

Phase Transformations

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Heterogeneous Equilibria

Preparation of Solid State Materials

Heterogeneous Equilibria

In a heterogeneous system chemical equilibrium is a function of the chemical potential, μ , of the constituents. The chemical potential is one of the *intensive variables of the system*:

- pressure, p
- temperature, T
- chemical potential, μ .

The stable phase is the one possessing the lowest Gibbs free energy: $G = H - TS$. The three intensive variables influence both the enthalpy and the entropy.

The Phase Rule

Under some conditions condensed matter exists in a two phase regime. The constraints governing multiphase equilibria are expressed by the *Gibbs Phase Rule*:

$$V = C - P + 2 \tag{2.1}$$

where V is the variance, C is the number of components, and P is the number of phases.

A *phase* is defined as an agglomeration of matter having identifiable characteristics. The phase rule can be applied, for example, to define the solid-liquid equilibrium of a one-component system. With one component and two phases, the state of the system is determined by only one intensive variable (variant). For example, specification of the temperature fixes all other properties.

Phase Diagrams

These “phase boundaries” are commonly depicted in a phase diagram as shown in Figure 2.1. This diagram gives the equilibrium relations of a single component system.

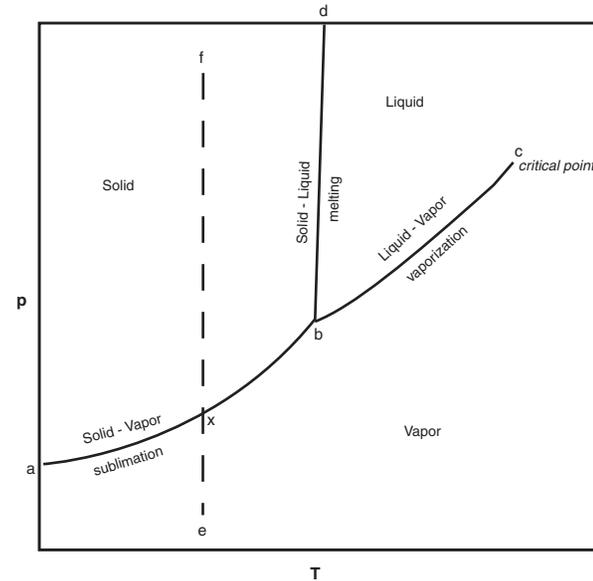


Figure 2.1
A one component phase diagram, pressure (p) vs. temperature (T).

Since composition is not a variable, only the intensive variables, temperature and pressure are of concern. The diagram consists of *univariant boundaries* and *bivariant fields*.

The boundaries obey the thermodynamic relation

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V} \tag{2.2}$$

which is known as the Clapeyron equation. As shown the S/V and L/V boundaries always have a positive slope because the system volume is increased by the phase transformation. For an ideal gas ($pV=RT$), the vapor phase

equilibrium is expressed by the Clausius-Clapeyron relation,

$$\frac{dp}{p} = \frac{\Delta H}{RT^2} \quad (2.3)$$

The critical point marks the point where the liquid / vapor interface ceases to exist. For example, above the critical temperature the density of the vapor equals the density of the liquid. An increase in pressure will not lead to nucleation of an interface.

Enthalpy is conserved in crossing a phase boundary. Thus,

$$\Delta H_{\text{sublimation}} = \Delta H_{\text{fusion}} (S/L) + \Delta H_{\text{vaporization}} (L/V) \quad (2.4)$$

Similarly, if two solid phases S_1 and S_2 exist

$$\Delta H_s(1) = \Delta H_{1-2}(1/2) + \Delta H_s(2) \quad (2.5)$$

The enthalpy changes are known as latent heats of transformation. This heat evolution accompanies all first order phase transformations. When $\Delta H = 0$ in crossing a phase boundary, the transformation is second or higher order.

The phase boundary defines the conditions under which one phase is exactly saturated with respect to the other. At this point, no change in an intensive variable can occur without creation of the new phase. Metastable, nonequilibrium phases can occur, however. For example, and undercooled liquid can be described by extending the L/V phase boundary to temperatures below the triple point, Figure 2.2. The deviation from equilibrium is characterized by a *negative* free energy change

$$\Delta G = kT \ln \left[\frac{p_2}{p_1} \right] \quad (2.6)$$

Thus, the vapor pressure of the metastable state is greater than for the equilibrium phase.

The *driving force* for a phase transformation is the magnitude of the negative free energy change, $|\Delta G|$.

