

Chapter 30: Statistical Mechanics Problems

1. For a diatomic molecule, the rotational energy is $\varepsilon_J = \tilde{B}hc J(J+1)$. (a.) Evaluate the rotational partition function of a heteronuclear diatomic molecule at 298.15 K by numerically summing the Boltzmann weighting factors over many energy levels in a spreadsheet. Take $\tilde{B}hc/kT = 0.00200$. The degeneracy of each level is $g_J = 2J + 1$. (b.) Compare your numerical answer to the partition function using the high temperature approximation: $q_r = kT/(\sigma\tilde{B}hc)$. (c.) Which rotational level has the maximum population of molecules? Why?

Answer: The plan is to note that summing over energy levels, the Boltzmann weighting factors are in the form $(2J + 1)e^{-\varepsilon_J/kT}$, with $\varepsilon_J = \tilde{B}hc J(J+1)$.

(a). The Excel spreadsheet to accomplish the sums is given below. The sum from $J = 0$ to $J = 90$ is required to find a five-significant figure value for the partition function. Not all rows are shown.

A1	B	C	D	E	F
2	Bhc/kT=	0.002			
3					
4	J	2J+1	BhcJ(J+1)/kT	$e^{-\varepsilon_J/kT}$	$(2J+1)e^{-\varepsilon_J/kT}$
5	0	1	0	1	1
6	1	3	0.004	0.99601	2.98802
7	2	5	0.012	0.98807	4.94036
8	3	7	0.024	0.97629	6.83400
9	4	9	0.04	0.96079	8.64710
10	5	11	0.06	0.94176	10.35941
11	6	13	0.084	0.91943	11.95261
12	7	15	0.112	0.89404	13.41066
13	8	17	0.144	0.86589	14.72009
14	9	19	0.18	0.83527	15.87013
15	10	21	0.22	0.80252	16.85289
16	11	23	0.264	0.76797	17.66339
17	12	25	0.312	0.73198	18.29954
18	13	27	0.364	0.69489	18.76206
19	14	29	0.42	0.65705	19.05436
20	15	31	0.48	0.61878	19.18229
21	16	33	0.544	0.58042	19.15392
22	17	35	0.612	0.54227	18.97928
23	18	37	0.684	0.50459	18.67000
24	19	39	0.76	0.46767	18.23899
25	20	41	0.84	0.43171	17.70013
26	⋮	⋮	⋮	⋮	⋮
27	90	181	16.38	7.696E-08	1.393E-05
28					
29				$q_r =$	500.33343

Cell D5 is “ $=\$C\$2*B5*(B5+1)$ ”. Cell E5 is “ $=EXP(-D5)$ ”. Cell F5 is “ $=C5*E5$ ”.

(b). For a heteronuclear diatomic, the symmetry number is one, $\sigma = 1$, since rotation by 180° gives a distinguishable state. The high temperature approximation then gives the rotational partition function as $q_r = kT/(\sigma\tilde{B}hc) = 1/0.00200 = 500.0$. The exact result is slightly higher at 500.333.

(c). The level with the maximum population is $J = 15$. While the Boltzmann distribution gives an exponentially decreasing probability of occupation of a given state with increasing J , the

degeneracy increases with increasing J . The product of a decreasing function and an increasing function has a maximum at intermediate value.

2. The fundamental vibration frequency for H^{35}Cl is 2885.3 cm^{-1} . Calculate the ratio of the number of molecules in the first excited vibrational state to the number in the ground vibrational state at 298.2 K .

Answer: The plan is to note that the ratio is given by Eq. 8.10.8 and that at 298.2 K $kT/hc = 207.224 \text{ cm}^{-1}$.

The Boltzmann probability of being in state i is: $p_i = n_i/N = e^{-\varepsilon_i/kT}/q$. The ratio of the number of molecules in states j and i is given by the ratio of the Boltzmann probabilities:

$$\frac{n_j}{n_i} = \frac{e^{-\varepsilon_j/kT}/q}{e^{-\varepsilon_i/kT}/q} = e^{-(\varepsilon_j - \varepsilon_i)/kT} = e^{-\Delta\varepsilon/kT} \quad \text{with } \Delta\varepsilon = \varepsilon_j - \varepsilon_i$$

For the first two vibrational states, $\Delta\varepsilon = h\nu_0$, giving:

$$\frac{n_1}{n_0} = e^{-hc\tilde{\nu}_0/kT} = e^{-2885.3 \text{ cm}^{-1}/207.224 \text{ cm}^{-1}} = 8.976 \times 10^{-7}$$

In other words, about one in a million are in the first excited vibrational state at room temperature.

3. The rotational constant for the linear molecule $\text{H-C}\equiv\text{N}$ is 1.4782 cm^{-1} .² Calculate the ratio of the number of molecules in excited rotational level $J = 3$ to the number in the ground rotational level $J = 0$ at 298.2 K . [Hint: take the rotational degeneracy $2J + 1$ into account.]

Answer: The plan is to note that the degeneracy is $2J + 1$ and that at 298.2 K the effective temperature is $kT/hc = 207.224 \text{ cm}^{-1}$. The ratio without taking degeneracy into account is given by Eq. 8.10.8

The Boltzmann probability of being in level i is: $p_i = n_i/N = g_i e^{-\varepsilon_i/kT}/q$, with g_i the degeneracy of level i . The ratio of the number of molecules in levels j and i is given by the ratio of the Boltzmann probabilities:

$$\frac{n_j}{n_i} = \frac{g_j e^{-\varepsilon_j/kT}/q}{g_i e^{-\varepsilon_i/kT}/q} = \left(\frac{g_j}{g_i}\right) e^{-(\varepsilon_j - \varepsilon_i)/kT} = \left(\frac{g_j}{g_i}\right) e^{-\Delta\varepsilon/kT} \quad \text{with } \Delta\varepsilon = \varepsilon_j - \varepsilon_i$$

The rotational energy is $\varepsilon_J = \tilde{B}hc J(J + 1)$. For rotational levels $J = 3$ and 0 :

$$\Delta\varepsilon = \tilde{B}hc [3(3 + 1) - 0(0 + 1)] = 12 \tilde{B}hc$$

For $\text{H-C}\equiv\text{N}$ the rotational constant is $\tilde{B} = 1.4782 \text{ cm}^{-1}$, giving:

$$\frac{n_3}{n_0} = \left(\frac{2 \cdot 3 + 1}{2 \cdot 0 + 1} \right) e^{-12 \tilde{B}hc/kT} = \left(\frac{7}{1} \right) e^{-12(1.4782 \text{ cm}^{-1})/207.224 \text{ cm}^{-1}} = \left(\frac{7}{1} \right) 0.9180 = 6.425$$

Even though the probability of being in a single rotational state with $J = 3$ is less than $J = 0$, the degeneracy gives roughly 6.5 times more molecules in $J = 3$ than $J = 0$ at room temperature.

4. Verify the units conversion factor, $\Gamma = 0.0259467$, for the translational partition function in Eqs. 30.3.1-30.3.2 for a $P^\circ = 1$ bar standard state.

Answer: The units conversion factor Γ is defined with $R = 8.3145 \text{ J K}^{-1} \text{ mol}$ and $P^\circ = 1 \text{ bar} = 1 \times 10^5 \text{ N m}^{-2}$. Moving the factor of h^3 into the first term and using $R/N_A = k$ gives:

$$\begin{aligned} \Gamma &= \left(\frac{2\pi k}{N_A 1000 \text{ g kg}^{-1}} \right)^{3/2} \frac{R}{N_A P^\circ h^3} = \left(\frac{2\pi k}{N_A h^2 1000 \text{ g kg}^{-1}} \right)^{3/2} \left(\frac{k}{P^\circ} \right) \\ &= \left(\frac{2\pi(1.3806488 \times 10^{-23} \text{ J K}^{-1})}{6.0221367 \times 10^{23} \text{ mol}^{-1} (6.6260755 \times 10^{-34} \text{ J s})^2 (1000 \text{ g/kg})} \right)^{3/2} \left(\frac{1.3806488 \times 10^{-23} \text{ J K}^{-1}}{1 \times 10^5 \text{ N m}^{-2}} \right) \\ &= 0.02594674 \pm 8 \times 10^{-8} = 0.02594674(8) \end{aligned}$$

We estimated the uncertainty using the “*Uncertainty Calculator*” applet that is available on the text book Web site and companion CD. The input formula was:

$$\left((2 \cdot \pi \cdot k / N_A / h^2 / 1000)^{1.5} \cdot k / 1e5 \right)$$

For the units note that for energy $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$ and for pressure $1 \text{ N m}^{-2} = 1 \text{ J m}^{-3}$. The units of k/h^2 are $1/(\text{J s}^2 \text{ K})$. The units of k/P° are $\text{m}^3 \text{ K}^{-1}$:

$$\Gamma \sim \left(\frac{1}{\text{J kg}^{-1} \text{ s}^2} \right)^{3/2} \left(\frac{1}{\text{g mol}^{-1} \text{ K}} \right)^{3/2} (\text{m}^3 \text{ K}^{-1})$$

The units of $\text{J kg}^{-1} \text{ s}^2$ are $(\text{kg m}^2 \text{ s}^{-2})(\text{kg}^{-1} \text{ s}^2) = \text{m}^2$.

$$\Gamma \sim (\text{m}^{-3}) \left(\frac{1}{\text{g mol}^{-1} \text{ K}} \right)^{3/2} (\text{m}^3 \text{ K}^{-1}) \sim \left(\frac{1}{\text{g mol}^{-1}} \right)^{3/2} \left(\frac{1}{\text{K}} \right)^{5/2}$$

These final units are grouped with the factors of $(\mathcal{M}/\text{g mol}^{-1})^{3/2}$ and $(T/\text{K})^{5/2}$ to give an overall unitless result. Note that the factor of N_A in q_i°/N_A is the molecule count and in this context is unitless, giving q_i°/N_A as overall unitless.

5. (a). Calculate the translational partition function in the form $q_{i,m}^\circ/N_A$ for hydrocyanic acid, $\text{H-C}\equiv\text{N}$, at 298.2 K. (b). Calculate the rotational partition function of $\text{H-C}\equiv\text{N}$ at 298.2 K. Hydrocyanic acid is linear with rotational constant 1.4782 cm^{-1} .²

Answer: (a). Using isotope averaged atomic masses from the periodic table, the molar mass of $\text{H-C}\equiv\text{N}$ is 27.03 g mol^{-1} . The standard state translational partition function is:

$$\frac{q_{i,m}^\circ}{N_A} = \Gamma (\mathcal{M}/\text{g mol}^{-1})^{3/2} (T/\text{K})^{5/2} = 0.0259467 (27.03)^{3/2} (298.15)^{5/2} = 5.597 \times 10^6$$

or lots and lots of accessible translational states per molecule: $q_{t,m} = N_A(5.597 \times 10^6)$.

(b). The rotational symmetry number is $\sigma = 1$, since $\text{H-C}\equiv\text{N}$ is unsymmetrical. The rotational partition function at 298.2 K is given using Eqs. 30.1.39 and 30.1.40:

$$q_r = \frac{kT}{\sigma \tilde{B}hc} = \frac{207.224 \text{ cm}^{-1}}{1.4782 \text{ cm}^{-1}} = 140.187$$

Once again, there are a large number of accessible rotational states.

6. Does anharmonicity have a significant effect on the vibrational partition function? The vibrational constants for diatomic Mg_2 are $\tilde{\nu}_e = 51.12 \text{ cm}^{-1}$, $\chi_e \tilde{\nu}_e = 1.64 \text{ cm}^{-1}$, and $\eta_e \tilde{\nu}_e = 0.0162 \text{ cm}^{-1}$. Using the zero-point energy as the zero in energy, determine the vibrational partition function at 298.2 K by explicit summation for three cases. (a). Assume a harmonic oscillator with the observed vibrational frequency $\tilde{\nu}_o$. Calculate $\tilde{\nu}_o$ using the first and second anharmonicity corrections, extending Eq. 27.5.11 as: $\tilde{\nu}_o = \tilde{\nu}_e - 2\chi_e \tilde{\nu}_e + 13/4 \eta_e \tilde{\nu}_e$. (b). Assume an anharmonic oscillator including only the first anharmonicity correction, Eq. 27.5.8. (c). Assume an anharmonic oscillator including the first and second anharmonicity corrections, Eq. 27.5.5. [Hint: for the anharmonic oscillator cases, extend the sums until the vibrational energy reaches a maximum, which corresponds to the dissociation limit.]

