

Worked out examples on partition functions

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1 Translational partition function

For a temperature of 273 K and a volume of $2.24 \times 10^{-2} \text{ m}^3$ determine the translational partition function for Argon gas. The translational partition function is

$$z_{tr} = \left(\frac{2\pi m k T}{h^2} \right)^{3/2} V$$

$$m = 40 \text{ g mol}^{-1} = 6.64 \times 10^{-26} \text{ kg per atom}$$

$$kT = 3.77 \times 10^{-21} \text{ J}$$

$$z_{tr} = 4.79 \times 10^{30} \text{ states per atom}$$

2 Vibrational partition function

The vibrational frequency of oxygen is 1580 cm^{-1} . Determine the vibrational partition function for oxygen gas. The vibrational partition function is

$$z_{vib} = \frac{\exp\left(-\frac{h\nu}{2kT}\right)}{1 - \exp\left(-\frac{h\nu}{kT}\right)}$$

The vibrational frequency in Hz is 4.737×10^{13} , so that

$$\theta_{vib} = \frac{h\nu}{k} = 2274 \text{ K}$$

At room temperature (300 K) $\theta_{vib}/T = 7.58$, which indicates that the vibrational energy is almost 8 times higher than the thermal energy. This would imply that the vibrational partition function will predominantly have contribution from the ground state. Inserting these quantities into the vibrational partition function expression gives a value of 1.0005.

3 Rotational partition function

The length of the bond in oxygen molecule is 1.2074 \AA . Determine the rotational partition function for oxygen at 300 K. The rotational partition function for a diatomic is

$$z_{rot} = \frac{8\pi^2 I k T}{\sigma h^2} = \frac{T}{\sigma \theta_{rot}},$$

where I is the moment of inertia μR^2 , σ is a symmetry factor which accounts for equivalent orientations of the molecule and is 1 for a heteronuclear diatomic and 2 for a homonuclear molecule. For a polyatomic molecule, z_{rot} becomes

$$z_{rot} = \left(\frac{8\pi^2 I k T}{h^2} \right)^{3/2} \frac{\pi I_a I_b I_c}{\sigma}.$$

Note that for a polyatomic the rotational partition function is a product of three terms corresponding to rotation about three perpendicular axes. Returning to the problem at hand, the moment of inertia of oxygen molecule is

$$I = \mu R^2 = \frac{mR^2}{2} = \frac{\left(0.016 \frac{\text{kg}}{\text{mol}}\right) (1.207410^{-10} \text{m})^2}{2 \left(6.023 \times 10^{23} \frac{\text{molecules}}{\text{mol}}\right)} = 1.937 \times 10^{-46} \text{ kg m}^2,$$

from which we determine the rotational temperature to be

$$\theta_{rot} = \frac{h^2}{8\pi^2 I k} = 2.08 \text{ K}$$

At room temperature, $T/\theta_{rot} \approx 150$, which indicates that the thermal energy is almost 150 times higher than the rotational energy and we expect the rotational partition function to have extensive contribution from the excited states. As expected, we find that the rotational partition to be $z_{rot} = T/(\sigma\theta_{rot}) = 72$.

4 Entropy of a monoatomic ideal gas

The entropy may be obtained from its relation to the Helmholtz energy

$$S = - \left(\frac{\partial A}{\partial T} \right)_{V,N},$$

which in turn is related to the partition function as

$$A = -kT \ln Z.$$

If the energy is known, as is the case here, it is easier to obtain the entropy from the classical thermodynamical definition of the Helmholtz energy

$$A = U - TS.$$

For a monoatomic ideal gas there is only a translational contribution to the entropy and the average energy is given by the equipartition principle

$$S = (U - A)/T = (3/2NkT - A_{tr})/T$$

with

$$A_{tr} = \frac{z_{tr}^N}{N!} = -NkT \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{3/2} \frac{V}{N} e \right].$$

In writing out the last equality we have used the Stirlings approximation for

$$N! = N^N e^{-N} \sqrt{2\pi N}$$

The entropy of a monoatomic ideal gas is hence

$$S = Nk \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{3/2} \frac{V}{N} e^{5/2} \right]$$

4.1 Absolute entropy of argon

The expression for the entropy may be used to obtain the absolute entropy of monoatomic gases, say argon at 300 K and 1 atm. The translational partition function of argon at 300 K is

$$z_{tr} = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V = 2.47 \times 10^{32} V$$

so that

$$\frac{S}{N} = k \ln \left(2.47 \times 10^{32} \frac{V}{N} e^{5/2} \right).$$

Using the equation of state to replace V/N by $kT/p = 4.10 \times 10^{-26}$ we get that the absolute entropy of argon is

$$S/N = 158.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

5 Chemical equilibrium of the water-gas reaction

The water-gas reaction is $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{H}_2\text{O} + \text{CO}$ for which the experimentally determined equilibrium constants are 2.0, 2.8, and 3.5, at 1295, 1565, and 1823 K respectively. Determine the equilibrium constant at 1565 from the partition function.

