

## Chapter 4 Point Defects

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## 4.1 Classification of Point defects

Contrary to the perfect lattices discussed in the preceding chapter, all real crystals contain defects differentiated according to their dimension. The zero-dimensional defect is called a *point defect*, implying that it involves only one atom site surrounded by an otherwise perfect lattice. However, the presence of a point defect may affect the properties of its nearest neighbors, and by elastic interactions, a sizable region of the lattice around the defect. In that sense, all defects are three-dimensional.

Two types of point defects are intrinsic to elemental solids, meaning that they form spontaneously in the lattice without any external intervention. These two are the *vacancy* (V) and the *self-interstitial atom* (SIA), shown schematically in a 2-D representation in the upper panels of Fig. 4.1. The vacancy is simply an atom missing from a lattice site, which would otherwise be occupied in a perfect lattice. The self-interstitial is an atom lodged in a position between normal lattice atoms; that is in an interstice. The qualification “self” indicates that the interstitial atom is of the same type as the normal lattice atoms.

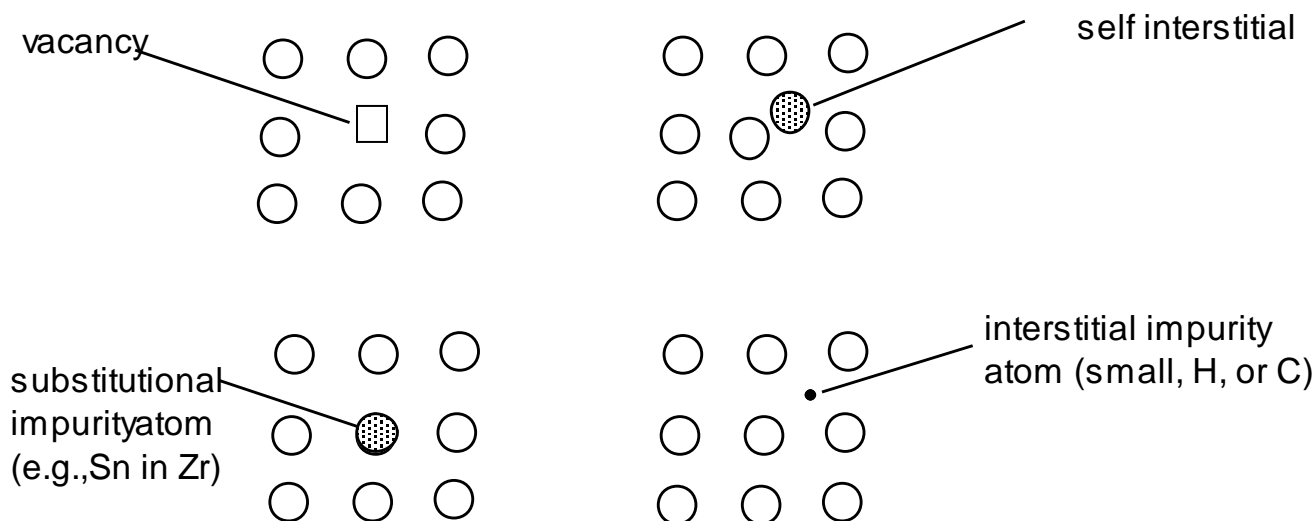
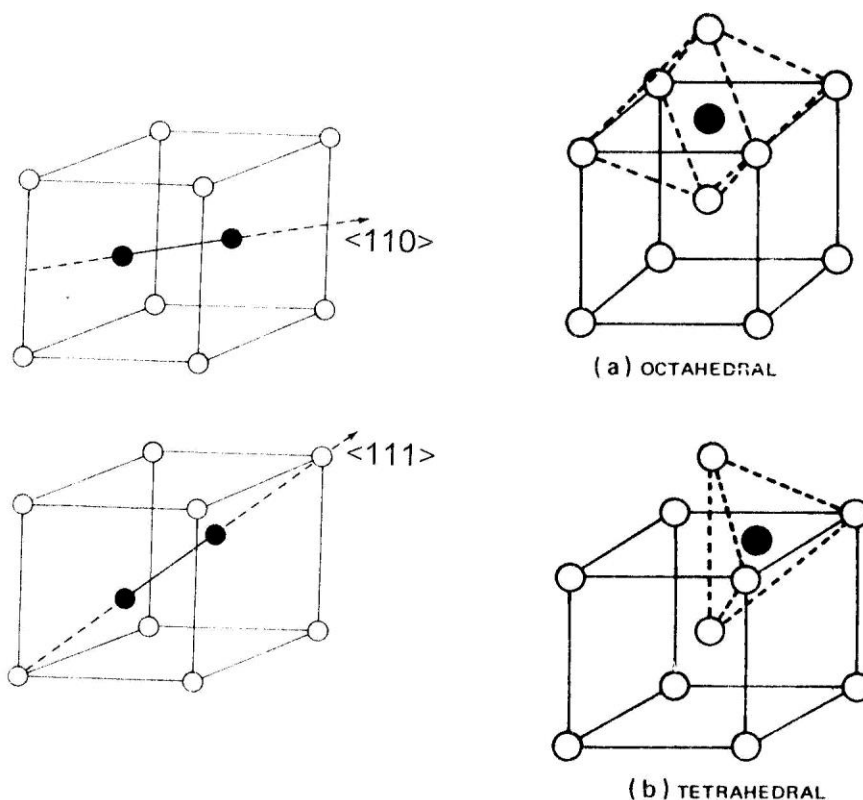


Fig. 4.1 Point Defects in an Elemental Crystal with examples of elemental impurities

The lower two panels in Fig. 4.1 show the two basic ways that a foreign (or impurity) atom exists in the crystal lattice of a host crystal. Large impurity atoms, usually of the same type as the host atoms (e.g., both metals, as nickel in iron), replace the host atoms on regular lattice positions. These are called *substitutional impurities*. The structure of the lattice is not disturbed, although nearby host atoms may be slightly displaced from their normal lattice sites. Small atoms (compared to the vacancy size) that are also chemically dissimilar from the host atoms can occupy interstitial positions without appreciably distorting the surrounding host crystal. They are termed *interstitial impurities*. Typical examples are carbon in iron and hydrogen in zirconium.

