Chapters 1-2

1. State, in symbols, the *Conservation Laws* for the number of particles and their total energy.

(1.6a)



(1.6b)



1. What does the symbol  signify?

(1.10)



(1.10) (1.10) (1.10)



1. Write an expression for the *molecular partition function, q.*

(2.6)



(2.8)



1. State the minimum and maximum value that *q* can take.



1. What is the difference between *energy states* and *energy levels*?

Each energy state has a set of unique quantum numbers associated with it. If there are *g* energy states that are degenerate (i.e. that have the same energy), they form single energy level with degeneracy *g.* Rotational energy levels are a particular example of this. A level with total angular momentum quantum number *J* has a degeneracy of (2*J*+1), corresponding to an equi-energetic state labelled by the azimuthal quantum number *MJ*.

1. Explain the term *accessible states.*

The number of states, that can be populated by the system of interest at a particular temperature.

1. Write an expression for the *occupation number, ni*, of *quantum state i*.

(2.7)



Chapter 3-5

1. Based on the *molecular partition function, q, w*rite an expression for the internal energy, *U* of an assembly of particles, explaining the meaning of the terms you use.

(3.5)



In this expression, *T* is the temperature in kelvin and *k* is the Boltzmann constant. *U* is the internal energy (at temperature *T*) and *U*(0) the internal energy at *T* = 0 K. *N* is the total number of particles. *q* is the molecular partition function. Finally, beta is 1/*kT*..

1. Discuss any small change d*U* in the internal energy, *U,* in terms of work done and heat taken in.

The first law of thermodynamics states that any change in internal energy can be written as a sum of the amount of heat going into the system and the amount of work done by the system.

1. How can the *Boltzmann expression*be justified?

See section 3.5.

1. What is the *canonical partition function, Q*?

The canonical partition function is the equivalent of the microcanonical partition function *q*. However, *q* is valid for molecules that do not interact at constant energy, volume, and number of particles and is a sum-over-molecular states. *Q* on the other hand deals with N interacting particles at constant volume, temperature, and total number of particles. It is a sum-over-system states.

1. Explain the concept of an *ensemble*.

An ensemble describes a collection of particles, which behave according to certain pre-set rules, e.g. in the canonical ensemble the total number of particles, the volume, and the temperature are all constant.

1. How are the *canonical* and *molecular* partition functions related?

In both cases one is dealing with N particles at constant volume. However, in the canonical partition function *Q,* these particles are interacting and their temperature is constant, whereas for *q,* the particles are not interacting and total energy is conserved.

1. What is meant by *distinguishability* and *indistinguishability*?

Distinguishability of particles means that there is some label or characteristic of the particles that allows one to distinguish between them in principle, e.g. a particle with rotational degrees-of-freedom (which could be interrogated spectroscopically) or a particle in a solid-state lattice (with an defined lattice address) can clearly be seen to be intrinsically identifiable. Indistinguishability is precisely the opposite, where such any such label or characteristic is absent, e.g. translation motion is inherently indistinguishable.

1. How are *canonical* and *molecular* partition functions for distinguishable and *indistinguishable* particles related?

, (5.3)



Chapter 6-8

1. Sketch the temperature dependence of the *upper state* and *lower state* populations in a 2-level system.

See Fig 6.2

1. Sketch the temperature dependence of the *total energy* in a 2-level system, and relate this to the consequent *heat capacity*.

See Section 6.4

1. Outline the derivation of an expression for the *translational partition function, q*trs.

See Section 8.2 for more details. The derivation starts with the particle-in-a-box and the partition function associated with the energies of this system. These energies are closely spaced and therefore the summation over energy levels in the partition function can be replaced by a integration. This integration is a standard integral and therefore this leads to a closed-form expression for the translation partition function. The three directions of motion are independent of each other and so the overall partition function is the partition functions for each of the three directions multiplied together.

1. State the *mass dependence* of the *translational partition function*.

The mass dependence of the translational partition function comes directly from the mass dependence of the eigenenergies of the particle-in-a-box problem. Those eigenenergies are inversely proportional to the mass, leading to a smaller spacing with increasing mass. A smaller spacing means that the number of available states increases at a given temperature, which leads to an increase in the partition function. The translational partition function is proportional to the mass, thus leading to an increase in the partition function with increasing mass, something expected from the energies of the particle-in-a-box.

1. Write expressions for the thermodynamic functions *A, U, p, CV*, and *S* using the *canonical partition function, Q.*

See section (7.6) to (7.9).