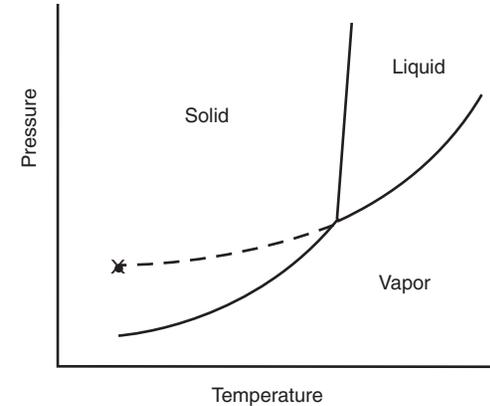


Figure 2.2
Single component phase diagram. The dashed line shows the virtual phase boundary for the metastable liquid.

$$\begin{aligned} \Delta G &= G(\text{product}) - G(\text{reactant}) \\ &= 0 \text{ equilibrium} \\ &< 0 \text{ reaction} \end{aligned} \quad (2.7)$$

Metastability arises when the rate of transformation is limited. The source of these *kinetic* limitations may be chemical, such as a local potential barrier or nonchemical, such as elastic strain or the need to create an interface.

Transformation Order

The system free energy changes continuously when a phase transition occurs at the equilibrium values of the intensive variables (a phase boundary). However, derivations of the free energy with respect to temperature and pressure may be discontinuous.

Based on equation 1.1

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \quad (2.8)$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad (2.9)$$

When a volume and entropy change are associated with a phase transition, the *first derivatives of the free energy show a discontinuous change*. This property describes a *first order transition*.

A *second order* transition is characterized by continuous changes in both G and its first derivatives, but a discontinuous change is its second derivatives.

$$-T\left(\frac{\partial^2 G}{\partial T^2}\right)_V = C_V \quad (2.10)$$

$$V\left(\frac{\partial^2 G}{\partial V^2}\right)_T = \frac{1}{K} \quad (2.11)$$

$$-K\left[\frac{\partial}{\partial V}\left(\frac{\partial G}{\partial T}\right)_V\right]_T = \alpha \quad (2.12)$$

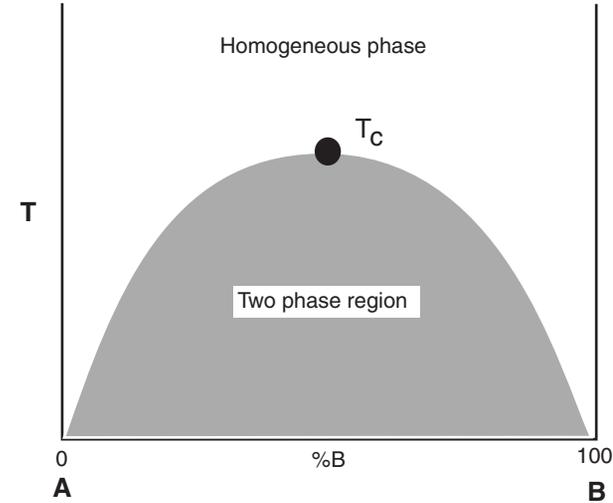


Figure 2.3
Phase diagram for liquid / liquid phase separation. T_c is the critical temperature for the system.

This behavior creates in specific heat, compressibility, and the coefficient of thermal expansion, respectively. Sublimation, melting, and vaporization are typical of first order phase transitions. All three occur with a well defined, characteristic latent heat. Order-disorder transitions are typical second order phenomena.

Higher order transformations are strictly defined by the rate of approach of the system to the phase boundary. Consider a binary alloy that can exist as either a homogeneous random solid solution or a heterogeneous two-phase mixture. The phase diagram is shown in Figure 2.3. At high temperatures the entropy component of the free energy favors random mixing in a single phase. At low temperatures the enthalpy or bonding preference of the A and B atoms is more important. The nearest neighbor interactions can be expressed as

$$H = N_{AA}H_{AA} + N_{AB}H_{AB} + N_{BB}H_{BB} \quad (2.13)$$

where H_{ij} are the interaction energies and N_{ij} are the densities of pairs, ij .

An order parameter $\psi(T)$ is defined as

$$\psi(T) = [A]_A(T) - [A]_B(T) \quad (2.14)$$

relating the identities of the nearest neighbors of component A. When approaching the critical temperature, T_c , at constant composition from the low temperature side, $\psi(T)$ tends to zero. The behavior of the order parameter near the transformation is typically fitted to a power law

$$\psi(T) = (T_c - T)^\beta \quad (2.15)$$

The critical exponent β is a universal feature of systems with critical points.