Aside from their identities relative to the host atoms, the SIA and the impurity interstitial differ in the way that they reside in the lattice. As shown in Fig. 4.2



**Fig. 4.2 Interstitials in the bcc lattice. Left: SIA; Right: impurity interstitial**

using the bcc lattice as an example, the self-interstitial, displaces a host atom from its normal lattice position, creating a dumbbell-shaped pair. This configuration is also called a *split interstitial*. The orientation of the dumbbell (or of the atomic configuration associated with the extra atom, in general) and the distance between the two atoms are determined by the condition that potential energy of the lattice be at a minimum.

The small interstitial impurity atoms, on the other hand, occupy definite sites without significant distortion of the host lattice. However, even the small distortion of the neighboring host atoms requires energy, which limits the solubility of the interstitial impurity. These sites are named after the shape of the polyhedron formed by joining the host atoms surrounding the interstitial. The examples shown on the right-hand side of Fig. 4.2 for the bcc lattice are *octahedral* and *tetrahedral* sites. These two interstitial sites offer the most space for the impurity atom to reside in, but which site is occupied is a sensitive function of the interaction energy between the impurity atom and the host atom.

## 4.2 Equilibrium Concentrations of Point Defects in Elemental Crystals

In Sect. 2.4 of Chap. 2, it was shown that the condition of chemical equilibrium is the minimization of the Gibbs energy at constant temperature and pressure. The system in this case consists of atoms on regular lattice sites and the intrinsic point defects randomly distributed on some lattice sites. Even though there is only one element involved, thermodynamically the system consists of two components, the regular atoms and the empty sites in case of a vacancy or atoms on interstitial sites in case of the SIA. In thermodynamic analyses, the two types of point defects are treated as independent entities.

The reason that point defects form spontaneously lies in the components of the Gibbs energy of formation<sup>1</sup>. For a single point defects, denoted by  $j$  ( $j=v$  for a vacancy or  $j=i$  for an SIA), the Gibbs energy contains two terms:

$$g_j = h_j - Ts_j \quad (4.1)$$

where  $h_j$  and  $g_j$  are differences in energy and  $s_j$  the difference in entropy for the processes shown in Figure 4.3 and 4.4. As illustrated in Fig.4.3, vacancy formation can be regarded as the movement of an atom from the interior of the crystal to its surface. When an SIA is formed (Fig.4.4.) the process is reversed as an atom is moved from the surface to the inside of the solid.

### Enthalpy

The enthalpy change accompanying creation of the point defects,  $h_j$ , is, from equation 2.1:

$$h_j = E_j - \sigma \Delta v_j \approx E_j \quad (4.2)$$

where the formation energy  $E_j$ , the dominant contribution, is the energy required to create a mole of point defects from the perfect lattice.  $E_j$  is positive for both vacancy and SIA creation, but is much larger for the latter than the former.  $\Delta v_j$  is the volume of a mole of vacant lattice sites, which is nearly the same as the molar volume<sup>2</sup>,

$$\Delta v_j = \frac{M}{\rho} \quad (4.3)$$

where  $M$  is the atomic weight of the element and  $\rho$  is its density.

The  $\sigma \Delta v$  term in  $h_j$  represents the work involved in the change in system volume as a surface atom is moved between the interior site and the surface (see Figs. 4.3 and 4.4).  $\sigma$  is the hydrostatic stress ( $\text{N/m}^2$  or  $\text{J/m}^3$ ), which is positive in tension.

### Entropy

The two parts of the entropy involved in formation of point defects are expressed by the equation:

<sup>1</sup> In this book, thermodynamic and transport properties are expressed in units of J/mole or kJ/mole. The literature often uses electron volt (eV) units. The relation between the two is 96.5 kJ/mole per eV. If eV is used, the gas constant  $R$  is replaced by Boltzmann's constant,  $k_B$ .

<sup>2</sup> If the above atomic units are used,  $V$  is replaced by the atomic volume  $\Omega = V/N_{Av}$ , where  $N_{Av}$  is Avogadro's number.

$$s_j = s_{vib}^j + s_{mix}^j \quad (4.4)$$

The  $s_{vib}$  component results from the difference between the vibrational motion of the atoms around the point defect from that of atoms in the perfect lattice. This term is (Ref. 1, Sect. 6.3):

$$s_{vib} = k_B \ln(\nu / \nu')^\alpha \quad (4.5)$$

where  $\nu$  is the vibration frequency of atoms in the perfect crystal, which could be either the Einstein or Debye frequencies (sect.2.1 of ref [1] and  $\nu'$  is the vibration frequency of the atoms immediately surrounding the point defect and  $k_B$  is Boltzmann's constant. Around a vacancy, the nearest-neighbor atoms relax into the hole, and in so doing, vibrate at a lower frequency. For this case,  $\nu/\nu' > 1$  and  $s_{vib} > 0$ . The more tightly-packed atoms surrounding the SIA vibrate at a higher frequency than those in the perfect lattice, so  $\nu/\nu' < 1$  and  $s_{vib} < 0$ .

