**Solutions Manual to**

***Principles of Electronic Materials and Devices***

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**CHAPTER 1**

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Water molecules are polar. A water jet can be bent by bringing a charged comb near the jet. The polar molecules are attracted towards higher fields at the comb's surface (Photo by SK)

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# Chapter 1

**Answers to "Why?" in the text**

**Page 31:**

Oxygen has an atomic mass of 16 whereas it is 14 for nitrogen. The O2 molecule is therefore heavier than the N2 molecule. Thus, from , the rms velocity of O2 molecules is smaller than that of N2 molecules.

**Page 34, footnote 11**

For small extensions, the difference between the engineering and instantaneous strains due to a temperature change are the same. Historically, mechanical and civil engineers measured extension by monitoring the change in length, *L*; and the instantaneous length *L* was not measured. It is not trivial to measure both the instantaneous length and the extension simultaneously. However, since we know *Lo* and measure *L*, the instantons length *L* = *Lo* + *L*. Is the difference important? Consider a sample of length *Lo* that extends to a final length *L*due to a temperature change from*To*to*T*. Let ** = (*L**Lo*) / *Lo* = *L*/*Lo* be the engineering strain.

The engineering definition of strain and hence the thermal expansion coefficient is

Engineering strain = 

so that thermal expansion from *To*to*T* gives,

 ∴  ∴  (1)

where** = *L*/*Lo* is the engineering strain as defined above

Physics definition of strain and hence the thermal expansion coefficient is

Instantaneous train = 

so that thermal expansion from *To*to*T* gives,

 ∴  ∴  (2)

We can expand the ln(1 + **) term for small **, so that Equation (2)essentially becomes Equation (1)

**1.1 Virialtheorem**The Li atom has a nucleus with a +3*e* positive charge, which is surrounded by a full 1*s* shell with two electrons, and a single valence electron in the outer 2*s* subshell. The atomic radius of the Li atom is about 0.17 nm. Using the Virial theorem, and assuming that the valence electron sees the nuclear +3*e* shielded by the two 1s electrons, that is, a net charge of +*e*, estimate the ionization energy of Li (the energy required to free the 2*s* electron).Compare this value with the experimental value of 5.39 eV. Suppose that the actual nuclear charge seen by the valence electron is not +*e* but a little higher, say +1.25*e*, due to the imperfect shielding provided by the closed 1*s* shell. What would be the new ionization energy? What is your conclusion?

**Solution**

First we consider the case when the outermost valence electron can see a net charge of +*e*. From Coulomb’s law we have the potential energy



 = 1.354 × 1018 J or 8.46 eV

Virial theorem relates the overall energy, the average kinetic energy, and average potential energy through the relations

and

Thus using Virial theorem, the total energy is

= 4.23 eV

The ionization energy is therefore **4.23 eV.**

Consider now the second case where the electronsees +1.25*e* due to imperfect shielding. Again the Coulombic*PE* between +*e* and +1.25*e* will be



= 1.692 × 1018 J or10.58 eV

The total energy is,



The ionization energy, considering imperfect shielding, is **5.29 eV**. This value is in closer agreement with the experimental value. Hence the second assumption seems to be more realistic.

**1.2 Virial theorem and the He atom** In Example 1.1 we calculated the radius of the H-atom using the Virial theorem. First consider the He+ atom, which as shown in Figure 1.75a, has one electron in the K-sell orbiting the nucleus. Take the *PE* and the *KE* as zero when the electrons and the nucleus are infinitely separated. The nucleus has a charge of +2*e* and there is one electron orbiting the nucleus at a radius *r*2. Using the Virial theorem show that the energy of the He+ ion is

 *Energy of He+ ion* [1.48]

Now consider the He-atom shown in Figure 1.75b. There are two electrons. Each electron interacts with the nucleus (at a distance *r*1) and the other electron (at a distance 2*r*1). Using the Virial theorem show that the energy of the He atom is

 *Energy of He atom* [1.49]

The first ionization energy *EI*1 is defined as the energy required to remove one electron from the He atom. The second ionization energy *EI*2 is the energy required to remove the second (last) electron from He+. Both are shown in Figure 1.75 These have been measured and given as *EI*1 = 2372 kJ mole1 and *EI*2= 5250 kJ mol1. Find the radii *r*1 and *r*2 for He and He+. Note that the first ionization energy provides sufficient energy to take He to He+, that is, He →He+ + *e* absorbs 2372 kJ mol1. How does your *r*1 value compare with the often quoted He radius of 31 pm?



**Figure 1.75:** (a) A classical view of a He+ ion. There is one electron in the *K*-shell orbiting the nucleus that has a charge +2*e*.(b) The He atom. There are two electrons in the *K*-shell. Due to their mutual repulsion, they orbit to void each other.

**Solution**

Virial theorem relates the overall energy, the average kinetic energy, and average potential energy through the relations

 (1)

Now, consider the *PE* of the electron in Figure 1.75a. The electron interacts with +2*e* of positive charge, so that



which means that the total energy (average) is

 (2)

whichis the desired result.

Now consider Figure 1.75b. Assume that, at all times, the electrons avoid each other by staying in opposite parts of the orbit they share. They are "diagonally"opposite to each other. The PE of this system of 2 electrons one nucleus with +2*e* is

*PE* = *PE* of electron 1 (left) interacting with the nucleus (+2*e*), at a distance *r*1

+ *PE* of electron 2 (right) interacting with the nucleus (+2*e*), at a distance *r*1

+ *PE* of electron 1 (left) interacting with electron 2 (right) separated by 2*r*1

∴ 

∴ 

From the Virial theorem in Equation (1)

 (3)

We are given,

*EI*1 = Energy required to remove one electron from the He atom = 2372 kJ mole1 = 25.58 eV

*EI*2 = Energy required to remove the second (last) electron from He+ = 5250 kJ mol1 = 54.41 eV

The eV values were obtained by using



We can now calculate the radii as follows. Starting with Equation 2 for the ionization of He+,



from which,

***r*2** = 2.65×1011 or **26.5 pm**

The calculation of *r*1 involves realizing that Equation (3) is the energy of the whole He atom, with 2 electrons. If we remove 1 electron we are left with He+ whose energy is Equation (2). Thus the



∴ 

∴ 

from

***r*1** = 3.19×1011 or **31.9 pm**

very close to the quoted value of 31 pm in various handbooks or internet period tables

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**1.3 Atomic mass and molar fractions**

*a.*Consider a multicomponent alloy containing *N*elements. If *w*1, *w*2, ..., *wN* are the weight fractions of components 1,2,..., *N* in the alloy and *M*1, *M*2, ..., *MN*, are the respective atomic masses of the elements, show that the atomic fraction of the *i*-th component is given by

  *Weight to atomic percentage*

*b.*Suppose that a substance (compound or an alloy) is composed of *N* elements, *A, B, C,*... and that we know their atomic (or molar) fractions *nA*, *nBnC*, .... Show that the weight fractions *wA*, *wB*, *wC*,....are given by



 *Atomic to weight percentage*

*c.*Consider the semiconducting II-VI compound cadmium selenide, CdSe. Given the atomic masses of Cd and Se, find the weight fractions of Cd and Se in the compound and grams of Cd and Se needed to make 100 grams of CdSe.

*d.*A Se-Te-P glass alloy has the composition 77 wt.% Se, 20 wt.% Te and 3 wt.% P. Given their atomic masses, what are the atomic fractions of these constituents?

**Solution**

***a.***Suppose that *n*1*, n*2*, n*3*,…,ni,…, nN* are the atomic fractions of the elements in the alloy,

*n*1 + *n*2 + *n*3 +… + *nN* = 1

Suppose that we have 1 mole of the alloy. Then it has *ni* moles of an atom with atomic mass *Mi* (atomic fractions also represent molar fractions in the alloy). Suppose that we have 1 gram of the alloy. Since *wi* is the weight fraction of the *i*-th atom, *wi* is also the mass of *i*-th element in grams in the alloy. The number of moles in the alloy is then *wi*/*Mi*. Thus,

Number of moles of element*i* = *wi/Mi*

Number of moles in the whole alloy = *w*1*/M*1 + *w*2/*M*2 +…+ *wi/Mi* +…+*wN/MN*

Molar fraction or the atomic fraction of the *i*-th elements is therefore,



∴ 

***b.***Suppose that we have the atomic fraction *ni* of an element with atomic mass *Mi*. The mass of the element in the alloy will be the product of the atomic mass with the atomic fraction, *i.e*. *niMi*. Mass of the alloy is therefore

*nAMA + nBMB*+…+*nNMN* = *M*alloy

By definition, the weight fractionis, *wi* = mass of the element *i*/Mass of alloy*.* Therefore,



***c****.*The atomic mass of Cd and Se are 112.41 g mol1 and 78.96 g mol1. Since one atom of each element is in the compound CdSe, the atomic fraction, *n*Cd and *n*Se are 0.5. The weight fraction of Cd in CdSe is therefore

= **0.587 or 58.7%**

Similarly weight fraction of Se is

= **0.4126 or 41.3%**

Consider 100 g of CdSe. Then the mass of Cd we need is

Massof Cd = *w*Cd*M*compound = 0.587 × 100 g = **58.7 g**(Cd)

and Mass of Se = *w*Se*M*compound = 0.413× 100 g = **41.3 g**(Se)

***d.***The atomic fractions of the constituents can be calculated using the relations proved above. The atomic masses of the components are *M*Se = 78.6 g mol1, *M*Te = 127.6 g mol1,and *M*P = 30.974 g mol1. Applying the weight to atomic fraction conversion equation derived in part (a) we find,

**∴ *n*Se = 0.794 or 79.4%**

**∴ *n*Te = 0.127 or 12.7 %**

**∴*****n*P= 0.0785 or 7.9%**

**1.4 Mean atomic separation, surface concentration and density** There are many instances where we only wish to use reasonable estimates for the mean separationbetween the host atoms in a crystal and the mean separationbetween impurities in the crystal. These can be related in a simple way to the atomic concentrationof the host atoms and atomic concentrationof the impurity atoms respectively. The final result does not depend on the sample geometry or volume. Sometimes we need to know the number of atoms per unit area *n*s on the surface of a solid given the number of atoms per unit volume in the bulk,*nb*. Consider a crystal of the material of interest which is a cube of side *L* as shown in Figure 1.76. To each atom, we can attribute a portion of the whole volume, which is a cube of side *a*. Thus, each atom is considered to occupy a volume of *a*3. Suppose that there are *N* atoms in the volume *L*3. Thus, *L*3 = *Na*3.

*a*. If *nb* is the bulk concentration of atoms, show that the mean separation *a* between the atoms is given by .

*b*. Show that the surface concentration *n*s of atoms is given by .

*c.* Show that the density of the solid is given by where *M*at is the atomic mass. Calculate the atomic concentration in Si from its density (2.33 g cm3)

*d.* A silicon crystal has been doped with phosphorus. The P concentration in the crystal is 1016 cm3. P atoms substitute for Si atoms and are randomly distributed in the crystal. What is the mean separation between the P atoms?

**Figure 1.76** Consider a crystal that has volume *L*3. This volume is proportioned to each atom, which is a cube of side *a*3.

**Solution**

***a.*** Consider a crystal of the material which is a cube of volume *L*3, so that each side has a length *L* as shown in Figure 1.76. To each atom, we can attribute *a portion of the whole volume*. For simplicity, we take the volume proportioned to an atom to be *a*3, that is, each atom is considered to occupy a volume of *a*3.

The actual or true volume of the atom does not matter. All we need to know is how much volume an atom has around it given all the atoms are identical and that adding all the atomic volumes must give the whole volume of the crystal.

Suppose that there are *N* atomsin this crystal. Then *nb*= *N/L*3is the atomic concentration in the crystal, the number of atoms per unit volume, the so-called bulk concentration. Since *N* atoms make up the crystal, we have

*Na*3 = Crystal volume = *L*3

The separationbetween any two atoms is*a*, as shown in Figure 1.76. Thus,

 (1)

Equation 1 can be derived even more simply because an atom has a volume of *a*3. In this volume are is only 1 atom. So *nba*3 must be 1, which leads to Equation 1.

The above idea can be extended to finding the separation between impurity atoms in a crystal. Suppose that we wish to determine the separation *d* between impurities,then we can again follow a similar procedure. In this case, the atoms in Figure 1.76 are impurities which are separated by *d*. We again assign a portion of the whole volume (for simplicity, a cubic volume) to each impurity. Each impurity atom therefore has a volume *d*3(because the separation between impurities is *d*). Following the above arguments we would find,

 (2)

***b.*** We wish to find the number of atoms per unit area*ns* on the surface of a solid given the atomic concentration*nb* in the bulk. Consider Figure 1.76.Each atom as an area *a*2, so that within this surface area there is 1 atom. Thus

Surface area of 1 atom × Surface concentration of atoms = 1

or *a*2*ns* = 1

∴  (3)

Equation (3) is of course based on the simple arrangement of atoms as shown in Figure 1.75. In reality, the surface concentration of atoms depends on the crystal plane at the surface. Equation (3), however, is a reasonable estimate for the order of magnitude for *ns* given *nb*.

***c.***We candetermine the density ** from the atomic concentration *nb* and vice versa. The volume in Figure 1.75 has*L*3*nb* atoms. Thus, the density is

 (4)

For Si, the atomic mas *M*at = 28.09 g mol1, so that with ** given as 2.33 g cm3,

=**5.00×1022 cm.**

***d*.** The P concentration in the crystal is 1016 cm3. P atoms substitute for Si atoms and are randomly distributed in the crystal. We can use Equation (2)



= **4.64×108 m = 46.4 nm**

**1.5 The covalent bond**Consider the H2 molecule in a simple way as two touching H atoms as depicted in Figure 1.77. Does this arrangement have a lower energy than two separated H atoms? Suppose that electrons totally correlate their motions so that they move to avoid each other as in the snapshot in Figure 1.77.The radius *ro* of the hydrogen atom is 0.0529 nm. The electrostatic potential energy *PE* of two charges *Q*1 and *Q*2 separated by a distance *r* is given by *Q*1*Q*2/(4*πε*o*r*).Using the Virial Theorem as in Example 1.1, consider the following:

*a*.Calculate the total electrostatic potential energy (*PE*) of all the charges when they are arranged as shown in Figure 1.77. In evaluating the *PE* of the whole collection of charges you must consider all pairs of charges and, at the same time, avoid double counting of interactions between the same pair of charges. The total *PE* is the sum of the following: electron 1 interacting with the proton at a distance*ro* on the left, proton at *ro* on the right, and electron 2 at a distance 2*ro* + electron 2 interacting with a proton at *ro* and another proton at 3*ro* + two protons, separated by 2*ro*, interacting with each other. Is this configuration energetically favorable?

*b*.Given that in the isolated H-atom the *PE* is 2 ×(13.6 eV), calculate the change in *PE* in going from two isolated H-atoms to the H2 molecule. Using the Virial theorem, find the change in the total energy and hence the covalent bond energy. How does this compare with the experimental value of 4.51 eV?

**Figure 1.77** A simplified view of the covalent bond in *H*2. A snapshot at one instant.

**Solution**

***a.***Consider the *PE* of the whole arrangement of charges shown in the figure. In evaluating the *PE* of all the charges, we must avoid double counting of interactions between the same pair of charges. The total *PE* is the sum of the following:

Electron 1 interacting with the proton at a distance*ro* on the left, with the proton at *ro* on the right and with electron 2 at a distance 2*ro*

+ Electron 2 on the far left interacting with a proton at *ro* and another proton at 3*ro*

+Two protons, separated by 2*ro*, interacting with each other



Substituting and calculating, we find***PE*** =1.0176 × 1017 J or -**63.52 eV**

The negative *PE* for this particular arrangement indicates that this arrangement of charges is indeed energetically favorable compared with all the charges infinitely separated (*PE* is then zero).

***b.***The potential energy of an isolated H-atom is -2× 13.6 eV or -27.2 eV. The difference between the *PE* of the H2 molecule and two isolated H-atoms is,

Δ*PE*= ­(63.52) eV2(-27.2) eV=9.12eV

We can write the last expression above as the change in the total energy.



This change in the total energy is negative. The H2 molecule has lower energy than two H-atoms by 4.56 eV which is the bonding energy. This is very close to the experimental value of 4.51 eV. (Note: We used a*ro*value from quantum mechanics - so the calculation was not totally classical!).

**1.6 Ionic bonding and CsCl**The potential energy *E* per Cs+-Cl−pair within the CsCl crystal depends on the interionic separation *r* in the same fashion as in the NaCl crystal,

 *Energy per ion pair in ionic crystals*[1.48]

where for CsCl, *M* = 1.763, *B* = 1.192×10104 J m9 or 7.442×105 eV (nm) 9 and *m* = 9. Find the equilibrium separation (*ro*) of the ions in the crystal and the ionic bonding energy, that is, the ionic cohesive energy; and compare the latter value to the experimental value of 657 kJ mol1. Given the *ionization energy* of Cs is 3.89 eV and the *electron affinity* of Cl (energy released when an electron is added) is 3.61 eV, calculate the atomic cohesive energy of the CsCl crystal as joules per mole.

**Solution**

Bonding will occur when potential energy *E*(*r*) is minimum at *r = r*0 corresponding to the equilibrium separation between Cs+ and Cl− ions. Thus, differentiating *E*(*r*) and setting it equal to zero at *r = ro* we have



∴ 

∴ 

∴  (1)

Thus substituting the appropriate values we have



∴***ro* = 3.57× 1010 m** or **0.357 nm**.

The minimum energy is the energy at *r = ro*, that is



which in terms of eV is

 (2)



= − 6.32eV per ion pair, or 3.16 eV per ion.

The amount of energy required to break up a CsCl crystal into Cs+and Cl− ions = 6.32eV per pair of ions.

The corresponding *ionic cohesive energy* is

*E*cohesive = (6.32 eV)(1.602× 1019 J eV1)(6.022× 1023 mol1)

= **610 kJ mol─1 of Cs+Cl ion pairsor610 kJmol─1of Cs+ ions and Cl−ions.**

(Not far out from the experimental value given the large numbers and the high index, *m* = 9, involved in the calculations.)

The amount of energy required to remove an electronfrom Cl− ion = 3.61 eV.

The amount of energy released when an electron is put into the Cs+ ion= 3.89 eV.

Bond Energy per pair of Cs-Cl atoms = 6.32 eV + 3.61 eV – 3.89 eV = **6.04 eV**

**Atomic cohesive energy** in kJ/mol is,

*E*cohesive = (6.04 eV)(1.6 × 1019 J eV1)(6.022× 1023 mol1)

=**582 kJ mol─1 of Cs or Cl atom (*i.e.* per mole of Cs-Cl atom pairs)**

**= 291kJ mol─1 of atoms**

------------------------

*Notes:*

1. Various books and articles report different values for *B* and *m* for CsCl, which obviously affect the calculated energy; *ro* is less affected because it requires the (*m*1)throot of *mB*. Richard Christman(*Introduction to Solid State Physics*, John Wiley and Sons, 1988) in Table 5-1 gives,*m* = 10.65 and *B* = 3.44 × 10120, quite different than values here, which are closer to values in Alan Walton, *Three Phases of Matter* (2nd Edition), Clarendon (Oxford University) Press, 1983 (pp. 258-259).