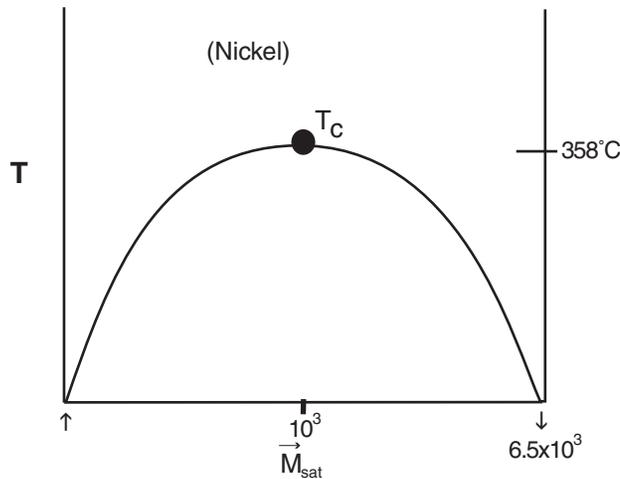


Figure 2.4
Phase diagram for order-disorder transitions in the magnetization of nickel. The critical temperature in this example corresponds to the Curie Temperature, above which spin correlation ceases to exist.

EXAMPLE 2.1

What is the order parameter which describes the ferromagnetic / paramagnetic phase transition?

The system free energy is defined as

$$G = H - TS - H_{ext} \bar{M} \quad (2.16)$$

The exchange interaction is a nearest neighbor interaction which is lowest in energy for parallel spins. The magnetization \bar{M} is a measure of the concentration of parallel spins. Alternatively, $\uparrow=A$ and $\downarrow=B$ and the phase diagram shown in Figure 2.4 applies.

When all spins are parallel, a large interaction energy is required to reverse a spin against its neighbors. As the temperature is raised more spins possess the internal energy to reverse and the system tends to disorder. At the Curie point, T_c , the correlation in spin alignment approaches zero. The specific heat of the system displays a singularity at T_c rather than a discontinuous step. The transformation is, hence, not second order, but of *higher* order.

The order parameter is given by the magnetic susceptibility

$$\begin{aligned} \chi_T &= \left(\frac{\partial \bar{M}}{\partial H} \right)_T \\ &= (T_c - T)^\beta. \end{aligned} \quad (2.17)$$

Below T_c a cooperative phenomenon produces long range order, beyond near neighbor correlations. At T_c the two equally probable spin orientations give rise to large system fluctuations.

Transformation Path

The path of a phase transformation is determined by the reaction rate. The fastest process is chosen. Two primary paths are characteristic of first order solid state transformations: nucleation and growth or spinodal decomposition.

Nucleation and growth requires the initial formation of a small volume of the product phase. In the earliest stages this nucleus may not possess the exact concentration of the product. However, a sharp interface with the surrounding matrix must exist. The transformation proceeds by growth or advancing of the interface.

Spinodal decomposition features a small compositional fluctuation that exists over a large volume. There is no sharp interface, initially. As the transformation proceeds, the fluctuation grows in intensity until two separate phases are produced.

Two Component Systems

Equilibrium in multicomponent system is governed by both physical and chemical interactions. Physical interactions, such as hardcore repulsion, govern the mutual stabilization and mixing of the components, particularly in the liquid phase. Chemical interactions lead to the formation of new compounds in the solid phase and govern the competition among interactions. The liquid state typically exhibits complete miscibility of the components, while the solid phase tends to limit the solubility of one in the other.

Miscibility

Complete miscibility in the solid phase connotes alloy formation. The appropriate phase diagram is shown in Figure 2.5. The system consists of two components, *A* and *B*.