The major component of the entropy change accompanying point defect formation is  $s_{mix}$ , the *entropy of mixing* (also called the *configurational entropy*). This term, is a positive quantity that contributes negatively to the system free energy, and thus promotes the formation of the point defects. This is due to randomly mixing  $N_V$  vacancies with  $N$  atoms. In this case the expression for  $s_{mix}$  is:

$$s_{mix} = -k_B \left[ \left( \frac{N}{N + N_V} \right) \ln \left( \frac{N}{N + N_V} \right) + \left( \frac{N_V}{N + N_V} \right) \ln \left( \frac{N_V}{N + N_V} \right) \right] \quad (4.6)$$

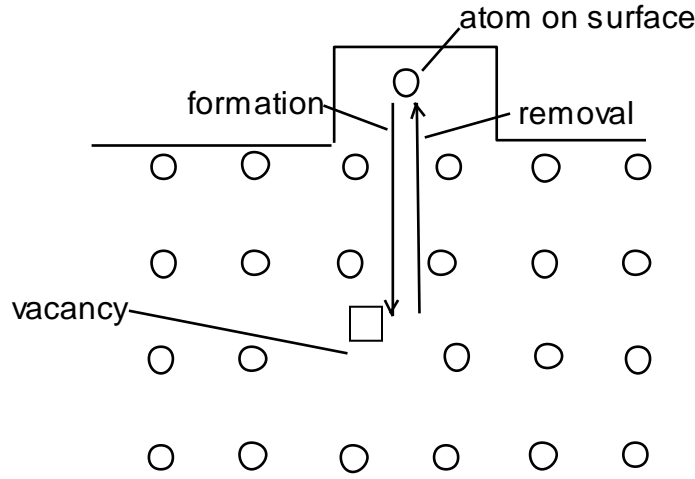
The reason for this behavior is that  $s_{mix}$  is a measure of randomness, and the introduction of point defects into a perfect crystal reduces the system's state of order. The entropy of mixing is responsible for the spontaneous existence of point defects at equilibrium; the magnitude of the positive energy of point defect formation,  $\epsilon_{PD}$ , governs the concentration of these species at thermal equilibrium, as discussed in the following section.

### 4.2.1 Vacancy formation

Figure 4.3 shows the creation of a vacancy by moving an interior atom to the surface of the solid, as described by the equilibrium reaction:



Where “null” denotes the perfect crystal,  $V$  is a single vacancy, and  $A_{surf}$  is an atom on the surface of the solid. The equilibrium is maintained because of the equality of the formation and removal rates depicted in Fig. 4.3. The components of the Gibbs energy equation,  $g_V = h_V - Ts_V$ , are considered as property differences between the right and left hand sides of Eq (4.6). The enthalpy to create a mole of vacancies is  $h_V = E_V - \sigma V$ , a process that involves breaking interatomic bonds.



**Fig. 4.3 Vacancy Formation**

The Gibbs energy of a solid containing  $N_V$  moles of vacancies and  $N$  moles of atoms is:

$$G_V = G(0) + N_V(E_V - \sigma_V \Delta v - T s_{vib}) - T(N + N_V)s_{mix} \quad (4.8)$$

where  $G(0)$  is the Gibbs energy of  $N$  moles of the perfect lattice (no vacancies). Even though the middle term in parentheses is always positive, the  $s_{mix}$  term is negative, effectively assuring that the minimum value of  $G_V$  cannot occur without vacancies. The equilibrium vacancy concentration is obtained from Eq (4.8) using the general criterion for equilibrium in a system at constant temperature and pressure, namely, that  $G_V$  be a minimum. Since  $N \gg N_V$ , this criterion yields:

$$\left( \frac{dG_V}{dN_V} \right)_N = (E_V - \sigma \Delta v_V - T s_{vib}) + k_B T = 0 \quad (4.9)$$

$N_V/N$  is the *site fraction* of vacancies, denoted by  $C_V$ . This concentration unit is the solid-state analog of the mole fraction unit that appears in the equilibrium equations in gases and liquids. The above equation is rewritten as:

$$C_V = N_V / N = e^{s_{vib}/k_B} e^{-E_V/k_B T} e^{\sigma \Delta v/k_B T} \approx e^{s_{vib}/k_B} e^{-E_V/k_B T} \quad (4.10)$$

$s_{vib}$  is usually approximated as zero, principally because it is unknown for most elements, and is small for those elements for which it has been measured. The term involving the stress can be

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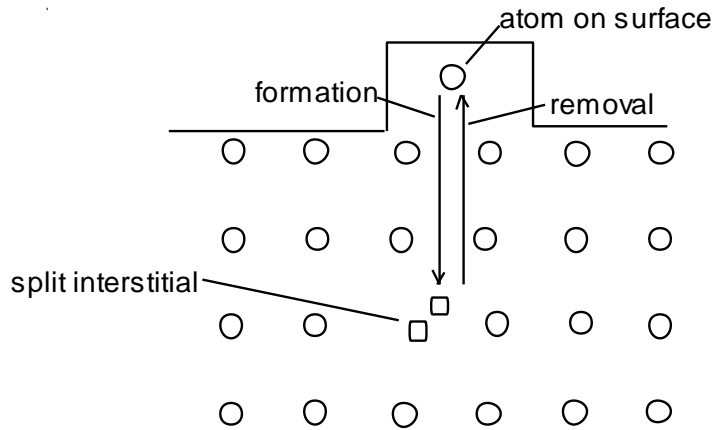
estimated using the following values:  $\sigma = 100 \text{ MPa}$ ,  $\Delta v = 2.4 \times 10^{-5} \text{ m}^3/\text{mole}$ ,  $R = 8.314 \text{ J/K-mole}$  and  $T = 1200 \text{ K}$ . This combination yields  $\sigma\Delta v/RT = 0.25$ , so that the exponential of this factor in Eq (4.9) is  $\sim 0.8$ . For most applications, this factor is sufficiently close to unity to be set equal to unity, and Eq (4.9) reduces to:

$$C_V = e^{-E_V/k_B T} \quad (4.9a)$$

**Example #1:** The formation energy of vacancies in copper is  $100 \text{ kJ/mole}$  ( $1 \text{ eV/atom}$ ). At  $1300 \text{ K}$  (which is just below the melting point) what fraction of the lattice sites are empty? Using these values in Eq (4.9a), the site fraction of vacancies is  $C_V = 10^{-4}$ . This value is too small to influence properties such as the density, but even smaller values of  $C_V$  are critical in determining transport properties such as self-diffusion (see following chapter).

