Appendix 4A Heat Capacity of Ideal Gases

We can determine the heat capacity from the energy content of materials as a function of temperature. The simplest material to model is an ideal gas, where according to the kinetic theory of gases the average kinetic energy \( (KE) \) per mole of atoms is given by Equation 4A.1:

\[
KE = \frac{3}{2}RT
\]

where \( R \) is the universal gas constant of 8.31 J/mole \cdot K. In an ideal gas, such as the inert gases, the kinetic energy is due to the velocity of the moving atoms.

The first law of thermodynamics is that energy is conserved. If the only ways to input energy \( E \) into a system are by transferring heat \( Q \) into the system or by doing work \( W \) on the system, then the first law of thermodynamics in differential form is shown in Equation 4A.2.

\[
dE = dQ + dW
\]

If a gas is compressed so that the volume decreases by \( dV \), and this requires a pressure \( P \), then the work performed on the gas (input) is \( P \cdot dV \).

For an ideal gas, at temperatures such as room temperature and above, there is no potential energy, because there is no bonding between the atoms; all of the internal energy is kinetic energy \( (E = KE) \). When heat is added to an ideal gas, the velocity of the atoms increases, and this increases the kinetic energy of the gas. If the volume of the ideal gas is held constant \( (dV = 0) \), then the increment of work in Equation 4A.2 is equal to 0 \( (dW = P \cdot dV = 0) \). All of the heat transferred \( (dQ) \) to an ideal gas increases the kinetic energy of the atoms by \( dKE \). For an ideal gas at constant volume, the change in kinetic energy is equal to the change in internal energy, and this is equal to the heat transferred \( (dE = dKE = dQ) \). From Equations 4.2, 4A.1, and 4A.2, the heat capacity of a mole of an ideal gas at constant volume is expressed in Equation 4A.3.

\[
C_V = \left( \frac{dQ}{dT} \right)_{V=\text{const}} = \frac{d \left( \frac{3}{2}RT \right)}{dT} = \frac{3R}{2}
\]

In diatomic gases, such as nitrogen, and gases of molecules, such as methane, the atoms in the molecules vibrate relative to each other and the molecules can rotate, and the vibration and rotation results in larger values of the heat capacity of these gases.

For gases, the specific heat at constant pressure and at constant volume are significantly different. For example, with ideal gases, the heat capacity at constant pressure minus the heat capacity at constant volume is equal to the universal gas constant.
Appendix 4B Molar Heat Capacity of Solids and Liquids

For the analysis of the heat capacity of liquids and solids, we assume that when the material is at a temperature of zero kelvin, this is zero kinetic energy and zero potential energy. The atoms are at their equilibrium interatomic positions. This is a different definition of zero potential energy than we used when developing interatomic potentials, where zero potential energy corresponded to the atoms separated to infinity. Energy is a scalar quantity, and the zero point can be defined wherever it is convenient; then energy changes are calculated relative to this zero. The kinetic energy resulting from the lattice vibrations is due to the velocity of the atoms as they vibrate about an equilibrium interatomic separation, and the potential energy increases as a result of the lattice vibrations displacing the atoms away from the equilibrium interatomic separation. When an atom is at the maximum displacement from the equilibrium interatomic position at a turning point, the kinetic energy in this lattice vibration is zero and the potential energy is a maximum. Then when the atoms pass through the equilibrium interatomic position, the kinetic energy of the lattice vibration is a maximum and the potential energy is zero. These energy changes are similar to the kinetic and potential energy changes of a pendulum. At any particular instant for an individual atom, the kinetic energy and potential energy do not equal each other. However, when the kinetic energy and potential energy due to lattice vibrations are summed over all the atoms in the material, the kinetic energy and potential energy sums are equal, and the time-averaged kinetic energy and potential energy due to lattice vibrations for an individual atom are equal.