1. Use the defining equations for *enthalpy* (*H* = *U* + *pV)*and for *Gibbs free energy* (*G* = *H* – *TS),* together with the expressions you wrote in question 20 to derive expressions for the thermodynamic functions *H* and *G.*

See section (7.10) and (7.11)

Chapter 8 - 9

1. Show that expressions for the thermodynamic variables *U, p,* and *CV*, derived from *partition functions* correspond to those based on the *ideal gas law* and the *kinetic theory of gases*.

See section (8.3)

1. Outline the derivation of the *Sackur-Tetrode* equation.

See section (8.4) for more details. Start from the toolkit function for S as a function of Q. Using the fact that a featureless monatomic gas has indistinguishable particles, this can be converted to q and the expression simplified using Stirling’s approximation. The correct expression for the micro-canonical partition function is then used to obtain the Sackur-Tetrode equation.

1. Write **two** expressions showing the functional dependence of the entropy of an ideal monatomic gas, *S(p, T, M) and S(V, T, M)* on the variables shown.



1. Explain the dependence of the entropy of an ideal monatomic gas on temperature, mass, and volume in terms of the underlying quantum mechanical description.

The underlying description is that of the particle-in-a-box. An increase in volume or mass will decrease the spacing between the energy levels, leading to an increase in *q*, since more states are accessible at that temperature. As a consequence, the entropy will increase as well. An increase in temperature will result in more states being accessible (irrespective of the underlying quantum mechanical description), resulting in a larger value of the micro-canonical partition function, *q*. Thus, in this case too, the entropy will increase.

1. Explain how contributions to the *canonical partition function* from various *energy modes* can be expressed using *factorisation*.

If one assumes that all modes are only weakly coupled, so that they can be looked at independently, factorisation of Q can be achieved using the various uncoupled energy modes. Firstly, the movement of the centre-of-mass can always be looked at as independent of internal degrees-of-freedom, thus allowing one to consider translation on its own. Decoupling of electronic degrees-of-freedom assumes the use of Born-Oppenheimer approximation, allowing one to look at electronic energies independent of energy due to nuclear motion. Vibration and Rotation are usually coupled. However, by assuming that the rigid rotor and harmonic oscillator approximations hold, rotation and vibration are also no longer coupled. This leads to the following expression:



Chapter 10-12

1. Explain the meaning of the term *characteristic rotational temperature.*

The characteristic rotational temperature gives a measure of the spacing between two rotational energy levels (in kelvins).

1. Explain the meaning of the term *rotational symmetry number,* .

The rotational symmetry number is an expression of the symmetry of the molecule. It represents the number of ways atoms within a molecule can be exchanged without changing the geometry or structure of the molecule.

1. Explain the behaviour of the rotational heat capacity as the temperature tends towards zero kelvin.

As the temperature tends towards zero kelvin, then at some low temperature only two states will be available to the system. As a consequence the system will start to behave like a two-level system, which means that the rotational heat capacity will exhibit a Schottky anomaly.

1. State the *mass dependence* and the *temperature dependence* of the *rotational partition function.*

As temperature increases, more states become accessible and therefore the rotational partition function increases, which indeed happens, since *q* is proportional to *T.* An increase in mass means an increase in the reduced mass, which is inverse proportional to the characteristic rotational temperature. An increase in mass therefore leads to a decrease in the characteristic rotational temperature, which means that the spacing between states decreases, resulting in an increase in the rotational partition function. Alternatively, the rotational partition function is inversely proportional to the rotational temperature, which in its turn is inversely proportional to the reduced mass. This means that the rotational partition function is proportional to the reduced mass. Thus, an increase in the mass will lead to an increase in the rotational partition function.

1. Compare the magnitudes of *characteristic temperatures* for *vibration* and for *rotation* in simple molecules*.*

In general the magnitude of the characteristic temperature for vibration will be greater than the characteristic temperature for rotation, particularly if the molecules contain hydrogen.

1. What is the most probable value of *q*vib for light simple molecules at room temperature?

One.

1. Under which conditions or for which kinds of vibration does the SHO approximation break down?

The SHO approximation will break down in situations, where one is dealing with large amplitude motion, e.g torsional motion. Large amplitude motion will have considerable anharmonic components, whereas torsional motion can turn at sufficiently high temperatures into internal rotation for which a different description is needed.