### 4.2.2 Self-interstitials

The process analogous to that in Fig. 4.3 for forming SIAs in elemental crystals is illustrated in Fig. 4.4.



**Fig. 4.4 Formation of self-interstitials**

The equilibrium concentration (as a site fraction) of SIAs is given by:

$$C_I = e^{s_{\text{vib}}/R} e^{-E_I/RT} e^{-\sigma\Delta v/RT} \cong e^{-E_I/RT} \quad (4.11)$$

For copper, the interstitial formation energy is  $E_I \sim 300 \text{ kJ/mole}$  or  $3.1 \text{ eV/atom}$ , which is about three times larger than the energy required to create a vacancy in this metal. As a result, the equilibrium concentration of interstitials is very much smaller than that of vacancies (by 8 orders of magnitude at  $1300 \text{ K}$ ). This is true of all elements, so thermally-generated interstitials can usually be neglected in most applications. However, in the presence of high-energy radiation, the two types of point defects are created at equal rates, and interstitials cannot be ignored.

Although the vibration entropy and stress terms are usually omitted, for the few applications where they are necessary, understanding how they differ for the two types of point defects is useful.

### 4.2.3 Point-defect formation as a chemical reaction

An approximate but extremely simple method for treating point defect equilibria regards the process as a pseudo-chemical reaction and directly utilizing the well-known theory of chemical-reaction equilibria. The “reaction” that produces vacancies is given by Eq (4.1). The law of mass action expresses the equilibrium constant for this reaction by:

$$K_v = \frac{\text{activity of vacancies} \times \text{activity of surface atoms}}{\text{activity of atoms in perfect lattice}} \quad (4.12)$$

Because the concentrations of atoms in the undisturbed lattice and on the surface are much greater than that of the point defect, they are essentially unaffected by point defect formation. Consequently, their activities can be taken to be unity. The activity of the vacancies, however, is equal to their site fraction  $C_v$ . This choice is based on the results of the previous detailed analysis that produced Eq (4.9).

The other feature of chemical-reaction theory that is adapted for the vacancy formation process is the relation between the equilibrium constant and the Gibbs energy change of the reaction (see Eq (2.69) of Chap. 2). The Gibbs energy change for forming a mole of vacancies,  $g_v$ , is equal to the sum of the three terms in parentheses in Eq (4.8). Applying these adaptations to the process of vacancy formation, Eq (4.9) yields:

$$K_v = C_v = e^{-g_v/k_B T} \quad (4.13)$$

which is identical to Eq (4.9) obtained by the exact method. A similar application of chemical equilibrium theory applies to self-interstitials as well.

### 4.2.4 Ordered compounds

In ordered compounds, two sub-lattices exist so that at least six types of defects can in principle, exist: vacancies in the A sub-lattice, vacancies in the B sub-lattice, A atom interstitials, B-atom interstitials and the so-called antisite defects, A atoms in the B sub-lattice and B atoms in the A sublattice. Although these are all possible, some will be energetically favored over the others, and because the dependence is exponential, only a few of the six may be stable.

## 4.3 Point Defects in Ionic Crystals [1]

Binary ionic solids consist of a nonmetal and a metal arranged on a crystal structure bonded by Coulomb forces (Chap. 3). A subset of ionic solids of particular importance in nuclear technology are oxides, the most important of which is uranium dioxide. Because of the multiplicity of valence states of uranium and the relative ease with which they can form, this



oxide is one of the most difficult to understand. It has been the subject of more research than any other metal oxide.

Characterization of a binary ionic crystal requires specification of:

- the metal and the nonmetal
- their normal valences (oxidation states)
- the crystal structure
- the types of point defects that spontaneously form

Because of the importance of ceramics such as  $\text{UO}_2$ ,  $\text{PuO}_2$ ,  $\text{ThO}_2$  and  $\text{ZrO}_2$  in light-water reactors (either as fuel or corrosion product), the above list will be focused as follows:

- oxygen is the nonmetal; its only stable state is  $\text{O}^{2-}$ .
- the metal is tetravalent in its most stable state, so the formula is  $\text{MO}_2$
- the crystal structure is fluorite (Fig. 3.15), consisting of a simple-cubic anion ( $\text{O}^{2-}$ ) sublattice intermingled with a face-centered cubic cation ( $\text{M}^{4+}$ ) sublattice. Oxygen and metal interstitials have their own sublattices so the solid with point defects has four different sublattices.

