

Appendix: Zero-Point Energy and Thermal Corrections to Energy, Enthalpy, and Gibbs Free Energy

For more information on the statistical mechanical theory described in this Appendix, see references 1 and 2.

For the purposes of the calculations of the thermodynamic properties of the molecules in this exercise, it will be assumed that the molecules are in a system at constant volume V and temperature T and do not interact with each other. (These are reasonable assumptions as we are only considering the reactant and product molecules separately in the calculations and not how the molecules interact when they react). In this case, all of the thermodynamic properties of the molecule can be computed from the *single-molecule canonical partition function*,

$$q = \sum_i e^{-\beta \varepsilon_i}, \quad (1)$$

where the sum is over all states i of the molecule, ε_i is the energy of state i , and $\beta = 1/(k_B T)$. The partition function is proportional to the number of thermally accessible states at the temperature T . The *probability* of a molecule occupying a state i is

$$p_i = \frac{e^{-\beta \varepsilon_i}}{q}, \quad (2)$$

from which the *average energy* of the molecule can be obtained as

$$\langle \varepsilon \rangle = \sum_i \varepsilon_i p_i = \frac{\sum_i \varepsilon_i e^{-\beta \varepsilon_i}}{\sum_i e^{-\beta \varepsilon_i}}. \quad (3)$$

Alternatively, it can be shown that the average energy is given by a partial derivative of the partition function with respect to β with the number of molecules N and volume V fixed,

$$\langle \varepsilon \rangle = - \left(\frac{\partial \ln q}{\partial \beta} \right)_{N,V} = - \frac{1}{q} \left(\frac{\partial q}{\partial \beta} \right)_{N,V}. \quad (4)$$

Assuming that the total energy of the molecule is the sum of independent translational, rotational, vibrational, and electronic degrees of freedom, i.e.

$$\varepsilon_i = \varepsilon_{iT} + \varepsilon_{iR} + \varepsilon_{iV} + \varepsilon_{iE}, \quad (5)$$

where the subscripts “T”, “R”, “V”, and “E” denote translational, rotational, vibrational, and electronic contributions, respectively, the single-molecule partition function can be written simply as a product of partition functions for these various contributions, i.e.

$$q = q_T q_R q_V q_E. \quad (6)$$

The partition functions q_T , q_R , q_V , and q_E for translational, rotational, vibrational, and electronic degrees of freedom, respectively, are each given by an equation identical to eq (1), except with the summation over all states replaced by one over translational, rotational, vibrational, or electronic states and energies only.

At most temperatures, the spacing between translational energy levels is very small compared with the thermal energy $k_B T$, which allows the *translational partition function* to be simplified to

$$q_T = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} V = \frac{V}{\Lambda^3}, \quad (7)$$

where m is the mass of the molecule and $\Lambda = \frac{h}{(2\pi m k_B T)^{1/2}}$ is the thermal wavelength. For an ideal gas of N molecules, $PV = Nk_B T$, where P is the pressure, so

$$q_T = \frac{Nk_B T}{P\Lambda^3}, \quad (8)$$

From eq (7) or (8), the *average translational energy* of a molecule is found to be

$$\langle \varepsilon_T \rangle = -\frac{1}{q_T} \left(\frac{\partial q_T}{\partial \beta} \right)_{N,V} \approx \frac{3}{2} k_B T. \quad (9)$$

This particularly simple result for the average translational energy of a molecule is an example of the *equipartition theorem*, which states that any term in the Hamiltonian for the system's energy that is quadratic with respect to momentum or position contributes $\frac{1}{2} k_B T$ to the average energy, provided that the temperature is sufficiently high that the spacing between energies levels is small compared with $k_B T$. (This is called the *classical* or *high-temperature limit*, where so many energy levels are occupied that the distribution of occupied energy levels can be treated as effectively continuous.) The translational energy of each molecule is the sum of three terms that are quadratic in the momenta in the x , y , and z , directions, respectively, leading to the factor of $\frac{3}{2} k_B T$ above.

