

## 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  $g_n$  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  $10^{-47} \text{ kg m}^2$ . 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  $\nu$  of  $ICl$  is  $384 \text{ cm}^{-1}$ . 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  $^{79}Br^{81}Br \rightleftharpoons ^{81}Br^{79}Br$ . The fundamental vibrational frequency of  $^{79}Br^{81}Br$  is  $323.33 \text{ cm}^{-1}$ . 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  $I_2 \rightleftharpoons 2I$ , calculate the equilibrium constant at 1000K. The relevant data are as follows. The ground electronic state of I is  $^2P$  whose degeneracy is 4. The rotational and vibrational frequencies of  $I_2$  are  $0.0373 \text{ cm}^{-1}$  and  $214.36 \text{ cm}^{-1}$  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 ( $\alpha$  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/ $\text{cm}^{-1}$
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:

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

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

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

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

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