1. Deduce the most significant contributions to the value of *q*vib at room temperature in
   1. *carbon dioxide* and

degenerate bending mode;

* 1. *trichloromethane.*

A bending mode involving the Cl-C-Cl angle. This mode is degenerate

Chapter 13 & 14

1. Check that the value of for CO2 is 1.091 at 300 K.



1. Explain why most molecules have *electronic partition functions* whose values differ little from unity, whereas the same is not true of atoms.

Most molecules or stable ions have closed-shell, singlet (i.e. non-degenerate) ground states, O2 being a notable exception to this rule. Moreover, for most molecules and stable ions the first excited state is not accessible, unless the temperature is very high. The situation is different for atoms, where the ground state is often degenerate, due to coupling between spin and orbital angular momentum components. This coupling can also lead to low-lying (i.e. thermally accessible) excited states.

1. Define the term *residual entropy* and discuss its origin in the species FClO3.

The residual entropy is defined as the difference between the calorimetric entropy and the spectroscopic entropy. In the case of FClO3 its origin lies in the fact that the assumption of zero entropy at 0 K for the calorimetric entropy may not hold. In other words, disorder may be present in the lattice due to a small orientation force during the crystallization process. As such in the worst case scenario, the orientation of FClO3 is random, giving rise to residual entropy and gives rise to a difference between the (measured) calorimetric entropy and the (calculated) spectroscopic entropy.

Chapter 15

1. Explain the terms in the expression for the equilibrium constant shown below:



16.2 Essay Problems

1. Describe what is meant by the term “two-level system” and give three appropriate examples.
2. Discuss the Boltzmann approach to the statistical modelling of molar entropies of gaseous atomic species. Expand your discussion to indicate how this approach can be extended to model the entropies of diatomic gases, such as H2(g), so as to accommodate the fact that the molecule has translational, rotational, vibrational and electronic contributions to its overall entropy.
3. Explain the dependence of the entropy of an ideal monatomic gas on temperature, mass, and volume in terms of the underlying quantum mechanical description.

16.3 Numerical Problems

1. Given that 2 states lie 10 kJ mol−1 apart, what are their relative populations at 25 °C?



1. Consider a system like in Figure 1.2, which has three equidistant energy levels , , and .



* 1. Calculate the statistical weight for each of the configurations with *N*=20, *E* = 20.

|  |  |  |  |
| --- | --- | --- | --- |
| *n0* | *n1* | *n2* | *N*!*/(n0*!*n1*!*n2*!*)* |
| 10 | 0 | 10 | 1.85×105 |
| 9 | 2 | 9 | 9.24×106 |
| 8 | 4 | 8 | 6.23×107 |
| 7 | 6 | 7 | 1.33×108 |
| 6 | 8 | 6 | 1.16×108 |
| 5 | 10 | 5 | 4.66×107 |
| 4 | 12 | 4 | 8.82×106 |
| 3 | 14 | 3 | 7.75×105 |
| 2 | 16 | 2 | 2.91×104 |
| 1 | 18 | 1 | 3.80×102 |
| 0 | 20 | 0 | 1 |

* 1. Plot a graph of your results and comment on its significance.

Even for a relatively simple system with a small number of particles, the distribution is already peaked, with a small change in configuration leading to a change in the number of configurations by an order of magnitude. Extending this to 1023 particles will only make this more evident.

1. The molar entropy, S, of a collection of distinguishable molecules may be estimated using the following equation:



* 1. Explain the thermodynamic significance of each of the terms in this equation.

*S* = entropy;

*U* = internal energy;

*U(0)* = internal energy at *T* = 0 K;

*R =* universal gas constant;

*q =* molecular partition function.

* 1. Give the equivalent of the above equation for a collection of indistinguishable molecules. Use Stirling’s approximation to simplify your answer.



In each of parts a. to c. below, two different numerical values of entropy are given. Account for the differences between these values, supporting your explanations with arguments based on statistical concepts.

1. Comment on the significance of each of the statements given below

Reminder:

(8.17)



* 1. At constant volume, raising the temperature from 298.15K to 400K, causes the molar entropy of argon to rise from 154.84JK−1 mol−1 to 158.50JK−1 mol−1.

Given (8.17) the entropy change is given as:



Thus:



According to the question, the entropy for Argon changes by 3.66 J K-1 mol-1, which is close to the predicted value from statistical thermodynamics (using the particle-in-a-box formalism).