2. The experimental value of 657 kJ mol1(6.81 eV per ion pair) for the ionic cohesive energy (the ionic lattice energy) is from T. Moeller et al, *Chemistry with Inorganic Qualitative Analysis,* Second Edition, Academic Press, 1984) p. 413, Table 13.5.

3. Some authors use the term molecular cohesive energy to indicate that the crystal is taken apart to molecular units e.g. Cs+Cl−, which would correspond to the ionic cohesive energy here. Further, most chemists use "energy per mole" to imply energy per mole of chemical units, and hence the atomic cohesive energy per mole would usually refer to energy be per Cs and Cl atom pairs. Some authors refer to the atomic cohesive energy per mole as cohesive energy per mole of atoms, independent of chemical formula.

4. Equation (1) is



which can be substituted into Equation (2) or [1.48] to eliminate *B*, that is, find the minimum energy of a pair of Cs+-Cl ions, *i.e.*



∴ 

which is called the **Born-Landé equation**.

**1.7 Ionic bonding and LiCl**Equation 1.48 can be used to represent the *PE* of the ion pair inside the LiC crystal. LiCl has the NaCl structure with *M* = 1.748, *m* = 7.30, *B* = 2.341089 J m7.30. Further, the ionization energy of Li (Li →Li + *e*) is 520.2 kJ mol1. The electron affinity of Cl (energy associated with Cl + *e*→ Cl) is 348.7 kJ mol1(a) Calculate the equilibrium separation of ions the LiCl crystal. (b) Calculate the bonding energy per ion pair in the LiCl crystal. (c) Calculate the atomic cohesive energy of the LiCl crystal. (c) Calculate the density of LiCl.

**Solution**

Figure 1Q07-1 shows the crystal structure of NaCl. LiCl has the same crystal structure.

**(a)** The minimum in energy is at



∴ 

∴ 

∴ 

Thus, substituting the appropriate values we have



∴***ro* = 2.612× 1010 m** or **0.261 nm**.

**(b)**The minimum energy is the energy at *r = ro*, that is





= 1.33× 1018 J per of Li+-Cl ions

= −8.32 eV per ion pair, or 4.18 eV per ion.

The bond energy is therefore

*E*bond = *E*min= **8.317 eV per ion pair, or4.18 eV per ion.**

**(c)** In (b) we calculatedthe amount of energy required to break up Li+-Cl− pair into Li+and Cl− ions = 8.317 eV per pair of ions.

The corresponding *ionic cohesive energy* is

*E*ionic-cohesive = (8.317 eV)(1.602× 1019 J eV1)(6.022× 1023 mol1)

= **802 kJ mol─1 of Li+Cl ion pairs or 802 kJ mol─1of Li+ ions and Cl−ions.**

Consider the electron affinity of Cl and the ionization energy of Li, then by definition, we have

Energy required to remove an electron from Cl− ion = 348.7 kJ mol1 = 3.614 eV per ion.

Energy released when an electron is put into the Li+ ion= 520.2 kJ mol1 = 5.392 eV per ion.

Bond Energy per pair of Cs-Cl atoms = 8.317 eV + 3.614 eV – 5.392 eV = **6.539 eVor 6.54 eV**

**Atomic cohesive energy** in kJ/mol is,

*E*atomic-cohesive = (6.539 eV)(1.602× 1019 J eV1)(6.022×1023 mol1)

= **631 kJ mol─1 of Cs or Cl atom (*i.e.* per mole of Cs-Cl atom pairs)**

**= 315 kJ mol─1 of atoms**

**(d)**We know the interionic separation, which is *r*o. The lattice parameter *a*is

*a* = 2*ro* = 2(2.61×1010 m) = **5.22×1010 m**

We can find the atomic masses of Li and Cl from Appendix C or from any periodic table. The density is given as



∴ = 1,980 kg m3 or **1.98 g cm3**.

**Figure 1Q07-1**Left: A schematic illustration of a cross section from solid NaCl. Solid NaCl is made of Cl− and Na+ ions arranged alternatingly, so the oppositely charged ions are closest to each other and attract each other. There are also repulsive forces between the like-ions. In equilibrium, the net force acting on any ion is zero. The interionic separation *ro* and the lattice parameter *a* are shown; clearly *a* = 2*ro*. (b) Solid NaCl and the definition of the unit cell with a lattice parameter *a*. There are 4 Na+ and 4 Cl ions in the unit cell. Clearly, *a* = 2*ro*.

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*Comments:*The values for *m*, and *B* are from Richard Christman, *Fundamental of Solid State Physics*, Wiley and Sons (New York), 1987, Ch 5, Table 5-1, p130. Cl electron affinity from <https://en.wikipedia.org/wiki/Electron_affinity_(data_page)> and Li ionization energy from <https://en.wikipedia.org/wiki/Molar_ionization_energies_of_the_elements> (22 October 2016)

We can compare the results from this calculation with some published experimental and calculated values as in table 1Q07-1. The calculated values above are not too far out from experimental values. Usually*m* and *B*are determined by using experimental values for the elastic coefficients as will be apparent in Question 1.9 where elastic coefficients are related to *m* and *B*)

**Lattice energy** of an ionic crystal is the energy of formation of the crystal from its ions.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | **Ionic cohesive**  **kJ mol─1** | **Atomic cohesive per Li-Cl pair**  **kJ mol─1** | **Atomic cohesive energy per atom**  **kJ mol─1** | ***ro***  **(nm)** | ***a***  **(nm)** | ******  **(g cm)** |
| **1Q07 (This question)** | **802** | **631** | **315** | **0.261** | **0.522** | **1.98** |
|  |  |  |  |  |  |  |
| **Wikipedia** |  |  |  |  | **0.514** | **2.068** |
| **Kittel, 7Ed, p73, Table 7** | **832.6** |  |  | **0.257** |  |  |
| **Moeller** | **834** |  |  | **0.257** |  |  |
| **Ashcroft and Mermin, Table 20.5, p406** | **831.1** |  |  |  |  |  |

C. Kittel, *Silid State Physics*, 7th Edition, John Wiley and Sons, New York, 1996; p73, Table 7.

T. Moeller et al, *Chemistry with Inorganic Qualitative Analysis,* Second Edition, Academic Press, 1984) p. 413, Table 13.5.

N.W. Ashcroft and N.D. Mermin, *Solid State Physics*, Saunders College, 1976; Table 20.5 (p406) data, originally from M.P. Tossi, Solid State Physics, Vol. 16 (Edited by F. Seitz and D. Turnbull), Academic Press, New York, 1964, p54

**1.8 Madelung constant**If we were to examine the NaCl crystal in three dimensions, we would find that each Na+ ion has

6 Cl−ions as *nearest* neighbors at a distance *r*

12 Na+ ions as *second* nearest neighbors at a distance **

8 Cl−ions as *third* nearest neighbors at a distance **

and so on. Show that the electrostatic potential energy of the Na+ atom can be written as

 *Madelung constant M for NaCl*

where*M*, called **Madelung constant**, is given by the summation in the square brackets for this particular ionic crystal structure (NaCl). Calculate *M* for the first three terms and compare it with *M* = 1. 7476, its value had we included the higher terms. What is your conclusion?

**Solution**

From Coulomb’s law of electrostatic attraction we know that the *PE* between two charges *Q*1 and *Q*2 separated by a distance *r* is given by



First we consider the interaction between Na+ ion and 6Cl− ions at distance *r*. Applying Coulomb’s law we have



Similarly, we now consider 12 Na+ ions as *second* nearest neighbors at a distance **



and 8 Cl─ ions as *third* nearest neighbors at a distance **



and similarly we can consider the next nearest set of neighbors and so on. Therefore, the overall *PE* of the Na+ ion is



or 

where clearly 

Considering just the first three terms we have *M* = 2.133. This is considerably different from the value *M* = 1.7464, the value obtained when higher order terms are considered. This implies that the next nearest neighbors have substantial effect on the potential energy.

*Note:* See Appendix A for the explanation on how the PE of ions in the crystal is usually written.

**\*1.9 Bonding and bulk modulus**In general, the potential energy *E* per atom, or per ion pair, in a crystal as a function of interatomic (interionic) separation *r* can be written as the sum of an attractive *PE* and a repulsive *PE,*

 *General PE curve for bonding*[1.49]

where*A* and *n* are constants characterizing the attractive PE and *B* and *m* are constants characterizing the repulsive *PE*. This energy is minimum when the crystal is in equilibrium. The magnitude of the minimum energy and its location*ro*define the bonding energy and the equilibrium interatomic(or interionic) separation respectively.

When a pressure *P* is applied to a solid, its original volume *Vo* shrinks to *V* by an amount *ΔV = V − V0*. The bulk modulus *K* relates the volume strain Δ*V/V* to the applied pressure *P* by

*P*= −*K*(Δ*V/Vo*) *Bulk modulus definition* [1.50]

The bulk modulus *K* is related to the energy curve. In its simplest form (assuming a simple cubic unit cell) *K* can be estimated from Equation 1.50 by

 *Bulk modulus* [1.51]

where *c* is a numerical factor, of the order of unity, given by*b/p* where *p* is the number of atoms or ion pairs in the unit cell and *b* is a numerical factor that relates the cubic unit cell lattice parameter *ao* to the equilibrium interatomic (interionic) separation *ro* by *b* =  *ao*3*/ro*3

*a.*  Show that the bond energy and equilibrium separation are given by

 and 

*b.*Show that the bulk modulus is given by

 or 

*c.*For a NaCl type crystal, Na+ and Cl ions touch along cube edge so that *ro* = (*ao*/2). Thus, *a*3 = 23*ro*3 and *b* = 23 = 8. There are 4 ion pairs in the unit cell, *p* = 4. Thus, *c* =*b/p* = 8/4 = 2. Using the values fromExample 1.3, calculate the bulk modulus of NaCl.

**Solution**

***a.***Interatomic separation *r* = *ro* is the distance at minimum *E*(*r*), Therefore we differentiate *E*(*r*) and set it equal to zero*.i.e.*



∴ 

∴ 

∴  or 

∴  (1)

The potential energy is minimum at *r = ro*and is related with bonding energy *E*(*ro*) = −*E*bond. From the equation for*ro* we have



and isolate for *B*,

 (2)

Substitute for *B* in the energy relation





∴  (3)

∴  (4)

***b.***Show that the bulk modulus is given by

 or 

From the definition of Bulk modulus mentioned in the problem statement above



First, we find, *i.e.*



∴ 



Again, substituting the value of *B* in the above relation, *i.e.*we have



∴ 

∴ 

Now substitute for the second derivative in the equation for the Bulk modulus



or  (5)

From the relationship for the bonding energy,



Now, consider the expression for *K* and rearrange it as



*i.e.* 

***c.***From Example 1.3, the bonding energy for NaCl is *M* = 1.748, *n* = 1, *m* = 8, *ro* = 0.281 × 109 m, *c* = 2. Therefore,

= 4.022 × 1028.

Substitute the above value for*A* in the expression for *K* in Equation (5),

= **25.1 × 109 Pa or 25.1 GPa**

------------------------

*Note:* Experimental value is roughly 2.4×1010 Pa or 24 GPa. The calculated value is quite close. (L.M. Thomas and J. Shanker, "Equation of State and Bulk Modulus for NaCl",Physica Status Solidi B, *189*, 363 (1995))

*Comment:* Equation (3) written as



is often called **Born-Landé equation** for the lattice energy of a crystal(after Max Born and Alfred Landé)

**1.10 Van der Waals bonding**Below 24.5 K, Ne is a crystalline solid with an FCC structure. The interatomic interaction energy per atom can be written as

(eV/atom)

where*ε* and *σ* are constants that depend on the polarizability, the mean dipole moment, and the extent of overlap of core electrons. For crystalline Ne, *ε* = 3.121 × 103 eV and *σ* = 0.274 nm.

*a*.Show that the equilibrium separation between the atoms in an inert gas crystal is given by *ro*= (1.090)*σ*. What is the equilibrium interatomic separation in the Ne crystal?

*b*. Find the bonding energy per atom in solid Ne.

*c*.Calculate the density of solid Ne (atomic mass = 20.18).

**Solution**

***a.*** Let *E* = potential energy and *x* = distance variable between the atoms. The energy *E* is given by



The force *F* on each atom is given by



∴ 

When the atoms are in equilibrium, this net force must be zero. Using *ro* to denote equilibrium separation,



∴ 

∴ 

∴ 

∴ ***ro* = 1.090*σ***

For the Ne crystal, *σ* = 2.74 × 1010 m and *ε* = 0.003121 eV. Therefore,

***ro*** = 1.090(2.74 × 1010 m) = **2.99 × 1010 m for Ne.**

***b.***Calculate energy per atom at equilibrium:



∴ 

∴ ***E*(*ro*) =× or  eV**

Therefore the **bonding energy in solid Ne is 0.027 eV per atom or 2.6 kJ / mole**

***c.*** To calculate the density, remember that the unit cell is FCC, and density = (mass of atoms in the unit cell) / (volume of unit cell). There are 4 atoms per FCC unit cell, and the atomic mass of Ne is 20.18 g/mol. (See Figure 1Q10-1)

**Figure 1Q10-1:**Left: An FCC unit cell with close-packed spheres. Right: Reduced-sphere representation of the FCC unit cell.

Since this is an FCC crystal structure, let *a* = lattice parameter (side of cubic cell) and *R* = radius of atom. The shortest interatomic separation is *ro* = 2*R* (atoms in contact means nucleus to nucleus separation is 2*R* (see Figure 1Q10-1).

*R* = *ro*/2

and 2*a*2 = (4*R*)2

∴ 

∴ *a* = 4.228 × 1010 m or **0.423 nm**

The mass (*m*Ne) of 1 Ne atom in grams is the atomic mass (*M*at) divided by *NA* (Avogadro's number) because *NA* number of atoms have a mass of *M*at grams,

*m*Ne = *M*at / *NA*

∴ 

There are 4 atoms per unit cell in the FCC lattice. The density*ρ*can then be found by

*ρ* = (4*m*Ne) / Volume of unit cell

or *ρ* = (4*m*Ne) / *a*3= [4 × (3.351 × 1026 kg)] / (4.228 × 1010 m)3

∴ ***ρ* = 1774 kg/m3**

In g/cm3, this density is:

***ρ* =**= **1.77g/cm3**

The density of solid Ne is 1.77 g cm3.

------------------------

*Notes:*

1. Except for He, all inert gas crystal structures are FCC.

2. The calculated value is very close to the experimental value for *a*(below 24 K, or 246 °C), which is 0.44 nm. (*e.g.*https://www.webelements.com/neon/crystal\_structure.html, 22 October 2016). The values of **and** for Ne are from C. Kittel, *Solid State Physics, Seventh Edition*, John Wiley and Sons, New York, 1996; Table 4, p60. Values in SI units are given below

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | **He** | **Ne** | **Ar** | **Kr** | **Xe** |
| **** x 10-21 J** | 0.14 | 0.5 | 1.67 | 2.25 | 3.2 |
| **** (meV)** | 0.874 | 3.121 | 10.424 | 14.045 | 19.975 |
| **** (nm)** | 0.256 | 0.274 | 0.34 | 0.365 | 0.398 |

3. There is an excellent undergraduate level description and discussion of Lennard-Jones potential for two isolated atoms and atoms in the FCC crystal in Alan Walton, *Three Phases of Matter, Second Edition*, Clarendon Press (Oxford University Press), Oxford, 1983; pp43-47 for two isolated atoms and pp259-261 for atoms in the crystal.

**1.11Kinetic molecular theory**

*a.*In particular Ar-ion laser tube the gas pressure due to Ar atoms is about 0.1 torr at 25 °C when the laser is off.What is the concentration of Ar atoms per cm3 at 25 °C in this laser? (760 torr = 1 atm = 1.013×105Pa.)

*b.*In the He-Ne laser tube He and Ne gases are mixed and sealed. The total pressure *P* in the gas is given by contributions arising from He and Ne atoms

*P* = *P*He + *P*Ne

where *P*He and *P*Ne are the *partial pressures* of He and Ne in the gas mixture, that is, pressures due to He and Ne gasses alone,

 and 

In a particular He-Ne laser tube the ratio of He and Ne atoms is 7:1, and the total pressure is about 1 torr at 22 °C. Calculate the concentrations of He and Ne atoms in the gas at 22 °C. What is the pressure at an operating temperature of 130°C?

**Solution**

***a****.*From the Kinetic molecular theory for gases, we have



where, *R* is the gas constantconstant, *T* is the temperature. The number of Ar atoms per unit volume is



We are given 13.33 Pa

Therefore the number of Ar atoms per unit volume*n*Arwill be

= **3.24 × 1021m3** or **3.24 × 1015 cm3**

***b****.*Let *n*He = *N*He/*V*, the concentration of He atoms; *n*Ne = *N*Ne/*V*, the concentration of Ne atoms.Given that the total pressure is the sum of the pressure by He and Ne gasses

*P* = *P*He + *P*Ne

∴ 

∴ 

∴ 

Thus at *T* = 22 °C (295 K) for Ne,

****

**=4.09× 1021 m3 or 4.09× 1015 cm3.**

Given that *n*He is 7 times that of *n*Ne, *i.e*.

*n*He = 7×*n*Ne = **2.86× 1022 m3** or **2.86× 1016 cm3**.

At *T* = 130 °C(403 K), the atomic concentrations of He and Ne remain unchanged (the tube has the same volume, neglecting the thermal expansion). Thus, the new pressure *P*′ and initial pressure *P* are related by

****

so that the new pressure *P*' is **1.37 torr.**

**\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_**

**1.12 Kinetic Molecular Theory**Calculate the effective (rms) speeds of the He and Ne atoms in the He-Ne gas laser tube at room temperature (300 K).

**Solution**

|  |  |
| --- | --- |
| **Figure 1Q12-1:** The gas atoms in the container are in random motion. | **Figure 1Q12-2:** The He-Ne gas laser. |

To find the root mean square velocity (*v*rms) of He atoms at *T* = 300 K:

The atomic mass of He is (from Periodic Table) *M*at = 4.0 g/mol. Remember that 1 mole has a mass of *M*at grams. Then, one He atom has a mass (*m*) in kg given by:



From the kinetic theory (visualized in Figure 1Q12-1),



∴ = **1368 m/s**

The root mean square velocity (*vrms*) of Ne atoms at *T* = 300 K can be found using the same method as above, changing the atomic mass to that of Ne, *M*at = 20.18 g/mol. After calculations, the mass of one Ne atom is found to be 3.351 × 1026 kg, and the root mean square velocity (*v*rms) of Ne is found to be ***v*rms = 609 m/s**.

