2 Essentials of T-c Phase Diagrams

This Chapter 2 explains the concepts behind T-c phase diagrams, which are maps of the phases that exist in an alloy of chemical composition c at temperature T.[1] A T-c phase diagram displays the phases in thermodynamic equilibrium, and these phases are present in the amounts f, and with chemical compositions that minimize the total free energy of the alloy. The emphasis in this Chapter 2 is on deriving T-c phase diagrams from free energy functions $F(c, T)$.[2] The constraint of solute conservation is expressed easily as the "lever rule." The minimization of the total free energy leads to the more subtle "common tangent construction" that selects the equilibrium phases at T from the $F(c)$ curves of the different phases. For binary alloys, the shapes of $F(c)$ curves and their dependence on temperature are used to deduce eutectic, peritectic, and continuous solid solubility phase diagrams. Some features of ternary alloy phase diagrams are also discussed.

If atoms occupy sites on a lattice throughout the phase transformation, free energy functions can be calculated with a minimum set of assumptions about how different atoms interact when they are brought together. Because the key features of phase diagrams can be obtained with general types of interactions between atoms, systems with very different types of chemical bonding, e.g., both oil in water and iron in copper, can show similar phase transitions. In these unmixing cases, the individual atoms or molecules prefer their like species as neighbors (see Fig. 1.4). The opposite case of a preference for unlike atom neighbors leads to chemical ordering at low temperatures, which requires the definition of an order parameter, L. These generalization of chemical interactions should not be lamented for their loss of rigor, but celebrated as a way to identify phenomena common to many phase transitions. Such "emergent" behavior can be missed if there is too much emphasis on the electronics of chemical bonding and atom vibrations. Nevertheless, we must be wise enough to know the predictive power available at different levels of generalization.

2.1 Overview of the Approach

Temperature promotes disorder in a material, favoring higher-entropy phases such as liquids, but the chemical bond energy favors ordered crystals at low tempera-

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[1] Pressure is assumed constant, or negligible.

[2] The usage of phase diagrams is deferred to Chapter 5.

tures. This information alone is sufficient to predict a phase change with temperature, but adding a bit more detail about the energy and entropy rewards us with considerably more information about alloy phase diagrams, and this is the essence of the present chapter.

The thermodynamic functions of the alloy, E and S, depend on the spatial arrangement of the atoms in the alloy.[3] In what follows, a minimal atomistic model is constructed to calculate thermodynamic functions and predict the equilibrium phases in alloys at different combinations of T and chemical composition c. This minimal model successfully predicts the main features of T-c phase diagrams for binary A-B alloys (A and B are the two species of atoms). Sometimes the free parameters in this approach, the pairwise atomic bond energies, can be tuned to fit phase transitions in a specific material, and sometimes the alloy thermodynamics can be extrapolated successfully into regions where no experimental data exists. Convenience for calculation is a virtue and a priority for this chapter, but we must be aware of the two types of risks it entails

1. A good parameterization of atom positions may require more detail than is possible with a simple model.
2. Even if the parameterizations of atom positions are excellent, calculating the energy or entropy from these parameterizations may require more sophisticated methods.

Part II of this book addresses these two issues in more detail. Nevertheless, the simple models developed in this chapter are often useful semiquantitatively, and are useful benchmarks for assessing the value added by more sophisticated treatments.

This book will not emphasize methods to calculate the energy of the phases, E, as is done today by electronic structure calculations, such as density functional theory with plane wave pseudopotentials.[4] Nevertheless, because the energies of the electrons in a material are set by the positions of the nuclei (i.e., the configurations of atoms), a good parameterization of atom configurations can accommodate more advanced analyses, too. Here we obtain E from local atomic arrangements, typically as a sum of energies of chemical bonds between the nearest-neighbor pairs of atoms. The entropy of an alloy also depends on atom configurations, often local ones.

For alloy thermodynamics we need expressions for $E(c)$ and $S(c)$, for which the Helmholtz free energy is

$$F(c,T) = E(c) - T\Big[S_{\text{config}}(c) + S_{\text{vib}}(c,T)\Big]\,. \tag{2.1}$$

In a first approximation, the electronic energy $E(c)$ is assumed to be independent of temperature, as is the way configurations are counted to obtain the configurational entropy $S_{\text{config}}(c)$. If $E(c)$ and $S_{\text{config}}(c)$ depend only on local atom configurations

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[3] This restates the paradigm that the atom arrangements in a material determine its properties, including thermodynamic properties.