At high temperatures the kinetic energy of a mole of the atoms in a solid or liquid is equal to the same value as in the classical gas. The average of the kinetic energy and potential energy due to lattice vibrations for a mole of atoms at temperature ($T$) are equal, as shown in Equation 4B.1.

$$PE = KE = \frac{3}{2}RT$$  \hspace{1cm} 4B.1

The total internal energy ($E$) at high temperatures due to the lattice vibrations is then the sum of the kinetic and potential energy, as shown in Equation 4B.2.

$$E = KE + PE = 3RT$$  \hspace{1cm} 4B.2

If an increment of heat ($dQ$) is added to a solid or liquid at constant volume, then from the first law of thermodynamics we can set $dQ = dE$ because at constant volume the increment of work must be zero ($dW = P \, dV = 0$). Then the heat capacity at constant volume is given by Equation 4B.3.

$$C_v = \left( \frac{dQ}{dT} \right)_{V=\text{const}} = \left( \frac{dE}{dT} \right)_{V=\text{const}} = \frac{d(3RT)}{dT} = 3R$$  \hspace{1cm} 4B.3

This is the value of the classical high-temperature heat capacity of liquids or solids, as shown in Figure 4.2. The heat capacity at constant volume of all solids and liquids at temperatures above the Debye temperature ($\theta_D$) is approximately $3R$. For most materials, the heat capacity is close to $3R$ at room temperature. If the specific heats in Table 4.1 are converted to heat capacities, the values are all approximately equal to $3R$, or $25 \text{ J/mole \cdot K}$, as shown in Example Problem 4.1. At lower temperatures, the heat capacity deviates from the classical high-temperature limit, as shown in Figure 4.2. At low temperatures, the heat capacity is described by quantum mechanical models. Also, there is a jump in the heat capacity when materials undergo phase transformations, as shown for UHMWPE in Figure 4.3b. After phase transformations, the heat capacity returns to $3R$ for solids and liquids at temperatures above the Debye temperature.
Example Problem 4B.1

(a) Calculate the kinetic energy in joules per mole for a solid material at 300 K, and convert this to eV per atom; assume that this is a high temperature for this material. (b) Calculate the kinetic energy for a solid material at 300 K in eV per atom, using Boltzmann’s constant.

Solution

a) In the classical high-temperature limit, the total internal energy is given by $3RT$, half of this internal energy is kinetic and half is potential; therefore the kinetic energy is

$$KE = \frac{3}{2}RT = 1.5 \left(8.31 \frac{J}{\text{mole} \cdot \text{K}}\right)300 \text{ K} = 3740 \frac{J}{\text{mole}}$$

To calculate the kinetic energy per atom, first divide the kinetic energy per mole by Avogadro’s number.

$$KE = 3740 \frac{J}{\text{mole}} \left(\frac{1 \text{ mole}}{6.023 \times 10^{23} \text{atoms}}\right) = 621 \times 10^{-21} \frac{J}{\text{atom}}$$

Next, convert the kinetic energy to eV/atom.

$$KE = 621 \times 10^{-21} \frac{J}{\text{atom}} \left(\frac{1 \text{ eV}}{1.602 \times 10^{-19} J}\right) = 388 \times 10^{-4} \frac{\text{eV}}{\text{atom}} = 0.039 \frac{\text{eV}}{\text{atom}}$$

b) The same result is obtained by using Boltzmann’s constant ($k = 8.62 \times 10^{-5}$ eV/atom $\cdot$ K) instead of $R$ in Equation 4.1.

$$KE = \frac{3}{2}kT = 1.5 \left(8.62 \times 10^{-5} \frac{\text{eV}}{\text{atom} \cdot \text{K}}\right)300 \text{ K} = 0.039 \frac{\text{eV}}{\text{atom}}$$

Boltzmann’s constant is the universal gas constant converted to eV/atom.