------------------------

*Note:* Radiation emerging from the He-Ne laser tube (Figure 1Q12-2) is due to the Ne atoms emitting light, all in phase with each other, as explained in Ch. 3. When a Ne atom happens to be moving towards the observer, due to the Doppler Effect, the frequency of the laser light is higher. If a Ne atom happens to moving away from the observer, the light frequency is lower. Thus, the random motions of the gas atoms cause the emitted radiation not to be at a single frequency but over a range of frequencies due to the Doppler Effect. \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

**\*1.13 Kinetic molecular theory and the Ar ion laser**An argon ion laser has a laser tube that contains Ar atoms that produce the laser emission when properly excited by an electrical discharge. Suppose that the gas temperature inside the tube is 1300 °C (very hot).

*a.*Calculate the mean speed (*v*av), rms velocity (*v*rms=) and the rms speed (*v*rms,*x*=) in one particular direction of the Ar atoms in the laser tube, assuming 1300 °C. (See Example 1.11.)

*b.*Consider a light source that is emitting waves and is moving towards an observer, somewhat like a whistling train moving towards a passenger. If *fo* is the frequency of the light waves emitted at the source, then, due to the *Doppler effect*, the observer measures a higher frequency *f* that depends on the velocity *v*Ar of the source towards to observer and the speed *c* of light,



It is the Ar ions that emit the laser output light in the Ar-ion laser. The emission wavelength*λo* = *c*/*fo* is 514.5 nm. Calculate the wavelength *λ*registered by an observer for those atoms that are moving with a mean speed *v*av toward the observer. Those atoms that are moving away from the observer will result in a lower observed frequency because *v*Ar will be negative. Estimate the width of thewavelengths (the difference between the longest and shortest wavelengths) emitted by the Ar ion laser.

**Solution**

***a****.*From Example 1.11 the mean speed is given by



*m* is the mass of a gas atom. *T* = 1300 °C = 1573 K. Atomic mass of Ar is *M*at = 39.95 g mol1, therefore the mass of the Ar atom is

= 6.634× 1023 g or 6.634 × 1026 kg

Mean speed is given by



∴***v*av = 913.32 m s1**.

Root mean square RMS velocity is



∴ ***v*rms= 991.31 m s1**.

RMS speedalon*x*,*v*rms,*x* = in one particular direction is

= **572.33 m s1**.

***b****.* First we consider the case when the source is moving towards the observer with average speed, *v*av, the frequency observed is



where *fo* = *c*/*λo* = 3×108 m s1/ 514.5 ×109 m = 5.8309 × 1014 s1, *v*Ar as calculated above is 912.32 m s1. Therefore the frequency is

= 5.830922× 1014 s1

The corresponding wavelength is therefore, *λ*1 = c/*f*1 = 3×108 m s1/ 5.830922× 1014 s1 = **514.4984 nm**.

In the case when the emitting source is moving away from the observer, the frequency is

= 5.830886× 1014 s1

The corresponding wavelength is therefore, *λ*2 = *c*/*f*2 = 3×108 m s1/ 5.830886× 1014 s1 = **514.5016 nm**. The range of wavelengths observed by the observer is between**514.4984 nm and 514.5016 nm**. The wavelength (spectral) width is

Δ*λ*= *λ*2 – *λ*1 = 514.5016 − 514.4984 nm **= 0.0032 nm, very small.**

------------------------

*Note:* The question asks for the change in the wavelength or the width in the emitted wavelengths. Four decimal places were kept in the calculations of frequency and wavelength because we are interested in these changes and the changes in the frequency and wavelength are small. It may be thought that we should similarly use higher accuracy in the velocity calculations and a more accurate *c* value *etc* but that's not necessary because the change in the frequency is actually 2*fov*Ar/*c*:



= 2(5.8309 × 1014 s1)(913.32 m s1) / (3 × 108 m s1) = 3.55 × 109 s1 = **3.55 GHz.**

*Note to the Instructor:* Some students are known to convert a range of frequencies to a range of wavelengths by taking Δ*λ*= *c*/Δ*f*, which is wrong. To convert a small range of frequencies Δ*f* to a range of wavelengths Δ*λ*, take*λ* = *c/f* and differentiate it,



∴ = 3.13 × 1012 m **=0.00313 nm**

very close to the above calculation of 0.0032 nm.

**1.14 Heat capacity of gases** Table 1.9shows the experimental values of the molar heat capacity for a few gases at 25 °C. Assume that we can neglect the vibrations of the atoms in the molecules. For each calculate the observed degree of freedom *f*observed, that is *f* in *Cm* = *f*(*R*/2). For each find the expected *f*expected by considering translational and rotational degrees of freedom only. What is your conclusion?

**Table 1.9** Heat capacities for some gases at room temperature at constant volume, *CV* in J mol1 K1.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Gas** | Ar | Ne | Cl2 | O2 | N2 | CO2 | CH4 | SF6 |
| ***CV*** | 12.5 | 12.7 | 25.6 | 21.0 | 20.8 | 28.8 | 27.4 | 89.0 |

**Solution**

If a gas atomor molecule has *f* degrees of freedom, then its molar heat capacity at constant volume is given by

*CV* = *f*(*R/*2)= *f*(4.158 J mol1 K1).

Thus we can obtain the experimental *f* as

= 3.00

which for the Ar gas gives

= 3.00

This is exactly what we expect since the Ar gas consists of single Aratoms moving around randomly in the tank. The Ar values have been entered into Table 1Q14-1. The remainder of the gases are similarly calculated and entered into Table 1Q14-1.

First, notice that for monoatomic gases such as Ar and Ne, *f*observed and *f*expected agree very well.

For diatomic molecules such as Cl2, O2, N2, we expect 5 degrees of freedom (DOF), 3 translational and 2 rotational, ignoring the vibrational degrees of freedom. O2 and N2 follows the expected behavior at room temperature; but not Cl2. The latter exhibits more DOF than 5 because the Cl2 molecules can gain energy through the vibrations of thetwo Cl atomsheld together by a bond that acts as a spring (ClCl). The vibrational DOF would normally contribute 2 additional (*R*/2) values but at room temperature their contribution is not full. (Full contribution means *R/*2 per DOF)

CO2 is actually a linear molecule and should have 5 translational and rotational DOF without the vibrations. It shows nearly 7 DOF, arising from various vibraions.

Both CO2 and CH4 should have full 3 translational and 3 rotational DOF, *i.e.f*expected = 6. However, their DOF is more than 6. Again there is a contribution from vibrational DOF.

SF6 should have 3 translational and 3 rotational degrees of freedom, 6 in total but it exhibits some 21 DOF. Clearly vibrations play a very important role in this gas

**Table 1Q14-1** Heat capacities for some gases at room temperature at constant volume, *CV* in J mol1 K1 and observed and expected *f*.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Gas** | Ar | Ne | Cl2 | O2 | N2 | CO2 | CH4 | SF6 |
| ***CV*** | 12.5 | 12.7 | 25.6 | 21.0 | 20.8 | 28.9 | 27.4 | 89.0 |
| ***f*observed** | 3.01 | 3.05 | 6.16 | 5.05 | 5.00 | 6.95 | 6.59 | 21.40 |
| ***f*expected (translation + rotation only)** | 3 | 3 | 5 | 5 | 5 | 5 | 6 | 6 |

*Note:* Data in Table 1.9 on elements are from <https://en.wikipedia.org/wiki/Heat_capacities_of_the_elements_(data_page)> (23 October 2016), data on CH4, CO2and SF6 gases from <http://encyclopedia.airliquide.com/Encyclopedia.asp?GasID=41>(23 October 2016).

**\*1.15 Degrees of freedom in a gas molecule** A monatomic molecule such as Ar has only three degrees of freedom (DOF) for motion along the three independent directions *x*, *y*, and *z*. In a system in which there are two independent atoms such Cl and Cl, the total number of DOF *f* is 6 because each atom has 3 degrees of freedom. Once we form a Cl2 molecule, the original 6 DOF in *KE* are partitioned as shown in Figure 1.78 The Cl2 molecule has 3 translational degrees of freedom, 2 rotational and 1 vibrational, summing to the original 6. The vibrational degree of freedom itself has *KE* and *PE* terms with each having an average of *kT* so that a vibrational degree of freedom actually has *kT* of energy rather than *kT*. The *PE* term arises from the stretching and compression of the bond (which acts like a spring) during the vibrations. Put differently, each vibrational DOF has two subdegrees of freedom associated with *KE* and *PE* terms, each of which has (1/2)*kT* of energy.Let *na* be the number of atoms in a molecule. Then 3*na* is the total number of kinetic energy based DOF. There will always be 3 translational DOF for the molecule and at most 3 rotational degrees of freedom. There may be one or more vibrational DOF because there may be many ways in which the atoms in the molecule can vibrate, but there is a maximum. If *f*rot and *f*vib are the rotational and vibrational DOF, then

3*na* = 3 + *f*rot + *f*vib.

1. What is the vibrational DOF for Cl2. What is the maximum molar heat capacity at constant volume *CV* for Cl2?Given Table 1.9, what is the vibrational contribution?
2. What is the vibrational DOF for SF6. The molar heat capacity at constant volume for the SF6 gas at 300 K is 89.0 J mol1 K1 but at 700 K, it is 141 J mol1 K1. How many vibrational DOF do you need to explain the observations at these two temperatures?

**Figure 1.78** The partitioning of degrees of freedom in a diatomic molecule.

**Solution**

***a.*** The Cl2 molecule has 2 atoms, joined by a spring (bond). There are 2 rotational DOF, we neglect the rotation about the bond (as shown in Figure 1.78). Thus, the general rule for the DOF,

3*na* = 3 + *f*rot + *f*vib

gives

*f*vib = 3*na* 3 *f*rot = 3(2)  3  2 = 1

Thus, the Cl2 molecule has 1 vibrational DOF, which itself has 2 "subdegrees" of freedom arising from the *KE* and *PE* terms. The molar constant volume heat capacity *CV* at most should be

*CV* = translational DOF × (*R*/2)

+ rotational DOF × (*R*/2)

+ vibrational DOF × *R*

∴ *CV* = 3(*R/*2) + 2(*R/*2) + 1*R* = (7/2)*R* = **29.1 J mol1 K1**

Table 1.9 gives *CV* for Cl2 at 300 K as 25.6 J mol1 K1, not the expected full value of 29.1 J mol1 K1; less than the expected.

Without the vibrations this *CV* would have been 5(*R*/2) or 20.79 J mol1 K1. The difference between the measured and 20.79 J mol1 K1 is the vibrational contribution to *CV*, that is

Vibrational contribution to *CV* at 300 K = 25.6  20.79 = 4.81 J mol1 K1.

The full vibrational contribution would have been 1*R*, that is 8.316 J mol1 K1. Clearly, the vibrational contribution is about half its full capacity.

***b.*** The SF6 molecule has 7 atoms. There are 3 rotational DOF. Thus, the general rule for the DOF,

3*na* = 3 + *f*rot + *f*vib

gives

*f*vib = 3*na* 3 *f*rot = 3(7)  3  3 = 15

Thus, the SF6 molecule has 15 vibrational DOF, with each having 2 "subdegrees" of freedom arising from the *KE* and *PE* terms. The molar constant volume heat capacity *CV* at most should be

*CV* = translational DOF × (*R*/2)

+ rotational DOF × (*R*/2)

+ vibrational DOF × *R*

∴ *CV* = 3(*R/*2) + 3(*R/*2) + 15*R* = 18*R*  = **149.7 J mol1 K1**

Consider now the *CV*-contributions from translational and rotational motions only (non-vibrational contribution), represented by *CV*(TR)

*CV*(TR) = 3(*R/*2) + 3(*R/*2) = **25 J mol1 K1**

The measured vibrational contribution *CV*(V) at 300 K is therefore

*CV*(V) = *CV*(Measured) *CV* (TR) = 89 J mol1 K125 J mol1 K1 = **64 J mol1 K1**

It is clear that the vibrational contribution is very strong; stronger than the translational and rotational contribution. Consider

Vibrational DOF *= CV*(V) */R* =(64 J mol1 K1) / (8.3145 J mol1 K1) =**7.7**

Recall that with the vibrational DOF, each DOF has an average energy of *R*, and be considered to be made up of KE and PEassociated "subdegrees" of freedom; each with an energy *R/*2. Clearly at least half the vibrations are contributing to *CV*.

Now consider *CV* at 700 K (427 °C), which is 141 J mol1 K1. Thus, the vibrational contribution to the molar heat capacity is

*CV*(V) = *CV*(Measured) *CV* (TR) = 141 J mol1 K125 J mol1 K1 = **116 J mol1 K1**

The vibrational DOF is

Vibrational DOF *= CV*(V) */R* =(116 J mol1 K1) / (8.3145 J mol1 K1) =**14.0**

It is clear that nearly all the vibrations are now contributing to the heat capacity.

-----------

*Comments:*

1. There is always a "degree" of confusion when it comes to "degrees of freedom". Some books simply assign 2 degrees of freedom to a particular mode of vibration so that this particular mode of vibration contributes 〈*KE*〉 = (1/2)*kT* and〈*PE*〉 = (1/2)*kT* or, in total,*kT*. Some authors prefer to keep the term "degree of freedom" to describe *an independent mode of vibration*. These are also called normal modes of vibration of a molecule. With this approach, the number of vibrational modes is always 3*na*3 *f*rotation. Clearly, each mode of vibration then has an average energy of 〈*KE*〉+ 〈*PE*〉 = *kT*.As an example, consider the water molecule (H2O). This has *na* = 3 so that

*f*vib = 3*na* 3 *f*rot = 3(3)  3  3 = 3

There are 3 vibrational degrees of freedom for the H2O molecule as shown in Figure 1Q15-1. These are independent modes of vibration and each has, on average, *kT* of energy so that *CV* for the maximum water vapor should be

*CV* = 3(*R/*2) + 3(*R/*2) + 3*R* = 6*R*  = **49.9 J mol1 K1**

Water vapor at 200 °C has a *CV* = 27.6 J mol1 K1 and at 1000 °C, *CV* = 33.1 J mol1 K1so that vibrational contribution at 1000 °C is only 25% (from<https://en.wikipedia.org/wiki/Water_(data_page)> (23 October 2016))

**Figure 1Q15-1**  Vibrational degrees of freedom (modes) in the H2O molecule. There are 3 vibrational degrees of freedom.

In the Cl2 molecule (Cl-Cl), the bond has only 1 mode of vibration (stretching and compressing the bond)

2. The heat capacity data for SF6 gas from "Suphur Hexafluoride", Solvay Fluor und Derivate GmbH (Hans-Böckler-Allee 20, D-30173 Hannover, Germany); company brochure version 7 on SF6, p27. This is available online at [http://www.solvay.com/en/binaries/SF6-Sulphur-Hexafluoride-EN-254640.pdf (23](http://www.solvay.com/en/binaries/SF6-Sulphur-Hexafluoride-EN-254640.pdf%20(23) October 2016)

Heat capacity data for SF6. Data are given below and the temperature dependence shown in Figure 1Q15-1.

|  |  |
| --- | --- |
| **T (K)** | **CV ( J mol-1 K-1)** |
| **298** | **97.25** |
| **373** | **112.45** |
| **400** | **116.39** |
| **473** | **125.89** |
| **500** | **128.54** |
| **573** | **134.51** |
| **600** | **136.07** |
| **673** | **140.21** |
| **700** | **141.1** |
| **773** | **144.35** |

**Figure 1Q15-1***CV* vs *T* for SF6 gas

**ADDENDUM**

Consider a CH4 molecule in methane gas (see Table 1.9 for its molar heat capacity)molecule has 5 atoms. There are 3 rotational DOF. Thus, the general rule for the DOF,

3*na* = 3 + *f*rot + *f*vib

gives

*f*vib = 3*na* 3 *f*rot = 3(5)  3  3 = 9

Thus, the CH4 molecule has 9 vibrational DOF, with each having 2 "subdegrees" of freedom arising from the *KE* and *PE* terms. The molar constant volume heat capacity *CV* at most should be

*CV* = translational DOF × (*R*/2)

+ rotational DOF × (*R*/2)

+ vibrational DOF × *R*

∴ *CV* = 3(*R/*2) + 3(*R/*2) + 9*R* = 12*R*  = **99.8 J mol1 K1**

Table 1.19 gives *CV* for CH4 at 300 K as 27.4 J mol1 K1, not the expected full value of 99.8 J mol1 K1. Just the translational and rotational DOF would give 25 J mol1 K1. Clearly the vibrational contribution is very small at room temperature.

**1.16 Dulong-Petit rule for metals** Consider the room temperature experimental specific heats of those 22 metals listed in Table 1.10. They are listed in increasing atomic mass from Li to Bi. Plot *cs* vs. 1/*M*atand find the best line that goes through the origin. What is the slope of this best line? Now consider Be, which is a very light metal. It has *cs*= 1.825 J g1 K1, *M*at = 9.012 g mol1. What is its molar heat capacity? What is your conclusion?(To avoid points cluttering in one region of the plot, you can also try a log-log plot.)

**Table 1.10** Specific heat capacity in J g1 K1 and atomic mass for selected metals at 25 °C

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Metal | Li | Na | Mg | Al | K | Ca | Ti | V | Cr | Fe | Co |
| *M*at | 6.94 | 22.99 | 24.3 | 26.98 | 39.1 | 40.08 | 47.87 | 50.94 | 51.99 | 55.85 | 58.93 |
| *cs* | 3.58 | 1.228 | 1.023 | 0.897 | 0.757 | 0.647 | 0.523 | 0.489 | 0.449 | 0.444 | 0.421 |
| Metal | Cu | Zn | Zr | Mo | Ag | Sb | Ta | W | Au | Pb | Bi |
| *M*at | 58.93 | 65.39 | 91.22 | 95.94 | 107.86 | 121.76 | 180.95 | 183.84 | 196.97 | 207.2 | 208.99 |
| *cs* | 0.385 | 0.388 | 0.278 | 0.251 | 0.235 | 0.207 | 0.14 | 0.132 | 0.129 | 0.13 | 0.122 |

**Solution**

Figure 1Q16-1 shows the data in Table 1.10 plotted as *cs* vs. 1/*M*at. The data can be easily fitted with a best line that passes through the origin as shown by the dashed line. There are many points that are cluttered around small 1/*M*at values (large *M*at). Figure 1Q16-2 shows a log-log plot of *cs* vs. 1/*M*at. Clearly, the experimental points now are stretched out much more discernable. The present data can be found in the Excel worksheet in Table 1Q16-1.