For rotational motion of a *linear molecule* that behaves as a freely rotating rigid rotor (i.e. all rotational energy is kinetic and atoms are connected by rigid bonds), the *rotational partition function* in the *high-temperature limit* is

$$q_R \approx \frac{k_B T}{\sigma h c \bar{B}} = \frac{T}{\sigma \theta_R}, \quad \text{if } T \gg \theta_R = \frac{h c \bar{B}}{k_B}, \quad (10)$$

where σ is the symmetry number (the number of ways the molecule can be rotated that interchange identical atoms, =1 for an asymmetric and =2 for a symmetric linear molecule), \bar{B} is the rotational constant, and θ_R is the *characteristic rotational temperature* of the molecule. The rotational temperature defines where the high-temperature limit applies. The corresponding *rotational partition function* for a *nonlinear molecule* in the *high-temperature limit* is

$$q_R \approx \frac{\pi^{\frac{1}{2}}}{\sigma} \left[\frac{T^{\frac{3}{2}}}{(\theta_{R,A} \theta_{R,B} \theta_{R,C})^{\frac{1}{2}}} \right], \quad \text{if } T \gg \theta_{R,A} = \frac{h c \bar{B}_A}{k_B}, \theta_{R,B} = \frac{h c \bar{B}_B}{k_B}, \theta_{R,C} = \frac{h c \bar{B}_C}{k_B}, \quad (11)$$

where σ is the symmetry number, and \bar{B}_A , \bar{B}_B , and \bar{B}_C are the three rotational constants and $\theta_{R,A}$, $\theta_{R,B}$, and $\theta_{R,C}$ the corresponding characteristic rotational temperatures for rotational motion around the three different principal axes of rotation. The rotational temperatures of most typical molecules are on the order of a few kelvin or less, and so the high-temperature approximation generally applies at typical temperatures studied. You should make this assumption in your calculations.

In the *high-temperature approximation*, the equipartition theorem holds for rotational motion, and so the *average rotational energy* of a molecule is

$$\langle \varepsilon_R \rangle = -\frac{1}{q_R} \left(\frac{\partial q_R}{\partial \beta} \right)_{N,V} \approx \begin{cases} k_B T & \text{(linear molecule)} \\ \frac{3}{2} k_B T & \text{(nonlinear molecule)} \end{cases}, \quad \text{if } T \gg \theta_R. \quad (12)$$

(The rotational energy of a freely rotating rigid rotor is the sum of terms that are quadratic in the angular momentum, two for a linear molecule and three for a nonlinear molecule corresponding to the number of independent axes or rotation in these respective types of molecules.)

Assuming that the vibrational modes of the molecule are *harmonic*, the *vibrational partition function* (measured with respect to the bottom of the harmonic potential wells) can be written exactly as

$$q_V = \prod_j \frac{e^{-\beta hc \bar{\nu}_j/2}}{1 - e^{-\beta hc \bar{\nu}_j}} = \prod_j \frac{e^{-\theta_{V,j}/(2T)}}{1 - e^{-\theta_{V,j}/T}}, \quad \text{where } \theta_{V,j} = \frac{hc \bar{\nu}_j}{k_B}, \quad (13)$$

$\bar{\nu}_j$ is the vibrational wavenumber of mode j , $\theta_{V,j}$ is the *characteristic vibrational temperature* of mode j , and the product (denoted by the large \prod symbol) is over the n_V normal modes of the molecule ($n_V = 3n - 6$ for a nonlinear molecule and $n_V = 3n - 5$ for a linear molecule, where n is the number of atoms in the molecule).

For a molecule with harmonic vibrational normal modes, the *average vibrational energy* including the zero-point energy (ZPE) can be calculated exactly as

$$\langle \varepsilon_V \rangle = -\frac{1}{q_V} \left(\frac{\partial q_V}{\partial \beta} \right)_{N,V} = \frac{hc}{2} \sum_j \bar{\nu}_j \left(\frac{1 + e^{-\beta hc \bar{\nu}_j}}{1 - e^{-\beta hc \bar{\nu}_j}} \right) = \frac{k_B}{2} \sum_j \theta_{V,j} \left(\frac{1 + e^{-\theta_{V,j}/T}}{1 - e^{-\theta_{V,j}/T}} \right). \quad (14)$$

If the temperature is much higher than the characteristic vibrational temperatures of all the normal modes, this equation can be simplified further to

$$\langle \varepsilon_V \rangle \approx n_V k_B T, \quad \text{if } T \gg \theta_{V,j} \text{ for all } j. \quad (15)$$

This equation is another example of the *equipartition theorem* – in this case, for each of the n_V normal modes, the kinetic energy is quadratic in the momentum and the potential energy is quadratic in the position along the vibrational coordinate, so there are two quadratic terms in the Hamiltonian for each normal mode.