[4] These methods are powerful, and will grow in importance to materials science. This is a large topic, however, and deserves a course of its own.

in a crystal, it is efficient to use a fixed lattice and pairwise chemical bonds. For solid solution phases, it is also convenient to assume statistical randomness of atom occupancies of the sites on the lattice.[5] Two important T-c phase diagrams, unmixing and ordering, can be obtained readily by minimizing such an $F(c, T)$ on an Ising lattice. More generally, there is competition between multiple phases that cannot be placed naturally on the same lattice, so each phase has a different $F(c, T)$. Minimizing the total free energy by varying the compositions and fractions of the phases requires the "common tangent" algorithm that allows us to complete the set of the five main types of T-c phase diagrams for binary alloys. With these assumptions, the two general risks listed above can be stated more specifically

1. Chapter 7 goes beyond the assumed random environment of an *average* atom, i.e., the "point approximation." One approach is to use probabilities of local "clusters" of atoms, working up systematically from chemical composition (point), to numbers of atom pairs (pair), then tetrahedra. Usually the energy and entropy of materials originate from local characteristics of atom configurations, so this approach has an excellent record of success.
2. How accurately can we account for the energy and entropy of the material? For example, the electronic energy, which provides the thermodynamic E, need not be confined to neighboring pairs of atoms. The energy of delocalized electrons in a box or in a periodic crystal is introduced in Chapter 6. This Chapter 2 ignores the entropy caused by the thermal vibrations of atoms, $S_{\mathrm{vib}}(c, T)$, the entropy from disorder in magnetic spins, $S_{\mathrm{mag}}(c, T)$, and the entropy from disorder in electron state occupancies, $S_{\mathrm{el}}(c, T)$. These will have to be assessed later.[6]

2.2 Intuition and Expectations about Alloy Thermodynamics

2.2.1 Free Energies of Alloy Phases

Alloys often transform to different phases at different temperatures. We have already mentioned the liquid at high temperatures and ordered structures at low temperature. Here, listed from high to low temperature, are some typical phases that are found for an alloy system ("system" meaning a range of compositions for specified chemical elements), with considerations of the Helmholtz free energy, $F(c) = E(c) - TS(c)$, for each phase

- The phase of maximum entropy dominates at the highest temperatures. For most materials this is a gas of isolated atoms, but at lower temperatures most

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[5] Or, analogously for an order parameter, the sublattice occupancies are assumed random.

[6] A textbook could start to develop phase diagrams by using $S_{\mathrm{vib}}(c, T)$ and ignoring $S_{\mathrm{config}}(c)$, but this would be unconventional.

Box 2.1 Configurational and Dynamical Sources of Entropy

We take the statistical mechanics approach to entropy, and count the configurations of a system with equivalent macrostates, giving the Ω for Eq. 1.10. For counting:

- Procedures to count atom arrangements (or spin arrangements) are independent of temperature.
- On the other hand, procedures to count states explored with thermal excitations, such as atom vibrations or electronic excitations, do depend on temperature.

This separation works well for the thermodynamics of crystals at modest temperatures. If atom mobility becomes extremely rapid while some vibrations become very slow, as when a liquid changes its viscosity with temperature, its reliability may be in doubt.

The reader should know that at a temperature of 1,000 K or so, S_{vib} is typically an order-of-magnitude larger than S_{config} (compare Figs. 2.9a and 10.3). It is possible for S_{vib} to be similar for different phases, however, so the difference in entropy caused by vibrations is not always dominant in a phase transition. Nevertheless, S_{vib} usually does depend on atom configurations, and this is developed for independent harmonic oscillations in Section 7.8. At high temperatures, however, vibrations change their frequencies, and normal modes of vibration interact with each other, so the statistical mechanics of harmonic vibrations needs significant modifications (Chapter 24).

alloys form a liquid phase with continuous solubility of A and B-atoms. (There are cases of chemical unmixing in the liquid phase, however, for which the thermodynamics of Eq. 2.19 is again relevant.)

- At low-to-intermediate temperatures, the equilibrium phases and their chemical compositions depend in detail on the free energy versus composition curves $F_{\xi}(c)$ for each phase ξ. Usually there are chemical unmixings, and the different chemical compositions frequently prefer different crystal structures. The chemical unmixings may not require precise stoichiometries (e.g., a precise composition of A_2B_3) because some spread of compositions may provide entropy to make off-stoichiometric compositions favorable (e.g., $A_{2-\delta}B_{3+\delta}$).
- At the lowest temperatures, the equilibrium state for a general chemical composition is a combination of crystalline phases, usually with precise stoichiometries. These often correspond to crystal structures that have unique sites for the different atom species, and a high degree of long-range order.[7]

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[7] At low temperatures, atoms usually do not have enough mobility to form these precise structures, so some chemical disorder is often observed.