Answer: The plan is to determine the vibrational energies in reference to the energy of the $\nu = 0$ level at the required levels of approximation.

The observed harmonic oscillator fundamental is at:

$$\tilde{\nu}_o = \tilde{\nu}_e - 2\chi_e \tilde{\nu}_e + 13/4 \eta_e \tilde{\nu}_e = 51.12 \text{ cm}^{-1} - 2(1.64 \text{ cm}^{-1}) + 13/4 (0.0162 \text{ cm}^{-1}) = 47.893 \text{ cm}^{-1}$$

The energy levels are:	harmonic	$\tilde{G}_\nu = \tilde{\nu}_o(\nu + 1/2)$
	first-anharmonicity	$\tilde{G}_\nu = \tilde{\nu}_e(\nu + 1/2) - \chi_e \tilde{\nu}_e(\nu + 1/2)^2$
	first and second-anharmonicity	$\tilde{G}_\nu = \tilde{\nu}_e(\nu + 1/2) - \chi_e \tilde{\nu}_e(\nu + 1/2)^2 + \eta_e \tilde{\nu}_e(\nu + 1/2)^3$

The zero point energies are:	harmonic	ZPE = $\tilde{G}_0 = \tilde{\nu}_o/2$
	first-anharmonicity	ZPE = $\tilde{G}_0 = \tilde{\nu}_e/2 - \chi_e \tilde{\nu}_e/4$
	first and second-anharmonicity	ZPE = $\tilde{G}_0 = \tilde{\nu}_e/2 - \chi_e \tilde{\nu}_e/4 + \eta_e \tilde{\nu}_e/8$

The spreadsheet implementing these calculations and the corresponding Boltzmann weighting factors is given below. The vibrational partition function is the sum of the Boltzmann weighting factors. For the harmonic case, states up to $\nu = 40$ are necessary to obtain a good estimate of the sum. For the harmonic calculation not all rows are shown to save space. Summing through $\nu = 40$ gives $q_v = 4.846$. Using the first-anharmonicity correction, the vibrational energy is maximum at $\nu = 15$, which corresponds to the dissociation energy. Summing through $\nu = 15$ gives $q_v = 5.898$. The first-anharmonicity correction increases the number of accessible states by 22% over the harmonic approximation. For the full expression, using the first and second-anharmonicity corrections, the vibrational energy is maximum at $\nu = 24$. Summing through $\nu = 24$ gives the

best estimate of the partition function as $q_v = 6.613$. Using only the first-anharmonicity correction underestimates the partition function by 11%.

v_e	51.12	cm ⁻¹				
$\chi_e v_e$	1.64	cm ⁻¹				
$j_e v_e$	0.0162	cm ⁻¹				
v_o	47.89265	cm ⁻¹				
	harmonic: v_o		$v_e(v+\frac{1}{2})-\chi_e v_e(v+\frac{1}{2})^2$		full	
ZPE	23.946325		25.15		25.152025	cm ⁻¹
v	ϵ_v	$e^{-\epsilon_v/kT}$	ϵ_v	$e^{-\epsilon_v/kT}$	ϵ_v	$e^{-\epsilon_v/kT}$
0	0	1	0	1	0	1
1	47.89265	0.793647903	47.84	0.793849573	47.89265	0.793647903
2	95.7853	0.629876994	92.4	0.640251444	92.6511	0.639476101
3	143.67795	0.499900556	133.68	0.524610591	134.37255	0.52286025
4	191.5706	0.396745028	171.68	0.436714565	173.1542	0.433618785
5	239.46325	0.314875859	206.4	0.369345179	209.09325	0.364575932
6	287.3559	0.249900565	237.84	0.317352066	242.2869	0.310614436
7	335.24855	0.19833306	266	0.277028442	272.83235	0.268043515
8	383.1412	0.157406617	290.88	0.245686631	300.8268	0.234172175
9	431.03385	0.124925431	312.48	0.221366973	326.36745	0.207017892
10	478.9265	0.099146807	330.8	0.202636774	349.5515	0.185105522
11	526.81915	0.078687655	345.84	0.188450735	370.47615	0.167327012
12	574.7118	0.062450293	357.6	0.178053922	389.2386	0.15284253
13	622.60445	0.049563544	366.08	0.170914689	405.93605	0.141010078
14	670.4971	0.039336003	371.28	0.166679185	420.6657	0.1313349
15	718.38975	0.031218936	373.2	0.165141979	433.52475	0.123432776
16	766.2824	0.024776843	371.84	0.166229361	444.6104	0.117003133
17	814.17505	0.01966409			454.01985	0.111809169
18	862.0677	0.015606363			461.8503	0.107663023
19	909.96035	0.012385958			468.19895	0.104414603
20	957.853	0.009830089			473.163	0.101943073
21	1005.74565	0.00780163			476.83965	0.100150309
22	1053.6383	0.006191747			479.3261	0.098955801
23	1101.53095	0.004914067			480.71955	0.098292619
24	1149.4236	0.003900039			481.1172	0.098104182
25	1197.31625	0.003095258			480.61625	0.098341629
26	1245.2089	0.002456545				
⋮	⋮	⋮				
40	1915.706	9.66307E-05				
$q_v =$	sum =	4.845714312		5.898082748		6.613415718

The vibrational partition function in the harmonic approximation using Eq. 30.1.31 is slightly larger than we obtained stopping the sum at $v = 40$:

$$q_v = \frac{1}{1 - e^{-\tilde{\nu}/207.224 \text{ cm}^{-1}}} = \frac{1}{1 - e^{-47.893/207.224}} = 4.8465$$

Mg₂ is atypical. The bond strength in Mg₂ is small and the vibration is unusually anharmonic. For most stable common diatomics, such as O₂, N₂, CO, and HF, anharmonicity makes a negligible contribution to the vibrational partition functions, because there are so few accessible states.

7. Calculate the electronic partition function of atomic carbon at 298.2 K. The spectroscopic constants for the low-lying electronic states are given in Table 30.1.2.

Answer: The plan is to follow Example 30.1.3 to determine the electronic partition function.

Consider a general three level system with energies ε_0 , ε_1 , and ε_2 with corresponding degeneracies g_0 , g_1 , and g_2 , respectively. The general form of the partition function of a three-level system is given by the sum of the Boltzmann weighting factors over the three-levels:

$$q_e = \sum g_i e^{-\varepsilon_i/kT} = g_0 + g_1 e^{-\varepsilon_1/kT} + g_2 e^{-\varepsilon_2/kT}$$

Using the spectroscopic constants for C-atoms gives the partition function at room temperature:

$$q_e = 1 + 3 e^{-16.40/207.22} + 5 e^{-43.40/207.22} = 7.827 = 1 + 3(0.9239) + 5(0.8110) = 7.827$$

The low-energy electronic terms of the C-atom are closely spaced in energy compared to kT . C-atoms are an excellent example of a case that gives a significant error by assuming the electronic partition function is the ground state degeneracy.

8. Calculate the contribution of translation to the molar standard state entropy of $\text{H-C}\equiv\text{N}$ at 298.2 K. Compare this translation-only result to the literature value of the thermodynamic standard state absolute entropy.

Answer: The plan is to use the Sackur-Tetrode equation.

Using isotope averaged atomic masses from the periodic table, the molar mass of $\text{H-C}\equiv\text{N}$ is $27.026 \text{ g mol}^{-1}$. For standard state at 298.2 K, using Eq. 30.2.35°:

$$\begin{aligned} S_{m,298.15 \text{ K}}^\circ &= 26.6929 + 71.0587 + \frac{3}{2} R \ln(\mathcal{M}/\text{g mol}^{-1}) + 11.1037 \text{ J K}^{-1} \text{ mol}^{-1} \\ &= 26.6929 + 71.0587 + \frac{3}{2} R \ln(27.026) + 11.1037 \text{ J K}^{-1} \text{ mol}^{-1} \\ &= 149.972 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

Using Table 8.4.1 in the Data Section, $S_{298 \text{ K}}^\circ = 201.78 \text{ J K}^{-1} \text{ mol}^{-1}$. The difference is primarily the contribution of rotation.

9. Calculate the contribution of rotation to the molar entropy of $\text{H-C}\equiv\text{N}$ at 298.2 K. Combine the translational contribution from the previous problem with the rotational contribution. Compare this translation-rotation only result to the literature value of the thermodynamic standard state absolute entropy. Hydrocyanic acid is linear with rotational constant 1.4782 cm^{-1} .⁹

Answer: The plan is to use the Sackur-Tetrode equation for the translational contribution, $kT/hc = 207.224 \text{ cm}^{-1}$, the high temperature approximation or Equipartition rotational contribution of a diatomic molecule of $U - U(0) = RT$, and Eq. 30.2.27°.

The translational contribution is determined in the previous problem using the Sackur-Tetrode equation, $S_{m,298.15 \text{ K}}^\circ = 149.972 \text{ J K}^{-1} \text{ mol}^{-1}$. The rotational symmetry number is $\sigma = 1$, since

H–C≡N is unsymmetrical. The rotational partition function at 298.2 K is given using Eqs. 30.1.39 and 30.1.40: (see also Problem 5b.)

$$q_r = \frac{kT}{\sigma \tilde{B}hc} = \frac{207.224 \text{ cm}^{-1}}{1.4782 \text{ cm}^{-1}} = 140.186$$

The contribution of rotation of a linear molecule to the internal energy is $U - U(0) = RT$, as based on the high temperature approximation, Table 30.3.3, or correspondingly from Equipartition. Using Eq. 30.2.27° the molar rotational entropy is:

$$S_r = R \ln q_r + R = 8.31446 \text{ J K}^{-1} \text{ mol}^{-1} (\ln 140.186 + 1) = 49.413 \text{ J K}^{-1} \text{ mol}^{-1}$$

Neglecting vibration, the predicted molar standard state entropy is:

$$S_{m,298.15 \text{ K}} = 149.972 \text{ J K}^{-1} + 49.413 \text{ J K}^{-1} \text{ mol}^{-1} = 199.38 \text{ J K}^{-1} \text{ mol}^{-1}$$

Using Table 8.4.1 in the Data Section, $S_{298 \text{ K}}^\circ = 201.78 \text{ J K}^{-1} \text{ mol}^{-1}$ giving a 1.2% difference. The difference is primarily a small contribution from the doubly degenerate bending vibration.

10. Determine the contribution of a vibration to the internal energy of a substance. Use the zero-point vibrational level, $\nu = 0$, as the zero in energy. Repeat the derivation giving Eq. 30.3.13. However, this result was derived using Eq. 30.2.15°; use Eq. 30.2.6° as the basis of your derivation, instead.

Answer: The plan is to use Eq. 30.1.31, written in terms of β instead of kT with Eq. 30.2.6°.