Even at zero temperature, the average vibrational energy is non-zero. The vibrational energy at zero temperature is called the zero-point energy (ZPE) and can be found from eq (14) to be

$$\varepsilon_{\text{ZPE}} = \frac{hc}{2} \sum_j \bar{\nu}_j = \frac{k_B}{2} \sum_j \theta_{V,j}. \quad (16)$$

There is no general closed expression for the *electronic partition function*, which is given by a sum over electronic state as

$$q_E = \sum_i e^{-\beta \varepsilon_{iE}}, \quad (17)$$

where ε_{iE} is the energy of electronic state i and the sum is only over electronic states. So the *average electronic energy* must be calculated by direct summation over the electronic states, i.e.

$$\langle \varepsilon_E \rangle = \sum_i \varepsilon_{iE} p_{iE} = \frac{\sum_i \varepsilon_{iE} e^{-\beta \varepsilon_{iE}}}{\sum_i e^{-\beta \varepsilon_{iE}}}, \quad (18)$$

where the sum is only over electronic states. At typical temperatures the sum in the last two equations can generally be truncated after a very small number of terms, because the separation between electronic energy levels is usually very large and so the contributions of electronic excited states to the sum rapidly go to zero as the energy of the state increases.

The *total average energy of a molecule* is the sum of contributions from the translational, rotational, vibration, and electronic degrees of freedom, i.e.

$$\langle \varepsilon \rangle = \langle \varepsilon_T \rangle + \langle \varepsilon_R \rangle + \langle \varepsilon_V \rangle + \langle \varepsilon_E \rangle. \quad (19)$$

The *total average energy of a system of N non-interacting molecules* is

$$\langle E \rangle = N \langle \varepsilon \rangle. \quad (20)$$

For a very large number N of molecules (i.e. in the *thermodynamic limit*), the total average energy can be identified with the macroscopic *thermodynamic internal energy* U , i.e.

$$U = \langle E \rangle . \quad (21)$$

The *enthalpy* H is related to the internal energy U , pressure P , and volume V by

$$H = U + PV . \quad (22)$$

The *change in enthalpy* for a reaction is then

$$\Delta H = \Delta U + \Delta(PV) , \quad (23)$$

where ΔU is the change in internal energy for the reaction. Assuming the ideal gas law,

$$PV = Nk_B T , \quad (24)$$

for the molecules in the reaction, the *change in enthalpy* for a chemical reaction at constant temperature T is then

$$\Delta H = \Delta U + (\Delta n)k_B T , \quad (25)$$

where Δn is the change in the number of molecules in the reaction.

The *Gibbs free energy* G is related to the enthalpy H , entropy S , and temperature T by

$$G = H - TS . \quad (26)$$

The *change in Gibbs free energy* for a reaction at constant temperature T is then

$$\Delta G = \Delta H - T\Delta S . \quad (27)$$

The *total entropy* S of a system of N indistinguishable non-interacting molecules in the thermodynamic limit is

$$S = \frac{U}{T} + Nk_B(\ln q - \ln N + 1). \quad (28)$$

Assuming that the translational, rotational, vibrational, and electronic degrees of freedom of each molecule are independent of one another, the *total entropy* S can be written as a sum of contributions from each of these degrees of freedom, i.e.

$$S = S_T + S_R + S_V + S_E , \quad (29)$$

where the *translational contribution* S_T is

$$S_T = \frac{N\langle \varepsilon_T \rangle}{T} + Nk_B(\ln q_T - \ln N + 1) = Nk_B \left\{ \ln \left(\frac{k_B T}{P \Lambda^3} \right) + \frac{5}{2} \right\} , \quad (30)$$

the *rotational contribution* S_R is

$$S_R = \frac{N\langle \varepsilon_R \rangle}{T} + Nk_B \ln q_R , \quad (31)$$

the *vibrational contribution* S_V is

$$S_V = \frac{N\langle \varepsilon_V \rangle}{T} + Nk_B \ln q_V , \quad (32)$$

and the *electronic contribution* S_E is

$$S_E = \frac{N\langle \varepsilon_E \rangle}{T} + Nk_B \ln q_E , \quad (33)$$

where the average energy $\langle \varepsilon_i \rangle$ and partition function q_i of each of these degrees of freedom are given in equations above.

(Note: To calculate “per mole” thermodynamic properties, set the number N of molecules to be equal to the Avogadro constant N_A .)

References

1. P.W. Atkins, J. de Paula, *Physical Chemistry (10e)*, W.H. Freeman, 2014.
2. T. Engel, P. Reid, *Physical Chemistry (3e)*, Pearson, 2013.