

18.E: Partition Functions and Ideal Gases (Exercises)

A Libretexts Textmap organized around McQuarrie and Simon's textbook

Physical Chemistry: A Molecular Approach

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These are homework exercises to accompany [Chapter 18](#) of McQuarrie and Simon's "Physical Chemistry: A Molecular Approach" Textmap.

1) If the nucleus has a spin of s_n , then its spin degeneracy $g_n = 2s_n + 1$. The diatomic molecule formed from such a nucleus will have g_n^2 spin functions which have to be combined to form symmetric and antisymmetric functions. Carry out an analysis similar to that of H_2 for D_2 where the deuterium nucleus has a spin of 1.

2) Derive the thermodynamic functions from the polyatomic rotational partition function. 3) Carry out the integration for the rotational partition function of the symmetric top.

4) Calculate the total partition function and the thermodynamic functions of water at 1000K. The three moments of inertia of water are 1.02, 1.91 and 2.92 in 10^{-47} kg m^2 . The symmetry number is 2. The vibrational data is given in Fig. 3.5. Assume a non-degenerate electronic ground state.

5) Verify that the symmetry numbers for methane, benzene and SF_6 are 12, 12 and 24 respectively.

6) The ground state of Na is a doublet (two states with the same energy). Assuming this to be the zero of energy and assuming that the next energy level to be 2 eV higher than the ground state, calculate q_{el} .

7) The bond length r_{eq} of O_2 is 1.2 Å. The moment of inertia I is $mr_{eq}^2/2$ where m of O is $16 \times 1.66 \times 10^{-27} \text{ kg}$. Calculate \tilde{B} and the rotational partition function of O_2 at 300 K.

8) The vibrational frequency ν of ICl is 384 cm^{-1} . What is its vibrational partition function at 300 K? What is the fraction of molecules in the ground state ($n = 0$) and the first excited state $n = 1$? 9) Calculate the translational partition function of N_2 at 300 K. For volume, use the molar volume at 300 K.

10) An isotope exchange reaction between isotopes of bromine is $^{79}Br^{79}Br + ^{81}Br^{81}Br \rightleftharpoons ^{79}Br^{81}Br + ^{81}Br^{79}Br$

The fundamental vibrational frequency of $^{79}Br^{81}Br$ is 323.33 cm^{-1} . All the molecules can be assumed to have the same bond length and have a singlet ground electronic state. Calculate the equilibrium constant at 300K and 1000K.

11) For the reaction $I_2 \leftrightarrow 2I$, calculate the equilibrium constant at 1000K. The relevant data are as follows. The ground electronic state of I is $^2P_{3/2}$ whose degeneracy is 4. The rotational and vibrational frequencies of I_2 are 0.0373 cm^{-1} and 214.36 cm^{-1} respectively. The dissociation energy of I_2 is 1.5422 eV.

12) The representative molecular data for a few molecules is given in table 3.1. Using the relevant data, calculate the equilibrium constant for the reaction $H_2 + Cl_2 \rightleftharpoons 2HCl$ at 1000K. What is the value of the equilibrium constant as $T \rightarrow \infty$?

13) Eq. (3.50) is related to the Giauque function. Estimate the total molar Giauque function for molecules that behave as harmonic oscillators-rigid rotors.

14) The energy of a molecule in the rigid rotor – harmonic oscillator approximation is $E_{vib, rot} = (n + 1/2) h\nu + B J(J+1)$. Real molecules deviate from this behaviour due to the existence of anharmonicity (anharmonicity constant x_e), centrifugal distortion (centrifugal distortion constant D) and the interaction between vibration and rotation (α is the coupling constant between the vibrational and rotational modes). The expression for the energy when these effects are included is $E_{vib, rot} = h\nu(n + 1/2) + B J(J+1) - D J^2(J+1)^2 + \alpha(n + 1/2) J(J+1)$. Here, the third term is due to anharmonicity, the fourth term is due to centrifugal distortion and the last term is due to the interaction between vibration and rotation. Calculate the $q_{vib, rot}$ which includes the effects of these distortions.

Q18.4

Using the data in Table 8.6, calculate the fraction of sodium atoms in the first excited state at temperatures 300 K, 1000 K, and 2000 K.

S18.4

Using Equation 18.10, we can calculate the fraction of sodium atoms in the first excited state, with $g_{e1} = 2, g_{e2} = 2, g_{e3} = 4, g_{e4} = 2$:

$$f_2 = \frac{2e^{-\beta\epsilon_{e2}}}{2 + 2e^{-\beta\epsilon_{e2}} + 4e^{-\beta\epsilon_{e3}} + 2e^{-\beta\epsilon_{e4}} + \dots} \quad (18.E.1)$$

Using the data in Table 8.6, the numerator of this fraction becomes

$$2\exp\left[-\frac{16956.183\text{cm}^{-1}}{(0.6950\text{cm}^{-1}\text{K}^{-1})T}\right] \quad (18.E.2)$$

and the denominator becomes

$$2 + 2\exp\left[-\frac{16956.183\text{cm}^{-1}}{(0.6950\text{cm}^{-1}\text{K}^{-1})T}\right] + 4\exp\left[-\frac{16973.379\text{cm}^{-1}}{(0.6950\text{cm}^{-1}\text{K}^{-1})T}\right] + 2\exp\left[-\frac{25739.86\text{cm}^{-1}}{(0.6950\text{cm}^{-1}\text{K}^{-1})T}\right] + \dots$$

Using these values, we can find the values of f_2 at the different temperatures.

$$f_2(T = 300\text{K}) = 4.8 \times 10^{-36}$$

$$f_2(T = 1000\text{K}) = 2.5 \times 10^{-11}$$

$$f_2(T = 2000\text{K}) = 5.0 \times 10^{-6}$$

Q18.5

Using the data in the table, calculate the fraction of hydrogen atoms in the first excited state at 400 K, 1800 K, and 2100 K.

Electronic Configuration	Term Symbol	Degeneracy $g_e = 2J + 1$	energy/ cm^{-1}
1s	$^2S_{1/2}$	2	0
2p	$^2P_{1/2}$	2	82 258.907
2s	$^2S_{1/2}$	2	82 258.942
2p	$^2P_{3/2}$	4	82 259.272

S18.5

Use the equation:

$$f_2 = \frac{g_{e2}e^{-\beta\epsilon_{e2}}}{g_{e1} + g_{e2}e^{-\beta\epsilon_{e2}} + g_{e3}e^{-\beta\epsilon_{e3}} + \dots} \quad (18.E.3)$$

and

$$\beta \approx \frac{1}{T \cdot 0.6950 \text{ cm}^{-1}\text{K}^{-1}} \quad (18.E.4)$$

to get:

$$f_2 = \frac{e^{-\frac{82\,258.907\text{ cm}}{T \cdot 0.6950\text{ cm}^{-1}\text{K}^{-1}}}}{2 + 2e^{-\frac{82\,258.907\text{ cm}}{T \cdot 0.6950\text{ cm}^{-1}\text{K}^{-1}}} + 2e^{-\frac{82\,258.942\text{ cm}}{T \cdot 0.6950\text{ cm}^{-1}\text{K}^{-1}}} + 4e^{-\frac{82\,259.272\text{ cm}}{T \cdot 0.6950\text{ cm}^{-1}\text{K}^{-1}}}} \quad (18.E.5)$$

$$f_2(400\text{ K}) = 0.2498$$

$$f_2(900\text{ K}) = 0.2499$$

$$f_2(2100\text{ K}) = 0.2500$$

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