* 1. At constant temperature, lowering the pressure from 100kPa to 60kPa, causes the molar entropy of helium to rise from 126.15JK−1 mol−1 to 130.40 JK−1 mol−1.

Changing the pressure implies change the volume at the same time. Given (8.17) the entropy change is thus given as:



Thus:



According to the question, the entropy for Helium changes by 4.25 J K-1 mol-1, which is the same as the predicted value from statistical thermodynamics (using the particle-in-a-box formalism).

* 1. Under standard conditions of temperature and pressure, the entropy of neon is 146.33JK−1 mol−1,   
     whereas that of xenon is 169.68JK−1 mol−1.

Given (8.17) the entropy change is given as:



Thus:



According to the question, the entropy difference between neon and xenon is 23.35 J K-1 mol-1, which is close to the predicted value from statistical thermodynamics (using the particle-in-a-box formalism).

1. The following table shows the calorimetric and spectroscopic standard entropies of gaseous nitrogen and carbon monoxide.
   1. For each of the two substances, comment on any difference or agreement between these two values of the entropy for each of the two substances.

The calorimetric and spectroscopic entropies are clearly the same for nitrogen, but are different for carbon monoxide; CO has a residual entropy. This is caused by the fact that orienting forces during the crystallization of CO are very weak (small dipole moment), resulting in a lattice at 0 K, which is not perfectly crystalline. Given that there are two orientations for CO, one would expect a residual entropy of *R* ln 2 (5.76 J K−1 mol−1), which compares well with the observed value of 0.62*R* (5.15 J K−1 mol−1).

* 1. Explain why the spectroscopic entropies for these two molecules are not more similar, since nitrogen has the same characteristic temperature for rotation as carbon monoxide and an equally negligible contribution from the vibrational entropy.

The total entropy is given as:



The question makes clear that the difference is not caused by vibration. Both N2 and CO are stable (singlet, closed-shell) molecules, so excited electronic are highly unlikely to have an effect as well. Translational entropy depends on mass, temperature, and volume (or pressure). These observables are identical for both N2 and CO. Thus, the rotational entropy is the only possible cause for the observed difference between the two. The rotational entropy depends on temperature, characteristic rotational temperature, and symmetry number. Whereas the former two do not change in going from N2 to CO, the last term does. Given that



the entropy should change from N2 to CO as *R* ln 2 (5.7631 J K−1 mol−1). The actual change is 7.6492 J K−1 mol−1, which is quite close.

|  |  |  |  |
| --- | --- | --- | --- |
| *Substance* | *T*/K |  |  |
| Nitrogen | 77.35 | 18.3 | 18.30 |
| Carbon monoxide | 81.61 | 18.6 | 19.22 |

1. Consider the following data for the three lowest electronic states of atomic fluorine

|  |  |  |
| --- | --- | --- |
| *Electronic State* | *Energy/cm−1* | *Degeneracy* |
|  | 0 | 4 |
|  | 404 | 2 |
|  | 102406 | 6 |

Calculate the fraction of fluorine atoms in each of the first three electronic levels at 300 K.

First we convert the energy levels in K by multiplying their energies above by *hc/k* or 1.4388 (taking care to keep track of our units).

|  |  |  |
| --- | --- | --- |
| *Electronic State* | *Energy/K* | *Degeneracy* |
|  | 0 | 4 |
|  | 581.28 | 2 |
|  | 147598.21 | 6 |

Then, we need to use the Boltzmann Law (taking care of the degeneracies of the levels).



Thus, given the high excitation energy, *n*() must be zero. We are interested in the ratio between *n0* and *n1*, which means *q* and *N* cancel out and





Thus, 93.28% of F atoms are in the ground state, whereas 6.72% are in the first electronic excited state.

1. At 698.6 K the experimental value of the equilibrium constant, , for the reaction



is 55.1.

Given the following information, calculate the value of the equilibrium constant for the reaction at this temperature and compare it with the experimental value.

|  |  |  |  |
| --- | --- | --- | --- |
|  | H2 | I2 | HI |
| *M*/kg mol−1 | 2.016 10−3 | 0.2538 | 0.1279 |
|  | 85.4 | 0.0537 | 9.29 |
|  | 5980 | 306.6 | 3210 |

The standard change in internal energy at 0 K for this reaction, , is –8.052 kJ mol−−−1.



First of all, we note that we have the same number of terms on either side and therefore that terms are going to cancel.

Thus:















Hereby, it should be noted that the final answer agrees very well with the experimental value of 55.1.