The partition function for the vibration of a diatomic molecule or a single vibrational mode of a polyatomic in the harmonic approximation is given by Eq. 30.1.31. The version of this equation written in terms of β is the most convenient form:

$$q_v = \frac{1}{(1 - e^{-\beta h\nu_0})}$$

The internal energy is given by Eq. 30.2.6°. Using the chain rule, the required derivative is:

$$\left(\frac{\partial q}{\partial \beta}\right)_v = \frac{-1}{(1 - e^{-\beta h\nu_0})^2} (h\nu_0 e^{-\beta h\nu_0})$$

Substitution of the derivative and the vibrational partition function into Eq. 30.2.6° gives:

$$U - U(0) = -\frac{N(\partial q)}{q(\partial \beta)_v} = -\frac{N}{\left(\frac{1}{1 - e^{-\beta h\nu_0}}\right)} \frac{-h\nu_0 e^{-\beta h\nu_0}}{(1 - e^{-\beta h\nu_0})^2}$$

Cancelling the common factors gives the final result:

$$U - U(0) = \frac{N h \nu_0 e^{-\beta h \nu_0}}{1 - e^{-\beta h \nu_0}} \quad (30.3.13)$$

11. Find the contribution of a vibration to the enthalpy, $H_v - H_v(0)$. Assume the energy zero is at the bottom of the vibrational potential, giving the zero-point $v = 0$ vibrational level at $\epsilon_0 = \frac{1}{2} h\nu_0$. For vibrations $H_v - H_v(0) = U_v - U_v(0)$. The reason vibrational enthalpy and internal energy are equal is that even though $H \equiv U + PV$, the PV correction term is included in calculating the translational enthalpy. [Hint: Eq. 30.2.15° is most convenient for this problem. Note that Eq. 30.3.13 was derived with the $v = 0$, zero-point vibrational level as the reference energy.]

Answer: The plan is to take the derivative with respect to β based on Eq. 30.1.29 instead of Eq. 30.1.31 using Eq. 30.2.15° for the internal energy.

Based on Eq. 30.1.29, the logarithm of the partition function is:

$$q_v = \frac{e^{-\beta h\nu_0/2}}{1 - e^{-\beta h\nu_0}} \quad \ln q_v = -\frac{1}{2}\beta h\nu_0 - \ln(1 - e^{-\beta h\nu_0})$$

The derivative with respect to β is: $\left(\frac{\partial \ln q_v}{\partial \beta}\right)_v = -\frac{1}{2}h\nu_0 - \frac{h\nu_0 e^{-\beta h\nu_0}}{1 - e^{-\beta h\nu_0}}$

$$H_v - H_v(0) = U_v - U_v(0) = -N \left(\frac{\partial \ln q_v}{\partial \beta}\right)_v = \frac{1}{2}N h\nu_0 + \frac{N h\nu_0 e^{-\beta h\nu_0}}{1 - e^{-\beta h\nu_0}}$$

The first term in the sum is the zero-point vibrational energy, ZPE. The second term is identical to Eq. 30.3.13. In other words, the difference caused by shifting the energy zero to the zero-point vibrational level is just an additive term in the ZPE. This result is used in correcting SCF total electronic energies from *ab initio* electronic structure calculations to the spectroscopic reference energy.

12. For one mole of an ideal gas at 25°C and constant volume, the number of accessible states increases by 10% with a temperature increase of 20°C. Estimate to a single significant figure (don't use a calculator) the internal energy of the substance. Based on Equipartition neglecting vibration, the value of $U_m - U_m(0)$ for a monatomic ideal gas is $\frac{3}{2} RT$, for a diatomic ideal gas is $\frac{5}{2} RT$, for a linear triatomic is $\frac{5}{2} RT$, and for a bent triatomic is $\frac{6}{2} RT$. To which case does this result most closely correspond?

Answer: The plan is to use the estimate given by Eq. 30.2.13°.

For a 10% increase in the partition function, $\delta q/q = 0.10$. For the change in temperature of 10°C:

$$U_m - U_m(0) \approx 1000 \text{ kJ K mol}^{-1} \left(\frac{0.10}{20 \text{ K}}\right) \approx 5 \text{ kJ mol}^{-1}$$

As a factor of R: $[U_m - U_m(0)]/RT \approx 5 \text{ kJ mol}^{-1}/RT \approx 2$

This factor of 2RT is in rough neighborhood of the values for diatomics and linear triatomics.

13. We can find an approximate formula for the internal energy based on the order of magnitude of the change in accessible states by converting Eq. 30.2.16° to base-ten log: $\ln x = 2.303 \log x$:

$$U - U(0) = 2.303 nRT^2 \left(\frac{\partial \log q}{\partial T} \right)_V$$

$$\text{and at } 298.2 \text{ K: } U_m - U_m(0) = 1702 \text{ kJ K mol}^{-1} \left(\frac{\partial \log q}{\partial T} \right)_V \approx 2000 \text{ kJ K mol}^{-1} \left(\frac{\partial \log q}{\partial T} \right)_V$$

For one mole of an ideal gas at 298 K and constant volume, the number of accessible states increases by a factor of ten for a temperature increase of 20 K. Estimate to a single significant figure (don't use a calculator) the internal energy of the substance.

Answer: The plan is to let the initial partition function, before the temperature increase be q_0 . For a factor of ten increase $\partial \log q = \log 10q_0 - \log q_0 = \log 10 = 1$.

For the change in temperature of 10 K:

$$U_m - U_m(0) \approx 2000 \text{ kJ K mol}^{-1} \left(\frac{1}{20 \text{ K}} \right) \approx 100 \text{ kJ mol}^{-1}$$

14. A quick estimate of the rotational contribution to the Gibbs energy of a linear molecule at room temperature is available by converting $\ln x$ to $\log x$ and using $2.303RT = 5.71 \text{ kJ mol}^{-1}$:

$$G_m - G_m(0) = -2.303 RT \log \left(\frac{207.2 \text{ cm}^{-1}}{\sigma \tilde{B}} \right) \cong -6 \text{ kJ mol}^{-1} \log \left(\frac{207.2 \text{ cm}^{-1}}{\sigma \tilde{B}} \right)$$

Without using a calculator estimate the contribution of rotation to the molar Gibbs energy of CO_2 . The rotational constant for CO_2 is 0.379 cm^{-1} . [Hint: use $\log 10^n = n$]

Answer: The plan is to note that the symmetry number for CO_2 is $\sigma = 2$ since rotation by 180° gives an indistinguishable state.

The ratio of the available thermal kinetic energy to the molecular constants is roughly:

$$\left(\frac{207.2 \text{ cm}^{-1}}{\sigma \tilde{B}} \right) = \frac{207.2 \text{ cm}^{-1}}{2(0.379 \text{ cm}^{-1})} \cong \frac{100}{0.4} \cong 250$$

By course estimation: $\log 250 \approx \log 100 = 2$. The estimate of the molar Gibbs energy of rotation is then:

$$G_m - G_m(0) \cong -6 \text{ kJ mol}^{-1} \log 250 \cong -6 \text{ kJ mol}^{-1} (2) = -12 \text{ kJ mol}^{-1}$$

We will spend a lot of time on very careful calculations in this chapter. However, rough, approximate calculations are very helpful in building insight. The precise result for this problem is given in Example 30.3.1 as $-13.9 \text{ kJ mol}^{-1}$.

15. The atomic energy levels for low-lying states of atomic oxygen are given in Figure 30.1.7. These low-lying states are an example of a three-level system. Consider a three level system with energies ε_0 , ε_1 , and ε_2 with corresponding degeneracies g_0 , g_1 , and g_2 , respectively. The lowest energy level is defined as the energy zero, $\varepsilon_0 = 0$. (a). Show that the contribution of the electronic degree of freedom of a three-level system to the molar internal energy is given by:

$$U_m - U_m(0) = N_A \frac{g_1 \varepsilon_1 e^{-\varepsilon_1/kT} + g_2 \varepsilon_2 e^{-\varepsilon_2/kT}}{g_0 + g_1 e^{-\varepsilon_1/kT} + g_2 e^{-\varepsilon_2/kT}}$$

(b). Plot the electronic contribution to the molar internal energy of O-atoms as a function of temperature, in the range 10 K to 800 K.

Answer: The plan is to note that the electronic partition function for O-atoms, as a specific case, is given in Example 30.1.2; however, the necessary derivative is easier in terms of β rather than T.

(a). The partition function is the sum over the three levels, taking degeneracy into account:

$$q_e = g_0 + g_1 e^{-\beta\varepsilon_1} + g_2 e^{-\beta\varepsilon_2}$$

with $\beta = 1/kT$. The required derivative is: $\left(\frac{\partial q_e}{\partial \beta}\right)_V = -g_1 \varepsilon_1 e^{-\beta\varepsilon_1} - g_2 \varepsilon_2 e^{-\beta\varepsilon_2}$

Using this derivative, the partition function, and $\beta = 1/kT$, the contribution to the molar internal energy is given by Eq. 30.2.6°:

$$U_m - U_m(0) = -\frac{N_A \left(\frac{\partial q}{\partial \beta}\right)_V}{q} = N_A \frac{g_1 \varepsilon_1 e^{-\varepsilon_1/kT} + g_2 \varepsilon_2 e^{-\varepsilon_2/kT}}{g_0 + g_1 e^{-\varepsilon_1/kT} + g_2 e^{-\varepsilon_2/kT}}$$

This result is identical to the result using Eqs 30.1.1 and 30.1.2 for molecular partition functions:

$U - U(0) = N \sum \varepsilon_i e^{-\varepsilon_i/kT}/q$. Using the spectroscopic constants for O-atoms, from Example 30.1.2, at room temperature:

$$q_e = 5 + 3 e^{-158.265/207.22} + 1 e^{-226.977/207.22} = 6.7322$$

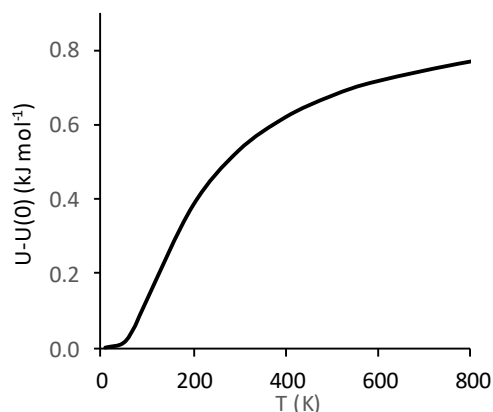
$$\begin{aligned} \text{and } U_m - U_m(0) &= \frac{N_A}{6.7322} [3(158.265 \text{ cm}^{-1}) e^{-158.265/207.22} + 1(226.977 \text{ cm}^{-1}) e^{-226.977/207.22}] \\ &= \frac{N_A}{6.7322} [3(158.265 \text{ cm}^{-1})(0.4659) + 1(226.977 \text{ cm}^{-1})(0.3344)] \\ &= N_A(44.14 \text{ cm}^{-1}) = (44.14 \text{ cm}^{-1})(11.96266 \text{ J mol}^{-1})(1 \text{ kJ}/1000 \text{ J}) \\ &= 0.528 \text{ kJ mol}^{-1} \end{aligned}$$

where we used the conversion $1 \text{ cm}^{-1} = 11.96266 \text{ J mol}^{-1}$ (from the inside front cover).

(b). The spreadsheet based on the preceding calculation at the given range of temperatures and the corresponding plot are shown below.

$g_0 =$	5	$\varepsilon_0 =$	0			
$g_1 =$	3	$\varepsilon_1 =$	158.265	cm^{-1}		
$g_2 =$	1	$\varepsilon_2 =$	226.977	cm^{-1}		

T (K)	kT/hc (cm ⁻¹)	e ^{-ε₁/kT}	e ^{-ε₂/kT}	q _e	U-U(0) (cm ⁻¹)	U-U(0) (kJ mol ⁻¹)
10	6.95	0.0000	0.0000	5	0.00	0.0000
50	34.8	0.0105	0.0015	5.033	1.06	0.0127
75	52.1	0.0480	0.0129	5.157	4.99	0.0597
100	69.5	0.1026	0.0382	5.346	10.73	0.1284
200	139	0.3203	0.1954	6.156	31.91	0.3817
298	207	0.4659	0.3344	6.732	44.14	0.5280
400	278	0.5659	0.4420	7.140	51.69	0.6183
500	348	0.6342	0.5204	7.423	56.48	0.6756
600	417	0.6842	0.5803	7.633	59.81	0.7155
800	556	0.7523	0.6648	7.922	64.14	0.7673
hc/k	=	1.4388	cm K			
1	cm ⁻¹ =	11.963	J mol ⁻¹			



16. Calculate the contribution of the electronic degree of freedom to the molar internal energy of atomic carbon at 298.2 K. The spectroscopic constants for the low-lying electronic states are given in Table 30.1.2.