The basic equation for the statistical thermodynamic calculation of the equilibrium constant is:

$$K_c = \frac{q_{\text{H}_2\text{O}} q_{\text{CO}}}{q_{\text{CO}_2} q_{\text{H}_2}} \exp \left(-\frac{\Delta E_0}{RT} \right)$$

where ΔE_0 is the difference in energy between the ground rotational/vibrational states of the reactants and products, and the q 's are the unit-volume partition function and may be written in terms of the partition functions for the different modes of motion

$$q = q_{\text{trans}} q_{\text{rot}} q_{\text{vib}}$$

It follows that the expression for K_c may be split into factors

$$K_c = K_{c(\text{trans})} K_{c(\text{rot})} K_{c(\text{vib})} \exp \left(-\frac{\Delta E_0}{RT} \right)$$

where $K_{c(\text{trans})}$ is

$$K_{c(\text{trans})} = \frac{q_{\text{H}_2\text{O}(\text{trans})} q_{\text{CO}(\text{trans})}}{q_{\text{CO}_2(\text{trans})} q_{\text{H}_2(\text{trans})}}$$

The equilibrium constant is dimensionless, and thus all fundamental constants in $K_{c(\text{trans})}$ cancel. But they do not in $K_{c(\text{rot})}$ because of the difference in the number of rotational degrees of freedom on the right, five, and the left, four.

Because the numbers of the molecules on the two sides of the equation are the same $K_{c(\text{trans})}$ may be written as

$$K_{c(\text{trans})} = \left(\frac{M_{\text{H}_2\text{O}} M_{\text{CO}}}{M_{\text{CO}_2} M_{\text{H}_2}} \right)^{3/2}$$

The rotational factor in K_c is

$$\begin{aligned} K_{c(\text{rot})} &= \frac{\sqrt{\pi(I_a I_b I_c)_{\text{H}_2\text{O}}} \left(\frac{8\pi^2 kT}{h^2} \right)^{3/2} \times I_{\text{CO}} \left(\frac{8\pi^2 kT}{h^2} \right)}{I_{\text{CO}_2} \left(\frac{8\pi^2 kT}{h^2} \right) \times I_{\text{H}_2} \left(\frac{8\pi^2 kT}{h^2} \right)} \times \frac{\sigma_{\text{CO}_2} \sigma_{\text{H}_2}}{\sigma_{\text{H}_2\text{O}} \sigma_{\text{CO}}} \\ &= \left(\frac{\sqrt{\pi(I_a I_b I_c)_{\text{H}_2\text{O}}} I_{\text{CO}}}{I_{\text{CO}} I_{\text{H}_2}} \right) \times \left(\frac{8\pi^2 kT}{h^2} \right)^{1/2} \times 2 \end{aligned}$$

If all moments of inertia are expressed in amu Å² a change is necessary in the factor containing the fundamental constants

$$K_{c(\text{rot})} = \left(\frac{2\sqrt{\pi(I_a I_b I_c)_{\text{H}_2\text{O}} I_{\text{CO}}}}{I_{\text{CO}} I_{\text{H}_2}} \right) \left(\frac{8\pi^2 kT \times 10^{-20}}{h^2 L_A} \right)^{1/2}$$

The second factor

$$\left(\frac{8\pi^2 kT \times 10^{-20}}{h^2 L_A} \right) = 114.8$$

The vibrational factor in K_c is

$$K_{c(\text{vib})} = \frac{q_{\text{vib}}(\text{H}_2\text{O}, 3 \text{ modes}) q_{\text{vib}}(\text{CO}, 1 \text{ mode})}{q_{\text{vib}}(\text{CO}_2, 4 \text{ modes}) q_{\text{vib}}(\text{H}_2, 1 \text{ mode})}$$

The molecular and other parameters are given in the table below

Property	CO ₂	H ₂	H ₂ O	CO
Heat of formation at 0 K (kJ mol ⁻¹)	-393.165	0.000	-238.935	-113.813
Bond length (10 ⁻¹⁰ m)	1.160	0.741	0.960	1.128
Bond angle (degrees)	180		104.5	
Moment of inertia (amu Å ²)	43.0	0.277	1.27 ¹	8.73
Vibration frequencies (cm ⁻¹)	2350	4160	3652	2168
	1320		3756	
	668		1595	
	668			

¹ $I_a I_b I_c$ for H₂O is 1.128

The vibrational partition functions, the energies of the states being measured from their respective ground state, are listed below.

Molecule	ω (cm ⁻¹)	q_{vib}
CO ₂	2350	1.13
	1320	1.43
	668	2.18
	668	2.18
H ₂	4160	1.02
H ₂ O	3652	1.04
	3756	1.04
	1595	1.30
CO	2168	1.16

The heat of the reaction at 0 K is

$$\Delta E_0 = -113.813 - 238.935 + 393.165 + 0.000 = +40.417 \text{ kJ mol}^{-1}$$

We finally obtain for K_c :

$$K_c = \left(\frac{18.02 \times 28.01}{44.01 \times 2.016} \right)^{3/2} \times \left(\frac{2 \times \sqrt{\pi 1.27} \times 8.73}{43.0 \times 0.277} \right) \times \sqrt{114.8} \times 0.208 \times \exp(-3.115)$$
$$= 2.98$$