

PART II

THE ATOMIC ORIGINS OF THERMODYNAMICS AND KINETICS

Free energy is a central topic of this book because a phase transition occurs in a material when its free energy, or a derivative of its free energy, has a singularity. Chapter 2 showed how to use the dependence of free energy on composition or order parameter to obtain thermodynamic phase diagrams. Chapters 3 and 4 discussed the kinetics of diffusion and nucleation, which can be calculated with an activated state rate theory that uses a free energy of activation. Chapter 5 showed how the free energies of equilibrium phases and the free energies of activation give rise to competition between thermodynamic and kinetic phenomena in phase transformations such as alloy solidification, glass formation, and thin film reactions.

The Gibbs free energy is

$$G = E - TS + PV .$$

Chapter 6 discusses the sources of energy of materials that are important for phase transitions. The next Chapter 7 addresses the important sources of entropy, and Chapter 8 discusses effects of pressure. Finally, Chapter 9 explains chemical effects on diffusion in alloys, which depend on the free energy of an activated state. This coverage of E , S , P , and ΔG^* comprises Part II of the book.

This Chapter 6 explains the different types of energies that are important for the thermodynamics of materials phases and materials microstructures, and some techniques for calculating them. It begins with the chemical bond between two atoms – a fundamentally quantum mechanical phenomenon that depends on the coherent interference of an electron wavefunction with itself, giving an electron density that is not a linear sum of densities from two separate atoms. In a periodic solid or in a large box for electrons, the number of electron states depends on a wavevector k , which can be used to obtain the spectrum of electron energies. The concepts presented here are important, but quantitative results require quantum chemical computer calculations.

At a more general, but more phenomenological level, interatomic potentials are described and used to explain the elastic behavior of solids. The elastic energy of a misfitting solid particle in a matrix is discussed, and this misfit energy is generally important for precipitation reactions in solid materials. Surface energy is also described, along with the Wulff construction for predicting the shapes of crystals and precipitates.

6.1 Molecular Orbital Theory of Diatomic Molecules

6.1.1 Interacting Atoms

Start with two isolated atoms, A and B. There are states for a single electron about each atom of energy ϵ_A and ϵ_B , set by the Schrödinger equations

$$-\frac{\hbar^2}{2m}\nabla^2\psi_A(\vec{r}) + V_A(\vec{r})\psi_A(\vec{r}) - \epsilon_A\psi_A(\vec{r}) = 0, \quad (6.1)$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi_B(\vec{r}) + V_B(\vec{r})\psi_B(\vec{r}) - \epsilon_B\psi_B(\vec{r}) = 0, \quad (6.2)$$

where ψ_A and ψ_B are single-electron wavefunctions at atoms A and B. As isolated atoms, their nuclei are far apart. Now bring the nuclei close enough together so their wavefunctions overlap. Our goal is to understand what the individual electrons do in the presence of both atoms, and understand the chemical bond in the new diatomic molecule.

We seek single-electron wavefunctions for the diatomic molecule. The potential

proves to be a real challenge because the potential for one electron depends on the presence of the second electron. The effect of the second electron is to push around the first electron, but this alters the potential and wavefunction of the second electron. Iterative methods are the most accurate for this problem, but here assume that the total potential is simply the sum of potentials of the isolated atoms

$$V(\vec{r}) = V_A(\vec{r}) + V_B(\vec{r}) . \quad (6.3)$$

This approach does not always work, especially when there are large electron transfers between atoms, which alter the atomic potentials. The approach works best when the overlap of the atom wavefunctions is small, and the potentials tend to retain their original character. We make a related assumption that a single electron is in a wavefunction ψ constructed from the original atomic wavefunctions

$$\psi(\vec{r}) = c_A \psi_A(\vec{r}) + c_B \psi_B(\vec{r}) . \quad (6.4)$$

It is important to remember that ψ pertains to a single electron, so the coefficients c_A and c_B are less than 1 (the atomic wavefunctions ψ_A and ψ_B accommodate one electron each). This ψ is a “molecular orbital” for one electron. We started with two electrons though, so we need to find two molecular orbitals. To do so, lay out the molecular Schrödinger equation twice and do two standard tricks: 1) multiply by $\psi_A^*(\vec{r})$ and $\psi_B^*(\vec{r})$

$$-\frac{\hbar^2}{2m} \psi_A^*(\vec{r}) \nabla^2 \psi(\vec{r}) + \psi_A^*(\vec{r}) V(\vec{r}) \psi(\vec{r}) - \epsilon \psi_A^*(\vec{r}) \psi(\vec{r}) = 0 , \quad (6.5)$$

$$-\frac{\hbar^2}{2m} \psi_B^*(\vec{r}) \nabla^2 \psi(\vec{r}) + \psi_B^*(\vec{r}) V(\vec{r}) \psi(\vec{r}) - \epsilon \psi_B^*(\vec{r}) \psi(\vec{r}) = 0 , \quad (6.6)$$

and 2) integrate

$$\langle A|H|A\rangle c_A + \langle A|H|B\rangle c_B - \epsilon(c_A + \langle A|B\rangle c_B) = 0 , \quad (6.7)$$

$$\langle B|H|A\rangle c_A + \langle B|H|B\rangle c_B - \epsilon(\langle B|A\rangle c_A + c_B) = 0 , \quad (6.8)$$

where the integrals are written in Dirac notation. Equations 6.7 and 6.8 can be arranged as a matrix equation

$$\begin{bmatrix} \langle A|H|A\rangle - \epsilon & \langle A|H|B\rangle - \epsilon\langle A|B\rangle \\ \langle B|H|A\rangle - \epsilon\langle B|A\rangle & \langle B|H|B\rangle - \epsilon \end{bmatrix} \begin{bmatrix} c_A \\ c_B \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} . \quad (6.9)$$

6.1.2 Definitions and Conventions

Before solving Eq. 6.9 for ϵ and then for c_A and c_B , we evaluate some terms and change notation. The integrals $\langle A|B\rangle$ and $\langle B|A\rangle$ are not zero – the wavefunctions are centered on different atoms, but the tails of these wavefunctions overlap. These are “overlap integrals,” defined as S

$$S \equiv \langle A|B\rangle = \langle B|A\rangle . \quad (6.10)$$