Clearly, we can draw a best line passing through the origin. Using Excel's trend line feature, the best line through the origin is given as

*y* = 25.1*x* or 

which has a best fit *R*2 value of 0.9967, which represents a very good fit given the large number of data points. The interpretation is straightforward. Suppose that *Cm* is the molar heat capacity. 1 mole any substance has a mass of *M*at grams. The specific heat capacity, according to the Dulong-Peit rule, is then given by



wherethat *Cm* = 3*R* = 25 J mol1 K1. Clearly, this is exactly what is predicted from the plots in Figure 1Q16-1 and 2 inasmuch as the slope of the best line through the origin is 25.1 J mol1 K1; as a corollary we can state that the experimental molar heat capacity of metals from the data in Table 1.10 is **25.1 J mol1 K1**. The best line in Figure 1Q16-1 is the **experimenta**l **Dulong-Petit rule**.

Consider Be now, which is a very light metal. Its molar heat capacity is given by



which is much less than the Dulong-Petit rule. Clearly, the Dulong-Petit rule fails in this case. Figure 1Q16-3 shows the Be point in the plots. It lies far below the Dulong-Petit line.

**Figure 1Q16-1** Plot of *cs* vs. 1/*M*at for various metals. The best line is forced through the origin

**Figure 1Q16-2** A log-log plot of *cs* vs. 1/*M*at for various metals. The dashed line is the best line representing *cs* = *y* = *mx* = 25.1*x* = 25.1/*M*at, which goes through the origin;remember thoughthe origin cannot be shown in a log-log plot.

**Figure 1Q16-3** A log-log plot of *cs* vs. 1/*M*at for various metals. The red point is the Be value, which is far away from the Dulong-Petit rule

**Table 1Q17-1** Excel worksheet with *cs* and *M*at data

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Metal | Mat (g / mol) | *cs* [J / (g K)] | **1/Mat** | ***cs* [J / (g K)]** |
| Li | 6.94 | 3.58 | **0.144092** | **3.58** |
| Na | 22.99 | 1.228 | **0.043497** | **1.228** |
| Mg | 24.3 | 1.023 | **0.041152** | **1.023** |
| Al | 26.98 | 0.897 | **0.037064** | **0.897** |
| K | 39.1 | 0.757 | **0.025575** | **0.757** |
| Ca | 40.08 | 0.647 | **0.02495** | **0.647** |
| Ti | 47.87 | 0.523 | **0.02089** | **0.523** |
| V | 50.94 | 0.489 | **0.019631** | **0.489** |
| Cr | 51.99 | 0.449 | **0.019234** | **0.449** |
| Fe | 55.85 | 0.449 | **0.017905** | **0.449** |
| Co | 58.93 | 0.421 | **0.016969** | **0.421** |
| Cu | 58.93 | 0.385 | **0.016969** | **0.385** |
| Zn | 65.39 | 0.388 | **0.015293** | **0.388** |
| Zr | 91.22 | 0.278 | **0.010963** | **0.278** |
| Mo | 95.94 | 0.251 | **0.010423** | **0.251** |
| Ag | 107.86 | 0.235 | **0.009271** | **0.235** |
| Sb | 121.76 | 0.207 | **0.008213** | **0.207** |
| Ta | 180.95 | 0.14 | **0.005526** | **0.14** |
| W | 183.84 | 0.132 | **0.00544** | **0.132** |
| Au | 196.97 | 0.129 | **0.005077** | **0.129** |
| Pb | 207.2 | 0.13 | **0.004826** | **0.13** |
| Bi | 208.99 | 0.122 | **0.004785** | **0.122** |

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**1.17 Heat capacity**

*a*.Calculate the heat capacity per mole and per gram of N2 gas, neglecting the vibrations of the molecule. How does this compare with the experimental value of 0.743 J g1 K1?

*b*.Calculate the heat capacity per mole and per gram of CO2 gas, neglecting the vibrations of the molecule. How does this compare with the experimental value of 0.648 J K1 g1? Assume that CO2 molecule is linear (O-C-O), so that it has two rotational degrees of freedom.

*c*.Based on the Dulong-Petit rule, calculate the heat capacity per mole and per gram of solid silver. How does this compare with the experimental value of 0.235 J K1 g1?

*d*.Based on the Dulong-Petit rule, calculate the heat capacity per mole and per gram of the silicon crystal. How does this compare with the experimental value of 0.71 J K1 g1?

**Solution**

***a****.*N2 has 5 degrees of freedom: 3 translational and 2 rotational. Its molar mass is

*M*at = 2 × 14.01 g/mol = 28.02 g/mol.

Let *Cm*= heat capacity per mole, *cs*= specific heat capacity (heat capacity per gram), and *R* = gas constant,then:



∴ ***cs*** = *Cm* / *M*at = (20.8 J K1 mol1)/(28.02 g/mol) = **0.742 J K1 g1**

This is close to the experimental value.

***b.***CO2 has the linear structure O=C=O. Rotations about the molecular axis have negligible rotational energy as the moment of inertia about this axis is negligible. There are therefore 2 rotational degrees of freedom. In total there are 5 degrees of freedom: 3 translational and 2 rotational. Its molar mass is

*M*at= 12.01 + 2 × 16 = 44.01 g/mol.

and 

∴ ***cs*** = *Cm* / *M*at = (20.8 J K1 mol1)/(44.01 g/mol) = **0.47 J K1 g1**

This is *smaller* than the experimental value 0.648 J K1 g1. The 5 degrees of freedom assigned to the CO2 molecule did not include molecular vibrations and “vibrations” of the atoms that include “flexing” or bond bending.

***c.***For solid silver, there are 6 degrees of freedom: 3 vibrational *KE* and 3 elastic *PE* terms. Its molar mass is,

*M*at= 107.87 g/mol.



∴ ***cs*** = *Cm* / *M*at = (24.9 J K1 mol1)/(107.87 g/mol) = **0.231 J K1 g1**

This is very close to the experimental value.

***d.***For a solid, heat capacity per mole is 3*R*. The molar mass of Si is *M*at = 28.09 g/mol. Thus,



∴ ***cs*** = *Cm*/ *M*at = (24.9 J K1 mol1)/(28.09 g/mol) = **0.886 J K1 g1**

The experimental value is substantially less and is due to the failure of classical physics. One has to consider the quantum nature of the atomic vibrations and also the distribution of vibrational energy among the atoms. We need to use the Debye model of a solid to be able to predict the correct specific heat capacity, which is covered in Chapter 4.

**1.18Dulong-Petit atomic heat capacity**Express the Dulong-Petit rule for the molar heat capacity as heat capacity per atom and in the units of eV K─1per atom, called the **atomic heat capacity**. CsI is an ionic crystal used in optical applications that require excellent infrared transmission at very long wavelengths (up to 55 μm). It has the CsCl crystal structure with one Cs+ and one I─ion in the unit cell. Calculate the specific heat capacity of CsI and compare it with the experimental value of 0.20 J K1 g1. What is your conclusion?

**Solution**

Molar heat capacity from Dulong-Petit rule is given by

= 25 J K1 mol1

The above relation provides us with the heat capacity per mole. In one mole of a substance there are *NA*(=6.022 × 1023) molecules or atoms. Therefore, the heat capacity per atom will be

*C*at =**4.15 × 1023J K1atom1**

In terms of eV K1, the heat capacity will be

*C*at = = **2.59 × 104 eV K1 atom1**

In the Dulong-Petit rule, *C*atdoes not depend on the type of atom. It is the same for all types of atoms in the crystal.Cs and Ihave *M*at(Cs) = 132.91 g mol1 and *M*at(I) = 126.90 g mol1. There are equal number of Cs+and I─atoms. Consider a mass *m* of CsI that has 1 mole (*NA* atoms) of Cs+ and 1 mole of I─. There will be 2*NA* atoms in total in this sample, and the heat capacity will be 2*NAC*at = 2(3*R*). The Cs atoms in this sample will have a mass *M*at(Cs)and I atoms will have a mass *M*at(I) so that the sample mass *m* = *M*at(Cs) + *M*at(I) = 132.91 g + 126.90 g.

The specific heat capacity of CsIwill be,

= **0.1924 J K1 g1**

Another method of calculating the specific heat capacity of CsI is by considering the unit cell. In one unit cell of CsCl type structure, there is the central atom of Cs+ and ×8 = 1 atom of I. The heat capacity of the unit cell is,

*C*cell = 2*C*at

The specific heat capacity of CsI is then



∴ 

which is the same calculation above.

*Conclusion:* The Dulong-Petit rule applies well to CsI.

*Note:*The Dulong-peit rule is blind to the species of atoms in the solid. Take a solid that has two types of atoms *A* and *B*. If  is the mean atomic mass in the solid, *i.e.* where,*nA*is the atomic fraction of *A*, *nB*the atomic fraction of *B* (so that *nA* + *nB* = 1), and *MA* and *MB* are the atomic weights (g mol1) of *A* and *B*, then the Dulong-petit rule is

 J K1 g1

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*a.*Calculate the specific heat capacity of Pb–Sn solder assuming that its composition is 38 wt.% Pb

and 62 wt.% Sn.

*b.* Calculate the specific heat capacitiesof Pb and Sn individually as *csA* and *csB*, respectively, and then calculate the *cs* for the alloy using

 *Alloy specific heat capacity*

where *wA* and *wB* are weight fractions of *A* (Pb) and *B* (Sn) in the alloy (solder). Compare your result with part (a). What is your conclusion?

*c.* ZnSe is an important optical material (used in infrared windows and lenses and high power CO2 laser optics) and also an important II-VI semiconductor that can be used to fabricate blue-green laser diodes. Calculate the specific heat capacity of ZnSe, and compare the calculation to the experimental value of 0.345 J K1 g1.

**Solution**

***a.***In the Dulong-Petit rule, the molar heat capacity *Cm* = 3*R* does not depend on the species (type) of atom. Stated differently, the atomic heat capacity (heat capacity per atom) *C*at = 3*R*/*NA* = 3*k*, does not depend on the chemical nature of the atom. It is the same for all types of atoms in the crystal.

Consider 1 mole of a compound that has *nA* moles of A and *nB* moles of B; and *nA* + *nB*= 1. Let *m* be the mass of the compound. The atomic masses are *MA* and *MB*. The heat capacity will be

Heat capacity = (*nANA*)*C*at + (*nBNA*)*C*at=*Cm*.

The sample mass *m* is given by

*m* = (*MA*(*nA*) + *MB*(*nB*)) grams,

since atomic masses are g mol1. The specific heat capacity is then

 (1)

where the mean atomic mass is defined by

 (2)

------------------------

*Note:* This is what would be called *a trivial derivation* that is a direct consequence of the fact that the Dulong-Petit rule does *not* depend on the species of atoms making up the crystal.

------------------------

We can now apply Equation (1). *M*at for Pb = 207.2 g mol1 and *M*at for Sn = 118.7 g mol1. The atomic fractions of Pb and Sn are



and 

The specific heat capacity using Equation (1) is



∴  = **0.1764 J g1K1**

***b.*** The specific heat capacity for Pb is  = 0.2106 J K1 g1

The specific heat capacity for Sn is  = 0.1207 J K1 g1

The specific heat capacity of the alloy is



*cs*=(0.2106 J K1 g1)(0.38)+ (0.1207 J K1 g1)(0.62) = **0.1764 J K1 g1**

*Conclusion:* This is the same as the calculation in Part *a*. The Dulong-Petit rule allows the overall specific heat capacity *cs* of an alloy to be readily calculated from individual specific heat capacities *csA* and *csB* weighted by their weight fractions *wA* and *wB* in the alloy; not their atomic fractions.

***c.***The atomic mass of Zn, *M*at = 65.41 g mol1 and for Se,*M*at = 78.96 g mol1. In the molecule ZnSe, *n*Zn = *n*Se = 0.5, so the specific heat capacity of the compound ZnSe is therefore

**0.3463 J K1 g1.**

The value is in close agreement with the experimental value 0.345 J K1 g1.

**ADDENDUM**

Another equivalent way of calculating the specific heat capacity is as follows. The specific heat capacity of a compound consisting of *A* and *B* is



∴ 

The specific heat capacity of PbSn solder with composition 38 wt.% Pb and 62 wt.% Sn is therefore

∴ *cs* =  = **0.1764 J K1 g1**

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*Note:* Typical values quoted on the internet for *cs* for a 60-40 type Sn-Pb soldersare 0.150 J K1 g1

**1.20 Molecular collisions** Consider the atmosphere as made up from 80% N2 and 20% O2 gases. At a pressure *P*, the N2 and O2 gases will have partial pressure of *P*N and *P*O respectively so that *P* = *P*N + *P*O. If *n*N and *n*O are the concentration of *N*2 and O2 molecules respectively then *P*N = *n*N*kT*, and *P*O = *n*O*kT*, Consider a vacuum chamber in which the total pressure is 105torr. Assume 27 °C.

*a.* Calculate the concentrations of N2 and O2 gases in the chamber.

*b.* Suppose that we simply consider the collisions of N2 with N2 and O2 with O2 and neglect N2 and O2 collisions. Calculate the mean free path for N2 and O2 molecules. See Table 1.11

*c.* What are the mean free paths for each gas if the gas were in the container alone at 105torr.

*d.* Obviously the calculation in *b* is not correct because we neglected collisions between N2 and O2. Suppose that we try to improve our calculations by using some average value for the collisional radius *r* by averaging that involves the relative concentrations of molecular species in the tank, that is,



where the subscript 1 refers to molecular species 1 (N2) and 2 to species 2 (O2) and we take *n* = *n*1 + *n*2 in the mean free path equation since all molecules are involved in the collisions. Calculate the mean free path using these parameters. What is your conclusion?

**Table1.11** Radii for molecular or atomic collisions in gases. (Data from Walter J. Moore, Physical Chemistry, 5th Edition Longman, London, 1971)

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Molecule or atom | He | Ne | Ar | N2 | O2 | CO2 |
| *r* (nm) | 0.100 | 0.117 | 0.143 | 0.158 | 0.148 | 0.230 |

**Solution**

***a.*** Equation 1.30 for N2 (species 1) andO2 (species 2) gives

*P*1 = *n*1*kT* and *P*1 = *n*1*kT*

so that *P*=*P*1*+P*2 = *n*1*kT +n*2*kT* = (*n*1 + *n*2)*kT* = *nkT*

where  *n = n*1 *+ n*2.

that is *n* = *P* / *kT* = (1×105torr)(133.32 Pa/torr) / (1.3807×1023 J/K)(300 K)

∴ *n* = 3.219×1017 m3.

The individual concentrations of N2 and O2 are thus,

*n*1 = 0.80*n* = 0.80(3.219×1017 m3) = 2.575×1017 m3

and *n*2 = 0.20*n* = 0.20(3.219×1017 m3) = 6.438×1016 m3

***b.*** Now, consider N2 molecules colliding with N2 molecules, and ignore the presence of O2 molecules. Equation 2.29, with *r*1 = 0.158 nm (Table 1.11) gives the mean free path (MFP) as

 = **8.75 m**

and similarly for O2 colliding with O2, ignoring the presence of N2, and using *r*2 = 0.148 nm,

 = **39.9 m**

***c.*** Now assume all the molecules are N2 and *P* = 1 torr. *n* remains the same as above as *P* = 1 torr, and *n*1 = *n* = 3.219×1017 m3, so that the new mean free path is

 = **7.00 m**

Similarly for only O2 at *P* = 1 torr, *n*2 = *n,* and the new mean free path is

= **7.98 m**

***d.*** Consider the original case with 80% N2 and 20% O2 and *P* = 105torr. The total concentration is *n* is the same, 3.219×1017 m3, and is the concentration of both N2 and O2. The mean radius for collisions is now



∴ *r* = 0.156×109 m or 0.156 nm

The mean free path now between molecular collisions of any type is Equation 2.29 with the total concentration *n* (=3.219×1017 m3) and *r* (= 0.156 nm) given by the average above.

= **7.18 m.**

One clear conclusion in this case is that as long as the pressure*P* (e.g. 1 05torr) is given, the mean free path of molecules between collisions does not depend strongly on the species of molecules; compare the values for 1′, 2′ and , which range over 7.00 to 7.98 m.

*comment*: This is certainly true here inasmuch as N2 and O2 have collisional radii that are similar. If we had CO2 at *P* = 105torr, then the mean free path for molecular collisions is only 3.3 m. The collisional radius does affect the mean free path.

**1.21SF6 insulating gas in HV switchgear**. SF6 (sulfur hexafluoride) is a gas that has excellent insulating properties and is widely used in high voltage electric power applications, such as gas insulated switchgear and circuit breakers up to megavolts. Six F atoms surround the S atom so that there are 6 bonds in total along ±*x* and ±*y* and ±*z* directions. The SF6 gas in a particular sealed switchgear container has a pressure of 500 kPa (roughly 5 atm). Assume the temperature is 27 C (300K). (a) What is the SF6 concentration in the tank? (b) What is the heat capacity *CV* at constant volume per mole, assuming that we can neglect all vibrations of the molecule (but not rotations)? How does this compare with the reported experimental value in Table 1.9? (c) The diameter of the SF6 molecule is roughly 0.48 nm. What is the mean free path of SF6 molecules in the container?

**Solution**

**(a)** Equation 1.30 gives

*n* = *P* / *kT* = (500×103 Pa) / (1.3807×1023 J/K)(300 K)

∴ *n* = 1.207×1026 m3.

**(b)** SF6 has 3 translational and 3 rotational degrees of freedom. *Neglecting vibrations*, we have

*CV* = 3(*R*/2) + 3(*R/*2) = 3*R* = 25 J mol1.

The experimental value is 89 J mol1 K1, so that 89 – 25 = 64 J mol1 K1 is due to vibrations of the atoms in the molecule

**(c)** The radius of SF6, *r* = 0.48 / 2 = 0.24 nm

= 8.1×109 m or **8.1 nm.**

*Authors note:* Suppose we take a snap-shot of the molecules in the tank and try to calculate the mean separation *d*from

= 2.02 nm

This is less than because a molecule can pass several other molecules (travel farther than *d*) before it collides with another molecule.

**Figure 1Q21**The SF6 molecule

**\*1.22 Mean free path and gas discharge in Ar-ion laser** Consider the collisions of a free electron with the molecules of a gas inside a laser tube. The much lighter electron is much faster than the heavier gas molecules. From an electron's perspective, the molecules look stationary. Suppose that the electron has just collided with a gas molecule. It moves off in a particular direction and travels a distance , the mean free path of the electron, and collides again with another or a second molecule, as shown in Figure 1.79. As long as the electron is within the cross sectional area *S* of the second molecule, it will collide with it. Clearly, within the volume *S*, there must be at least one molecule inasmuch as the electron collides once after traveling the distance . If *n* is the concentration of molecules, then *nS* = 1, so that

 *Mean free path of electrons colliding with atoms or molecules*

Consider the argon gas inside an Ar-ion laser tube. The pressure of the gas in the tube is roughly 0.1 torr. The gas temperature during operation is approximately 1300 °C. A large applied electric field *E* accelerates a free electron somewhere in the gas. As the electron accelerates, it gains energy from the field and when it impacts an Ar atom, it ionizes it to Ar+ and releases a free electron that can also be accelerated, and so on. The ionization energy of the Ar atom is 15.8 eV. The radius of an Ar atom is approximately 0.143 nm. (a) What is the concentration of Ar atoms in the tube? (b) What is the mean free path of collisions between Ar atoms? (c) What is the mean free path of an electron colliding with Ar atoms? (d) Suppose that the electron is traveling along the force of the field *F* = *eE* so thatso that it gains an energy *Fd* in moving a distance *d*.What should be the electric field that would impart sufficient energy to the electron over a distance  so that upon collision it may be able to ionize the Ar atom.