#### 4.3.1 Types of point defects

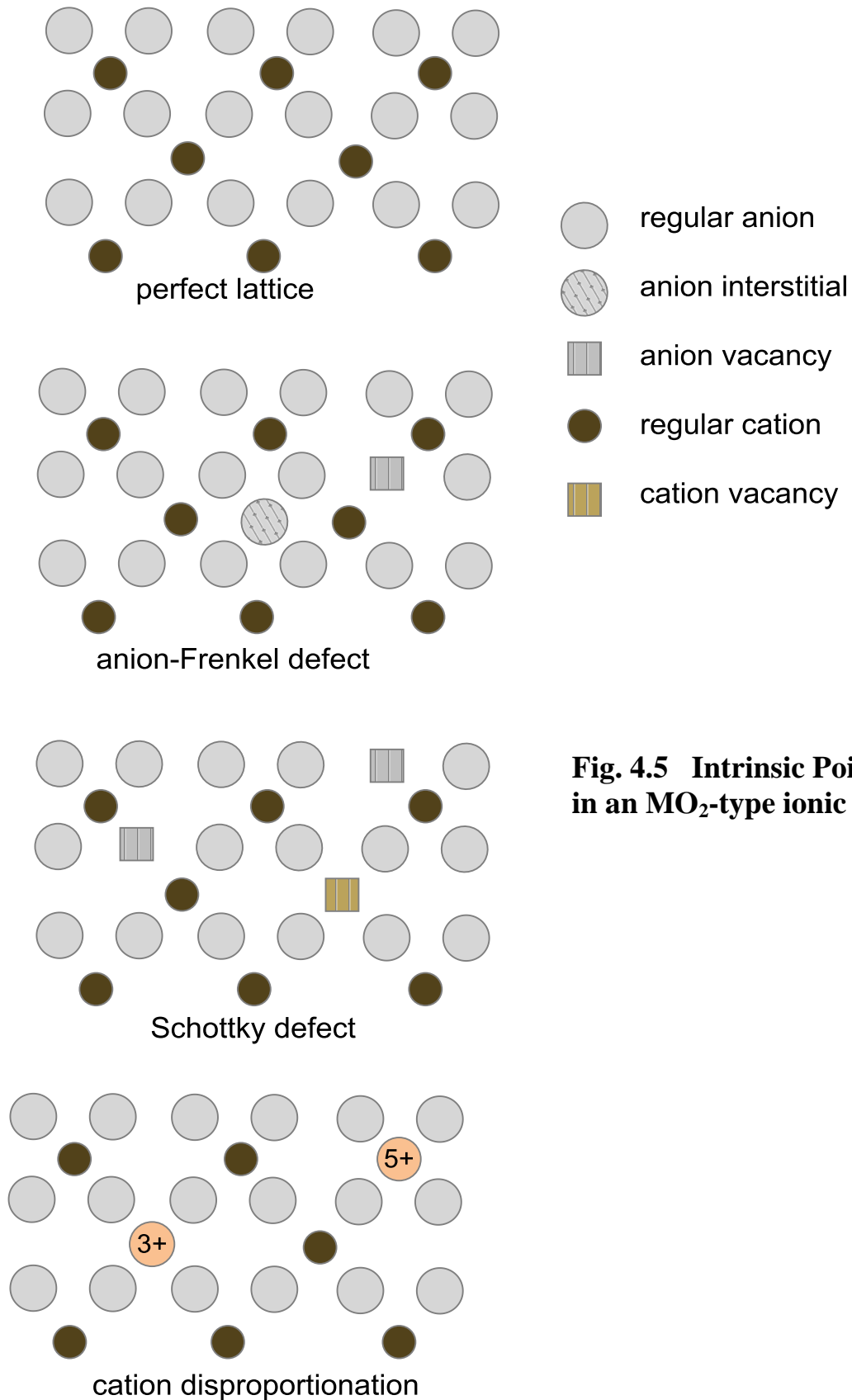
Point defects in ionic solids can be either *structural* or *electrical*. As in elemental solids, a structural defect is either a missing ion (*vacancy*) or an ion in an irregular (*interstitial*) position. Because the cations and anions carry electrical charges, vacancy and interstitial formation are not independent processes. The top two drawings of Fig. 4.5 show the structural defects in the fluorite structure of  $\text{MO}_2$ . The principal defect is the *anion Frenkel defect*, which is created by displacement of an oxygen ion from its normal lattice position. The resulting structure consists of a vacant site on the anion sublattice and an  $\text{O}^{2-}$  ion in an interstitial position<sup>3</sup>. This combination obeys electrical neutrality. The middle drawing is a *Schottky* defect. In this case, electrical neutrality requires that two anion vacancies be created for every cation vacancy.

Schottky and Frenkel defects are created independently. In a particular crystal, one is dominant while the other is either absent or a minor contributor. In  $\text{UO}_2$ , for example, the major defect is anion-Frenkel, but Schottky defect formation occurs to a lesser extent. The defects in Fig. 4.5 are termed *intrinsic* because they occur without the assistance of an impurity cation. *Extrinsic* point defects are generated by the presence of *aliovalent* (alio = different) cations such as  $\text{Q}^{5+}$  or  $\text{Q}^{3+}$  that replace  $\text{M}^{4+}$  on the cation sublattice. A foreign 4+ cation causes no electrical disturbance in the  $\text{MO}_2$  lattice.

The bottom diagram of Fig. 4.5 is a purely electrical point defect that occurs only with cations that exhibit oxidation states other than the stable 4+ state. This is termed *disproportionation*; it amounts to loss or gain of an electron from  $\text{M}^{4+}$ . It occurs only when the cation has valence states that are close in energy (such as  $\text{U}^{4+}$  and  $\text{U}^{5+}$  and  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$ ).

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<sup>3</sup> The actual anion Frenkel defect in  $\text{UO}_2$  is more complex than that shown in Fig. 4.5 ( see Sect. 16.5)  
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**Fig. 4.5 Intrinsic Point defects in an  $\text{MO}_2$ -type ionic crystal**

### 4.3.2 Kroger-Vink Notation

The accepted method for characterizing defects in ionic solids is that due to Kroger and Vink [2]. In this method, the defect's charge is identified by the deviation from the absolute charge of the ions in the perfect lattice. In the oxide  $\text{MO}_2$ , for example,  $\text{M}^{4+}$  and  $\text{O}^{2-}$  in their normal lattice sites would be considered uncharged and identified as  $\text{M}_\text{M}$  and  $\text{O}_\text{O}$ . The normal letter denotes the species and the subscript is the sublattice on which the species resides. Thus in  $\text{MO}_2$   $\text{M}_\text{M}$  stands for cation  $\text{M}^{4+}$  on the cation sublattice.  $\text{M}_\text{I}$  and  $\text{O}_\text{I}$  designates occupation of the appropriate interstitial sites by a metal ion and/or an oxygen ion. As shown below, symbols for the charges of the various species (relative to the normal charges of 4+ for cations and 2- for anions) need to be added to the symbols.

