Problem 1:

Explain the following observations:

(a) Materials that crystallize in the CsCl structure are ionic or metallic in their bonding, never covalent.

(b) Materials that crystallize in the Cu₃Au structure are never ionic.

(c) Materials that crystallize in the β-ZnS structure are covalent or ionic.

(d) Materials that crystallize in the NaCl structure may be ionic, like NaCl, or metallic, like TiC. But they are never covalent.

(e) The NaCl structure is fcc with additional atoms in all octahedral voids. The NiAs structure is hcp with additional atoms in all octahedral voids. In NaCl it makes no difference which, Na or Cl, I take to be the interstitial ion, but in NiAs I must take Ni as the interstitial specie.
Problem 2:

(a) The Second Law of Thermodynamics states that the entropy of an isolated system can only increase. Use this fact to show that when a binary system has fixed temperature, pressure and chemical content, its Gibbs free energy can only decrease.

(b) Show that if the system of part (a) has heterogeneous composition, the solute (1) will diffuse down the gradient in the relative chemical potential, \( \bar{\mu} = \mu_1 - \mu_2 \).

(c) Diffusion usually obeys Fick’s First Law. For a one-dimensional concentration gradient

\[
J = -nD \frac{dc}{dx}
\]

This “law” makes it appear that the driving force for diffusion is the concentration gradient, rather than the chemical potential gradient. Explain.

(d) Let a crystalline solid have a one-dimensional gradient in the composition of an interstitial species. Let the solute diffuse by performing random, discrete atom jumps from plane to plane in the crystal. Derive an expression for the diffusivity, D, that appears in Fick’s First Law.
Problem 3:

Explain the following observations about the thermal properties of materials:

(a) The valence electrons in a metal are energetic particles that wander throughout the metal at high velocity. Nonetheless, they contribute very little to the heat capacity of the metal.

(b) While they contribute very little to the heat capacity of a metal, the valence electrons are almost completely responsible for its thermal conductivity. The thermal conductivity increases with the electrical conductivity.

(c) But the highest room temperature thermal conductivity is found in diamond, which is an insulator with almost no electrical conductivity.

(d) When diamond transforms to the more stable form of carbon, graphite, its electrical conductivity rises dramatically, but its thermal conductivity decreases.

(e) But other good insulators, such as silica glass, have such low values of the thermal conductivity at room temperature that they are used as thermal insulators.
Problem 4:

(a) The kinetics of a nucleated phase transformation that happens on cooling are qualitatively represented by a c-curve of the sort given in the notes. Briefly explain why the kinetic curve has this characteristic shape.

(b) Sketch a similar figure that represents the transformation kinetics of a material that solidifies into either a crystalline solid or a glass on cooling. Locate the “glass transition temperature” $T_g$, on the plot.

(c) Sketch a similar figure that represents the transformation kinetics of a solid that transforms on cooling by either a nucleated or a martensitic transformation. Define and explain the “$M_s$” and “$M_f$” temperatures of the martensite.

(d) Consider a polygranular material that has the kinetic transformation curve you sketched in part (c). Describe the heat treatment process you would use to achieve a microstructure that has bands of relatively equiaxed grains along the grain boundaries of the parent structure, with martensitic material filling the grain interiors of the parent structure.

(c) Now consider a nucleated transformation that happens on heating. Sketch and explain the kinetic transformation curve.
Problem 5:

Explain the following observations:

(a) Nuggets of pure gold can be found in nature.

(b) Nuggets of metallic iron are almost never found in nature.

(c) While aluminum is one of the most common elements in nature, metallic aluminum was technologically unavailable until fairly recent times.

(d) One good reason to recycle aluminum beverage cans is that, if thrown on the side of the road, they remain there as eyesores for a very long time.

(e) While aluminum beverage cans remain unchanged for very long times in air, fine particles of metallic Al can oxidize so rapidly, even at low temperature, that aluminum-bearing dusts are likely to explode.
Problem 1:

(a) Ionic binary compounds (AB) are commonly found in one of three crystal structures. Which are they?

(b) How would you predict which of those structures a particular AB ionic compound would adopt?

(c) Two of those structures are also common in 50-50 metallic compounds (AB). One is not. Which and why?

(d) The Cu₃Au structure is never found in binary ionic compounds. Why?

(e) A Cu₃Au pattern is often found in ternary ionic compounds (e.g., BaTiO₃) that have the perovskite or related structures. Given the result of part (d), how can you explain this?
Problem 2:

(a) The Second Law of Thermodynamics states that the entropy of an isolated system can only increase. Use this fact to show that when a binary system has fixed temperature, pressure and chemical content, its Gibbs free energy can only decrease.