**Figure 1.79** The mean free path of an electron in a gas. The electron has a negligible size compared with the scattering gas atom and the electron is much faster than the gas atom. Assume the gas atoms are stationary in determining the mean free path .

**Solution**

**(a)** Equation 1.30 can be used to find the concentration of Ar atoms, that is,

*n* = *P* / *kT* = (0.1 torr × 133.3 Pa/torr) / (1.3807×1023 J/K)(1300 + 273 K)

∴ *n* = 6.138×1020 m.

**(b)** Let Ar = mean free path of collisions between Ar atoms, then

= 0.0141 m

**(c)** Let *e* = mean free path of an electron colliding with Ar atoms, then

= 0.0254 m

**(d)** When an electron moves a distance *d* along the force of the field *F* = *eE*, it gains energy *dE* = *eEd*. Thus, when it moves a distance  without a collision, its energy reaches *E* = *eE*.The electron will ionize the Ar atom if *E* = *EI*, the ionization energy of the electron, or more. Thus we need,

*E* = *eE* = *EI*= (15.8 eV) × (1.6022×1019 J/eV)

∴ = **624.5 V m1 or 6.25 V cm1**

------------------------

*Note:* The actual field during discharge is somewhat higher than this because multiple ionizations are normally needed. If we know the applied field, we can calculate the distance over which, say *e*′, the electron accelerates before it collides with an Ar atom. Obviously *e*′<*e*.

*Comments:*

1. The approach in this question is highly simplified to highlight the concept and find very rough estimates rather than carry out accurate calculations. In fact, the cross section*r*2 that is involved in the ionization of an Ar atom is smaller than the actual cross section of the Ar atom, because the projectile electron may not necessarily ionize the Ar atom during its interactions with it. (The cross section also depends on the energy of the electron.).

2. As shown in Ch. 7, the breakdown in gases can be described by Paschen curves. Ina Paschen curve, the breakdown voltage (*V*br) is plotted against the pressure× electrodespacing product (*Pd*).Let's take *P* = 0.1 torr and *d* = 40 cm so that *Pd* = 4 torr⋅cm. The corresponding *V*br = 300 V and the field is very roughly *V*br/*d* = 300 V / 40 cm = 7.5 V cm1, which is, as expected, higher than our calculation. (See Gas Discharge Tubes and Paschen's Lawat <http://www.g3ynh.info/disch_tube/intro.html>, 25 October 2016)

**1.23 Thermal expansion**

*a***.**If*λ* is the thermal expansion coefficient, show that the thermal expansion coefficient for an area is 2λ. Consider an aluminum square sheet of area 1 cm2. If the thermal expansion coefficient of Al at room temperature (25 °C) is about 24 × 106 K1, at what temperature is the percentage change in the area +1%?

*b*. A particular incandescent light bulb (100 W, 120 V) has a tungsten (W) filament of length 57.9 cm, and a diameter of 63.5 μm. Calculate the length of the filament at 2300 °C, the approximate operating temperature of the filament inside the bulb. The linear expansion coefficient λ of W is approximately 4.50×106 K1 at 300 K. How would you improve your calculation?

**Solution**

***a.***Consider a rectangular area with sides *xo* and *yo*. Then at temperature *T0*,



and at temperature *T*,



that is

.

We can now use that  and neglect the term  because it is very small in comparison with the linear term  (*λ*<<1) to obtain,



So, the thermal expansion coefficient for an area is



The area of the aluminum sheet at any temperature is given by



where *Ao* is the area at the reference temperature *T0*. Solving for *T* we obtain,

= **233.3 °C**.

***b.***The linear expansion coefficient *λ* of tungsten (W) is approximately 4.50×106 K1 at 300 K. The length of W at 2300 °C (2573 K) is required. Considering the linear expansion coefficient *λ* is temperature independent the length will be



= 57.9 cm [1+ 4.50×106 K1(2573 K – 300 K)] = **58.49 cm.**

From Fig 1.20, we note that thethermal expansion coefficient is a function of temperature. The linear expansion coefficient *λ*of W at 2573 K is approximately 7.70×106 K1. The calculated length now will be



= 57.9 cm [1+ 7.70×106 K1(2573 – 300)] = **58.91 cm.**

------------------------

*Note:* The diameter of the filament is not required in the length expansion calculations; it is given for information only, to get a feel for its dimensions. Perhaps a better calculation would use an average **av*i.e.* (7.70×106 + 4.50×106)/2 = 6.1×106. This would give

*L* = 57.9 cm [1+ 6.1×106 K1(2573 – 300)] = **58.70 cm.**

**1.24 Thermal expansion of Si** The expansion coefficient of silicon over the temperature range 120-1500 K is given by Okada and Tokumaru (1984) as

 *Silicon linear expansion coefficient*

where *λ* is in K1 (or °C1) and *T* is in Kelvins.

*a.*By expanding the above function around 20 °C (293 K) show that,

 *Silicon linear expansion coefficient*

*b.*The change  in the density due to a change *δT* in the temperature, from Example 1.8, is given by



Given density of Si as 2.329 g cm3 at 20 ºC, calculate the density at 1000 ºC by using the full expression, and by using the polynomials expansion of *λ*. What is your conclusion?

**Solution**

a. We use Taylor series for series expansion of the function about a point. Taylor series expansion of a function *f*(*x*) about a point x = a is given by



We have to expand the thermal expansion coefficient about *a* = *T*0 = 293 K,

*f*(*x*) =

*f*(*a*)== 2.5086 × 106 K1.

*f′*(*a)*=

= 8.6632 × 109 K1.

*f*′(*a*) == - 4.7678 × 1011 K1.

Therefore the expansion will result in



∴ 

***b.***The expansion coefficient at 1000 °C (1273 K) will be



∴ *λ*(1273 K) = 4.4269×106 K1.

The density of Si at 293 K is 2.329 g cm3, the density at 1000 °C (1273 K) is thus

*ρ* =

= 2.329 g cm3 3 (2.329 g cm3)( 4.4269×106 K1)(1273 K – 293 K)= 2.2987 g cm3.

The density changes from 2.329g cm3 to 2.2987 g cm3, which 1.3% and it is a very small change.*For most engineering applications, we can therefore take the density to be approximately constant*.

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Note: The full citation is: Yasumasa Okada and YozoTokumaru " Precise determination of lattice parameter and thermal expansion coefficient of silicon between 300 and 1500 K", J. Applied Physics, *56,* 314 (1984); <http://dx.doi.org/10.1063/1.333965>.

**1.25Thermal expansion of GaP and GaAs**

*a.*GaP has the zinc blende structure. The linear expansion coefficient in GaP has been measured as follows: *λ*=4.65×106 K1 at 300 K; 5.27×106 K1 at 500 K;5.97×106 K1 at 800 K. Calculate the coefficients*A*, *B* and *C* in



where *To* = 300 K. The lattice constant of GaP,*a*, at 27 ºC is 0.5451 nm. Calculate the lattice constant at 300 ºC.

*b.*The linear expansion coefficient of GaAs over 200 K-1000 K is given by

** = 4.25×5.82×**2.82×*T*2  *GaAs linear expansion coefficient*

where *T* is in Kelvins. The lattice constant *a* at 300 K is 0.56533 nm. Calculate the lattice constant and the density at ─40 °C.

**Solution**

***a.*** Given that at

*T* = 300 K, *λ* = 4.65×106 K1

*T* = 500 K, *λ* = 5.27×106 K1

*T* = 800 K, *λ* = 5.97×106 K1

Thermal expansion coefficient is written as



Substitute the value of *T*0, and *λ* for 300 K in the above relation neglecting higher order terms



∴ ***A*= 4.65×106 K1**

At 500 K, the equation becomes



or  (1)

At 800 K, the equation becomes



or  (2)

Solving the two simultaneous equations (1) and (2) we have,

***B* = 3.407×109K2**

and ***C* = -1.533×1012 K3**

The equation for *λ*(*T*) thus becomes

****

We wish to find *a* at 300 °C or at 573 K (*=T*1), given *a*0 = 0.56533 nm at 300 K (= *T*0). The temperature range is *T*0 to *T*1 or 300 K to 573 K and the average temperature

*T*av = (*T*1 + *T*0) / 2 = (573 + 300)/2=436.5 K.

At *T* = *T*av, the thermal expansion coefficient is denoted as **av, and given by

and, ****

∴  ****av = 5.0864×106 K1**

The lattice constant *a*1 at *T*1 = 573 K is

= 0.5451 nm [1+ 5.0864×106 K1(573 – 300)] = **0.54586 nm**.

The most accurate solution is of course to integrate *T*) from *T*0 to *T*1, that is,

****

we can easily evaluate the integral to find,

*a*1 = **0.54586 nm**,

essentially the same as the simpler calculation using an average **av in the temperature range *T*0 to *T*1.

------------------

*Comment:* If we use the room temperature (300 K)******value then

= 0.5451 nm [1+ 4.65×106 K1(573 K – 300 K)]

= **0.54579 nm**.

This is 1.2% smaller than the actual value above.

------------------

***b.*** Let *T*1 = 40 °C = 40 + 273 K = 233 K. The average temperature *T*av over the range 233 to 300 K is

*T*av = (*T*1 + *T*0) / 2 = (233 + 300)/2 = 266.5 K.

At *T* = *T*av, the thermal expansion coefficient is denoted as **av, and given by

and, ****

∴  ****av = 4.0519×106 K1**

The lattice constant at ─40°C is

= 0.56533 nm [1+ 4.0519×106 K1(233 K – 300 K)]

= **0.56518 nm**.

It is left as an exercise to shows that if we integrate **, that is

****

yields ***a*1 = 0.56518** as the calculation above.

If we use the room temperature coefficient**0 = **(300 K) = 4.0500×106 K1, then*a*1= 0.56502 and is out by 2.9%.

To calculate the density, we need to know the number and type of atoms in the unit cell. Referring to the diamond crystal structure in Figure 1Q25-1, we can identify the following types of atoms

8 corner atoms labeled C,

6 face center atoms (labeled FC) and

4 inside atoms labeled 1,2,3,4.

The effective number of atoms within the unit cell is:

(8 Corners) × (1/8 C-atom) + (6 Faces) × (1/2 FC-atom) + 4 atoms within the cell (1, 2, 3, 4) = 8

**Figure 1Q25-1:** The diamond crystal structure, the unit cell (left)and GaAs (right).

In the GaAs crystal, shown in Figure 1Q25-1 (right), it is apparent that there are 4 Ga and 4 As atoms in the unit cell. The concentration of Ga (or As) atoms per unit volume (*n*Ga) is



There are 4/*a*3 Ga-As pairs per m3. We can calculate the mass of the Ga and As atoms from their relative atomic masses in the Periodic Table. Taking *M*at(Ga) = *M*Ga = 69.72 g/mol for Ga and *M*at(As) = *M*As = 74.92 g/mol for As, the density of the crystal is



or 

∴ 

*i.e.* ***ρ* = 5.322× 103 kg m3**or **5.322 g cm3**

**1.26 Bimetal cantilever devices** Consider two thin plate strips of equal length that are welded to each other as shown in Figure 1.80a. Suppose that metal *B* has a large thermal expansion coefficient *B* than *A*. *A* and *B* are of equal length *Lo* at *To*. When the temperature increases by *T*, *B* extends more than *A* so that the extension in lengths can only be accommodated if the two-metal system bends to form an arc of a circle centered at *O* as in Figure 1.80b. Center-to-center separation of the strips is *d*/2 so that the strip thickness is *d* and the two metals are assumed to have the same thickness. Suppose that *LA* and *LB* are the new lengths (along the center of the strip), then

*LA* = *Lo*(1 + *A**T*) and *LB* = *Lo*(1 + *B**T*)

Figure 1.80 (a) Two different thin metals of identical length at *To*. (b) The lengths are different at a higher temperature. *B* expands more than *A*. The two metals bend to form an arc of a circle centered at *O* with a radius *R*. The arc subtends an angle ** at *O*.

Both lengths have the same angle ** at *O* as shown in Figure 1.80b. Show that

 *Bending of a bimetallic strip*

Show that the deflection *h* (very small) can be calculated from the geometry once we know ** , that is, for small **

* Bend height of a bimetallic strip*

(Hint: *Lo*/*R*≈ sin** and (*R**h*)/*R* ≈cos** and then expand in terms of small ** )

Consider a steel-brass bimetallic strip cantilever as in Figure 1.80a, that is 1 mm thick and 100 mm long. The thermal expansion coefficient for steel is 10×10°C1, and for brass, it is 20×10°C1. If the bimetallic strip is flat at 20 °C, what is the deflection at 100 °C?

**Solution**

Both strip lengths (*A* and *B*) have the same angle ** at *O* as shown in Figure 1.80b. If *R* is the radius of curvature from *O* to the strip,

(*R**d*/4)** = *LA* = *Lo*(1 + *A**T*)

and (*R* 3*d*/4)**= *LB* = *Lo*(1 + *B**T*)

so that subtracting one from the other, we get,

 *Bending of a bimetallic strip* 

Clearly,** is proportional to the temperature change *T* and to the differential thermal expansion coefficient (*B**A*). It can be easily calculated given *Lo, d, A*and*B.*

The deflection *h* can be calculated from the geometry once we know **. We can use straightforward trigonometry to find *h* from *Lo* and ** in Figure 1.80b, that is,

*Lo*/*R*≈sin**

and (*R**h*)/*R*≈cos**

so that we can eliminate *R* (not measurable) between these two equations and solve for *h*

**

Usually ** is small, and we can expand cos** and sin** to find\*

* Bend height of a bimetallic strip* (2)

Take *A* to be steel, *A* = 10×10°C1 and *B* to be brass, *B* = 20×10°C1. The temperature change *T* = 100 – 20 °C. Given the bimetal dimensions are *Lo* = 100 mm and *d* = 1 mm, Equation (1) gives,

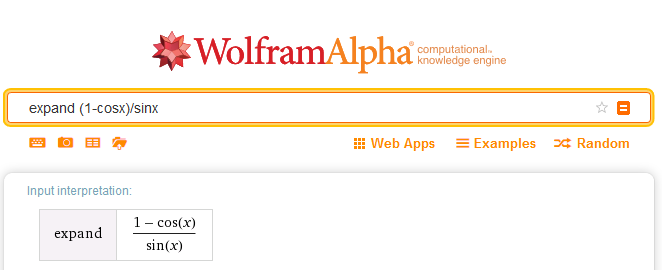
= 0.16 rad or 9.17°.

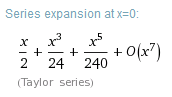
The deflection is

**= 8.0 mm

or the deflection is 0.1 mm per °C change.

------------------

\**Comment:* Using http://www.wolframalpha.com 1(



so that the first term in the expansion is **/2

**1.27 Electrical noise**Consider an amplifier with a bandwidth *B* of 5 kHz, corresponding to a typical speech bandwidth. Assume the input resistance of the amplifier is 1 MΩ. What is the rms noise voltage at the input? What will happen if the bandwidth is doubled to 10 kHz? What is your conclusion?

**Solution**

Bandwidth: *B* = 5 × 103 Hz

Input resistance: *R*in = 106Ω

Assuming room temperature: *T* = 300 K

The noise voltage (or the rms voltage, *vrms*) across the input is given by:

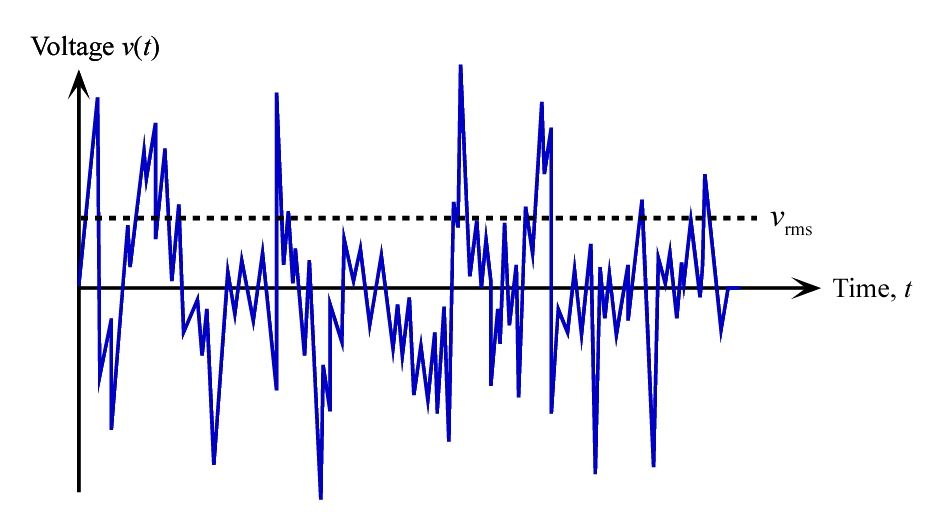


∴ ***v*rms= 9.10 × 106 V** or **9.1 μV**

If the bandwidth is doubled: *B′*= 2 × 5 × 103 = 10 × 103 Hz

∴ **= 1.29 × 105 V** or **12.9 μV**

The larger the bandwidth, the greater the noise voltage. 510 kHz is a typical speech bandwidth and the input signal into the amplifier must be much greater than 13 μV for amplification without noise added from the amplifier itself.



**Figure 1Q27-1:** Random motion of conductions electrons in a conductor results in electrical noise.

**1.28 Thermal activation**A certain chemical oxidation process (e.g., SiO2) has an activation energy of 2 eV atom1.

*a.*Consider the material exposed to pure oxygen gas at a pressure of 1 atm. at 27 °C. Estimate how many oxygen molecules per unit volume will have energies in excess of 2 eV? (Consider numerical integration of Equation 1.24)

*b*.If the temperature is 900 °C, estimate the number of oxygen molecules with energies more than 2 eV. What happens to this concentration if the pressure is doubled?