In place of + and - signs, deviant charges are denoted by apostrophes (') for negative states and dots (•) for positive states. Thus, the anion vacancy is designated by  $\text{V}_\text{O}^{\bullet\bullet}$ , where V stands for vacancy, the subscript O indicates the vacancy occupies a regular anion sublattice site and the two dots show that the vacant site is doubly-positively charged with respect to the anion that would normally occupy the site ( $\text{O}^{2-}$ ).

The defect symbols in  $\text{MO}_2$  are summarized below

$\text{V}_\text{O}^{\bullet\bullet}$  = doubly-positively charged anion vacancy

$\text{V}_\text{M}^{\prime\prime\prime\prime}$  = vacancy on the cation sublattice. This species carries four negative charges relative to the regular cation. This charge state is designated by the quadruple apostrophe

$\text{M}_\text{I}^{\bullet\bullet\bullet\bullet}$  = cation on an interstitial site designated by I. The dots indicate the number of positive charges attached to the cation, relative to the empty interstitial site

$\text{O}_\text{I}^{\prime\prime}$  = oxygen ion located on an interstitial site (I). It carries two negative charges

$\text{M}_\text{M}'$  = trivalent metal ion (i.e.,  $\text{M}^{3+}$ ) on a normal cation sublattice site ( $\text{M}$ ). Compared to the tetravalent ion  $\text{M}^{4+}$ , the trivalent ion carries one negative charge

$\text{M}_\text{M}^\bullet$  =  $\text{M}^{5+}$  on a cation sublattice site ( $\text{M}$ ). It is positively charged.

$\text{Q}_\text{M}^\bullet$  = pentavalent impurity cation ( $\text{Q}^{5+}$ ) on a regular cation site. It has one extra positive charge compared to  $\text{M}^{4+}$  on a regular cation sublattice site

$\text{Q}_\text{M}'$  = trivalent impurity cation ( $\text{Q}^{3+}$ ) on a regular cation site. It is negatively charged.

The concentration unit is typically site fraction or moles/unit volume, for which the symbols for component i are  $C_i$  and  $[i]$ , respectively.

### 4.3.3 Site Fractions

In addition to Kroger-Vink notation, defect concentrations in ionic solids can be expressed as *site fractions* in a manner analogous to that applied to elemental crystals (see Eq (4.9)). Using

MO<sub>2</sub> as an example, these defect site fraction measures are connected to Kroger-Vink notation. For the ions in the normal lattice sites these are:

Cation:

$$C_M = \frac{[M_M]}{[M_M]^*} \quad (4.14)$$

Anion:

$$C_O = \frac{[O_O]}{[O_O]^*} \quad (4.15)$$

The starred concentrations are:

[O<sub>O</sub>]<sup>\*</sup> = concentration of sites on the anion (oxygen) sublattice.

[M<sub>M</sub>]<sup>\*</sup> = concentration of sites on the cation sublattice.

anion vacancy:

$$C_{VO} = \frac{[V_O^{\bullet\bullet}]}{[O_O]^*} \quad (4.16)$$

anion interstitial:

$$C_{IO} = \frac{[O_I^{\bullet}]}{[I_O]^*} \quad (4.17)$$

cation vacancy:

$$C_{VM} = \frac{[V_M^{\bullet\bullet}]}{[M_M]^*} \quad (4.18)$$

cation interstitial:

$$C_{IM} = \frac{[M_I^{\bullet\bullet\bullet}]}{[I_M]^*} \quad (4.19)$$

(4.12f)

aliovalent cation

$$C_{M'M} = \frac{[M_M']}{[M_M]^*} \text{ or } C_{M\bullet M} = \frac{[M_M^{\bullet}]}{[M_M]^*} \quad (4.20)$$

aliovalent impurity

$$C_{Q'M} = \frac{[Q_M']}{[M_M]^*} \text{ or } C_{Q\bullet M} = \frac{[Q_M^{\bullet}]}{[M_M]^*} \quad (4.21)$$

$C_O$  in Eq (4.15) is a macroscopic measure of the gross oxygen concentration in the metal oxide. On the other hand, the site fractions  $C_{VO}$ , etc. are measures of the concentrations of atomic-size point defects.

For the fluorite structure of  $MO_2$

$$[O_o]^* = 2[M_M]^* \quad (4.22)$$

The concentration of cation sites is:

$$[M_M]^* = \frac{\rho_{ox}}{M_{ox}} = \frac{\rho_{ox}}{M_M + 32} \quad (4.23)$$

where  $\rho_{ox}$  is the mass density of the oxide ( $g/cm^3$ ) and  $M_{ox}$  is its molecular weight ( $g/mole$ ).

$[I_M]^*$  = concentration of interstitial sites for cations

$[I_O]^*$  = " " " anions

#### 4.3.4 Site-filling, electrical neutrality and equilibrium

The point-defect volumetric concentrations defined in the preceding section are employed in three types of equations:

1. *site-filling*: these equations identify the species that occupy anion and cation sublattice sites.

In the  $MO_2$  crystal structure, these are:

cation sites:

$$[M_M] + [V_M^{\bullet\bullet}] = [M_M]^* \quad (4.24)$$

which says that a cation sublattice site must contain either a metal ion or a vacancy. The metal ion may need to be divided into the various valence states and any impurity cations.

Similarly, the anion site-filling condition is:

anion sites:

$$[O_o] + [V_o^{\bullet\bullet}] = [O_o]^* \quad (4.25)$$

2. *electric neutrality, or charge balance*: this equation satisfies the requirement that the oxide be electrically-neutral. Using  $MO_2$  as an example, but without multiple cation valences or cation impurities:

$$2[V_o^{\bullet\bullet}] + 4[M_I^{\bullet\bullet\bullet}] = 4[V_M^{\bullet\bullet}] + 2[O_I^{\bullet}] \quad (4.26)$$

3. *equilibrium equations*: describe the thermodynamics among point defects or between point defects and the external gaseous environment (Sect. 4.3.7).