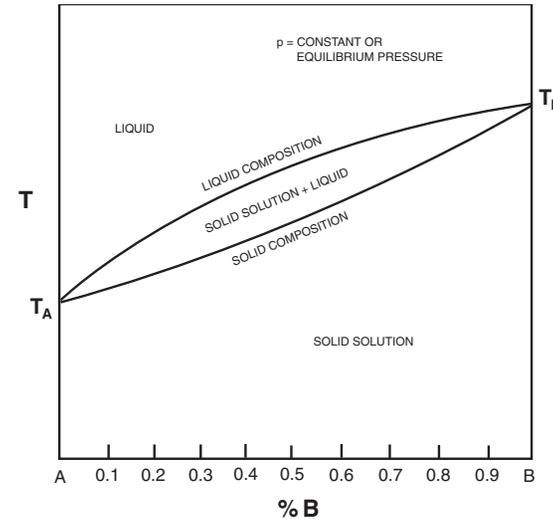
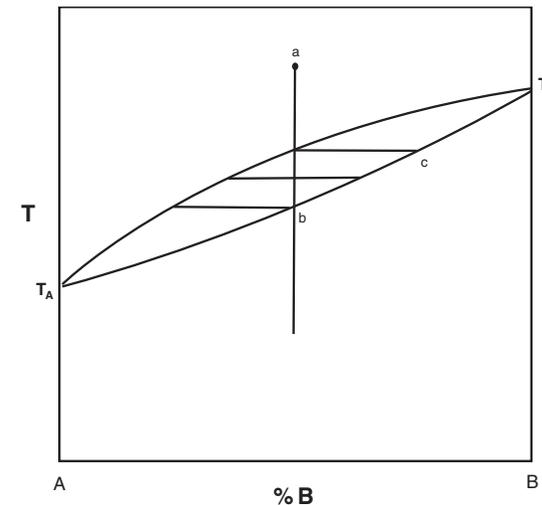


Figure 2.5
Binary phase diagram for a completely miscible system.



Compositional change dependence on fraction solidified.

The melting point of *B* is higher than that of *A*. At temperatures above T_B (melting point of component *B*) the system is in the liquid phase for all compositions. It is instructive to follow the state of the system at an intermediate composition as the temperature is lowered from $T > T_B$.

The temperature and composition of point *a* specify a liquid phase. According to the Phase Rule the variance of the system at point *a* is three. Therefore, all three intensive variables are free to change, while the liquid phase is maintained. An underlying assumption of phase diagrams with Temperature vs. Composition axes is that the pressure of the system is held constant. Thus, as shown in the diagram, the *isobaric* variance is two: small changes in temperature or composition do not result in a phase change.

Upon cooling from point *a*, the system will eventually approach the liquidus phase boundary. This boundary defines liquid compositions which are in equilibrium with solid compositions (the solidus) at specified temperatures. Thus, a solid of composition *c* is in equilibrium with a liquid of composition *a* at the liquidus temperature. Note that this new, two phase equilibrium is isobarically univariant. Specification of *either* the temperature or the composition is sufficient to determine the state of the system. Several features of this region of the phase diagram are important.

— The composition *c* of the solid is richer in component *B* than is the liquid from which it crystallizes. Thus *the liquid preferentially rejects the component with the highest melting point.*

— Upon crystallization *the latent heat of fusion, ΔH_f , of each component is evolved.*

— The final equilibrium state of a crystal solidified from a liquid of composition *a* is a solid of composition *a* (as shown by point *b*). The actual composition of the solid will vary continuously between *c* and *a*, because diffusion is much slower in the solid than the liquid. Equilibration of the solid at composition *a* will occur only after heat treatment of the solid at very high temperatures for very long times.

The rules for selection of components which freeze into a single solid phase (an alloy) have been enumerated by Hume-Rothery:

- 1) The components must be isomorphous so that only a single solid phase results.
- 2) The lattice constants of the solids should not differ by more than ~10%.
- 3) The valences and electronegativities for the components should be similar in order to avoid compound formation.

Immiscibility

An exemplary phase diagram for an immiscible system is shown in Figure 2.6. The melting point of component *B* is greater than that of *A*. The liquidus boundaries describe the conditions for solidification of solid *A* or solid *B* from the

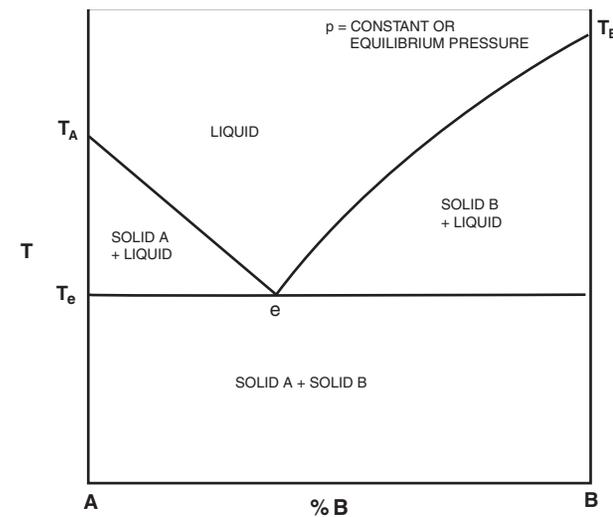


Figure 2.6
Eutectic phase diagram for an immiscible system.