Answer: The plan is to use Eq. 30.2.6° after following Example 30.1.2 to determine the electronic partition function.

Consider a general three level system with energies ϵ_0 , ϵ_1 , and ϵ_2 with corresponding degeneracies g_0 , g_1 , and g_2 , respectively. The derivation of the contribution of a three-level system to the molar internal energy is given in the previous problem. Using the spectroscopic constants for C-atoms gives the partition function at room temperature:

$$q_e = g_0 + g_1 e^{-\beta\epsilon_1} + g_2 e^{-\beta\epsilon_2} = 1 + 3 e^{-16.40/207.22} + 5 e^{-43.40/207.22} = 7.827$$

The electronic contribution to the molar internal energy is:

$$\begin{aligned} U_m - U_m(0) &= N_A \frac{g_1 \epsilon_1 e^{-\epsilon_1/kT} + g_2 \epsilon_2 e^{-\epsilon_2/kT}}{g_0 + g_1 e^{-\epsilon_1/kT} + g_2 e^{-\epsilon_2/kT}} \\ &= \frac{N_A}{7.827} [3(16.40 \text{ cm}^{-1}) e^{-16.40/207.22} + 5(43.40 \text{ cm}^{-1}) e^{-43.40/207.22}] \\ &= \frac{N_A}{7.827} [3(16.40 \text{ cm}^{-1})(0.9239) + 5(43.40 \text{ cm}^{-1})(0.8110)] \\ &= N_A(28.29 \text{ cm}^{-1}) = (28.29 \text{ cm}^{-1})(11.96266 \text{ J mol}^{-1})(1 \text{ kJ}/1000 \text{ J}) \\ &= 0.3385 \text{ kJ mol}^{-1} \end{aligned}$$

where we used the conversion $1 \text{ cm}^{-1} = 11.96266 \text{ J mol}^{-1}$ (from the inside front cover). The low-energy electronic terms of the C-atom are closely spaced in energy. C-atoms are an excellent example of a case that gives a significant error by assuming the electronic partition function is the ground state degeneracy.

17. Calculate the contribution of the electronic degree of freedom to the molar Gibbs energy of atomic oxygen at 298.2 K. The spectroscopic constants for the low-lying electronic states are given in Table 30.1.2.

Answer: The plan is to note that the electronic partition function for O-atoms is given in Example 30.3.1; the contribution to the Gibbs energy is given by Eq. 30.2.53.

The explicit sum over the Boltzmann weighting factors gives, using Figure 30.1.7 as shown in Example 30.1.2:

$$q_e = 5 + 3 e^{-158.265/207.22} + 1 e^{-226.977/207.22} = 5 + 1.39776 + 0.33443 = 6.7322$$

The electronic contribution to the molar Gibbs energy is:

$$\begin{aligned} G_e - G_e(0) &= -RT \ln q_e \\ &= -8.3145 \text{ J K}^{-1} \text{ mol}^{-1} (1 \text{ kJ}/1000 \text{ J})(298.15 \text{ K}) \ln 6.7322 = -4.727 \text{ kJ mol}^{-1} \end{aligned}$$

18. The nucleus of a deuterium atom has a spin of one, $I = 1$. In a magnetic field of strength B_0 , a deuterium nucleus has energy levels $\varepsilon = \gamma \hbar B_0 m_I$, with $m_I = +1, 0, -1$. The magnetogyric ratio, γ , is a constant that is different for each isotope of each element. For deuterium, $\gamma = 41.065 \text{ radians s}^{-1} \text{ T}^{-1}$, with the magnetic field strength given in tesla, T. For thermodynamic calculations, setting the lowest energy level at $\varepsilon = 0$ is most convenient. With the shifted zero in energy, the deuterium nuclear energies are at $\varepsilon = 0$ for $m_I = +1$, $\varepsilon = \gamma \hbar B_0$ for $m_I = 0$, and $\varepsilon = 2\gamma \hbar B_0$ for $m_I = -1$. Find the partition function and the contribution of the nuclear energy to the internal energy. [This three-level system is the basis of deuterium NMR spectroscopy. Deuterium NMR is common, especially for locking and shimming operations while doing conventional proton and ^{13}C NMR.]

Answer: The plan is to find the partition function as the sum of the three Boltzmann weighting factors. The derivative to determine the internal energy is easier with the Boltzmann weighting factors expressed in terms of β instead of kT .

The partition function is the sum of the Boltzmann weighting factors:

$$q_n = \sum e^{-\beta \varepsilon_i} = e^0 + e^{-\beta \gamma \hbar B_0} + e^{-2\beta \gamma \hbar B_0} = 1 + e^{-\beta \gamma \hbar B_0} + e^{-2\beta \gamma \hbar B_0}$$

The derivative with respect to β is: $\left(\frac{\partial q}{\partial \beta}\right)_v = -\gamma \hbar B_0 e^{-\beta \gamma \hbar B_0} - 2\gamma \hbar B_0 e^{-2\beta \gamma \hbar B_0}$

The contribution of the nuclear degree of freedom to the internal energy is given by Eq. 30.2.6°:

$$\begin{aligned} U - U(0) &= -\frac{N}{q} \left(\frac{\partial q}{\partial \beta}\right)_v = N \frac{\gamma \hbar B_0 e^{-\beta \gamma \hbar B_0} + 2\gamma \hbar B_0 e^{-2\beta \gamma \hbar B_0}}{1 + e^{-\beta \gamma \hbar B_0} + e^{-2\beta \gamma \hbar B_0}} \\ &= N \frac{\gamma \hbar B_0 e^{-\gamma \hbar B_0/kT} + 2\gamma \hbar B_0 e^{-2\gamma \hbar B_0/kT}}{1 + e^{-\gamma \hbar B_0/kT} + e^{-2\gamma \hbar B_0/kT}} = N\gamma \hbar B_0 \frac{e^{-\gamma \hbar B_0/kT} + 2 e^{-2\gamma \hbar B_0/kT}}{1 + e^{-\gamma \hbar B_0/kT} + e^{-2\gamma \hbar B_0/kT}} \end{aligned}$$

A magnetic field strength of 11.74 T gives a deuterium NMR transition frequency of 76.73 MHz and a proton NMR frequency of 500 MHz. At 76.73 MHz or $\nu = 76.73 \text{ s}^{-1}$, for one mole of deuterium nuclei:

$$N_A \gamma \hbar B_0 = N_A h \nu = 6.022 \times 10^{23} \text{ mol}^{-1} (6.6261 \times 10^{-34} \text{ J s}) (76.73 \times 10^6 \text{ s}^{-1}) = 0.03062 \text{ J mol}^{-1}$$

The small size of this energy explains why we don't normally bother considering nuclear degrees of freedom in thermodynamic problems. At 76.73 MHz the corresponding transition in wave numbers is:

$$\tilde{\nu} = \nu/c = 76.73 \times 10^6 \text{ s}^{-1} / 2.9979 \times 10^{10} \text{ cm s}^{-1} = 0.002559 \text{ cm}^{-1}$$

NMR transitions are very low energy transitions. The ratio to the thermal kinetic energy at room temperature is:

$$\gamma \hbar B_0 / kT = 0.002559 \text{ cm}^{-1} / 207.224 \text{ cm}^{-1} = 1.235 \times 10^{-5} \text{ giving } e^{-\gamma \hbar B_0 / kT} = 0.9999877$$

The average molar internal energy at 298.2 K is:

$$U - U(0) = 0.03062 \text{ J mol}^{-1} \frac{0.999988 + 2(0.999988)^2}{1 + 0.999988 + (0.999988)^2} = 0.03062 \text{ cm}^{-1}$$

In other words, the populations of the three levels are almost identical, so that the internal energy is near the maximum.

19. The translational partition function of a mobile species on a surface is:

$$q_t = \frac{2\pi mkT}{h^2} \sigma$$

where σ is the surface area (not to be confused with the rotational symmetry number). Find the contribution of translation to the molar internal energy of the species, $U_t - U_t(0)$.

Answer: The plan is to use Eq. 30.2.16° and $\ln q_t = \ln(2\pi mk\sigma/h^2) + \ln T$.

Substitution of the partition function into Eq. 30.2.16° with $n = 1 \text{ mol}$ gives:

$$U_t - U_t(0) = RT^2 \left(\frac{\partial \ln q}{\partial T} \right)_V = RT^2 \left(\frac{\partial (\ln(2\pi mk\sigma/h^2) + \ln T)}{\partial T} \right)_V = RT^2 \left(\frac{\partial \ln T}{\partial T} \right)_V$$

The derivative of the first term in the sum is zero, since the values are all constants. Then completing the derivative gives:

$$U_t - U_t(0) = RT^2 \left(\frac{1}{T} \right) = RT$$

This value is predicted by Equipartition, since there are two translational degrees of freedom on the surface with each degree of freedom contributing $\frac{1}{2} RT$ to the internal energy.

Alternately, the derivation can also be based on Eq. 30.2.12°:

$$U_t - U_t(0) = \frac{RT^2}{q} \left(\frac{\partial q}{\partial T} \right)_V = \frac{RT^2}{q} \left(\frac{\partial (2\pi mkT\sigma/h^2)}{\partial T} \right)_V = \frac{RT^2}{q} (2\pi mk\sigma/h^2)$$

$$= \frac{RT^2 (2\pi mk\sigma/h^2)}{(2\pi mkT\sigma/h^2)} = \frac{RT^2}{T} = RT$$

20. Find the relationship between the Helmholtz energy and the molecular partition function. Start with $A - A(0) = -kT \ln Q$, Eq. 30.2.40. Find the relationship between the Helmholtz energy and the molecular partition functions of rotation, vibration, and electronic degrees of freedom (just in the form $q_r q_v q_e$).

Answer: The plan is to parallel the derivation of Eq. 30.2.25° for the entropy.

The Helmholtz energy in terms of the ensemble partition function is $A - A(0) = -kT \ln Q$. For independent molecules the ensemble partition function is given by Eq. 30.1.13°. For very large numbers of systems, the factor of $N!$ can be expressed using Sterling's approximation, Eq. 30.2.24°:

$$Q \cong \left(\frac{qe}{N}\right)^N$$

Substitution into Eq. 30.2.40 gives: $A - A(0) = -NkT \ln\left(\frac{qe}{N}\right) = -nRT \ln\left(\frac{qe}{N}\right)$

To find the relationships to the molecular degrees of freedom, we parallel the process we used for the entropy and Gibbs energy, Eqs. 30.2.26° and 30.2.52°. The molecular partition function factors as $q = q_t q_{\text{int}}$ with $q_{\text{int}} = q_r q_v q_e$, Eq. 30.1.16°. The factors that arise from the correction for indistinguishability are grouped with the translational partition function:

$$A - A(0) = -nRT \ln\left(\frac{qe}{N}\right) - nRT \ln q_{\text{int}} = -nRT \ln\left(\frac{qe}{N}\right) - nRT \ln q_r q_v q_e$$

In other words, the contribution of internal degrees of freedom to the Helmholtz and Gibbs energies are identical. The Helmholtz energy is particularly useful in molecular dynamics simulations at constant volume. See the next problem to explore the relationship between Helmholtz and Gibbs energy.

21. Find the relationship between the Helmholtz energy and the molecular partition function. Start with $A - A(0) = -kT \ln Q$, Eq. 30.2.40. (See also Problem 30.20). From the resulting equation, derive Eq. 30.2.51°.

Answer: The plan is to parallel the derivation of Eq. 30.2.25° for the entropy.