1. Calculate the equilibrium constant, , at 1000 K for the isotopic exchange reaction



The characteristic vibrational temperature for H2 equals is 6215 K, and the ground electronic states of hydrogen and deuterium atoms are both doubly degenerate.

First of all, we note that we have the same number of terms on either side and therefore that terms are going to cancel.

Thus:



The vibrational temperature of H2 is 6215 K. The vibrational temperature of HD can be calculated using the ratio of the reduced masses of HD and H2. Thus,



Both these vibrational temperatures are much higher than the temperature under consideration. Thus, *q*vib(HD)=*q*vib(H2)=1. As a consequence, Kp,vib=1





The exothermicity is the change in the zero-point energies (Electronically, HD and H2 are the same. There is no rotational or translational energy left at 0 K, Thus, the only change is in the zero-point energies of reactants and products)



Thus,





1. Determine for the following reaction at 1000 K using the vibrational frequencies in the table below.



D2(g) + HF (g) = DF(g) + HD(g)

|  | ***ν / cm−1*** |
| --- | --- |
| D2 | 3115.5 |
| HF | 4138.3 |

First of all, we note that we have the same number of terms on either side and therefore that terms are going to cancel.

Thus:





The fundamental frequency of D2 is 3115.1 cm−1. The vibrational temperature of HD can be calculated using the ratio of the reduced masses of HD and H2. Thus,







All these vibrational temperatures are significantly higher than the temperature under consideration. Thus, *q*vib(HD)=*q*vib(D2)= *q*vib(DF)=*q*vib(HF)=1. As a consequence, Kp,vib=1





The exothermicity is the change in the zero-point energies. Thus,



Thus,





1. Calculate the equilibrium constant, , at 1000 K for the reaction



The first two electronic levels of atomic chlorine have the degeneracies, g, and a level splitting, , as shown below



The lowe st electronic level for molecular chlorine is a singlet and all higher levels are unoccupied at 1000 K. The dissociation energy of Cl2 is 239.5 kJ mol−1.

For Cl2, rot = 0.351 K and vib= 813K.

First of all, in this case the number of molecules on the left-hand side of the chemical equation and on the right-hand side are not equal. Thus, there will be very little cancellation and all terms need to be calculated separately and completely.



We use RT in the expression above, since the endothermicity of the reaction is given in kJ/mol. This saves a conversion back to J.

First, we will deal with the electronic degrees-of-freedom. These are given in wavenumbers, but need to be converted to Kelvin (or J) for ease of use.















1. Calculate the equilibrium constant, at 1000 K, for the reaction



The ground electronic state of the F atom is fourfold degenerate and the next energy state that is 404 cm−1 higher in energy is twofold degenerate. The internuclear distance in F2 is 1.418 Å and the fundamental vibrational frequency is 892 cm−1. The dissociation energy of F2 is 153.6 kJ mol−1.

First of all, in this case the number of molecules on the left-hand side of the chemical equation and on the right-hand side are not equal. Thus, there will be very little cancellation and all terms need to be calculated separately and completely.



We use RT in the expression above, since the endothermicity of the reaction is given in kJ/mol. This saves a conversion back to J.

First, we will deal with the electronic degrees-of-freedom. These are given in wavenumbers, but need to be converted to Kelvin (or J) for ease of use.

















1. Consider the following reaction



The following data relate to this reaction:

|  |  |  |
| --- | --- | --- |
| Electronic: |  |  |
|  |  |  |
|  |  |  |
|  |  |  |
|  |  |  |
|  |  |  |
|  |  |  |
| Vibrational: |  |  |
| Energetic: |  |  |

* 1. Show that = 1115.0, when the Cl-O distance is 1.56963 Å.









* 1. Calculate the equilibrium constant, , for this reaction at 1000K.



First of all, in this case the number of molecules on the left-hand side of the chemical equation and on the right-hand side are not equal. Thus, there will be very little cancellation and all terms need to be calculated separately and completely.



We use RT in the expression above, since the endothermicity of the reaction is given in kJ/mol. This saves a conversion back to J.

First, we will deal with the electronic degrees-of-freedom. These are given in wavenumbers, but need to be converted to Kelvin (or J) for ease of use

|  |  |  |
| --- | --- | --- |
| Electronic: |  |  |
|  |  |  |
|  |  |  |
|  |  |  |
|  |  |  |
|  |  |  |
|  |  |  |