liquid solution. The liquidus boundary is expressed by

$$\ln[A] = -\frac{\Delta H_f(A)}{R} \left[\frac{1}{T} - \frac{1}{T_A} \right] \quad (2.18)$$

The A and B liquidus are, thus, independent of each other. The solid phase consists of a mixture of crystallites or grains of 'pure A' and 'pure B'. The point e is a triple point called *the eutectic point* which denotes equilibrium between the liquid and solids A and B. This equilibrium condition between three phases must be a *point* on this phase diagram because it is isobarically invariant.

The liquidus and solidus define the composition of the solid C_S that will freeze from a liquid of composition C_L . The ratio of these two compositions is the *segregation coefficient* (or distribution coefficient) (see Figure 2.7).

$$k = \frac{C_S}{C_L} \quad (2.19)$$

Figure 2.7
Solute rejection
in a eutectic
system.

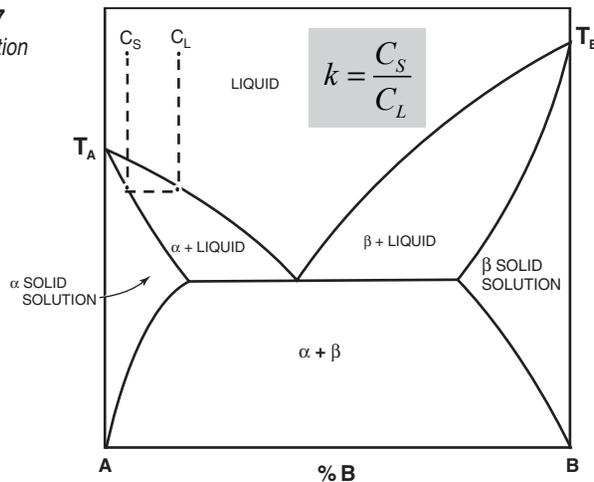


TABLE 2.1

Distribution Coefficients at the Melting Points of Ge and Si

ELEMENT	Ge	Si
Ag	4x10 ⁻⁷	—
Al	0.073	0.0020
As	0.02	0.3
Au	1.3 x 10 ⁻⁵	2.5 x 10 ⁻⁵
B	17	0.80
Bi	4.5 x 10 ⁻⁵	7 x 10 ⁻⁴
Cd	>1 x 10 ⁻⁵	—
Co	~10 ⁻⁶	8 x 10 ⁻⁶
Cu	1.5 x 10 ⁻⁵	4 x 10 ⁻⁴
Fe	~3 x 10 ⁻⁵	8 x 10 ⁻⁶
Ga	0.087	0.0080
Ge	1	0.33
In	0.001	4 x 10 ⁻⁴
Li	0.002	0.01
Mn	~10 ⁻⁶	~10 ⁻⁵
N	—	<10 ⁷ *
Ni	3 x 10 ⁻⁶	—
O	—	0.5
P	0.080	0.35
Pb	1.7 x 10 ⁻⁴	—
Pt	~5 x 10 ⁻⁶	—
S	—	10 ⁻⁵
Sb	0.0030	0.023
Si	5.5	1
Sn	0.020	0.016
Ta	—	10 ⁻⁷
Te	~10 ⁻⁶	—
Tl	4 x 10 ⁻⁵	—
V	<3 x 10 ⁻⁷	—
Zn	4 x 10 ⁻⁴	~1 x 10 ⁻⁵

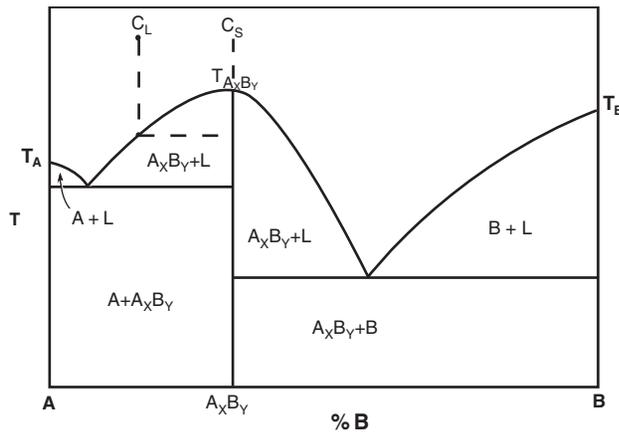
*Uncertain

Table 2.1 lists the segregation coefficients for some impurities in germanium and silicon. This factor determines the melt composition required to grow a crystal of a particular doping level.