The derivation of the relationship between the Helmholtz energy and the molecular partition function is given in the previous problem:

$$A - A(0) = -nRT \ln\left(\frac{qe}{N}\right)$$

This result can be expanded to separate the factor of "e":

$$A - A(0) = -nRT \ln\left(\frac{qe}{N}\right) = -nRT \ln\left(\frac{q}{N}\right) - nRT \ln e = -nRT \ln\left(\frac{q}{N}\right) - nRT$$

Using the definition of Gibbs energy with $PV = nRT$ for an ideal gas, this last result gives:

$$G \equiv A + PV \quad \text{or} \quad G - G(0) = A - A(0) + PV = -nRT \ln\left(\frac{q}{N}\right) - nRT + nRT = -nRT \ln\left(\frac{q}{N}\right)$$

Remember that e is just a number $e = 2.7183$.

22. Calculate the rotational partition function for HF at 298.15 K. Calculate the contribution of rotation to the molar entropy and molar Gibbs energy of HF.

Answer: The plan is to use the spectroscopic constants from Table 27.6.1, $kT/hc = 207.224 \text{ cm}^{-1}$, and the high temperature approximation or Equipartition rotational contribution of a diatomic molecule of $U - U(0) = RT$.

Table 27.6.1 lists $\tilde{B}_e = 20.9537 \text{ cm}^{-1}$. Using Eq. 30.1.39 with $\sigma = 1$, the rotational partition function is:

$$q_r = \frac{kT}{\sigma \tilde{B} hc} = \frac{207.224 \text{ cm}^{-1}}{\sigma \tilde{B}} = \frac{207.224 \text{ cm}^{-1}}{20.9537 \text{ cm}^{-1}} = 9.88961$$

The contribution of rotation of a linear molecule to the internal energy is $U - U(0) = RT$, from the high temperature approximation, Table 30.3.3, or correspondingly from Equipartition.

Using Eq. 30.2.26° the molar rotational entropy is:

$$S_r = R \ln q_r + R = 8.31446 \text{ J K}^{-1} \text{ mol}^{-1} (\ln 9.88961 + 1) = 27.3669 \text{ J K}^{-1} \text{ mol}^{-1}$$

Using Eq. 30.2.52°, the contribution to the molar Gibbs energy is:

$$\begin{aligned} G_r - G_r(0) &= -RT \ln q_r = -8.31446 \text{ J K}^{-1} \text{ mol}^{-1} (1 \text{ kJ}/1000 \text{ J})(298.15 \text{ K}) \ln 9.88964 \\ &= -5.6805 \text{ kJ mol}^{-1} \end{aligned}$$

As a check, note that for the rotational contribution, $H_r - H_r(0) = U_r - U_r(0)$; the factor of nRT in the conversion of the overall internal energy to enthalpy, $H = U + nRT$, is combined with the translational contribution. Then using the definition of Gibbs energy, $G \equiv H - TS$, and the entropy result, above:

$$\begin{aligned} G_r - G_r(0) &= H_r - H_r(0) - T S_r = U_r - U_r(0) - T S_r \\ &= 2.47896 \text{ kJ mol}^{-1} - 298.15 \text{ K} (27.3669 \text{ J K}^{-1} \text{ mol}^{-1}) (1 \text{ kJ}/1000 \text{ J}) \\ &= 2.47896 \text{ kJ mol}^{-1} - 8.15944 \text{ kJ mol}^{-1} = -5.6805 \text{ kJ mol}^{-1} \end{aligned}$$

Even though you might expect six significant figures given \tilde{B}_e , our treatment neglects centrifugal distortion and vibration-rotation interaction, which limits the accuracy of the statistical mechanical result. In addition, the statistical mechanical and thermodynamic values have limited precision and accuracy caused by experimental error. See Problem 30.24 for a spreadsheet that implements these calculations.

23. Calculate the rotational spectroscopic temperature and partition function for HF at 298.15 K. Calculate the contribution of rotation to the molar entropy and molar Gibbs energy of HF.

Answer: The plan is to use the spectroscopic constants from Table 27.6.1 and the conversion factor $hc/k = 1.438778 \text{ cm K}$.

Table 27.6.1 lists $\tilde{B}_e = 20.9537 \text{ cm}^{-1}$, giving the spectroscopic temperature:

$$\Theta_r = \frac{\tilde{B}hc}{k} = 20.9537 \text{ cm}^{-1}(1.438778 \text{ cm K}) = 30.1477 \text{ K}$$

Using Eq. 30.3.3 with $\sigma = 1$, the rotational partition function is:

$$q_r = \frac{T}{\sigma\Theta_r} = \frac{298.15 \text{ K}}{30.1477 \text{ K}} = 9.88964$$

The preceding problem gives the corresponding contribution of rotation to the molar entropy and Gibbs energy.

24. Calculate the rotational partition function for $^{24}\text{Mg}_2$ at 298.15 K. The bond length is $R_e = 3.07859 \text{ \AA}$. Calculate the contribution of rotation to the molar entropy and molar Gibbs energy of Mg_2 .

Answer: The plan is to use $kT/hc = 207.224 \text{ cm}^{-1}$, and the high temperature approximation or Equipartition rotational contribution of a diatomic molecule of $U - U(0) = RT$.

The molar mass of ^{24}Mg is $23.98504 \text{ g mol}^{-1}$. The reduced mass of $^{24}\text{Mg}_2$ is:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{\mathcal{M}_{\text{Mg}}/2}{N_A} (1 \text{ kg}/1000 \text{ g}) = 1.991406 \times 10^{-26} \text{ kg}.$$

With Eqs. 24.4.10 and 24.5.41, the rotational constant is: $\tilde{B}_e = \frac{\hbar}{4\pi \mu R_e^2 c}$

$$\tilde{B}_e = \frac{1.05457266 \times 10^{-34} \text{ J s}}{4\pi(1.991406 \times 10^{-26} \text{ kg})(3.8905 \times 10^{-10} \text{ m})^2(2.99792458 \times 10^{10} \text{ cm s}^{-1})} = 0.09287 \text{ cm}^{-1}$$

Using Eq. 30.1.39 with $\sigma = 2$, the rotational partition function is:

$$q_r = \frac{kT}{\sigma\tilde{B}hc} = \frac{207.224 \text{ cm}^{-1}}{2(0.09287 \text{ cm}^{-1})} = 1115.7$$

The contribution of rotation of a linear molecule to the internal energy is $U - U(0) = RT$, from the high temperature approximation, Table 30.3.3, or correspondingly from Equipartition.

Using Eq. 30.2.26° the molar rotational entropy is:

$$S_r = R \ln q_r + R = 8.31446 \text{ J K}^{-1} \text{ mol}^{-1}(\ln 1115.7 + 1) = 66.659 \text{ J K}^{-1} \text{ mol}^{-1}$$

Using Eq. 30.2.52°, the contribution to the molar Gibbs energy is:

$$\begin{aligned} G_r - G_r(0) &= -RT \ln q_r = -8.31446 \text{ J K}^{-1} \text{ mol}^{-1}(1 \text{ kJ}/1000 \text{ J})(298.15 \text{ K}) \ln 1115.7 \\ &= -17.395 \text{ kJ mol}^{-1} \end{aligned}$$

As a check, note that for the rotational contribution, $H_r - H_r(0) = U_r - U_r(0)$; the factor of nRT in the conversion of the overall internal energy to enthalpy, $H = U + nRT$, is combined with the translational contribution. Then using the definition of Gibbs energy, $G \equiv H - TS$, and the entropy result, above:

$$\begin{aligned} G_r - G_r(0) &= H_r - H_r(0) - T S_r = U_r - U_r(0) - T S_r \\ &= 2.47896 \text{ kJ mol}^{-1} - 298.15 \text{ K}(66.659 \text{ J K}^{-1} \text{ mol}^{-1})(1 \text{ kJ}/1000 \text{ J}) \\ &= 2.47896 \text{ kJ mol}^{-1} - 8.15944 \text{ kJ mol}^{-1} = -17.395 \text{ kJ mol}^{-1} \end{aligned}$$

The spreadsheet format is particularly convenient for statistical mechanical calculations. A spreadsheet that implements these calculations for translation, rotation, and vibration in diatomics is shown below. We are so lazy that we even included a section that calculates the molar mass from the molecular formula. The most abundant isotope specific masses are used. This spreadsheet applies to several problems:

A1	B	C	D	E	F	G	H	I	J
2		T	298.15	K	kt/hc =	207.224	cm ⁻¹		
3		μ	47.97008	g mol ⁻¹					
4		B	0.09287	cm ⁻¹					
5		σ	2						
6		ν_0	44.367	cm ⁻¹					
7		g_e	1						
8									
9	Contribution			ZPE (kJ mol ⁻¹)	U-U(0) (kJ mol ⁻¹)	H-H(0) (kJ mol ⁻¹)	S (J K ⁻¹ mol ⁻¹)	G-G(0) (kJ mol ⁻¹)	
10	translation	$q_t/N_A =$	13232012		3.71844	6.19739	157.12797	-40.65031	
11	rotation	$q_r =$	1115.669		2.47896	2.47896	66.65879	-17.39536	
12	vibration	$q_v =$	5.188517	0.26537	2.22304	2.22304	21.14545	-4.08147	
13	electronic	$q_e =$	1		0	0	0	0	
14	Total				8.42044	10.89939	244.93222	-62.12714	kJ mol ⁻¹
15	Formula	mass	#	mass (g mol ⁻¹)					
16	C	12		0			Constants		
17	H	1.007825		0			hc/k	1.4387782	cm K
18	N	14.00307		0			$N_A hc$	11.96266	J cm mol ⁻¹
19	O	15.99492		0			Γ	0.025946759	
20	P	30.97376		0			k	1.380649E-23	J K ⁻¹
21	S	31.97207		0			h	6.626076E-34	
22	F	18.9984		0			N_A	6.022137E+23	
23	Cl	34.96885		0			R	8.3144621	J K ⁻¹ mol ⁻¹
24	Br	78.91834		0			V°	24.78956875	L
25	Li	6.015122		0					
26	Na	22.98977		0					
27	Mg	23.98504	2	47.9701					
28	$\mu =$			47.9701	g mol ⁻¹				

Cell G2 is: “=D2/I17”

Cells D10:E12 are:

A1	B	C	D	E
9	Contribution			ZPE (kJ mol ⁻¹)
10	translation	$q_t/N_A =$	=119*D3^1.5*D2^2.5	
11	rotation	$q_r =$	=G\$2/D5/D4	
12	vibration	$q_v =$	=1/(1-EXP(-D6/G\$2))	=D6*G\$18/2/1000
13	electronic	$q_e =$		1

Cell F10 is: “=3*\$I\$23*\$D\$2/1000”

Cell G10 is: “=F10+I23*\$D\$2/1000”

Cell H10 is: “=\$I\$23*(LN(\$I\$24)+3*LN(\$D\$2)/2+3*LN(D3)/2)+11.1037”

Cell I10 is: “=-I23*D2*LN(D10)/1000”

25. Calculate the contribution of vibration to the molar entropy at 298.15 K for HCN, given the literature value of the observed bending vibration frequency at $\tilde{\nu}_o = 711.98 \text{ cm}^{-1}$ and the two stretching vibrations at 2096.85 cm^{-1} and 3311.47 cm^{-1} .³ The bending vibration is doubly degenerate. (See also Problems 8 and 9 for the contributions of translation and rotation.)

Answer: The plan is to use Eqs. 30.3.15 and 30.2.26 for the degenerate bending vibrations; the overall vibrational entropy is the sum of the entropy of each normal mode.