**Solution**

**Method 1:Estimation**

The activation energy (*EA*) is 2 eV per atom or

*EA* = (2 eV/atom)(1.602 × 1019 J/eV) = 3.204 × 1019 J/atom

***a.***We are given pressure *P* = 1 atm = 1.013 × 105 Pa and temperature *T* = 300 K. If we consider a portion of oxygen gas of volume *V* = 1 m3 (the unit volume), the number of molecules present in the gas (*N*) will be equal to the concentration of molecules in the gas (*n*), *i.e.*: *N* = *n*. And since we know *η* = *N*/*NA*, where *η* is the total number of moles and *NA* is Avogadro’s number, we can make the following substitution into the equation *PV* = *ηRT*:



isolating*n*, 

∴ *n* = 2.445 × 1025 m3

Therefore there are 2.445 × 1025 oxygen molecules per unit volume.

For an estimation of the concentration of molecules with energy above 2 eV, we can use the following approximation (remember to convert *EA* into Joules). If *nA* is the concentration of molecules with E > EA, then:



∴ 

∴ *nA* = 6.34 × 109 m3

However, this answer is only in the right order of magnitude. For a better calculation we need to use a numerical integration of *n*(*E*) from *EA* to ∞.

***b.***At *T* = 900 ºC + 273 = 1173 K and *P* = 1 atm, the same method as above can be used to find the concentration of molecules with energy greater than *EA*. After calculations, the following numbers will be obtained:

*n* = 6.254 × 1024 m3

*nA*= 1.61 × 1016 m3

This corresponds to an increase by a factor of 1025 compared to a temperature of T = 300 K.

Doubling the pressure doubles *n* and hence doubles *nA*. In the oxidation of Si wafers, high pressures lead to more rapid oxidation rates and a shorter time for the oxidation process.

**Method 2: Numerical Integration**

To find the number of molecules with energies greater than *EA* = 2 eV more accurately, numerical integration must be used. Suppose that *N* is the total number of molecules. Let

*y* = *nE*/*N*

where *nE* is the number of molecules per unit energy, so that *nEdE* is the number of molecules in the energy range *dE*.

Define a new variable *x* for the sake of convenience:



∴ *E* = *kTx*

where *E* is the energy of the molecules. Using partial differentiation:

*dE* = *kT dx*

The energy distribution function is given by:



substitute: 

simplify: 

Integration of *y* with respect to *E* can be changed to that with respect to *x* as follows:



∴  (substitute*dE* = *kT dx*)

We need the lower limit *xA* for *x* corresponding to *EA*



This is the activation energy *EA* in terms of *x*.

We also need the upper limit, *xB*which should be ∞, but we will take it to be a multiple of:

*xB* = 2 ×*xA* = 154.72

We do this because the numerical integration is difficult with very small numbers, e.g. exp(─*xA*) = 2.522 × 1034.

The fraction, *F*, of molecules with energies greater than *EA* (= *xA*) is:



At T = 300 K, P = 1 atm = 1.013 × 105Pa, and V = 1 m3, the number of molecules per unit volume is n:



∴ 

The concentration of molecules with energy greater than *EA* (*nA*) can be found using the fraction *F*:

***nA***= *nF*= (2.445 × 1025 m3)(2.519 × 1033) = **6.16 × 108 m3**

If we estimate *nA* by multiplying *n* by the Boltzmann factor as previously:



The estimateis out by a factor of about 10.

***b.***The concentration *nA* of molecules with energies greater than *EA* can be found at *T* = 900 °C + 273 = 1173 K, using the same method as in part ***a***. After calculations, the following values will be obtained:

*F* = 1.3131 × 108

*n* = 6.254 × 1024 m3

***nA* = 8.21 × 1016 m3**

If we compare this value to the one obtained previously through estimation (1.61 × 1016 m3), we see that the estimate is out by a factor of about 5. As stated previously, doubling the pressure doubles *n* and hence doubles *nA*. In the oxidation of Si wafers, high pressures lead to more rapid oxidation rates and a shorter time for the oxidation process.

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*Comment:* Calculations of the type in Method 1, are often called "back-of-an-envelope" calculations. A factor of ~5 in numbers around 1016 is not a big price to pay for a quick back-of-an-envelope calculation to estimate the order of magnitude for the number of atoms with energies exceeding *EA*

**1.29 Diffusion in Si**The diffusion coefficient of boron (B) atoms in a single crystal of Si has been measured to be 1.5 ×1018 m2 s1 at 1000 ºC and 1.1 ×1016 m2 s1 at 1200 ºC.

*a*.What is the activation energy for the diffusion of B, in eV/atom?

*b*.What is the pre-exponential constant *Do*?

*c*.What is the rms distance (in micrometers) diffused in 1 hour by the B atom in the Si crystal at 1200 ºC and 1000 ºC?

*d*.The diffusion coefficient of B in polycrystalline Si has an activation energy of 2.4-2.5 eV/atom and *Do* = (1.5-6) × 107 m2 s1. What constitutes the diffusion difference between the single crystal sample and the polycrystalline sample?

**Solution**

Given diffusion coefficients at two temperatures:

*T*1= 1200 °C + 273 = 1473 K *D*1 = 1.1 × 1016 m2/s

*T*2= 1000 °C + 273 = 1273 K *D*2 = 1.5 × 1018 m2/s

***a.***The diffusion coefficients *D*1 and *D*2 at *T*1 and *T*2 respectively are given by:

where *EA* is the activation energy in eV/atom and *q* = 1.6×1019 J/eV (conversion factor from eV to J).Since,



we can take the ratio of the diffusion coefficients to express them in terms of *EA* (eV):



∴  (in eV)

∴ 

∴ ***EA* = 3.47 eV/atom**

***b.***To find *Do*, use one of the equations for the diffusion coefficients:



∴ 

∴ ***D0*= 8.12 × 105 m2/s**

***c.***Given: time (*t*) = (1 hr) × (3600 s/hr) = 3600 s

At 1000 °C, rms diffusion distance (*L*1000 °C) in time *t* is given by:

*L*1000 °C

∴ ***L*1000 °C = 1.04 × 107 m** or **0.104 μm**

At 1200 °C:

*L*1200 °C

∴***L*1200 °C = 8.90 × 107 m** or **0.89 μm** (almost 10 times longer than at 1000 °C)

**d.**Diffusion in polycrystalline Si would involve diffusion along grain boundaries, which is easier than diffusion in the bulk. The activation energy is smaller because it is easier for an atom to break bonds and jump to a neighboring site; there are vacancies or voids, broken bonds, and strained bonds in a grain boundary.

**1.30 Diffusion in SiO2**The diffusion coefficient of P atoms in SiO2 has an activation energy of 2.30 eV/atom and *Do* = 5.73 × 109 m2 s1. What is the rms distance diffused in 1 hour by P atoms in SiO2 at 1200 °C?

**Solution**

Given: Temperature: *T* = 1200 °C + 273 = 1473 K

Diffusion coefficient: *Do* = 5.73 × 109 m2/s

Activation energy: *EA* = 2.30 eV/atom

Time: *t* = (1 hr) × (3600 s/hr) = 3600 s

Using the following equation, find the diffusion coefficient *D*:



∴ = 7.793 × 1017 m2/s

The rms diffusion distance (*L*1200 °C) is given as:

*L*1200 °C =

∴ ***L*1200 °C = 7.49 × 107 m** or **0.75 μm**

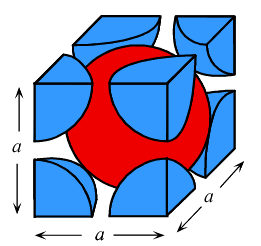
Comment: The P atoms at 1200 °C seem to be able to diffuse through an oxide thickness of about 0.75 μm.

**1.31 BCC and FCC crystals**

*a.*Molybdenum has the BCC crystal structure, has a density of 10.22 g cm3 and an atomic mass of 95.94 g mol1. What is the atomic concentration, lattice parameter a, and atomic radius of molybdenum?

*b.*Gold has the FCC crystal structure, a density of 19.3 g cm3 and an atomic mass of 196.97 g mol1. What is the atomic concentration, lattice parameter a, and atomic radius of gold?

**Solution**



**Figure 1Q31-1** BCC unit cell. The center atom is shown red. The cube diagonal is (*a*2 + *a*2 + *a*2)1/2. It is also 4*R.* Therefore 31/2*a* = 4*R*

**Table 1Q31-1** Characteristics of BCC and FCC unit cells

****

***a.***Since molybdenum has BCC crystal structure, there are 2 atoms in the unit cell. (See Figure 1Q31-1 and Table 1Q31-1 .) The density is



that is, 

Solving for the lattice parameter *a* we receive

= **3.147 × 1010 m = 0.3147 nm**

The atomic concentration*n*at is 2 atoms in a cube of volume *a*3, *i.e.*

= **6.415 × 1022 cm3 = 6.415 × 1028 m3**

For a BCC cell, the lattice parameter *a* and the radius of the atom *R* are in the following relation (listed in Table 1.3):

= **1.363 × 1010 m 0.1363 nm**

***b.***Gold has the FCC crystal structure (see Figure 1Q31-2), hence, there are 4 atoms in the unit cell (as shown in Table 1.3).

The lattice parameter *a* is

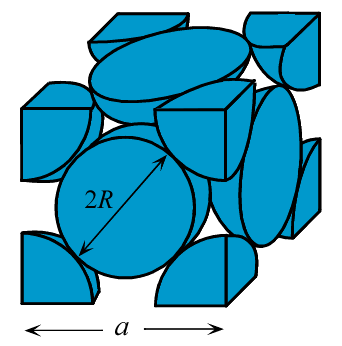
= **4.077 × 1010 m = 0.4077 nm**

The atomic concentration is

= **5.901 × 1022 cm3 = 5.901 × 1028 m3**

For an FCC cell, the lattice parameter *a* and the radius of the atom *R* are in the following relation (shown in Table 1.3):

= **1.442 × 1010 m = 0.1442 nm**



**Figure 1Q31-2** FCC unit cell

**1.32 BCC and FCC Crystals**

*a.*Tungsten (W) has the BCC crystal structure. The radius of the W atom is 0.1371 nm. The atomic mass of W is 183.8 amu (g mol1). Calculate the number of W atoms per unit volume and density of W.

*b.*Platinum (Pt) has the FCC crystal structure. The radius of the Pt atom is 0.1386 nm. The atomic mass of Pt is 195.09 amu (g mol1). Calculate the number of Pt atoms per unit volume and density of Pt.

**Solution**

***a.***Consider a cube diagonal with two corner atoms and the central atom in contact. The length of the diagonal is 4*R*. Therefore

*a*2 + *a*2 + *a*2 = (4*R*) 2

or 

Thus for W,0.3166 nm

In the BCC structure, the total number of atoms == 2 atoms.

The density of W is therefore



= 19.23 × 103 kg m3 or 19.23 g cm3

The atomic concentration of W with 2 atoms per unit cell is



**= 6.303×1028 m3 or 6.303×1022 cm3**

***b****.*Consider a face diagonal with corner atoms and the central atom in contact. The length of the diagonal is 4*R*. Therefore

*a*2 + *a*2 = (4*R*) 2

or 

Thus for Pt, 0.3920 nm

In the FCC structure, the total number of atoms == 4 atoms

The density of Pt is therefore



= **21.51 × 103 kg m3** or **21.51 g cm3**.

The atomic concentration of Pt with 4 atoms per unit cell is



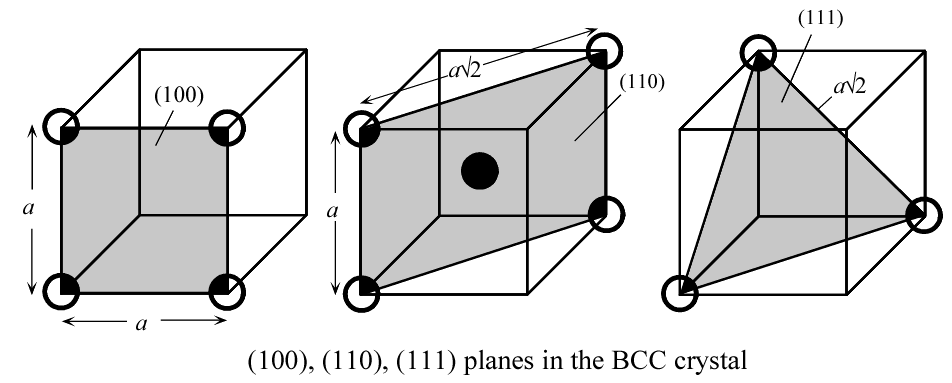
= **6.64×1028 m3** or **6.64×1022 cm3**.

**1.33 Planar and surface concentrations**Niobium (Nb) has the BCC crystal with a lattice parameter *a* = 0.3294 nm. Find the planar concentrations as the number of atoms per nm2 of the (100), (110) and (111) planes. Which plane has the most concentration of atoms per unit area? Sometimes the number of atoms per unit area *n*surface on the surface of a crystal is estimated by using the relation *n*surface = *n*bulk2/3 where *n*bulk is the concentration of atoms in the bulk. Compare *n*surface values with the planar concentrations that you calculated and comment on the difference. [*Note:* The BCC (111) plane does not cut through the center atom and the (111) has one-sixth of an atom at each corner.]

**Solution**

Planar concentration (or density) is the number of atoms per unit area on a given plane in the crystal. It is the surface concentration of atoms on a given plane. To calculate the planar concentration *n(hkl*) on a given (*hkl*) plane, we consider a bound area *A*. Only atoms whose centers lie on *A* are involved in the calculation of *n*(*hkl*). For each atom, we then evaluate what portion of the atomic cross section cut by the plane (*hkl*) is contained within *A*.

For the BCC crystalline structure the planes (100), (110) and (111) are drawn in Figure 1Q33-1.



**Figure 1Q33-1:** (100), (110), (111) planes in the BCC crystal

Consider the (100) plane.

Number of atoms in the area *a*×*a*, which is the cube face = (4 corners) × (1/4th atom at corner) = 1.

Planar concentration is

= **9.216 × 1018 atoms m2**

The most populated plane for BCC structure is (110).

Number of atoms in the area  defined by two face-diagonals and two cube-sides

= (4 corners) × (1/4th atom at corner) + 1 atom at face center = 2

Planar concentration is

= **1.303 × 1019atoms m2**

The plane (111) for the BCC structure is the one with rarest population. The area of interest is an equilateral triangle defined by face diagonals of length(see Figure 1Q33-1).The height of the triangle isso that the triangular area is. An atom at a corner only contributes a fraction (60°/360°=1/6) to this area.

So, the planar concentration is

= **5.321 × 1018 atoms m2**

For the BCC structure there are two atoms in unit cell and the bulk atomic concentration is



= **5.596 × 1028 atoms m3**

and the surface concentration is

= **1.463 × 1019 atoms m2**

**1.34 Diamond and zinc blende**Si has the diamond and GaAs has the zinc blende crystal structure. Given the lattice parameters of Si and GaAs, *a* = 0.543 nm and *a* = 0.565 nm, respectively, and the atomic masses of Si, Ga, and As as 28.08, 69.73 g/mol, and 74.92, respectively, calculate the density of Si and GaAs. What is the atomic concentration (atoms per unit volume) in each crystal?

**Solution**

Referring to the diamond crystal structure in Figure 1Q34-1, we can identify the following types of atoms

8 corner atoms labeled C,

6 face center atoms (labeled FC) and

4 inside atoms labeled 1,2,3,4.

The effective number of atoms within the unit cell is:

(8 Corners) × (1/8 C-atom) + (6 Faces) × (1/2 FC-atom) + 4 atoms within the cell (1,2,3,4) = 8



**Figure 1Q34-1:** The diamond crystal structure.

The lattice parameter (lengths of the sides of the unit cell) of the unit cell is *a*. Thus the atomic concentration in the Si crystal (*n*Si) is

= **5.0 × 1028 atoms per m3**

If *M*at is the atomic mass in the Periodic Table then the mass of the atom (*mat*) in kg is

*mat* = (103 kg/g)*Mat*/*N*A (1)

where *NA* is Avogadro’s number. For Si, *Mat* = *M*Si = 28.09 g/mol, so then the density of Si is

*ρ* = (number of atoms per unit volume) × (mass per atom) = *n*Si*mat*

or 

*i.e.* **= 2.33 × 103 kg m3** or **2.33 g cm3**

In the case of GaAs, it is apparent that there are 4 Ga and 4 As atoms in the unit cell. The concentration of Ga (or As) atoms per unit volume (*n*Ga) is

= **2.22 × 1028 m3**

*Total atomic concentration* (counting both Ga and As atoms) is twice *n*Ga.

***n*Total** = 2*n*Ga = **4.44 × 1028 m3**

There are 2.22 × 1028 Ga-As pairs per m3. We can calculate the mass of the Ga and As atoms from their relative atomic masses in the Periodic Table using Equation (1) with *Mat* = *M*Ga = 69.72 g/mol for Ga and *Mat* = *M*As = 74.92 g/mol for As. Thus,



or 

*i.e.* ***ρ* = 5.33 × 103 kg m3** or **5.33 g cm3**

**1.35 Zinc blende, NaCl and CsCl**

*a*.InAs is a III-V semiconductor that has the zinc blende structure with a lattice parameter of 0.606 nm. Given the atomic masses of In (114.82 g mol1) and As (74.92 g mol1), find the density.

*b*.CdO has the NaCl crystal structure with a lattice parameter of 0.4695 nm. Given the atomic masses of Cd (112.41 g mol1) and O (16.00 g mol1), find the density.

*c*. KCl has the same crystal structure as NaCl. The lattice parameter *a* of KCl is 0.629 nm. The atomic masses of K and Cl are 39.10 g mol1 and 35.45 g mol1 respectively. Calculate the density of KCl.

**Solution**

***a.***For zinc blende structure there are 8 atoms per unit cell (as shown in Table 1.3). In the case of InAs, it is apparent that there are 4 In and 4 As atoms in the unit cell. The density of InAs is then



= **5.66 × 103 kg m3 = 5.66 g cm3**

***b.***For NaCl crystal structure, there are 4 cations and 4 anions per unit cell. For the case of CdO we have 4 Cd atoms and 4 O atoms per unit cell and the density of CdO is



 = **8.24 × 103 kg m3 = 8.24 g cm3**

***c.***Similarly to ***b***, for the density of KCl we receive



= **1.99 × 103 kg m3 = 1.99 g cm3**

**1.36 Crystallographic directions and planes**Consider the cubic crystal system.

*a*. Show that the line [*hkl*] is perpendicular to the (*hkl*) plane.