Values of $k < 1$ are required for purification by zone refining.

A compound A_xB_y acts as a pseudo-binary component in the system AB . As shown in Figure 2.8, A_xB_y acts as an end point in a eutectic phase diagram for each of components A and B . When the melting point of the compound is the highest temperature boundary on the phase diagram, the compound *melts congruently*. In other words, for the composition A_xB_y , $C_L = C_S$ at equilibrium.

Figure 2.8
Phase diagram with compound formation in an immiscible system.



In some cases, a compound can have a small *region* of existence rather than a single, fixed composition. This region, as shown in Figure 2.9 is called an existence region. When an existence region exists, the composition of the solid compound will depend critically on the melt composition. When a compound consists of a highly volatile component, the composition in the vapor phase (partial pressures) is not the same as the compositions in the liquid and solid phases. The compound, therefore, *vaporizes incongruently*. Arsenic: gallium arsenide is a good example of a system of this type. The phase diagram of GaAs is similar to the one shown in Figure 2.9. The melting point of GaAs is a much higher temperature than for either

Ga or As. The eutectic points are shifted, therefore, to near the end points of the phase diagram.

The high vapor pressure of the arsenic component requires that three phases (vapor, liquid, and solid) be considered in the system equilibrium. Furthermore, the chemical potential of the arsenic in the liquid and solid ($[As]$ or $\%B$) is directly related to the arsenic partial pressure in the vapor phase (p_{As} or p_B). This added variant of the system has striking consequences in the determination of the composition of the compound. Bordering either side of the solid phase existence region of the compound are two regions containing both solid and liquid. In these three phase regions, the variance is computed to be one. Thus, the vapor pressure p_B must remain constant over the range $a \rightarrow b$. Since p_B is near zero at low $[B]$ (point a) and near the equilibrium partial pressure for the pure component at high $[B]$ (point d), a

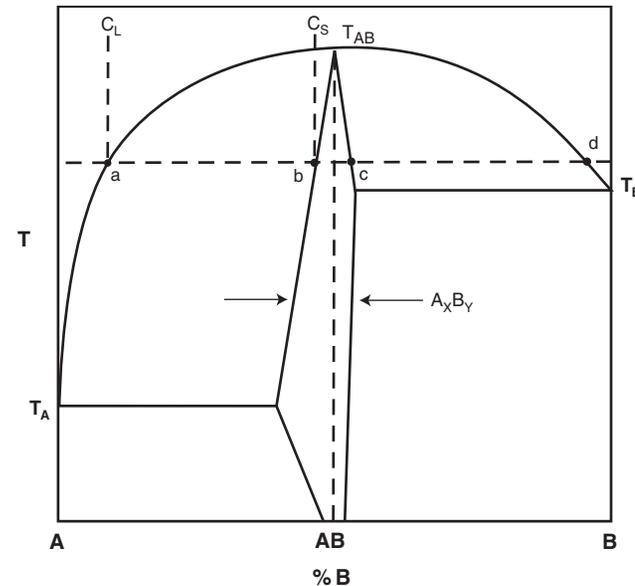


Figure 2.9
GaAs Phase diagram.

large change in p_B must occur over the short composition interval $b \rightarrow c$. It is for this reason that critical control of the arsenic vapor pressure over the solid/liquid interface is required for the growth of highly perfect gallium arsenide.

Crystal Growth

Introduction

Crystalline solids may be grown from either vapor or liquid phase components. Growth from the melt is the most direct process, involving no solvent or carrier gas. Growth from solution is favored for materials that decompose at the melting point. Growth from the vapor phase is most appropriate for thin layers involving volatile species. Growth rate limiting factors are 1) the formation of crystalline nuclei at the solid/liquid interface, 2) the removal rate of the latent heat, ΔH_f or ΔH_s , (this term is directly proportional to the temperature gradient at the growth interface), and 3) the incorporation of solute in the solid.