The Boltzmann weighting factor for the bending vibration is:

$$e^{-711.98 \text{ cm}^{-1}/207.224 \text{ cm}^{-1}} = 0.032200$$

Using Eq. 30.1.31, the vibrational partition function for each bending vibration is:

$$q_v = \frac{1}{1 - e^{-\tilde{\nu}_o/207.224 \text{ cm}^{-1}}} = \frac{1}{1 - e^{-711.98/207.224}} = 1.033270$$

The vibrational partition functions for the two stretches are 1.000035 and 1.000000115, respectively, which are too close to one to contribute significantly to the final entropy. The constant $N_A h c$ is given as (see inside front cover of the text):

$$\begin{aligned} N_A h c &= 6.0221367 \times 10^{23} \text{ mol}^{-1} (6.6260755 \times 10^{-34} \text{ J s}) (2.99792458 \times 10^{10} \text{ cm s}^{-1}) \\ &= 11.962658 \pm 1.0 \times 10^{-5} \text{ J cm mol}^{-1} = 11.962658(10) \text{ J cm mol}^{-1} \end{aligned}$$

giving: $N_A h c \tilde{\nu}_o = 11.96266 \text{ J cm mol}^{-1} (1 \text{ kJ}/1000 \text{ J}) (711.98 \text{ cm}^{-1}) = 8.51729 \text{ kJ mol}^{-1}$

The zero-point energy is: $\frac{1}{2} N_A h c \tilde{\nu}_o = \frac{1}{2} (8.51717 \text{ kJ mol}^{-1}) = 4.259 \text{ kJ mol}^{-1}$

Using Eq. 30.3.15, the contribution of each bending vibration to the molar internal energy is:

$$U_{m,v} - U_{m,v}(0) = \frac{N_A h \nu_o e^{-h\nu_o/kT}}{1 - e^{-h\nu_o/kT}} = 8.51729 \text{ kJ mol}^{-1} \frac{0.032200}{1 - 0.032200} = 0.283377 \text{ kJ mol}^{-1}$$

Using Eq. 30.2.26° the molar vibrational entropy of each bending vibration is:

$$\begin{aligned} S_v &= R \ln q_v + \frac{U_v - U_v(0)}{T} \\ &= 8.31446 \text{ J K}^{-1} \text{ mol}^{-1} (\ln 1.03327) + \frac{0.283377 \times 10^3 \text{ J mol}^{-1}}{298.15 \text{ K}} \\ &= 0.27212 \text{ J K}^{-1} \text{ mol}^{-1} + 0.95045 \text{ J K}^{-1} \text{ mol}^{-1} = 1.22253 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

For both bending vibrations the total is: $S_v = 2.4451 \text{ J K}^{-1} \text{ mol}^{-1}$

In Problem 9, we worked out the translational and rotational contributions to the molar standard state entropy: $S_{m,298.15 \text{ K}}^{\circ} = 199.38 \text{ J K}^{-1} \text{ mol}^{-1}$. Adding in the vibrational contribution gives:

$$S_{m,298.15\text{ K}}^{\circ} = 199.38 \text{ J K}^{-1} \text{ mol}^{-1} + 2.4451 \text{ J K}^{-1} \text{ mol}^{-1} = 201.83 \text{ J K}^{-1} \text{ mol}^{-1}$$

Using Table 8.4.1 in the Data Section, $S_{298\text{ K}}^{\circ} = 201.78 \text{ J K}^{-1} \text{ mol}^{-1}$ giving only a 0.02% difference.

26. Calculate the vibrational partition function at 298.15 K for Mg_2 , given the literature value of the fundamental vibration frequency, $\tilde{\nu}_0 = 47.89 \text{ cm}^{-1}$. Calculate the contribution of vibration to the zero point energy, and molar internal energy, entropy, and Gibbs energy of Mg_2 .

Answer: The plan is to use Table 30.3.3 and Eq. 30.3.15. (See Problem 6 for the calculation of $\tilde{\nu}_0 = 47.89 \text{ cm}^{-1}$ for Mg_2).

Using Eq. 30.1.31, the vibrational partition function is:

$$q_v = \frac{1}{1 - e^{-\tilde{\nu}_0/207.224 \text{ cm}^{-1}}} = \frac{1}{1 - e^{-47.89/207.224}} = 4.8463$$

The zero-point energy is $\frac{1}{2}N_A h c \tilde{\nu}_0$. The constant $N_A h c$ is given as (see inside front cover of the text):

$$\begin{aligned} N_A h c &= 6.0221367 \times 10^{23} \text{ mol}^{-1} (6.6260755 \times 10^{-34} \text{ J s}) (2.99792458 \times 10^{10} \text{ cm s}^{-1}) \\ &= 11.962658 \pm 1.0 \times 10^{-5} \text{ J cm mol}^{-1} = 11.962658(10) \text{ J cm mol}^{-1} \end{aligned}$$

giving: $N_A h c \tilde{\nu}_0 = 11.96266 \text{ J cm mol}^{-1} (1 \text{ kJ}/1000 \text{ J}) (47.89 \text{ cm}^{-1}) = 0.57289 \text{ kJ mol}^{-1}$

The zero-point energy is: $\frac{1}{2}N_A h c \tilde{\nu}_0 = \frac{1}{2}(0.57289 \text{ kJ mol}^{-1}) = 0.28645 \text{ kJ mol}^{-1}$

The Boltzmann weighting factor is: $e^{-47.89 \text{ cm}^{-1}/207.224 \text{ cm}^{-1}} = 0.79366$

Using Eq. 30.3.15, the contribution of a vibration to the molar internal energy is:

$$U_{m,v} - U_{m,v}(0) = \frac{N_A h \nu_0 e^{-h\nu_0/kT}}{1 - e^{-h\nu_0/kT}} = 0.57289 \text{ kJ mol}^{-1} \frac{0.79366}{1 - 0.79366} = 2.2035 \text{ kJ mol}^{-1}$$

Using Eq. 30.2.26° the molar vibrational entropy is:

$$\begin{aligned} S_v &= R \ln q_v + \frac{U_v - U_v(0)}{T} \\ &= 8.31446 \text{ J K}^{-1} \text{ mol}^{-1} (\ln 4.8463) + \frac{2.2035 \times 10^3 \text{ J mol}^{-1}}{298.15 \text{ K}} = 20.511 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

Using Eq. 30.2.52°, the contribution to the molar Gibbs energy is:

$$\begin{aligned} G_v - G_v(0) &= -RT \ln q_v = -8.31446 \text{ J K}^{-1} \text{ mol}^{-1} (1 \text{ kJ}/1000 \text{ J}) (298.15 \text{ K}) \ln 4.8463 \\ &= -3.912 \text{ kJ mol}^{-1} \end{aligned}$$

As a check, note that for the rotational contribution, $H_r - H_r(0) = U_r - U_r(0)$; the factor of nRT in the conversion of the overall internal energy to enthalpy, $H = U + nRT$, is combined with the translational contribution. Then using the definition of Gibbs energy, $G \equiv H - TS$, and the entropy result, above:

$$\begin{aligned}
 G_v - G_v(0) &= H_v - H_v(0) - T S_v = U_v - U_v(0) - T S_v \\
 &= 2.2035 \text{ kJ mol}^{-1} - 298.15 \text{ K}(20.511 \text{ J K}^{-1} \text{ mol}^{-1})(1 \text{ kJ}/1000 \text{ J}) \\
 &= 2.2035 \text{ kJ mol}^{-1} - 6.1154 \text{ kJ mol}^{-1} = -3.912 \text{ kJ mol}^{-1}
 \end{aligned}$$

See Problem 30.24 for a spreadsheet that implements these calculations.

27. The symmetry number, σ , in the rotational partition function may seem arbitrary at first. This problem is designed to explore the effects of the symmetry number on the properties of molecules. A good test case is to consider N_2 and CO . We will look at the contribution of rotation to the entropy of these two very similar diatomic molecules. The mass of N_2 is 28.02 g mol^{-1} and the mass of CO is 28.01 g mol^{-1} , so the contribution of translation to the entropy is essentially identical. The fundamental vibration frequencies of the two are very similar, $\tilde{\nu}_0$ for N_2 is 2359.6 cm^{-1} and for CO is 2170.2 cm^{-1} . The vibrational contribution to the entropy is essentially identical. Both molecules have singlet ground states. The rotational constants are also very similar, \tilde{B}_e for N_2 is 2.010 cm^{-1} and for CO is 1.9314 cm^{-1} . So, the only major difference is the symmetry.

(a). Using the result of part a, prove that the contribution of rotation to the molar entropy of a diatomic gas is:

$$S_m = R \ln \left(\frac{kT}{\tilde{B}_e hc} \right) + R - R \ln \sigma$$

(b). Using the result from part a, and assuming that the differences in \tilde{B}_e of N_2 and CO are negligible, calculate the theoretical difference in entropy of N_2 and CO . The experimental entropies are $191.61 \text{ J K}^{-1} \text{ mol}^{-1}$ for N_2 and $197.67 \text{ J K}^{-1} \text{ mol}^{-1}$ for CO . Compare theory and experiment.

(c). Evaluate the contribution of just the symmetry part of the rotational partition function to the equilibrium constant for the reaction: $\text{N}_2 + \text{CO}_2 \rightleftharpoons \text{CO} + \text{N}_2\text{O}$

Answer: The plan is to use Eq. 30.3.7 as the basis for this problem.

(a). Splitting out the symmetry number term from Eq. 30.3.7 for one mole gives:

$$S_{r,m} = R \ln \left(\frac{kT}{\sigma \tilde{B} hc} \right) + R = R \ln \left(\frac{kT}{\tilde{B} hc} \right) + R - R \ln \sigma$$

(b). The difference assuming equal rotational constants with $\sigma_{\text{N}_2} = 2$ and $\sigma_{\text{CO}} = 1$ is then:

$$\begin{aligned}
 S_r(\text{N}_2) - S_r(\text{CO}) &= -R \ln \sigma_{\text{N}_2} - (-R \ln \sigma_{\text{CO}}) \\
 &= 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} (\ln \sigma_{\text{CO}} - \ln \sigma_{\text{N}_2}) \\
 &= 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} (\ln 1 - \ln 2) = -5.763 \text{ J K}^{-1} \text{ mol}^{-1}
 \end{aligned}$$

with the experimental difference: $S_r(\text{N}_2) - S_r(\text{CO}) = 191.61 \text{ J K}^{-1} \text{ mol}^{-1} - 197.67 \text{ J K}^{-1} \text{ mol}^{-1} = -6.06 \text{ J K}^{-1} \text{ mol}^{-1}$. The difference in entropy is primarily given by symmetry.

(c). The contribution of the symmetry part of the rotational partition function to the equilibrium constant for the reaction using $\sigma_{\text{N}_2} = 2$, $\sigma_{\text{CO}_2} = 2$, $\sigma_{\text{CO}} = 1$, and $\sigma_{\text{N}_2\text{O}} = 1$ is

$$K_p = (1)(1)/(2)(2) = 0.25$$

28. Write your own spreadsheet that reproduces Example 30.4.1.

Answer: The cells C11:C18 are:

A	B	C
11	q_t/N_A	$=\$C\$24*\$C\$20^2.5*C6^1.5$
12	q_r	$=\$C\$21/C8/C5$
13	q_v	$=1/(1-EXP(-C4/\$C\$21))$
14	q_e	$=C7$
15	G-G(0) internal	$=-\$C\$22*\$C\$20*LN(C12*C13*C14)/1000$
16	G-G(0) (kJ mol ⁻¹)	$=-\$C\$22*\$C\$20*LN(C11*C12*C13*C14)/1000$
17	G(0) (kJ mol ⁻¹)	$=-C9*\$C\27
18	G (kJ mol ⁻¹)	$=C17+C16$

Cell G20 is “ $=(2*G18-C18-E18)$ ” and Cell G21 is “ $=G20/2$ ”.

29. The equilibrium constant expression in Eq 30.4.24° can be related directly to the bond length of the diatomic molecules: R_{AB} for the product and R_{BC} for the reactant. (a). Express Eq. 30.4.24° directly in terms of the bond lengths of the diatomic species. The result clearly shows the relationship between molecular structure and the position of equilibrium. (b). For atom-diatom exchange on the basis of rotation alone, if $R_{AB} > R_{BC}$ are products or reactants favored?

Answer: The plan is to use the definition of the rotational constant in terms of the moment of inertia of a diatomic molecule, Eqs. 24.4.10 and 24.5.41, to find the relationship to the bond lengths.