Appendix 4C The Entropy of Mixing B-Type Atoms into an A-Type Crystal

In this appendix, the entropy change is determined when $N_B$ B-type atoms are substituted into an A-type crystal. This entropy change is the entropy of mixing ($\Delta S_m$), which is the entropy of the atoms mixed relative to the entropy of the atoms separated. To create an A-type crystal mixed with substitutional B-type atoms, first the substitutional B-type atoms are placed in a lattice without any A-type atoms, and then all of the remaining sites are filled with A-type atoms. In the empty lattice, shown in Figure 4C.1a, assume that this is a large crystal with $N$ possible sites for placement of the first B-type atom.

![Figure 4C.1](image)

(a) A lattice with no atoms. (b) One B-type atom placed in the lattice. (c) Two B-type atoms placed in the lattice.
The number of ways to arrange one B-type atom \([\omega(1)]\) in a crystal with \(N\) possible sites is equal to \(N\), as shown in Equation 4C.1.

\[
\omega(1) = \frac{N}{1} \quad 4C.1
\]

The reason for dividing \(N\) by 1 in Equation 4C.1 will become apparent. Assume that the first B-type atom is placed as shown in Figure 4C.1b. If there are two substitutional B-type atoms, then there are \(N\) places for the first atom, but for the second atom there are only \(N - 1\) sites remaining after the first atom is placed. The atom arrangement after the placement of the second atom, shown in Figure 4C.1c, is identical if the first and second atom placements are interchanged, because the two B-type atoms are identical and cannot be distinguished from each other. With two B-type atoms, half of the total ways of arranging the atoms are identical, so that the number of ways of arranging two B-type atoms on \(N\) sites is the product of the number of ways of arranging each atom divided by 2, as shown in Equation 4C.2.

\[
\omega(2) = \binom{N}{1} \left( \frac{N-1}{2} \right) \quad 4C.2
\]

Equation 4C.3 provides the number of ways of arranging three identical substitutional B-type atoms on \(N\) sites.

\[
\omega(3) = \binom{N}{1} \left( \frac{N-1}{2} \right) \left( \frac{N-2}{3} \right) \quad 4C.3
\]

If there are \(N_B\) identical substitutional atoms that have \(N\) possible sites, the total number of different ways of arranging these is given by Equations 4C.4 and 4C.5

\[
\omega(N_B) = \binom{N}{1} \left( \frac{N-1}{2} \right) \left( \frac{N-2}{3} \right) \ldots \left( \frac{N - N_B + 1}{N_B} \right) \quad 4C.4
\]

\[
\omega(N_B) = \frac{N(N-1)(N-2) \ldots (N - N_B + 1)}{N_B!} \quad 4C.5
\]

where \(N_B! = 1 \times 2 \times 3 \times 4 \ldots \times N_B\). Multiplying the numerator and denominator of Equation 4C.5 by \((N - N_B)!\) results in Equation 4C.6.

\[
\omega(N_B) = \frac{N!}{N_B!(N - N_B)!} \quad 4C.6
\]

Once the B-type atoms are placed in the crystal, all of the A-type atoms are placed in the empty sites to complete the crystal. The entropy of randomly mixing \(N_B\) substitutional atoms into a crystal is then calculated from Equation 4.11, resulting in Equation 4C.7.

\[
\Delta S_m = k \ln \omega(N_B) \quad 4C.7
\]

\(\Delta S_m\) is simplified with Stirling’s approximation as given in Equation 4C.8.

\[
\ln N! \approx N \ln N - N \quad 4C.8
\]

To obtain Equation 4C.9.

\[
\Delta S_m = -kN \left[ \frac{N_B}{N} \ln \left( \frac{N_B}{N} \right) + \left( \frac{N - N_B}{N} \right) \ln \left( \frac{N - N_B}{N} \right) \right] \quad 4C.9
\]
The quantity \( N_B/N \) is the atom fraction of substitutional B-type atoms \((C_B)\), and \((N - N_B)/N\) is the atom fraction of host A-type atoms \((C_A)\), so that \( \Delta S_m \) can be written as Equation 4C.10 in terms of the atom fractions.

\[
\Delta S_m = -kN(C_A \ln C_A + C_B \ln C_B)
\]

Equation 4C.10 is the same as Equation 4.12.