(b) Show that if the system of part (a) has heterogeneous composition, the solute (1) will diffuse down the gradient in the relative chemical potential, $\bar{\mu} = \mu_1 - \mu_2$.

(c) Diffusion usually obeys Fick’s First Law. For a one-dimensional concentration gradient

$$J = -nD \frac{dc}{dx}$$

This “law” makes it appear that the driving force for diffusion is the concentration gradient, rather than the chemical potential gradient. Explain.

(d) Let a crystalline solid have a one-dimensional gradient in the composition of an interstitial species. Let the solute diffuse by performing random, discrete atom jumps from plane to plane in the crystal. Derive an expression for the diffusivity, D, that appears in Fick’s First Law.
Problem 3:

A binary system of atoms A and B has the simple eutectic phase diagram drawn below.

(a) Give the phases present, their compositions and their mole fractions at each of the three points indicated by dots in the phase diagram. (Assume an overall composition x = 0.1 and give plausible estimates for any other compositions you need.)

(b) Draw the expected microstructure of the solid that forms when a sample of composition 3 is cooled from the liquid phase. Explain why this microstructure should form.

(c) Suppose that a sample of composition 1 is held for a long time at the temperature indicated by the dot in the α-field, and is then cooled to room temperature. What microstructure is likely if the sample is cooled very rapidly? What microstructure if it is cooled slowly? Why?
Problem 4:

Explain the following observations concerning oxidation and corrosion:

(a) While very fine particles of iron can burn spontaneously in air (for example, the sparks thrown off during the machining of steel), a bulk sample of iron oxidizes at a negligible rate unless the temperature is very high.

(b) If the same bulk sample of iron is immersed in damp soil, it oxidizes (rusts) fairly quickly.

(c) If a bulk sample of iron is immersed in damp soil very near a piece of zinc, the iron corrodes just as it would if the zinc were not there. But if the iron is connected to the zinc by a thin metal wire, the iron immediately stops corroding, and is protected from further corrosion until the zinc has corroded away.

(d) If Fe is heavily doped with C or P, it becomes amorphous in structure. If amorphous Fe is brought into contact with ordinary, crystalline Fe in damp soil, it corrodes rapidly. However, if the amorphous Fe forms a continuous coating over the surface of the Fe, it is very resistant to corrosion. Explain.

(e) Fe remains bright and uncorroded for long periods of time in moist air and some damp soils, if it is alloyed with more than 8% Cr.
Problem 5:

Visible light spans a range of wavelength between 0.4-1.0 μm, corresponding to a photon energy between $\approx 1.2\text{eV}$ and $\approx 3\text{ eV}$.

(a) An old practical test says that if you can see through a piece of material, it is almost certainly a good insulator. Why?

(b) Why the modifier "almost"? How can a transparent material fail to be a good insulator?

(c) On the other hand, there are many good insulators that you cannot see through, including both opaque ceramics and brightly colored plastics. Describe at least one microstructure that creates an opaque insulator.

(d) A good choice for the window of a solar heater would have low absorption in the visible range and high absorption in the infrared. Why?

(e) What in the nature of a material would cause it to have good absorption in the infrared while being transparent in the visible? Would you expect common window glass to be such a material?
Problem 1:

(a) The NaCl structure is adopted by ionic and by metallic systems, but not by covalent ones. Why no covalent crystals? What characteristic would you expect in a metallic compound that took on the NaCl structure?

(b) The β-ZnS structure is common in covalent and ionic compounds, but not in metallic compounds. Why might you expect to find covalent compounds in this structure? What would be the characteristic feature of an ionic compound that crystallized in this structure?

(c) Would you expect to find ionic compounds in the Cu₃Au structure? Why (or why not)?
Problem 2:

The 2\textsuperscript{nd} law of thermodynamics has the consequence that the equilibrium of an isolated system requires that its entropy be maximum.

(a) Show that a system with fixed values of T, V and \{N\} is in equilibrium if and only if its Helmholtz free energy is a minimum with respect to any small change in its state.

(b) What is meant by a “metastable” equilibrium state? What conditions must hold for a metastable state to exist?

(c) Show that the free energy per unit volume of a one-component solid can be written

\[ F(T) = E_0(T) + \int_0^T c_v \left[ 1 - \frac{T}{T'} \right] dT' \]

where \(E_0\) is the binding energy and \(c_v\) is the isometric specific heat. Given the Debye model for the specific heat, show that phases that become stable at high T will ordinarily have lower values of the Debye temperature than those that appear at lower temperature.
Problem 3:

A binary system of atoms A and B has the simple eutectic phase diagram drawn below.