Solidification from the Liquid Phase

The liquid/solid equilibrium expressed by the system phase diagram plays the determining role in establishing the conditions for growth. The distribution coefficient, k , is typically less than one. This fact implies rejection of solute to the melt at the growing interface. As a result, a boundary layer, rich in solute is established at the interface as shown in Figure 2.10. The solute concentration of the liquid/solid interface C_i is, thus, greater than the average concentration

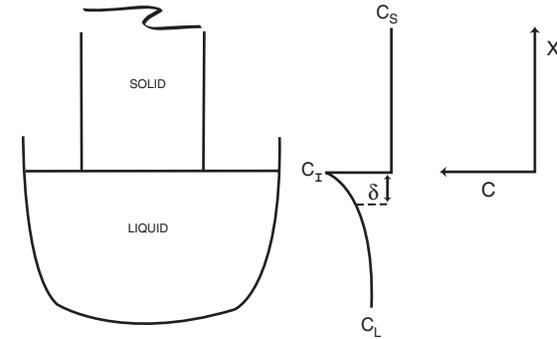


Figure 2.10

Solute distribution at the liquid /solid interface for Czochralski growth.

Note: a) $C_i > C_L$; b) the boundary layer, δ , will be dependent on stirring.

in the liquid, C_L . The magnitude of $(C_i - C_L)$ can be reduced by stirring or very slow freezing (allowing time for solute diffusion to homogenize the liquid).

When a boundary layer exists, the concentration of solute in the solid is governed by the equilibrium distribution coefficient.

$$k = \frac{C_s}{C_i} \quad (2.20)$$

The *operational* value of k determined by measuring composition of the liquid C_L and solid C_s is called k_{eff} , the effective distribution coefficient. The k_{eff} is related to the k of the phase diagram by the properties of the boundary layer.

$$k_{eff} = \frac{k}{k + (1-k) \exp\left[\frac{-\delta f}{D}\right]}$$

$$= \frac{C_s}{C_L} \quad (2.21)$$

$$> k$$

The derivation of expression (2.20) is found in two papers in J. Chem. Phys. 21, 1987, 1991 (1953) by Burton, Prim, and Slichter. D is the solute diffusion coefficient in the liquid, f is the growth rate, and δ is the boundary layer thickness.

In the limit $D \rightarrow 0$, $k_{eff} = 1$, because C_i maintains an artificially high value. When $\delta \rightarrow 0$ or $f \rightarrow 0$, the boundary layer disappears by stirring or diffusion, and $k_{eff} = k$. Random convection in the melt or thermal asymmetries can produce rapid fluctuations in f which produce heterogeneities in the impurity content through the correlated changes in k_{eff} . These microheterogeneities are called *impurity striations* because they extend across the growth interface.

Heterogeneity in impurity content results, naturally, from the *normal freezing process*. When $k < 1$, solute is rejected into the melt, and C_s gradually increases as the melt is solidified. The solute content in the solid increases as a consequence. Under conditions of $\delta = 0$, this increase is expressed by

$$C_s(x) = kC_L(0)(1-x)^{k-1} \quad (2.22)$$

where x is the fraction of the melt which has solidified, $C_s(x)$ is the solute concentration in the solid at $(1-x)$ melt

fraction, and $C_L(0)$ is the initial composition of the melt. The initial composition of the solid is $kC_L(0)$, and the final composition becomes very large. *Normal freezing* is an effective means of purification for low fractions of solidification.

The solute content in the melt can lead to spurious nucleation and polycrystallinity during growth. This result is a consequence of the lowering of the melting point of the solid by the solute (see Figure 2.7). The structure of the advancing liquid/solid interface is stable when small fluctuations from planarity are superheated and are instantaneously remelted. The condition for stability is shown in Figure 2.11. When the temperature gradient at the interface is too low, the melt will be locally undercooled and the fluctuations will grow. This *dendritic growth* is particularly common to solute systems with $k \ll 1$.