**Appendix 4D Derivation of the Equilibrium Concentration of Substitutional Point Defects in a Crystal**

In this section we derive the form of Equation 4.16 that gives the equilibrium concentration of point defects that substitute for atoms in a crystal, and in this example we use the vacancy. The Gibbs free energy \((G)\) of a crystal with \(N_v\) vacancies and \(N_O\) occupied sites is given by an equation similar to 4.18, as shown in Equation 4D.1:

\[
G = G_0 + N_v \Delta G_v = G_0 + N_v \Delta H_v - T \Delta S_m
\]

where \(G_0\) is the Gibbs free energy of a crystal without vacancies, \(\Delta H_v\) is the enthalpy required to create one vacancy, and \(\Delta S_m\) is the entropy change resulting from mixing the \(N_v\) vacancies into a perfect crystal. The entropy of mixing \((\Delta S_m)\) results from the probability that at each site it is possible that the site is occupied by an atom or vacant. The equilibrium concentration of vacancies that minimizes the Gibbs free energy is determined from Equation 4D.2.

\[
\frac{\partial G}{\partial N_v} = 0
\]

First we determine the partial derivative of the entropy of mixing term \((\Delta S_m)\) for vacancy substitutions. \(\Delta S_m\) is expressed in Equation 4C.10, and written for vacancies the result is Equation 4D.3.

\[
\Delta S_m = -kN(C_v \ln C_v + C_o \ln C_o)
\]

where \(C_v\) and \(C_o\) are defined in Equations 4D.4.

\[
C_v = \frac{N_v}{N} \text{ and } C_o = \frac{N_O}{N}
\]

Writing the entropy of mixing in Equation 4D.3 in terms of \(N_v\), \(N_O\), and the total number of sites \((N = N_O + N)\) results in Equation 4D.5.

\[
\Delta S_m = -kN \left[ \left( \frac{N_v}{N} \right) \ln \left( \frac{N_v}{N} \right) + \left( \frac{N_O}{N} \right) \ln \left( \frac{N_O}{N} \right) \right]
\]

Cancelling out \(N\) and rewriting the natural log functions as differences in logs results in Equation 4D.6.

\[
\Delta S_m = -k \left[ (N_v \ln N_v - \ln N) + N_O \ln N_O - \ln N \right]
\]
Multiplying terms and collecting terms in Equation 4D.6 results in Equation 4D.7.

\[
\Delta S_m = -k \left( N_v \ln N_v + N_o \ln N_o - N \ln N \right) \tag{4D.7}
\]

Equation 4D.7 can also be rewritten by noting that \( N = N_o + N_v \) as shown in Equation 4D.8.

\[
\Delta S_m = -k \left( N_v \ln N_v + N_o \ln N_o - (N_o + N_v) \ln (N_o + N_v) \right) \tag{4D.8}
\]

Now taking the partial derivative of \( \Delta S_m \) with respect to \( N_v \) and noting that the number of occupied sites \( (N_o) \) is a constant results in Equation 4D.9.

\[
\frac{\partial \Delta S_m}{\partial N_v} = -k \left[ \ln N_v + 1 - \ln (N_o + N_v) - 1 \right] \tag{4D.9}
\]

Equation 4D.9 can be rewritten as Equation 4D.10.

\[
\frac{\partial \Delta S_m}{\partial N_v} = -k \ln \frac{N_v}{N_o + N_v} = -k \ln \frac{N_v}{N} \tag{4D.10}
\]