### 4.3.5 Anion Frenkel defects

Frenkel defects can form from either cations or anions. Anion-Frenkel defects are produced by moving an anion from a regular site on the anion sublattice to a site on the anion interstitial sublattice. This process is expressed by:



The law of mass action for this reaction is expressed in terms of site fractions rather than volumetric concentrations:

$$K_{FO} = C_{VO} C_{IO} = e^{s_{FO}/k_B} e^{-E_{FO}/k_B T} \quad (4.28)$$

where the subscript FO denotes Frenkel defects on the anion (oxygen) sublattice. The  $\sigma\Delta v$  term that appears in Eq (4.10) for elemental crystals has been neglected in Eq (4.28).

If anion Frenkel defects are the only point defects in the crystal, electrical neutrality is:

$$[V_o^{\bullet\bullet}] = [O_i^{\bullet}] \quad (4.29)$$

or, in terms of site fractions (from Eqs (4.16) and (4.17)):

$$C_{VO} [O_o]^* = C_{IO} [I_o]^* \quad (4.30)$$

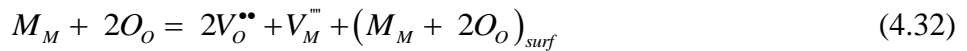
With this relation, Eq (4.28) permits determination of both point-defect site fractions:

$$C_{IO} = \sqrt{2K_{FO}} \quad C_{VO} = \sqrt{K_{FO}/2} \quad (4.31)$$

which assumes that  $2[I_o]^* = [O_o]^*$  (for  $MO_2$ ).

### 4.3.6 Schottky defects

Schottky defects consist of vacant sites on both the anion and cation sublattices (see Fig. 4.5 for the Schottky defect in  $MO_2$ ). The reaction producing a Schottky pair is:



Where  $V_M^{\bullet\bullet\bullet}$  and  $V_o^{\bullet\bullet}$  are vacancies on the cation and anion sublattices, respectively.

$(M_M + 2O_o)_{surf}$  represents bulk ions that have moved to the surface, leaving behind the vacancies.

The law of mass action for Eq (4.32) is:

$$K_S = C_{VO}^2 C_{VM} = e^{s_S/k_B} e^{-E_S/k_B T} \quad (4.33)$$

$K_S$  is the Schottky equilibrium constant expressed in terms of the entropy  $s_S$  and energy  $E_S$  of formation of a Schottky triplet.

In the absence of impurity cations and competing defect processes, charge neutrality is expressed by:

$$2[V_O^{\bullet\bullet}] = 4[V_M^{\bullet\bullet}] \quad (4.34)$$

or, dividing by Eq (4.22):

$$C_{VO} = C_{VM} \quad (4.35)$$

Combining Eqs (4.33) and (4.34) yields the individual vacancy site fractions:

$$C_{VO} = C_{VM} = \sqrt[3]{K_S} \quad (4.36)$$

If the oxide contains aliovalent impurity ions (i.e., ions of different valence from the principal cation), their concentrations are included in Eq (4.22) but the solution method would be similar to that employed in the anion-Frenkel analysis of Sect. 4.3.4.

If other defect formation processes are operative, the charge-neutrality condition of Eq (4.22) must include all charged species. For example, if anion Frenkel defects were dominant,  $C_{VO}$  would be determined by Eq (4.31), not Eq (4.36).

### 4.3.7 Gas-phase/defect equilibrium

Finally, a connection between point defect concentrations and the external environment is needed. For oxides such as  $MO_2$ , this is supplied by the equilibrium between the oxygen partial pressure in the gas phase and point defects in the solid. A possible reaction of this type is:



In the reverse of this reaction, an oxygen atom ( $\frac{1}{2} O_2$ ) enters a vacant anion sublattice site ( $V_O^{\bullet\bullet}$ ) at the same time extracting two electrons from the solid. The result is an  $O^{2-}$  ion on a previously-vacant anion sublattice site ( $O_O$ ). The equilibrium condition for the reaction is expressed by:

$$K = \frac{[V_O^{\bullet\bullet}][e']^2 \sqrt{p_{O_2}}}{[O_O]} \quad (4.38)$$

Gas-solid equilibria other than reaction (4.37) may connect the oxygen partial pressure with point-defect concentrations. The case of  $UO_2$  outlined in Chap. 16 provides a more realistic example.

## References

1. Per Kofstad, "Nonstoichiometry, Diffusion & Electrical Conductivity in Binary Metal Oxides", Wiley-Interscience (1972)
2. F. Kroger & H. Vink, Solid State Physics **3** (1956) 310

## Problems

**4.1.** A substance with the alumina-type( $M_2X_3$ ) crystal structure forms Schottky defects with an equilibrium constant  $K_s$ .

This material is doped with a cation impurity having a valence of +2. The fraction of the cation sites containing the impurity ion is  $x_{DM}$ . Derive the equation for the equilibrium fraction of vacancies on the anion sublattice in the doped crystal. Solve this equation for  $s_s = 4R$ ,  $\epsilon_x = 4$  eV,  $T = 1800$  K, and  $x_{DM} = 10^{-2}$ . Compare this result to the anion vacancy fraction in the undoped crystal and physically explain the difference.