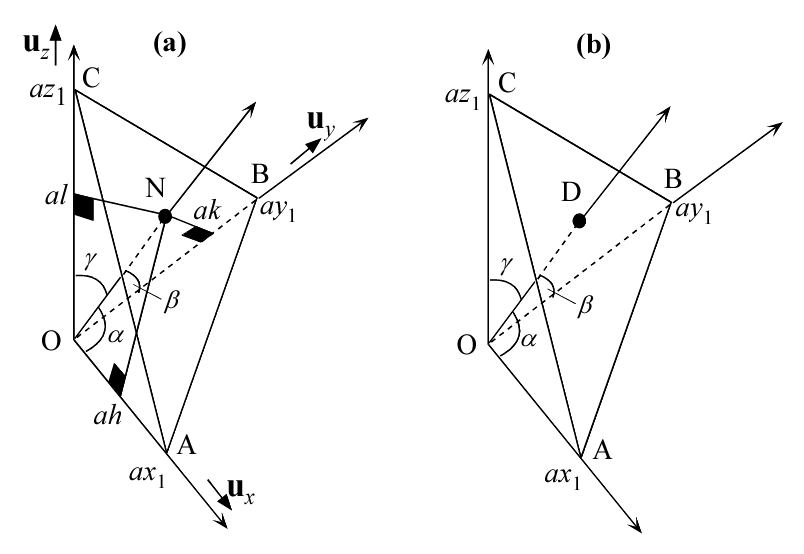
*b*. Show that the spacing between adjacent (*hkl*) planes is given by



**Solution**

This problem assumes that students are familiar with three dimensional geometry and vector products.

Figure 1Q36-1(a) shows a typical [*hkl*] line, labeled as **ON**, and a (*hkl*) plane in a cubic crystal. **u***x*, **u***y* and **u***z* are the unit vectors along the *x*, *y*, *z* coordinates. This is a cubic lattice so we have Cartesian coordinates and **ux**⋅**ux** = 1 and **u***x*⋅**u***y* = 0 etc.



**Figure 1Q36-1:** Crystallographic directions and planes

***a.***Given *a* = lattice parameter, then from the definition of Miller indices (*h* = 1/*x*1, *k* = 1/*y*1 and *l* = 1/*z*1), the plane has intercepts: *xo* = *ax*1 =*a*/*h*; *yo* = *ay*1 = *a*/*k*; *zo* = *az*1 = *a*/*l*.

The vector **ON** = *ah***u***x* + *ak***u***y* + *al***u***z*

If **ON** is perpendicular to the (*hkl*) plane then the product of this vector with any vector in the (*hkl*) plane will be zero. We only have to choose 2 non-parallel vectors (such as **AB** and **BC**) in the plane and show that the dot product of these with **ON** is zero.

**AB** = **OB****OA**= (*a*/*k*)**u***y* (*a*/*h*)**u***x*

**ON⋅AB** = (*ah***u***x* + *ak***u***y* + *al***u***z*) **⋅**((*a*/*k*)**u***y* (*a*/*h*)**u***x*) = *a*2*a*2 = 0

Recall that **u***x***u***x* = **u***y***u***y* =1 and **u***x***u***y* = **u***x***u***z* = **u***y***u***z*= 0

Similarly, **ON⋅BC** = (*ah***u***x* + *ak***u***y* + *al***u***z*)**⋅** ((*a*/*l*)**u***z* (*a*/*k*)**u***y*) = 0

Therefore **ON** or [*hkl*] is normal to the (*hkl*) plane.

***b.*** Suppose that **OD** is the normal from the plane to the origin as shown in Figure 1Q36-1(b). Shifting a plane by multiples of lattice parameters does not change the miller indices. We can therefore assume the adjacent plane passes through O. The separation between the adjacent planes is then simply the distance **OD** in Figure 1Q36-1(b).

Let *α*, *β* and *γ* be the angles of **OD** with the *x*, *y* and *z* axes. Consider the direction cosines of the line **OD**: cos*α* = *d*/(*ax*1) = *dh*/*a*; cos*β* = *d*/(*ay*1) = *dk*/*a*; cos*γ* = *d*/(*az*1) = *dl*/*a*

But, in 3 dimensions,(cos*α*)2 + (cos*β*)2 + (cos*γ*)2 = 1

Thus, (*d*2*h*2/*a*2) + (*d*2*k*2/*a*2) + (*d*2*l*2/*a*2) = 1

Rearranging, *d*2 = *a*2 / [*h*2 +*k*2+ *l*2]

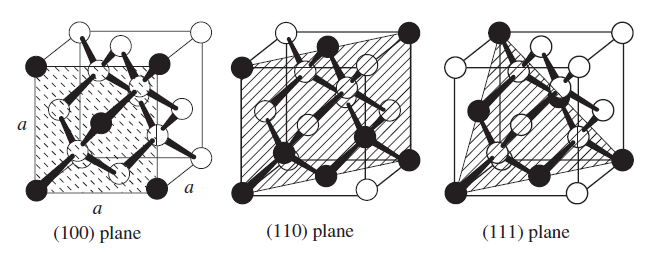
or, ***d*= *a*/ [*h*2 + *k*2 + *l*2]1/2**

**1.37 Si and SiO2**

*a*.Given the Si lattice parameter *a* = 0.543 nm, calculate the number of Si atoms per unit volume, in nm3.

*b*. Calculate the number of atoms per m2 and per nm2 on the (100), (110) and (111) planes in the Si crystal as shown on Figure 1.81. Which plane has the most number of atoms per unit area?

*c*. The density of SiO2 is 2.27 g cm3. Given that its structure is amorphous, calculate the number of molecules per unit volume, in nm3. Compare your result with (a) and comment on what happens when the surface of an Si crystal oxidizes. The atomic masses of Si and O are 28.09 and 16, respectively.



**Figure 1.81:** Diamond cubic crystal structure and planes. Determine what

portion of a black-colored atom belongs to the plane that is hatched.

**Solution**

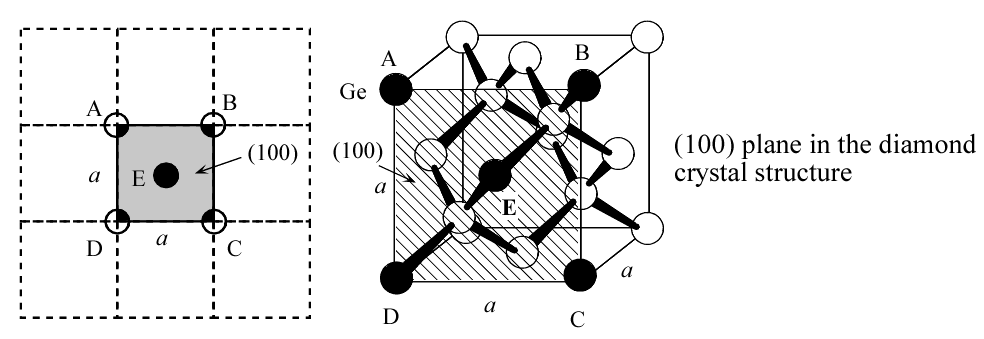
***a.***Si has the diamond crystal structure with 8 atoms in the unit cell, and we are given the lattice parameter *a* = 0.543 × 109 m and atomic mass *Mat* = 28.09 × 103 kg/mol. The concentration of atoms per unit volume (*n*) in nm3 is therefore:

**=50.0 atoms/nm3**

If desired, the density *ρ* can be found as follows:

= **2331 kg m3** or **2.33 g cm3**

***b.***The (100) plane has 4 shared atoms at the corners and 1 unshared atom at the center. The corner atom is shared by 4 (100) type planes. Number of atoms per square nm of (100) plane area (*n*) is shown in Fig. 1Q37-1:



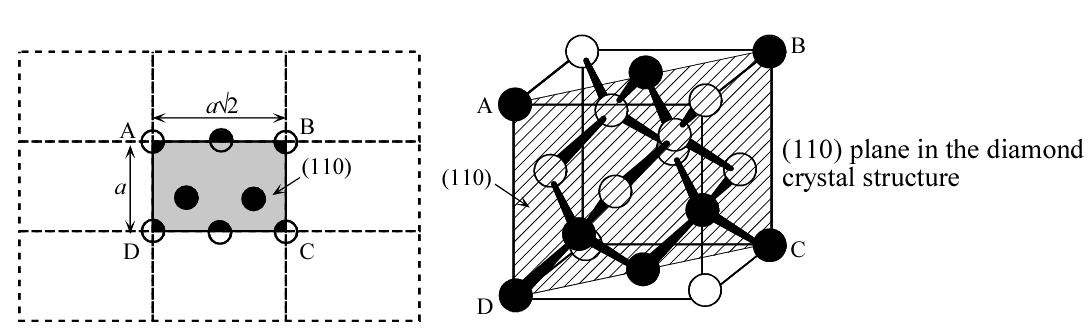
**Figure 1Q37-1:** The (100) plane of the diamond crystal structure.

The number of atoms per nm2, *n*100, is therefore:



∴ ***n*100 = 6.78 atoms/nm2** or **6.78 × 1018 atoms/m2**

The (110) plane is shown below in Fig. 1Q37-2. There are 4 atoms at the corners and shared with neighboring planes (hence each contributing a quarter), 2 atoms on upper and lower sides shared with upper and lower planes (hence each atom contributing 1/2) and 2 atoms wholly within the plane.



**Figure 1Q37-2:** The (110) plane of the diamond crystal structure.

The number of atoms per nm2, *n*110, is therefore:

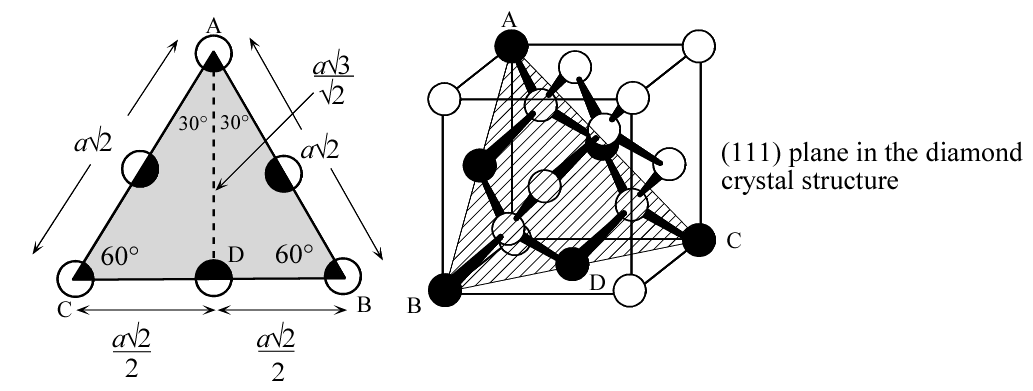


∴ 

∴ ***n*110 = 9.59 atoms/nm2** or **9.59 × 1018 atoms/m2**

This is the most crowded plane with the most number of atoms per unit area.

The (111) plane is shown below in Fig. 1Q37-3:



**Figure 1Q37-3:** The (111) plane of the diamond crystal structure

The number of atoms per nm2, *n*111, is therefore:



∴ 

∴ ***n*111 = 7.83 atoms/nm2** or **7.83 × 1018 atoms/m2**

***c.***Given:

Molar mass of SiO2: *M*at = 28.09 × 103 kg/mol + 2 × 16 × 103 kg/mol = 60.09 × 103 kg/mol

Density of SiO2: *ρ* = 2.27 × 103 kg m3

Let *n* be the number of SiO2 molecules per unit volume, then:



∴ = 2.27 × 1028 molecules per m3

Or, converting to molecules per nm3,



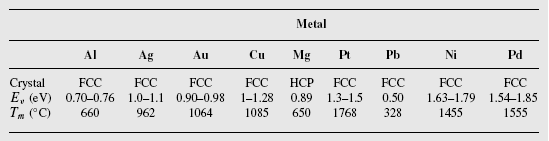
Oxide has less dense packing so it has a more open structure. For every 1 micron of oxide formed on the crystal surface, only about 0.5 micron of the Si crystal is consumed.

**1.38 Vacancies in metals**

*a.*The energy of formation of a vacancy in the copper crystal is about 1 eV. Calculate the concentration of vacancies at room temperature (300K) and just below the melting temperature, 1084 °C. Neglect the change in the density which is small.

*b.*The table below shows the energies of vacancy formation in various metals with *close-packed* crystal structures and the melting temperature *Tm*. Plot *Ev* in eV vs. *Tm* in Kelvins, and explore if there is a correlation between *a* and *Tm*. Some materials engineers take *Ev* to be very roughly 10*kTm*. Do you think that they are correct? (Justify.)

**Table 1.12** Energy of formation of vacancies for selected metals



**Solution**

***a****.* Equilibrium concentration of vacancies is given by



where *N* is atomic concentrations. Vacancy formation energy *Ev* = 1 eV × (1.6×1019 J eV1) = 1.6×1019 J. The atomic mass of Cu is *M*at = 63.54 g mol1 and the density at 293 K is 8.96 g cm3.

Atomic concentration is calculated as



= 8.49×1022 cm3 or 8.49×1028 m3

At *T* = 300 K



***nv***= **1.42 × 1012 m3 or *nv***= **1.42 × 106cm3.**

This implies that there is a vacancy in every 5.97 × 1010 atoms (= *N/nv*)

At *T* = 1084°C (1357 K)



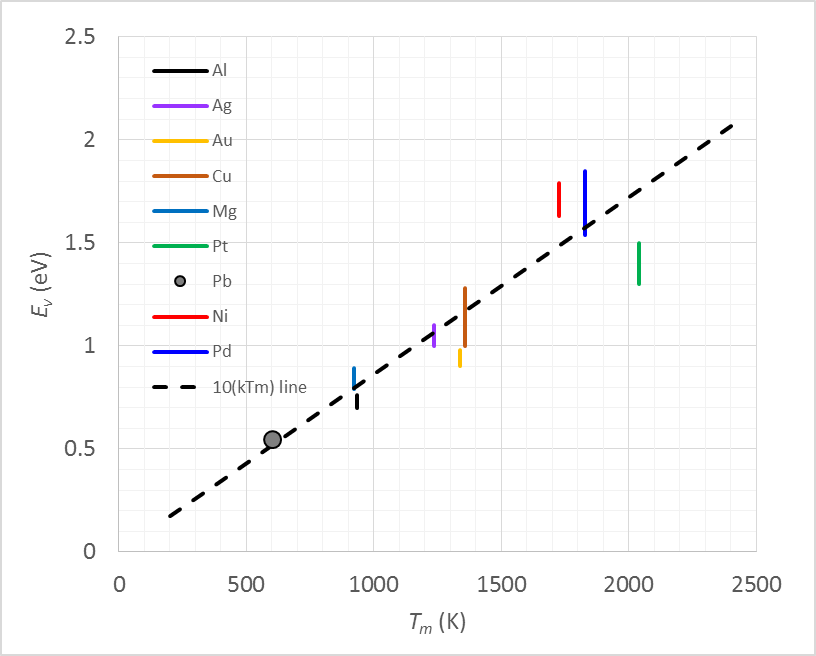
***nv***=**1.66× 1025 m3 or *nv***= **1.66× 1019cm3.**

This implies that 1 in 5115 atoms is a vacancy.

A better calculation would use the atomic concentration *N* at 1357 K by calculation the new density at 1357 K through the thermal coefficient of volume expansion. However, its effect on the final result is small.

***b.*** The vacancy formation *E*v and the melting temperature *Tm*in K are plotted in Figures 1Q38-1 and 1Q38-2. Table 1Q38-1 provides the values that were used in these plots.

The 10*kT*m line is also plotted on the same graph. It seems that this is a reasonable approximation to predicting *Ev*. Table 1.12 has range of values for most of the metals.



**Figure 1Q38-1:** Plot of vacancy formation energy versus melting temperature *T*m. The 10*kT*m line is also plotted on the same graph.

**Figure 1Q38-2:** Plot of vacancy formation energy versus melting temperature *T*m. The 10*kT*m line is also plotted on the same graph.

**Table 1Q38-1**Values used in Figure 1Q38-2

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Metal** | **k (eV/K)** | **8.62E-05** | **m =** | **10** |  |  |  |  |  |
|  | **Tm (C )** | **Tm (K)** | **Ev (eV)** | **Tm (K)** | **Ev (eV)** | **Tm (K)** | **Ev (eV)** | **Tm (K)** | **10(kTm)** |
| **Al** | **660** | **933** | **0.7** | **933** | **0.7** | **933** |  | **200** | **1.72E-01** |
| **Al** | **660** | **933** | **0.76** | **933** |  | **933** | **0.76** | **400** | **3.45E-01** |
| **Ag** | **962** | **1235** | **1** | **1235** | **1** | **1235** |  | **1000** | **8.62E-01** |
| **Ag** | **962** | **1235** | **1.1** | **1235** |  | **1235** | **1.1** | **1500** | **1.29E+00** |
| **Au** | **1064** | **1337** | **0.9** | **1337** | **0.9** | **1337** |  | **2000** | **1.72E+00** |
| **Au** | **1064** | **1337** | **0.98** | **1337** |  | **1337** | **0.98** | **2400** | **2.07E+00** |
| **Cu** | **1085** | **1358** | **1** | **1358** | **1** | **1358** |  |  |  |
| **Cu** | **1085** | **1358** | **1.28** | **1358** |  | **1358** | **1.28** |  |  |
| **Mg** | **650** | **923** | **0.79** | **923** | **0.79** | **923** |  |  |  |
| **Mg** | **650** | **923** | **0.89** | **923** |  | **923** | **0.89** |  |  |
| **Pt** | **1768** | **2041** | **1.3** | **2041** | **1.3** | **2041** |  |  |  |
| **Pt** | **1768** | **2041** | **1.5** | **2041** |  | **2041** | **1.5** |  |  |
| **Pb** | **328** | **601** | **0.55** | **601** | **0.55** | **601** | **0.55** |  |  |
| **Ni** | **1455** | **1728** | **1.63** | **1728** | **1.63** | **1728** |  |  |  |
| **Ni** | **1455** | **1728** | **1.79** | **1728** |  | **1728** | **1.79** |  |  |
| **Pd** | **1555** | **1828** | **1.54** | **1828** | **1.54** | **1828** |  |  |  |
| **Pd** | **1555** | **1828** | **1.85** | **1828** |  | **1828** | **1.85** |  |  |

*Comment:* Usually the vacancy formation energy *Ev* is deduced indirectly from monitoring a property, such the resistivity of the metal, right after it has been quenched etc.

\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

**1.39 Vacancies in silicon**

In device fabrication, Si is frequently doped by the diffusion of impurities (dopants) at high temperatures, typically 950─1200 ºC. The energy of vacancy formation in the Si crystal is about 3.6 eV. What is the equilibrium concentration of vacancies in an Si crystal at 1000 ºC. Neglect the change in the density with temperature which is less than 1percent in this case.

**Solution**

Vacancy formation energy *Ev* = 3.6 eV × (1.6×1019 J eV1) = 5.76×1019 J. The equilibrium concentration of vacancies is given by

 (1)

for which we need *N*, the atomic concentration. For Si the atomic mass *M*at = 28.09 g mol1 and density *ρ* = 2.33 g cm3. Therefore the atomic concentration is,

= 5.0×1022 cm3 or 5.0×1026 m3

At *T* = 1000°C (1273 K), equilibrium concentration of vacancies is,



***nv* = 2.8 × 1014 m3**or ***nv/Nat* = 5.6×1015**

We neglected the change in the density from 300 K to 1273 K. Its effect on the final result is small.