(a) Give the phases present, their compositions and their mole fractions at each of the three points indicated by dots in the phase diagram. (Assume an overall composition \( x = 0.1 \) and give plausible estimates for any other compositions you need.)

(b) Draw the expected microstructure of the solid that forms when a sample of composition 3 is cooled from the liquid phase. Explain why this microstructure should form.

(c) Suppose that a sample of composition 1 is held for a long time at the temperature indicated by the dot in the \( \alpha \)-field, and is then cooled to room temperature. What microstructure is likely if the sample is cooled very rapidly? What microstructure if it is cooled slowly? Why?
Problem 4:

(a) The specific heat of a typical metal lid is the sum of electronic and vibrational contributions. The electronic contribution is ordinarily negligible. Why?

(b) The thermal conductivity of a typical metal is the sum of electronic and vibrational contributions. The vibrational contribution is ordinarily negligible. Why?

(c) If we convert a single crystal of metal into a nanograin polycrystal, the thermal conductivity will ordinarily decrease while the diffusivity of any substitutional species will ordinarily increase. Why would you expect this?
Problem 5:

(a) The kinetics of a nucleated phase transformation are qualitatively represented by a c-curve of the sort given in the notes. Briefly explain why the kinetic curve has this characteristic shape.

(b) Sketch a similar figure that represents the transformation kinetics of a material that solidifies into either a crystalline solid or a glass on cooling. Locate the “glass transition temperature” $T_g$ on the plot.

(c) Sketch a similar figure that represents the transformation kinetics of a solid that transforms on cooling by either a nucleated or a martensitic transformation. Define and explain the “$M_s$” and “$M_f$” temperatures of the martensite.
Problem 6:

Briefly describe the properties you would want in a material to be used as an oxidation-resistant coating for a structural component in an engine that operates at high temperature in air. Why do such coatings ordinarily contain several different chemical components?
Problem 1:

(a) Almost all of the elements that crystallize in the hexagonal close-packed structure are metallic conductors. Why?

(b) There are at least a couple of elements that crystallize in the hexagonal close-packed structure and are electrical insulators. How can this be?

(c) The largest sphere that can be placed in a tetragonal void in a face-centered close-packed crystal of rigid, spherical atoms has radius

\[ r_{\text{tet}} = 0.225 \ R \]

where \( R \) is the radius of the spheres that make up the FCC lattice. What is the radius of the largest sphere that can be placed in a tetrahedral void in an HCP lattice of rigid spheres?
**Problem 2:**

The Second Law of Thermodynamics states that the entropy of an isolated system can only increase. The change in entropy in an infinitesimal change of state is

\[ dS = \frac{1}{T} \left[ dE + PdV - \mu dN \right] \]

where we have assumed a one-component fluid with temperature, \( T \), energy, \( E \), pressure, \( P \), volume, \( V \), chemical potential, \( \mu \), and mole number, \( N \).

(a) Let two solids have fixed volumes and chemical contents, and let their temperatures be different. Show that if they interact only with one another energy (heat) flows from the solid with higher \( T \) to the solid with lower \( T \).

(b) Consider an open system, with fixed volume, but in equilibrium with a reservoir that fixes its temperature and chemical potentials. Show that the equilibrium of the system is governed by its work function:

\[ \Omega = E - TS - \mu N \]

which must decrease in any spontaneous change.

(c) If we write \( \Omega \) as a function of the variables \((T,V,\mu)\), what are its partial derivatives?
Problem 3:

A binary system of atoms A and B has the simple eutectic phase diagram drawn below.

(a) Give the phases present, their compositions and their mole fractions at each of the three points indicated by dots in the phase diagram. (Assume an overall composition $x = 0.1$ and give plausible estimates for any other compositions you need.)

(b) Draw the expected microstructure of the solid that forms when a sample of composition 3 is cooled from the liquid phase. Explain why this microstructure should form.

(c) Suppose that a sample of composition 1 is held for a long time at the temperature indicated by the dot in the α-field, and is then cooled to room temperature. What microstructure is likely if the sample is cooled very rapidly? What microstructure if it is cooled slowly? Why?
Problem 4:

(a) Carbon diffuses through BCC iron much more rapidly than nickel does. Why?

(b) At low to moderate temperature, nickel diffuses through polycrystalline iron more rapidly than through single crystal iron. Why?

(c) If an iron-nickel alloy is quenched from high temperature, the diffusivity of nickel has an anomalously high value for a short time after the quench, but eventually decreases to its expected value. Why?
Problem 5:

The kinetics of precipitation of a phase $\beta$ from a polygranular $\alpha$ phase are described by the kinetic diagram given below, where $\tau$ is the time required to initiate the transformation and $\Delta T$ is the undercooling below the temperature at which $\beta$ precipitation becomes thermodynamically possible.