(a). Given the moment of inertia of a diatomic molecule is $I = \mu R^2$ with the rotational constant:

$$\tilde{B} = \frac{\hbar}{4\pi I c} = \frac{\hbar}{4\pi \mu R^2 c} \quad (24.4.10, 24.5.41)$$

The ratio for the rotational partition functions simplifies to:

$$\left(\frac{1/\tilde{B}_{AB}}{1/\tilde{B}_{BC}} \right) = \frac{\mu_{AB} R_{AB}^2}{\mu_{BC} R_{BC}^2}$$

From Eq. 30.4.24°, the equilibrium expression is:

$$K_p = \underbrace{\left(\frac{m_{AB} m_C}{m_A m_{BC}} \right)^{3/2}}_{\text{translation}} \underbrace{\frac{\mu_{AB} R_{AB}^2}{\mu_{BC} R_{BC}^2}}_{\text{rotation}} \underbrace{\left(\frac{1}{1 - e^{-h\tilde{\nu}_o(AB) c/kT}} \right)}_{\text{vibration}} \underbrace{\left(\frac{g_{AB} g_C}{g_A g_{BC}} \right)}_{\text{electronic zero-point energy shift}} e^{-\Delta E_o/RT}$$

(b). From this final expression, if $R_{AB} > R_{BC}$ the numerator is larger than the denominator, which favors products. Alternatively, thinking of the string of relationships, if R_{AB} increases compared to R_{BC} :

If $R_{AB} \uparrow$ then:

$I_{AB} \uparrow$, $\tilde{B}_{AB} \downarrow$, rotational level spacing \downarrow , accessible rotational states of products \uparrow , $K_p \uparrow$

The flow of the logic provides a concise summary of the relationships of fundamental quantum mechanics, spectroscopy, and thermodynamics. The progression is from the structural properties of individual molecules to the many-body phenomena of macroscopic equilibrium.

30. Use typical values of the partition functions, Eq. 30.3.5°, to estimate the equilibrium constant of the ideal gas reaction: $O_2 + F \rightleftharpoons OF + O$ at 298 K. This reaction is a possible reaction in ozone depletion in the stratosphere. Use $q_t/N_A = 1 \times 10^7$, $q_F = 100$, and $q_v = 1$. Since OF has an odd number of electrons, assume the ground state of OF is a doublet, $^2\Pi$. The bond dissociation energies are: $D_o(O_2) = 5.126 \text{ eV} = 494.6 \text{ kJ mol}^{-1}$ and $D_o(OF) = 1.61 \text{ eV} = 155 \text{ kJ mol}^{-1}$.

Answer: The zero point energy shift term is simplified by using the equivalent temperature in eV from Table 30.3.1, $kT/e = 0.02569 \text{ eV}$ at 298.15 K.

The equilibrium constant for $O_2 + F \rightarrow OF + O$ is:

$$K_p = \left(\frac{q_{OF}/N_A q_O/N_A}{q_{O_2}/N_A q_F/N_A} \right) e^{-\Delta E_o/RT}$$

with $\Delta E_o = [-D_o(OF)] - [-D_o(O_2)] = [-1.61 \text{ eV}] - [-5.126 \text{ eV}] = 3.52 \text{ eV} = 340. \text{ kJ mol}^{-1}$

The zero point shift term in eV is: $e^{-\Delta E_o/RT} = e^{-3.53 \text{ eV}/0.02569 \text{ eV}} = e^{-137} = 3.2 \times 10^{-60}$

Alternatively, the zero point shift term in kJ mol^{-1} is:

$$e^{-\Delta E_o/RT} = e^{-340 \times 10^3 \text{ J mol}^{-1}/(8.314 \text{ J K}^{-1} \text{ mol}^{-1} \cdot 298.2 \text{ K})} = e^{-137} = 3.2 \times 10^{-60}$$

The rotational symmetry numbers are $\sigma_{O_2} = 2$ and $\sigma_{OF} = 1$. The vibrations are too high in frequency to make a contribution ($> 500 \text{ cm}^{-1}$). At a low level of approximation we can take the electronic partition functions as the ground state degeneracies, which for atoms are given in Table 30.1.2. The ground state degeneracies are $g_{O_2} = 3$, $g_F = 4$, $g_{OF} = 2$, and $g_O = 5$. The equilibrium constant is roughly approximated:

$$K_p \cong \left(\frac{10^7 \cdot 10^7}{10^7 \cdot 10^7} \right) \left(\frac{100}{100/2} \right) \left(\frac{1}{1} \right) \left(\frac{2 \cdot 5}{3 \cdot 4} \right) e^{-137} \cong 5 \times 10^{-60}$$

translation rotation vibration electronic zero point shift

Products are favored by rotation and reactants are favored by electronic degeneracy. However, the order of magnitude of the equilibrium constant is dominated by the bond dissociation energies. Diatomic O_2 has the stronger bond, strongly favoring reactants.

One of the possible large errors in using “garden variety” estimates is in the rotational contribution. The rotational constants are $\tilde{B}_e(OF) = 1.0587 \text{ cm}^{-1}$ and $\tilde{B}_e(O_2) = 1.446 \text{ cm}^{-1}$, giving more precise values of the rotational partition functions:

$$q_r(\text{OF}) = \frac{207.224 \text{ cm}^{-1}}{1.0587 \text{ cm}^{-1}} = 196.7 \quad \text{and} \quad q_r(\text{O}_2) = \frac{207.224 \text{ cm}^{-1}}{2(1.446 \text{ cm}^{-1})} = 71.65$$

with $q_r(\text{OF})/q_r(\text{O}_2) = 196.7/71.65 = 2.75$ rather than the “garden variety” estimate of 2.

31. Use the “*Equilibrium Constants from Molecular Structure*” applet, “efs.html,” on the textbook Web site and companion CD to calculate the equilibrium constant for the reaction in the previous problem: $\text{O}_2 + \text{F} \rightleftharpoons \text{OF} + \text{O}$ at 298 K. The spectroscopic parameters are available as examples, or the values given in the previous problem can be input by hand. Compare with the approximate results from the previous problem.

Answer: The parameters were input using the “Examples” buttons to give the following results:

	A	+ B	-> C	+ D
formula	16O 16O	F	16O F	16O
Be (cm ⁻¹)	1.44567		1.0587	
symm. number	2		1	
v _o (cm ⁻¹)	1580.361		1028.7	
ground state degeneracy	3	4	2	5
D _o , dissociation E (eV)	5.126		1.61	
mass (g/mol)	31.9898	18.9984	34.9933	15.9949
qt/N _A	7205998.57628	3298009.78569	8244303.49681	2547705.22925
q _r	71.6712457528	1	195.736223382	1
q _v	1.00048771342	1	1.00703302432	1
H-H(0) (kJ/mol)	8.686	6.197	8.763	6.197
S (J/mol/K)	205.080	157.104	211.495	156.813
G-G(0) [internal] (kJ/mol)	-13.314	-3.436	-14.816	-3.989
G-G(0) (kJ/mol)	-52.458	-40.642	-54.293	-40.555
G(0) (kJ/mol)	-494.581	0.000	-155.340	0.000
G (kJ/mol)	-547.040	-40.642	-209.634	-40.555

Final reaction Gibbs Free Energy change: 337.493 kJ and K_p: 7.485e-60

These accurate calculations agree favorably with the “garden variety” estimates used in the previous problem. See also Problem 30.24 for a similar spreadsheet for a single species.

32. Consider the reaction $\text{AB} \rightarrow \text{A} + \text{B}$, where A and B are atoms. Predict the effect on the equilibrium constant if the following changes are made. (a). The AB molecule is a ground state triplet (like O₂) instead of a singlet. (b). The AB bond length is increased. (c). The AB force constant is increased. (d). The AB bond dissociation energy is increased. [In reality changing just one molecular parameter is impossible, bond strength changes have multiple effects. However, for the purposes of this exercise assume that the given change is done without changes in other parameters.]

Answer: The plan is to note if the change increases or decreases the number of accessible states and if the change is for a reactant or product.

The equilibrium constant is given in terms of the partition functions as:

$$K_p = \left(\frac{q^A/N_A q^B/N_A}{q^{AB}/N_A} \right) e^{-\Delta E_0/RT} = \left(\frac{q^A/N_A q^B/N_A}{q^{AB}/N_A} \right) \left(\frac{1}{q_r(AB)} \right) \left(\frac{1}{q_v(AB)} \right) \left(\frac{q_e(A) q_e(B)}{q_e(AB)} \right) e^{-\Delta E_0/RT}$$

with $\Delta E_0 = -\varepsilon_0(AB) = -[-D_0(AB)]$

(a). If the AB molecule is a ground state triplet (like O₂) instead of a singlet, the ground state degeneracy increases from one to three, and the number of accessible electronic states increases. Since AB is a reactant, increasing the number of accessible states shifts the equilibrium towards reactants.

(b). The rotational constant of a diatomic molecule is given by Eq.30.1.34 with moment of

inertia $I = \mu R^2$ for a diatomic molecule : $\tilde{B} = \frac{h}{4\pi \mu R^2 c}$

If the bond length of AB is increased, the moment of inertia is increased, the rotational constant is decreased, the rotational energy level spacing is decreased, and the number of accessible states is increased for AB. Since AB is a reactant, increasing the number of accessible states shifts the equilibrium towards reactants. In summary:

If $R_{AB} \uparrow$ then:

$I_{AB} \uparrow$, $\tilde{B}_{AB} \downarrow$, rotational level spacing \downarrow , accessible rotational states of reactants \uparrow , $K_p \downarrow$

(c). If the bond force constant of AB is increased, the fundamental vibration frequency of AB is increased, the vibrational energy level spacing is increased, and the number of accessible states is decreased. Since AB is a reactant, decreasing the number of accessible states shifts the equilibrium towards products. In summary:

If $k_{AB} \uparrow$ then:

$\tilde{\nu}_0(AB) \uparrow$, vibrational level spacing \uparrow , accessible vibrational states of reactants \downarrow , $K_p \uparrow$

(d). If the bond dissociation energy of AB is increased, the zero-point energy shift is increased, the overall energy states of AB are lowered, and the number of accessible AB states are increased. Since AB is a reactant, increasing the number of accessible states shifts the equilibrium towards reactants. AB becomes more stable and so is favored in the equilibrium state.

33. Calculate the equilibrium constant of the ideal gas dissociation $Mg_2 \rightleftharpoons Mg + Mg$ at 298.15 K. Assume the isotope is ²⁴Mg. The spectroscopic constants for Mg₂ are $R_e = 3.8905 \text{ \AA}$, $\tilde{\nu}_0 = 47.89 \text{ cm}^{-1}$, and $D_e = 0.04979(4) \text{ eV}$.¹ The ground state of Mg₂ is ¹Σ_g⁺ and the ground state of Mg-atoms is ¹S₀.

Answer: The molar mass of ²⁴Mg is 23.98504 g mol⁻¹. The mass of Mg₂ is 47.97954 g mol⁻¹ and with Eqs. 30.3.1° and 30.3.2°:

$$\frac{q_{t,Mg_2}^\circ}{N_A} = \Gamma (\mathcal{M}/g \text{ mol}^{-1})^{3/2} (T/K)^{5/2} = 0.0259472 (47.97954)^{3/2} (298.15)^{5/2} = 1.32320 \times 10^7$$

For Mg-atoms: $\frac{q_{i,\text{Mg}}^\circ}{N_A} = 0.0259472 (23.98504)^{3/2} (298.15)^{5/2} = 4.678223 \times 10^6$

The reduced mass of Mg₂ is: $\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{\mathcal{M}_{\text{Mg}}/2}{N_A} (1 \text{ kg}/1000 \text{ g}) = 1.991406 \times 10^{-26} \text{ kg}$.

