$390.0329799 \tag{11}$$

Vibrational partition function:

> $\nu := 1885.69[[cm^{-1}]]$

$$\nu := 1885.69 \left[\left[\frac{1}{cm}\right]\right] \tag{12}$$

> $qV := T \rightarrow \frac{1}{1 - \exp\left(-\frac{h \cdot c \cdot \nu}{k \cdot T}\right)}$

$$qV := T \rightarrow \frac{1}{1 - e^{-\frac{h\, c\, \nu}{k\, T}}} \tag{13}$$

> $simplify(qV(1000[[K]]))$

$$1.071045375 \tag{14}$$

Question 5:

> $q := T \rightarrow qT(T) \cdot qR(T) \cdot qV(T)$

$$q := T \rightarrow qT(T)\ qR(T)\ qV(T) \tag{15}$$

> $simplify(q(1000[[K]]))$

(16)

$$1.393543627\ 10^{32} \quad (16)$$

Question 6:

$$> pV := (v, T) \to \frac{\exp\left(-\frac{h \cdot c \cdot \nu \cdot v}{k \cdot T}\right)}{qV(T)}$$

$$pV := (v, T) \to \frac{e^{-\frac{h c \nu v}{k T}}}{qV(T)} \quad (17)$$

$$> simplify(\, pV(0, 1000[\![K]\!])\,)$$

$$0.9336672592 \quad (18)$$

$$> simplify(\, pV(1, 1000[\![K]\!])\,)$$

$$0.06193270834 \quad (19)$$

$$> simplify(\, pV(2, 1000[\![K]\!])\,)$$

$$0.004108166292 \quad (20)$$

$$> simplify(\, pV(3, 1000[\![K]\!])\,)$$

$$0.0002725059297 \quad (21)$$

Question 7:

$$> pVR := (v, J, T) \to \frac{(2 \cdot J + 1) \cdot \exp\left(-\frac{h \cdot c \cdot (\nu \cdot v + J \cdot (J+1) \cdot B)}{k \cdot T}\right)}{qV(T) \cdot qR(T)}$$

$$pVR := (v, J, T) \to \frac{(2 J + 1)\, e^{-\frac{h c (\nu v + J (1 + J) B)}{k T}}}{qV(T)\, qR(T)} \quad (22)$$

$$> simplify(\, pVR(1, 10, 1000[\![K]\!])\,)$$

$$0.002515098961 \quad (23)$$

Question 8:

$$> pR := (J, T) \to \frac{(2 \cdot J + 1) \cdot \exp\left(-\frac{h \cdot c \cdot J \cdot (J+1) \cdot B}{k \cdot T}\right)}{qR(T)}$$

$$pR := (J, T) \to \frac{(2 J + 1)\, e^{-\frac{h c J (J+1) B}{k T}}}{qR(T)} \quad (24)$$

$$> solve(diff(simplify(\, pR(J, 1000[\![K]\!])\,), J) = 0, J)$$

$$13.46483046, -14.46483046 \quad (25)$$

This tells us that the most probable state is either $J = 13$ or 14. Let's check both:

$$> simplify(\, pR(13, 1000[\![K]\!])\,)$$

$$0.04341190181 \quad (26)$$

> $simplify(pR(14, 1000[[K]]))$

$$0.04339758531 \quad (27)$$

The most probable state is in fact $J = 13$.

Question 9:

> $R := 8.3145101[[J \cdot K^{-1} \cdot mol^{-1}]]$

$$R := 8.3145101 \left[\left[\frac{m^2\, kg}{s^2\, K\, mol} \right]\right] \quad (28)$$

> $U := R \cdot T^2 \cdot diff(\ln(q(T)), T) :$

> $T := 1000[[K]]$

$$T := 1000 \; [[K]] \quad (29)$$

> $simplify(U)$

$$22388.90700 \left[\left[\frac{m^2\, kg}{s^2\, mol} \right]\right] \quad (30)$$

The molar internal energy is therefore 22.39 kJ/mol.

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