---------

*Authors Note:* Strictly, within proper thermodynamic treatment, Equation (1) should really be written in terms of the free energy of vacancy formation *Gv*, that is

 (2)

or  (3)

in which *Hv* is *Ev* (energy of vacancy formation) and *Sv* is the entropy change upon vacancy formation. The term exp(*Sv/k*) has been neglected. The uncertainties in *Ev* cause a bigger variation than the neglect of exp(*Sv/k*)

**1.40Pb-Sn solder**Consider the soldering of two copper components. When the solder melts, it wets both metal surfaces. If the surfaces are not clean or have an oxide layer, the molten solder cannot wet the surfaces and the soldering fails. Assume that soldering takes place at 250 ºC, and consider the diffusion of Sn atoms into the copper (the Sn atom is smaller than the Pb atom and hence diffuses more easily).

*a*. The diffusion coefficient of Sn in Cu at two temperatures is *D* = 1.69× 109 cm2 hr1 at 400 ºC and *D* = 2.48× 107 cm2 hr1 at 650 ºC. Calculate the rms distance diffused by an Sn atom into the copper, assuming the cooling process takes 10 seconds.

*b*.What should be the composition of the solder if it is to begin freezing at 250 ºC?

*c*.What are the components (phases) in this alloy at 200 ºC? What are the compositions of the phases and their relative weights in the alloy?

*d*.What is the microstructure of this alloy at 25 ºC? What are weight fractions of the *α* and *β* phases assuming near equilibrium cooling?

**Solution**

***a.***Given information:

Temperatures: *T*1 = 400 °C + 273 = 673 K *T*2 = 650 °C + 273 = 923 K

Diffusion coefficients: *D*1 = 1.69 × 109 cm2/hr = (1.69 × 109 cm2/hr)(0.01 m/cm)2 / (1 hr) × (3600 sec/hr)

*D*1 = 4.694 × 1017 m2/s

*D*2 = 2.48 × 107 cm2/hr = (2.48 × 107 cm2/hr)(0.01 m/cm)2 / (1 hr) × (3600 sec/hr)

*D*2 = 6.889 × 1015 m2/s

The diffusion coefficients *D*1 and *D*2 at *T*1 and *T*2 respectively are given by:

where *EA* is the activation energy in eV/atom and *q* = 1.6×1019 J/eV (conversion factor from eV to J). Since



we can take the ratio of the diffusion coefficients to express them in terms of *EA* (eV):



∴  (in eV)

∴  (in eV)

∴ *EA* = 1.068 eV/atom

Now the diffusion coefficient *Do* can be found as follows:



∴ = 4.638 × 109 m2/s

To check our value for *Do*, we can substitute it back into the equation for *D*2 and compare values:



∴ *D*2 = 6.870 × 1015 m2/s

This agrees with the given value of 6.889 × 1015 m2/s for *D*2.

Now we must calculate the diffusion coefficient *D*3 at *T*3 = 250 °C + 273 = 523 K (temperature at which soldering is taking place).



∴ D3 = 2.391 × 1019 m2/s

The rms distance diffused by the Sn atom in time *t* = 10 s (*Lrms*) is given by:

**= 2.19 × 109 m** or **2 nm**

***b.***From Figure 1Q40-1, 250 °C cuts the liquidus line approximately at 33 wt.% Sn composition (*Co*).

∴ ***Co* = 0.33** (Sn)

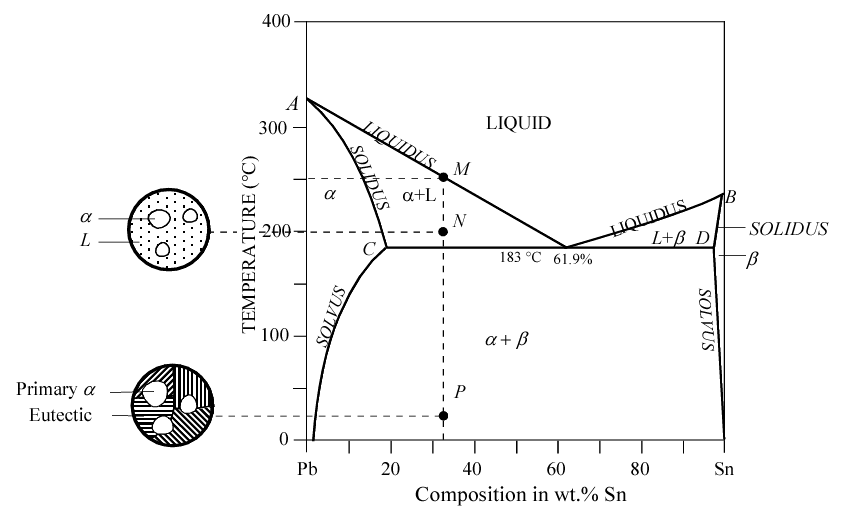
***c.***For *α*-phase and liquid phase (*L*), the compositions as wt.% of Sn from Figure 1.69 or 1Q31-1 are:

*Cα* = 0.18 and *CL* = 0.56

The weight fraction of *α* and *L* phases are:

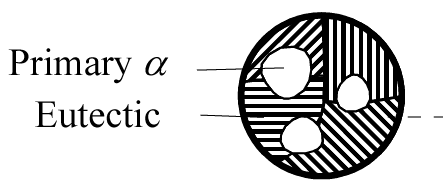
or**60 wt.% *α*-phase**

or**39.5 wt.% liquid phase**



**Figure 1Q40-1:** The equilibrium phase diagram of the Pb-Sn alloy.

***d.***The microstructure is a primary *α*-phase and a eutectic solid (*α* + *β*) phase. There are two phases present, *α* +*β*. (See Figure 1Q31-2)



**Figure 1Q40-2:** Microstructure of Pb-Sn at temperatures less than 183°C.

Assuming equilibrium concentrations have been reached:

*C′α* = 0.02 and *C′β* = 1

The weight fraction of *α* in the whole alloy is then:

or**68.4 wt.% *α*-phase**

The weight fraction of *β* in the whole alloy is:

or**31.6 wt.% *β*-phase**

**1.41Pb-Sn solder**Consider the 50% Pb-50% Sn solder.

*a*.Sketch the temperature-time profile and the microstructure of the alloy at various stages as it is cooled from the melt.

*b*.At what temperature does the solid melt?

*c*.What is the temperature range over which the alloy is a mixture of melt and solid? What is the structure of the solid?

*d.*Consider the solder at room temperature following cooling from 182 ºC. Assume that the rate of cooling from 182 ºC to room temperature is faster than the atomic diffusion rates needed to change the compositions of the *α* and *β* phases in the solid. Assuming the alloy is 1 kg, calculate the masses of the following components in the solid:

1. The primary*α*.

2. *α* in the whole alloy.

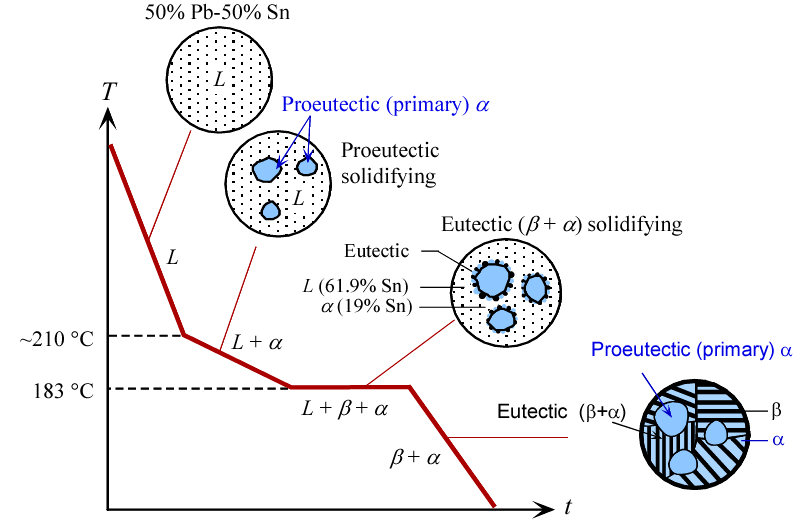
3. *α* in the eutectic solid.

4. *β* in the alloy (Where is the*β*-phase?)

*e.* Calculate the specific heat of the solder given the atomic masses of Pb (207.2) and Sn (118.71).

**Solution**

***a.***



**Figure 1Q41-1:** Temperature vs. time profile and microstructure diagram of 50% Pb-50% Sn.

All compositions are in weight %.

***b.***When 50% Pb-50% Sn is cooled from the molten state down to room temperature, it begins to solidify at point A at about 210 °C. Therefore the melting temperature (fusion temperature) is at 210 °C. (However, when going from solid to liquid (when the solid is heated) the solid begins to melt at 183 °C, so this would be the melting temperature.)

***c.***Between 210 °C and 183 °C, the liquid has the eutectic composition and undergoes the eutectic transformation to become the eutectic solid. Below 183 °C, all the liquid has solidified, and the structure is a combination of the solid *α*-phase and the eutectic structure (which is composed of *α* and *β* layers).

***d.*** At 182 °C, the composition of the proeutectic or primary *α* is given by the solubility limit of Sn in*α*,**19.2% Sn**.The primary or proeutectic*α* (pro-*α*) exists just above and below 183 °C (eutectic temperature), *i.e.* it is stable just above and below 183 °C. Thus the mass of pro-*α* at 182 °C is the same as at 184 °C. Applying the lever rule (at 50% Sn):



Assume that the whole alloy is 1 kg. The mass of the primary or proeutectic*α* is thus **27.9% of the whole alloy**; or **0.279 kg**. The mass of the total eutectic solid (*α*+*β*) is thus 1 - 0.279 = **0.721** or **72.1%** or **0.721 kg**.

If we apply the lever rule at 182 °C at 50% Sn, we obtain the weight percentage of *α* in the whole solid:



Thus the mass of *α* in the whole solid is **0.607 kg**. Of this, 0.28 kg is in the primary (proeutectic) *α* phase. Thus 0.607 - 0.279 or **0.328 kg** of *α* is in the eutectic solid.

Since the total mass of *α* in the solid is 0.607 kg, the remainder of the mass must be the *β*-phase. Thus the mass of the *β*-phase is 1 kg - 0.607 kg or **0.393 kg**. The *β*-phase is present solely in the eutectic solid, with no primary*β*, because the solid is forming from a point where it consisted of the *α* and liquid phases only.

***e.***Suppose that *nA* and *nB* are atomic fractions of *A* and *B* in the whole alloy,

*nA* +*nB* = 1

Suppose that we have 1 mole of the alloy. Then it has *nA* moles of *A* and *nB* moles of *B* (atomic fractions also represent molar fractions in the alloy). Suppose that we consider 1 gram of the alloy. Since *wA* is the weight fraction of *A*, *wA* is also the mass of *A* in grams in the alloy. The number of moles of *A* in the alloy is then *wA*/*MA* where *MA* is the atomic mass of *A*. Thus,

Number of moles of *A* = *wA/MA*.

Number of moles of *B* = *wB*/*MB*.

Number of moles of the whole alloy = *wA/MA* + *wB*/*MB*.

Molar fraction of A is the same as *nA*. Thus,

 and 

We are given the molar masses of Pb and Sn:

*M*Pb = 207.2 g/mol *M*Sn = 118.71 g/mol

Let *n* = mole (atomic) fraction and *W* = weight fraction. Then *W*Pb = weight fraction of Pb in the alloy. We know this to be 0.5 (50% Pb).

The mole fractions of Pb and Sn are *n*Pb and *n*Sn and are given by:



∴ = 0.3642

*n*Sn = 1 - *n*Pb = 1 - 0.3642 = 0.6358

The mole fraction of Pb is 0.3642 and that of Sn is 1─0.3642 = 0.6358.

The heat capacity of a metal is 3*R* per mole, where *R* is the gas constant. We want the specific heat capacity *Cs* (heat capacity per gram of alloy). 1 mole of the alloy has a mass *M*PbSn:

*M*PbSn = *n*Pb*M*Pb + *n*Sn*M*Sn

Thus the specific heat capacity *Cs* (*i.e.* heat capacity per gram) is:



∴ 

∴ ***cs* = 0.165 J K1 g1**

**1.42 Gruneisen'sruleandmetals**AlandCubothhavemetallicbondingandthesamecrystalstructure. Assuming that the Gruneisen's parameter **for Al is the same as that for Cu, **= 2.1, estimate thelinear expansion coefficient **of Al, given that its bulk modulus *K* = 75 GPa, *cs* = 900 J K-1 kg-1, and **= 2.7g cm-3. Compare your estimate with the experimental value of 23.510-6K-1.

**Solution**

Given that, *K* = 75 GPa = 75×109 J m3

*cs* = 900 J kg1K1

and *ρ* = 2.7 g cm3 = 2.7×103 kg m3

Grüneisen's laws can be written as



∴ =**22.7×106 K1**

So the estimated value is close to the experimental value in the range(23.123.6)×106 K1 (see https://en.wikipedia.org/wiki/Thermal\_expansion (28 October 2016))

**1.43 Heat capacity and the thermal expansion coefficient of diamond** Given that diamond hasa bulk modulus of 443 GPa, specific heat capacity of510 J kg1 K1, and density of 3.51 g cm, *estimate* its linear expansion coefficientat room temperature taking the Grüneisen parameter as~1.

**Solution**

Given that, *K* = 443 GPa = 443×109 J m3

*cs* = 510 J kg1K1

and *ρ* = 3.51 g cm3 = 3.51×103 kg m3

Grüneisen's laws is



∴ = 1.35×106 K1

Experimental values are around 1×106 K1 (*e.g.* S. Adachi *Properties of Group IV, III-V and II-VI Semiconductors*, John Wiley and Sons, Chichester, 2005; p31, Table 2.5.). Given that ** is only roughly 1, the estimate is not bad.

*Note: K* and *cs* are from Wikipedia and are very close to the values in Adachi's book above. Some books use *B* instead of *K*.

**APPENDIX**

**USEFUL INSTRUCTOR NOTES**

**A. Ionically Bonded Solids**

**Ionically Bonded Solids: Page 18, Section 1.3.4**

Figure 1.10 is for the potential energy of an in pair (Na+ and Cl ion pair) inside the crystal, and not for an isolated ion pair. For an isolated ion pair, the minimum in energy is around 4.27 eV. The attractive term in the PE curve in Figure 1.10 includes the Madelung constant; see Question 1.8. According to Figure 1.10,

Energy required to create Na+ and Cl from a pair of Na and Cl atoms ≈ 1.5 eV per Na-Cl pair

Energy to separate the crystal into Na and Cl atoms ≈ 6.3 eV per Na-Cl pair

Energy needed to separate the crystal into Na+ and Cl ions = 6.3 + 1.5 = 7.8 eV per Na+-Cl pair

Note: 7.8 eV per Na+-Cl pair = 753 kJ mol1

**Atomic cohesive energy** = Energy required to take the crystal apart to individual Na and Cl atoms = 6.3 / 2 = 3.15 eV per atom.

However, usually the atomic cohesive energy is quoted as kJ per mole for the whole NaCl crystal. This means that we need to convert 6.3 eV per Na-Cl pair to kJ per mole, which is 608 kJ mol1

**Lattice energy** of an ionic solid is the energy needed to break up the crystal into its ions (infinitely separated). According to Figure 1.10, the energy needed to go from the bottom of the *PE* curve to the *r* = ∞ point where ions are infinitely separated is 6.3 eV + 1.5 eV = 7.8 eV. This energy will ensure we have generated infinitely separated Na+ and Cl ions.7.8 eV per ion pair means 753 kJ mol1. Chemistry books quote the lattice energy for NaCl as769 kJ/mol (T. Moeller et al, *Chemistry with Inorganic Qualitative Analysis,* Second Edition, Academic Press, 1984, p. 413, Table 13.5.), which is very close (within 2%)

There are several good discussions available at the undergraduate level for students.

[1] J.R. Taylor *et al*, Modern Physics, Second Edition, Pearson, Upper Saddle River, 2004, pp416-417. Ionic bonding in the crystal is discussed.

[2] K. Krane, Modern Physics, Second Edition, Wiley, New York, 1996, pp335-338. Ionic bonding in the crystal is clearly explained. Further, the cohesive energy of the crystal is also calculated and the problem of double counting the ions is explained.

[3] F.J. Blatt, Modern, Physics, McGraw-Hill, New York, 1992, pp204-207. Ionic bonding in the Na+-Cl molecule (not the crystal) is described.

There is a simple explanation for the difference in the binding energy of a Na+-Cl pair in the molecule and in the crystal. In the crystal, we need to consider all neighboring ions around a given ion even though the energy was expressed per ion pair. The consideration of all the ions in the attractive potential energy term is represented by the Madelung constant *A*, which, for an FCC, is 1.75. One needs to modify the repulsion term as well, but if we leave this alone for a minute, then, given

Binding energyper ion pair in the molecule = 4.27 eV

Bonding energy per ion pair in the crystal = 7.8 eV

Ratio = 7.8/4.27 = 1.82, very roughly the Madelung constant.

**The sign of lattice energy** varies from book to book. Most physics textbooks like Kittel give the lattice energy as a positive quantity, which is understood to mean the energy we need to separate the crystal into its ions. Most chemistry books quote it as a negative number, that is, the energy of the crystal with respect to isolated ions. While the sign is non consistent in the literature, the meaning is nonetheless clear.

**Why do we plot "Potential energy per ion pair vs. separation" in Figure 1.10?**

The PE in this figure is actually twice the PE of a given ion in the NaCl structure. We can use the Madelung constant and obtain the energy of

First consider the PE of a single ion in the crystalas in Question 1.8 with the repulsive energy term included,



This is the same as Equation 1.4 on p17 in the textbook, where it is stated that this is for an ion pair. Consider the total potential energy*E*crystal of1 mole ofNaCl. This crystal has *NA*Na+ and *NA* Cl ions. *E*crystal is not simply(2*NA*)*E*one-ion because that would count each ion twice. The total energy is thus (1/2)(2*NA*)*E*one-ion. Then we can write the lattice energy of NaCl as



Remember that the NaClcrystal has *NA* number of ion pairs. Thus, we can interpret *E*one-ion as the *energy per ion pair*, which is the term that is used in Figure 1.10; and also used in other textbooks



**Figure 1.10** Sketch of the potential energy per ion pair in solid NaCl. Zero energy corresponds to neutral Na and Cl atoms infinitely separated.

**"After a year's research, one realizes that it could have been done in a week."**

Sir William Henry Bragg (As quoted by Alan L. Mackay, Dictionary of Scientific Quotations, Institute of Physics Publishing, Bristol, 1994, p. 37, apparently from Fifty Years of X-ray Diffraction ed. P.P. Ewald, Utrecht, 1962)