With Eqs. 24.4.10 and 24.5.41: $\tilde{B}_e = \frac{\hbar}{4\pi \mu R_e^2 c}$

$$\tilde{B}_e = \frac{1.05457266 \times 10^{-34} \text{ J s}}{4\pi (1.991406 \times 10^{-26} \text{ kg})(3.8905 \times 10^{-10} \text{ m})^2 (2.99792458 \times 10^{10} \text{ cm s}^{-1})} = 0.09287 \text{ cm}^{-1}$$

Using Eq. 30.1.39 with $\sigma = 2$, the rotational partition function is:

$$q_r = \frac{kT}{\sigma \tilde{B} h c} = \frac{207.224 \text{ cm}^{-1}}{\sigma \tilde{B}} = \frac{207.224 \text{ cm}^{-1}}{2(0.09287 \text{ cm}^{-1})} = 1115.7$$

Using Eq. 30.1.31, the vibrational partition function is:

$$q_v = \frac{1}{1 - e^{-\tilde{\nu}_0/207.224 \text{ cm}^{-1}}} = \frac{1}{1 - e^{-47.89/207.224}} = 4.8463$$

See Problem 30.24 for a spreadsheet that implements these calculations. The reaction products are atoms, while the reference point is for totally dissociated atoms. The zero-point energy shift is then just $\Delta E_0 = -\varepsilon_0(\text{Mg}_2) = -[-D_0(\text{Mg}_2)] = 0.04979(4) \text{ eV}$. In terms of bond energy, the reaction runs uphill from Mg₂. Using Table 30.3.1, $kT/e = 0.025693 \text{ eV}$ at 298.15 K, the zero-point energy shift term is:

$$e^{-\Delta E_0/RT} = e^{-0.04979 \text{ eV}/0.025693 \text{ eV}} = e^{-1.938} = 0.1440 \pm 0.0023$$

Even though the bond dissociation energy is unusually small, the zero-point energy shift term is still unfavorable. Considering each degree of freedom separately, the overall equilibrium constant is:

$$\begin{aligned} K_p &= \frac{q_{\text{Mg}}^\circ q_{\text{Mg}}^\circ}{q_{\text{Mg}_2}^\circ} e^{-\Delta E_0/RT} \\ &= \left(\frac{(4.678223 \times 10^6)^2}{1.32320 \times 10^7} \right) \left(\frac{1}{1115.7} \right) \left(\frac{1}{4.8463} \right) \left(\frac{1 \cdot 1}{1} \right) 0.1440 \\ &= \underset{\text{translation}}{1.65400 \times 10^6} \underset{\text{rotation}}{0.0008963} \underset{\text{vibration}}{0.20634} \underset{\text{electronic}}{1} \underset{\text{zero-point energy shift}}{0.1440} = 44.05 \pm 0.70 \end{aligned}$$

Mg₂ is 99% dissociated at 298.2 K and 1 bar, Eq. 20.2.8. Our expectation based on Lewis structures is that Mg₂ is not stable, since Mg atoms are closed shell.

34. Heat capacities are the fundamental building blocks of all thermodynamic properties. For example, Third Law absolute entropies are based entirely on the temperature dependence of the heat capacity of the pure substance and enthalpies of the phase transitions, which in turn require heat capacities for their measurement. (a). Prove that the constant volume heat capacity of a pure substance is given by:

$$C_v = \left(\frac{\partial U}{\partial T} \right)_v = 2nRT \left(\frac{\partial \ln q}{\partial T} \right)_v + nRT^2 \left(\frac{\partial^2 \ln q}{\partial T^2} \right)_v$$

(b). Show that the constant volume heat capacity of rotation of a linear molecule is nR .

Answer: The plan is to note that the constant volume heat capacity is the temperature derivative of the internal energy, $C_v = (\partial U / \partial T)_v$.

(a). Using Eq. 30.2.16° and the product rule:

$$U - U(0) = nRT^2 \left(\frac{\partial \ln q}{\partial T} \right)_v \quad 1$$

$$C_v = \left(\frac{\partial U}{\partial T} \right)_v = 2nRT \left(\frac{\partial \ln q}{\partial T} \right)_v + nRT^2 \left(\frac{\partial^2 \ln q}{\partial T^2} \right)_v \quad 2$$

(b). For rotations using Eq. 30.1.39: $q_r = \frac{kT}{\sigma B h c}$ or $\ln q_r = \ln \left(\frac{k}{\sigma B h c} \right) + \ln T$ 3

The derivatives are: $\left(\frac{\partial \ln q}{\partial T} \right)_v = \left(\frac{\partial \ln T}{\partial T} \right)_v = \frac{1}{T} \left(\frac{\partial T}{\partial T} \right)_v = 1/T$ and $\left(\frac{\partial^2 \ln q}{\partial T^2} \right)_v = -1/T^2$ 4

Substituting the derivatives into Eq. 2 gives:

$$C_v = \left(\frac{\partial U}{\partial T} \right)_v = 2nRT(1/T) + nRT^2(-1/T^2) = nR$$

as expected from Equipartition.

35. The Equipartition prediction of the contribution of a vibration to the molar heat capacity of a diatomic molecule is $C_v = R$, which is the maximum contribution at high temperatures. More accurately, the contribution of vibration to the internal energy of a diatomic molecule, in the harmonic approximation, is given by Eq. 30.3.13. (a). Determine the heat capacity of a diatomic molecule, in the harmonic oscillator approximation, using the following steps. (a). To make the derivation easier, start by showing that the vibrational contribution is given by:

$$U - U(0) = \frac{N h \nu_0 e^{-\beta h \nu_0}}{1 - e^{-\beta h \nu_0}} = \frac{N h \nu_0}{e^{\beta h \nu_0} - 1}$$

(b). Then, convert the heat capacity derivative to one written in terms of β :

$$C_v = \left(\frac{\partial U}{\partial T} \right)_v = \left(\frac{\partial U}{\partial \beta} \right)_v \left(\frac{\partial \beta}{\partial T} \right)_v = -\frac{1}{kT^2} \left(\frac{\partial U}{\partial \beta} \right)_v$$

(c). Show that: $C_v = \frac{N(h\nu_0)^2}{kT^2} \left(\frac{e^{\beta h \nu_0}}{(e^{\beta h \nu_0} - 1)^2} \right)$

(d). Finally show that: $C_v = \frac{N(h\nu_0)^2}{kT^2} \left[\frac{e^{-h\nu_0/kT}}{(1 - e^{-h\nu_0/kT})^2} \right]$

(e). Plot the molar heat capacity from $T = 10$ to 1000 K for a vibration frequency of 200.0 cm^{-1} . At what temperature, compared to $\tilde{\nu}_0$, does the vibration begin to make a significant contribution to the heat capacity?

Answer: The plan is to note that the constant volume heat capacity is the temperature derivative of the internal energy, $C_v = (\partial U / \partial T)_v$.

(a). Eq. 30.3.13 gives the contribution of a vibration to the internal energy as:

$$U - U(0) = \frac{N h \nu_0 e^{-\beta h \nu_0}}{1 - e^{-\beta h \nu_0}} \quad 1$$

This relationship is simplified by multiplying numerator and denominator by $e^{\beta h \nu_0}$:

$$\frac{N h \nu_0 e^{-\beta h \nu_0}}{1 - e^{-\beta h \nu_0}} \left(\frac{e^{\beta h \nu_0}}{e^{\beta h \nu_0}} \right) = \frac{N h \nu_0}{e^{\beta h \nu_0} - 1} \quad 2$$

(b). To make the derivative easier, using the product rule and Eq. 30.2.8:

$$C_v = \left(\frac{\partial U}{\partial T} \right)_v = \left(\frac{\partial U}{\partial \beta} \right)_v \left(\frac{\partial \beta}{\partial T} \right)_v = - \frac{1}{k T^2} \left(\frac{\partial U}{\partial \beta} \right)_v \quad 3$$

(c). Using the chain rule, the derivative is:

$$\left(\frac{\partial U}{\partial \beta} \right)_v = - \frac{N h \nu_0}{(e^{\beta h \nu_0} - 1)^2} \left(\frac{\partial (e^{\beta h \nu_0} - 1)}{\partial \beta} \right)_v = - \frac{N h \nu_0}{(e^{\beta h \nu_0} - 1)^2} e^{\beta h \nu_0} (h \nu_0) = - \frac{N (h \nu_0)^2 e^{\beta h \nu_0}}{(e^{\beta h \nu_0} - 1)^2} \quad 4$$

Substituting Eq. 4 into Eq. 3, the constant volume heat capacity is:

$$C_v = - \frac{1}{k T^2} \left(\frac{\partial U}{\partial \beta} \right)_v = \frac{N (h \nu_0)^2}{k T^2} \left(\frac{e^{\beta h \nu_0}}{(e^{\beta h \nu_0} - 1)^2} \right) \quad 5$$

Now, we do the reverse of step 2:

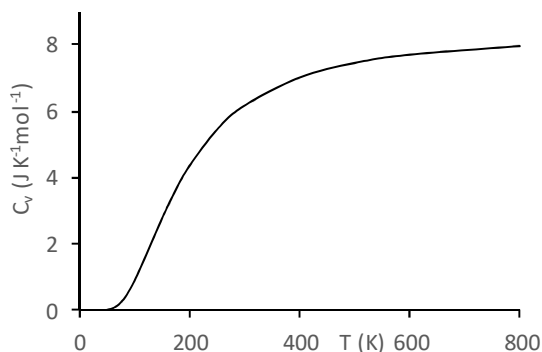
$$C_v = \frac{N (h \nu_0)^2}{k T^2} \left(\frac{e^{\beta h \nu_0}}{(e^{\beta h \nu_0} - 1)^2} \right) \left(\frac{e^{-\beta h \nu_0}}{e^{-\beta h \nu_0}} \right)^2 \quad 6$$

$$C_v = \frac{N (h \nu_0)^2}{k T^2} \left[\frac{e^{-\beta h \nu_0}}{(1 - e^{-\beta h \nu_0})^2} \right] = \frac{N (h \nu_0)^2}{k T^2} \left[\frac{e^{-h \nu_0 / k T}}{(1 - e^{-h \nu_0 / k T})^2} \right] \quad 7$$

(d). The spreadsheet and plot are shown below.

A1	B	C	D	E
2	$\nu_0 =$	400	cm^{-1}	
3				
4	T (K)	kT/hc (cm^{-1})	$e^{-h\nu_0/kT}$	C_v ($\text{J K}^{-1}\text{mol}^{-1}$)
5	10	6.9503	0.0000	0.0000
6	50	34.7517	0.0000	0.0110

7	75	52.1276	0.0005	0.2279
8	100	69.5034	0.0032	0.8776
9	150	104.2551	0.0216	2.7569
10	175	121.6310	0.0373	3.6195
11	200	139.0068	0.0563	4.3499
12	250	173.7585	0.1001	5.4433
13	298.15	207.2244	0.1451	6.1510
14	400	278.0137	0.2372	7.0172
15	500	347.5171	0.3163	7.4543
16	600	417.0205	0.3832	7.7053
17	800	556.0273	0.4870	7.9650
18				
19	hc/k	1.4387782	cm K	
20	N _A	6.0221E+23	mol ⁻¹	
21	h	6.6261E-34	J s	
22	k	1.3806E-23	J K ⁻¹	
23	c	2.9979E+10	cm s ⁻¹	



Cell C5 is “=B5/\$C\$19”. Cell D5 is “=EXP(-\$C\$2/C5)”. Cell E5 is:

$$=\$C\$20*(\$C\$21*\$C\$23*\$C\$2)^2/\$C\$22/\$B5^2*\$D5/(1-\$D5)^2$$

The heat capacity “begins to thaw” near a wave number equivalent temperature of $\tilde{\nu}_0/10$. The heat capacity approaches 10% of the full value at $\tilde{\nu}_0/4$ or equivalently at a temperature of $\Theta_v/4$, where Θ_v is the spectroscopic temperature of the transition. The high temperature limiting value is R , or $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, as expected from Equipartition.

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