(a) If the material is cooled as indicated by the upper arrow, the final microstructure contains nuclei of $\beta$ almost exclusively in the grain boundaries of the $\alpha$ grains. Why might you expect this?

(b) If the material is cooled and then heated, as indicated by the lower path in the figure, the final microstructure consists of a dense distribution of $\beta$ precipitates in the interiors of the $\alpha$ grains. Why?
Problem 6:

(a) It is desired to form a liquid film on a solid surface. The liquid-vapor interfacial tension is $\sigma_{LV}$, the solid-liquid tension is $\sigma_{SL}$, and the solid-vapor interfacial tension is $\sigma_{SV}$. For what relative values of these quantities should a film form spontaneously?

(b) The interfacial tensions are such that the film does not form spontaneously. Suggest two practical ways to modify them to promote wetting.
Problem 1:

(a) Materials that crystallize in the CsCl structure are ionic or metallic in their bonding, never covalent. Why would you expect this?

(b) Materials that crystallize in the Cu₃Au structure are never ionic. Why would you expect this?

(c) Materials that crystallize in the β-ZnS structure are covalent or ionic. Why would you expect this?

Problem 2:

The Second Law of Thermodynamics states that the entropy of an isolated system can only increase. The change in entropy in an infinitesimal change of state is

\[
dS = \frac{1}{T} \left[ dE + PdV - \sum_k \mu_k dN_k \right]
\]

where \( T \) is the temperature, \( E \) is the internal energy, \( P \) is the pressure, \( V \) is the volume, \( \mu_k \) is the chemical potential of the \( k \)th component and \( N_k \) is the mole number of the \( k \)th component.

(a) Let two solids have fixed volumes and chemical contents, and let their temperatures be different. Show that if they interact only with one another energy (heat) flows from the solid with higher \( T \) to the solid with lower \( T \).

(b) Let a solid have a fixed chemical content and be in thermal and mechanical contact with a reservoir that fixes its temperature and pressure. Show that the equilibrium of the system is governed by its Gibbs free energy,

\[
G = E - TS + PV
\]

which must decrease in any spontaneous change.

(c) Assume that, at equilibrium under ambient pressure, a solid has the structure, \( \beta \), at low temperature and \( \alpha \) at high temperature. Show that \( \beta \) must have the lower energy at low \( T \), while \( \alpha \) must have the higher entropy at high \( T \). Which do you believe has the higher Debye temperature?

Problem 3:

A binary system of atoms A and B has the complex phase diagram drawn below.
(a) A possible state of the system is indicated by the dot on the left-hand side of the diagram. Give the phases present, estimate the compositions of the phases, and estimate their fractions when the system is at equilibrium in the state shown by the dot.

(b) Let a liquid with the composition indicated by the vertical line on the left of the phase diagram be cooled slowly enough to preserve equilibrium. Describe the evolution of the system as it is cooled.

(c) Suppose that you are given the assignment of growing a single crystal of $\gamma$ phase that is to be used at room temperature (which, we shall assume, is the temperature at the bottom of the phase diagram). While it may not be possible to do this, it may be possible. Describe the process you would try and explain why it might work.

Problem 4:

Liquid silica, $\text{SiO}_2$, can solidify into crystalline quartz or into a glass.

(a) Sketch the expected form of the kinetic diagram (initiation time vs. temperature below melting point) that governs the solidification of liquid silica. [Assume, incorrectly, that there is only one crystalline phase.]

(b) Why is it always necessary to cool slightly below the melting point to initiate solidification?

(c) To promote glass formation it is common to add ionic species such as $\text{Na}^+$ to the silica melt. Why do these ionic species promote glass formation? How do they change the kinetic diagram for the transformation?

Problem 5:

(a) Plot the expected variation of the diffusivity with temperature for a substitutional solute in a polygranular solid, and explain the shape of the graph.

(b) Let the diffusivity of a substitutional specie in a given solid be measured at temperature $T$, under two conditions: (1) the solid has uniform temperature, $T$; (2) the solid has a temperature gradient, and $T$ is an intermediate temperature. Would the two measurements differ? How and why?
Problem 6:

(a) The liquid, L, forms a drop on the solid, S, in the vapor, V. Use a simple force balance between the interfacial tensions to find the "contact angle", $\theta$, that governs the shape of the drop. What assumption must you make about the mechanical properties of the solid?

(b) Under what conditions does the Young equation predict that the liquid will spread into a continuous film over the solid surface?

(c) Suppose the liquid does not "wet" the solid. What can you do to promote wetting?