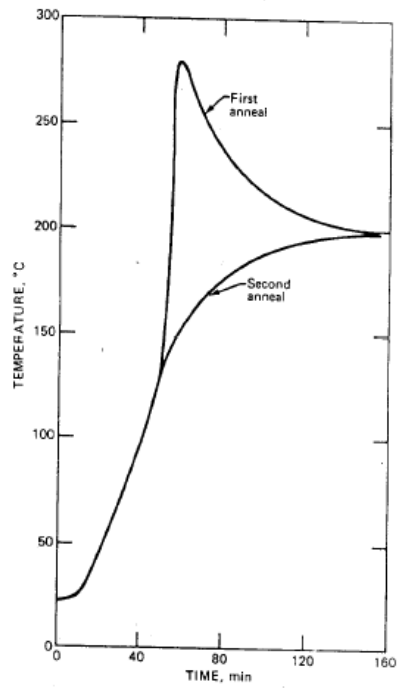
**4.2.** (a) Anion Frenkel and Schottky defects exist in comparable amounts in an  $M_2X$  type crystal. The anion X is divalent and the cation M is univalent. The defect equilibrium constants are  $K_{FX}$  and  $K_s$ , respectively. The number of anion interstitial sites is equal to the number of regular anion sites. What fraction of the anion and cation lattice sites are vacant? (b) Repeat part (a) for an MX type crystal.

**4.3** An  $M_2X$  type Crystal forms Schottky defects with equilibrium constant  $K_s$ . The crystal is doped with a cation site fraction  $x_{DM}$  of an impurity of the DX type. The common anion has a valence of -2. Derive the equation giving the cation vacancy fraction  $x_{VM}$ .

**4.4** The energy stored in graphite as displacements(i.e., vacancy-interstitial pairs, or Frenkel pairs) produced by low-temperature irradiation can be released if the temperature is raised beyond a critical point. The phenomenon is called "Wigner release" after the physicist who first predicted its existence. The phenomenon was responsible for overheating of an early British reactor at Windscale, UK.

The magnitude of the stored energy,  $Q$  J/g, for irradiation of a graphite specimen to a particular fast-neutron fluence is measured in the following experiment. Ten g of irradiated graphite are placed in a furnace and held at  $200^\circ\text{C}$  and the temperature is monitored as a function of time. the upper curve on the graph shows the temperature history. The sample is then cooled to room temperature and the anneal repeated. The lower curve shows the time-temperature behavior of the second anneal. There is no stored energy to be released in the second anneal, so the lower curve represents simple heat transfer between the sample and the furnace. The rate of heat addition is found to be represented by the function  $0.44(200-T)$  J/min, where  $T$  is in  $^\circ\text{C}$ . The temperature at which the two curves diverge is  $128^\circ\text{C}$  and the maximum temperature achieved in the first anneal is  $270^\circ\text{C}$ . The area between the two curves is  $4200^\circ\text{C-min}$ . The heat capacity of graphite is  $1.26$  J/g- $^\circ\text{C}$ .

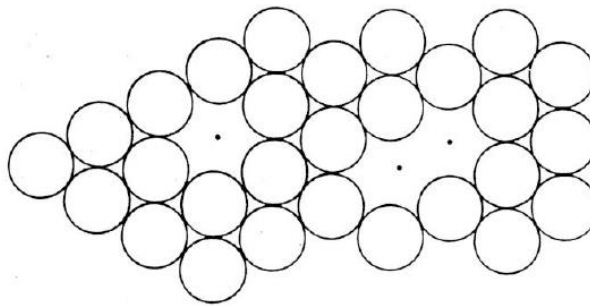




(a) Determine the value of the stored energy per gram of graphite. Hint: the rate of release of stored energy is written as a temperature-dependent function  $q(T)$ , which can be used in developing equations from which  $Q$  can be determined.

(b) If the stored energy is due to recombination of radiation-produced Frenkel pairs, what was the atomic fraction of these pairs prior to annealing. the formation energies of vacancies and interstitials in graphite are 500 and 1340 kJ/moles of defect, respectively. The figure above is the time vs. temperature plot of graphite placed in a furnace held at 200°C. Upper curve; sample previously irradiated at 55°C. Bottom curve: same sample after annealing. (after G.J.Dienes and G.H. Vineyard, *Radiation Effects in Solids*, p.100, Wiley-Interscience, Inc., New York, 1957)

**4.5** In addition to single vacancies, a small concentration of *divacancies* (denoted by  $V_2$ ) is present naturally in elemental solids. The equilibrium concentration of  $V_2$  is maintained by formation from single vacancies ( $V$ ) and thermal decomposition of the divacancies. The divacancy has a negative formation energy with respect to the single vacancies of which it is composed (i.e.,  $\epsilon_{V_2} < 0$ ). The entropy of formation of the divacancy from single vacancies is  $sv_2$ .



Vacancy and divacancy.

Using the “chemical reaction” equilibrium approach (notes, pp. 5 and 6):

- What is the “chemical reaction” that describes formation of the divacancies from single vacancies?
- Write the law of mass action that relates the equilibrium constant  $K_{V_2}$  for the reaction of part (a) to the site-fraction concentrations  $x_V$  of single vacancies and  $x_{V_2}$  of divacancies.
- Express the equilibrium constant  $K_{V_2}$  in terms of  $\epsilon_{V_2}$  and  $sv_2$ .
- Is  $sv_2$  positive or negative? Give reasons
- Does  $x_{V_2}$  increase or decrease as the temperature is increased? Show why with appropriate equations.

**4.6** An ionic crystal of the  $MX_2$  type forms Schottky defects, for which the energy of formation is 200 kJ/mole. By how much should the temperature be reduced from 2000K in order to reduce the concentration of anion vacancies by a factor of 10?

**4.7** The vacancy formation enthalpy of a metal is 1.5 eV. The material is under a pressure of 850 MPa, and the lattice parameter of this simple cubic metal is 0.286 nm. Make a plot of the equilibrium vacancy concentration versus the inverse of absolute temperature ( $K^{-1}$ ) (a) for the case where no pressure is applied and (b) for the case where the pressure above is

applied. How much does the vacancy concentration change at 1500 K when pressure is applied?