Inserting Equation 4D.10 into Equation 4D.2 and taking the partial derivative of the Gibbs free energy of the crystal with respect to \( N_v \) vacancies results in Equation 4D.11.

\[
\frac{\partial G_v}{\partial N_v} = \frac{\partial N_v \Delta H_v}{\partial N_v} - T \frac{\partial \Delta S_m}{\partial N_v} = \delta H_v - T k \ln \frac{N_v}{N} = 0 \tag{4D.11}
\]

In taking the partial derivative in Equation 4D.2, all other variables, such as temperature and pressure, are held constant. Solving Equation 4D.11 for the atom fraction of vacancies \( (N_v / N) \) results in Equation 4D.12.

\[
\frac{N_v}{N} = \exp \left( -\frac{\Delta H_v}{kT} \right) \tag{4D.12}
\]

Equation 4D.12 for the concentration of vacancies that minimizes the Gibbs free energy is of the same form as Equation 4.16.

**Appendix 4E Derivation of Fick’s Second Law of Diffusion**

Figure 4E.1 shows the plane view of the front face of a volume of material \( (\Delta V) \) that has a cross-sectional area \( (A) \) that is made by taking sections at \( x \) and \( x + \Delta x \) through the diffusion couple shown in Figure 4.15. At time \( t \) a flux of B-type atoms per square meter per second \( J_B(x, t) \) flows into the volume at \( x \), and a flux \( J_B(x + \Delta x, t) \) flows out of the volume at \( x + \Delta x \). If \( J_B(x, t) \) is larger than \( J_B(x + \Delta x, t) \), B-type atoms are accumulating in the volume \( (\Delta V) \) at a rate equal to the change in concentration \( \Delta C_B(x, t) \) times the volume \( (\Delta V) \) divided by the time \( (\Delta t) \) over which the change in concentration occurs. The rate
of accumulation of B-type atoms is also equal to the flux of B-type atoms into the volume minus the flux of B-type atoms out of the volume \( J_B(x, t) - J_B(x + \Delta x, t) \) times the area (A), as shown in Equation 4E.1.

\[
[J_B(x, t) - J_B(x + \Delta x, t)]A = \frac{\Delta C_B(x, t) \Delta V}{\Delta t} \tag{4E.1}
\]

The dimensions of each side of Equation 4E.1 are B-type atoms per second.

The increment of volume \( \Delta V \) is equal to \( \Delta x \) times the area (A), and area cancels on each side of the equation, resulting in Equation 4E.2.

\[
J_B(x, t) - J_B(x + \Delta x, t) = \frac{\Delta C_B(x, t) \Delta x}{\Delta t} \tag{4E.2}
\]

The left side of Equation 4E.2 is equal to the negative of the change in flux \([-\Delta J_B(x, t)]\). Making this substitution and dividing each side of Equation 4E.2 by \( \Delta x \) results in Equation 4E.3:

\[
-\frac{\Delta J_B(x, t)}{\Delta x} = \frac{\Delta C_B(x, t)}{\Delta t} \tag{4E.3}
\]

Rewriting Equation 4E.3 in differential form, assuming that the variables \( x \) and \( t \) are separable, and inserting \( J_B(x, t) \) from Fick’s first law of diffusion in Equation 4.38 results in Equation 4E.4:

\[
\frac{\partial J_B(x, t)}{\partial x} = -\frac{\partial D_B}{\partial x} \left[ \frac{\partial C_B(x, t)}{\partial x} \right] = \frac{\partial C_B(x, t)}{\partial t} \tag{4E.4}
\]

where \( D_B \) is the diffusion coefficient of the B-type material into A-type material. Assuming that \( D_B \) is not a function of \( x \) or \( t \) results in Equation 4E.5.

\[
D_B \frac{\partial^2 C_B(x, t)}{\partial x^2} = \frac{\partial C_B(x, t)}{\partial t} \tag{4E.5}
\]

Equation 4E.5 is Fick’s second law of diffusion.