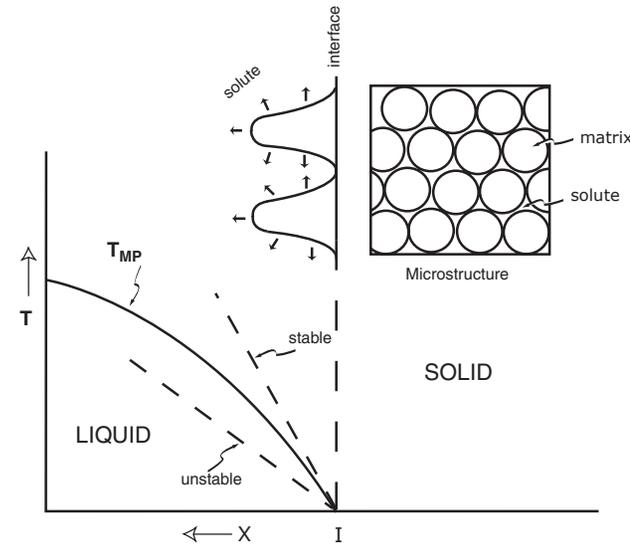


Figure 2.11
Conditions for
Stability
of the L/S
Interface

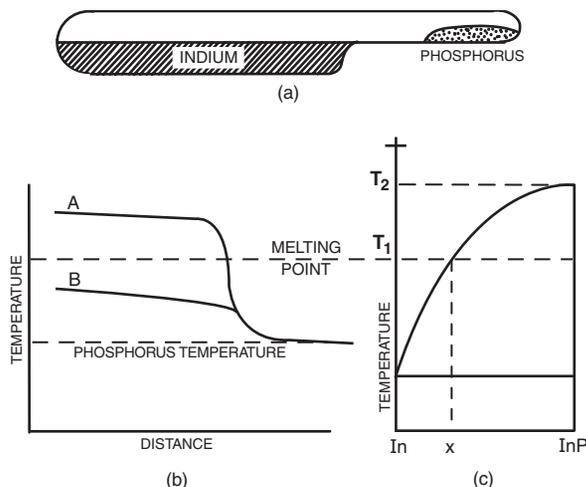
Cellular growth morphology results as solute is rejected laterally as well as ahead of the “growth fingers”. This general class of phenomena is called *constitutional supercooling*.

Growth from the Melt

The most direct method of preparing a crystal of a substance is solidification from the melt. A crucible is filled with constituents in the desired proportion of concentrations, the mixture is heated to a temperature above the melting point of the final solid, and the temperature is gradually lowered to near the equilibrium melting point of the solid so that crystallization may proceed. When a single crystal of material is desired, special techniques are employed to create only one crystalline nucleus and control the growth at only *one* solid/liquid interface.

The *crucible* should be a less efficient heat conductor than the crystal being grown. A key parameter in controlling crystal growth is the temperature gradient at the

Figure 2.12 The growth of indium phosphide using excess indium + as the solvent: (a) the indium container and phosphorus source; (b) temperature gradients in the furnace when growth is started, curve A, and at the conclusion of growth, curve B; (c) the indium-indium phosphide phase diagram.



liquid/solid interface. This gradient determines the path of dissipation of the latent heat of fusion, ΔH_f . Secondary nucleation can be suppressed only when the advancing interface is, also, the primary heat sink.

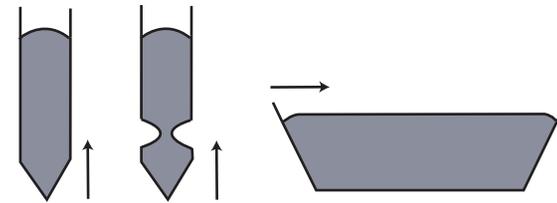


Figure 2.13 Types of crucibles used in growing crystals from the melt.

Crucibles can be oriented vertically or horizontally. They should be constructed of materials and with a finish that will discourage wetting of the melt or nucleation of the solid on the walls. When a high vapor pressure component is involved, a closed system must be employed to prevent losses through evaporation. A separate charge of the pure, volatile component is added to the closed system to provide control of the partial pressure and, hence, composition (see Figure 2.12).

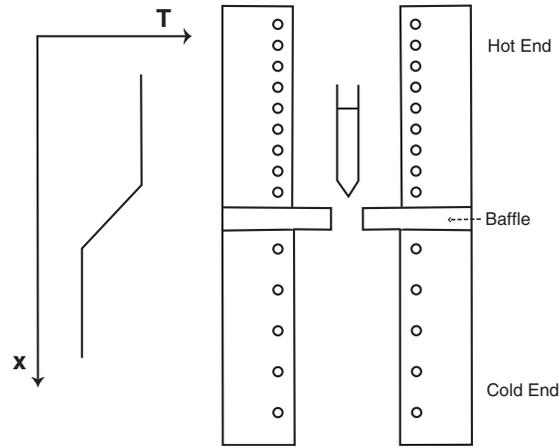
The three primary methods of growth from the melt are *gradient freeze*, *crystal pulling* and *zone melting*.

In the *gradient freeze* technique the system components are placed in a container that is heated at one end and cooled at the other. Provision is made for nucleation at the cold end by inserting a single crystal seed or a region of high curvature or taper. Some examples are shown in Figure 2.13. Solidification of the charge is accomplished by moving the charge relative to an established temperature gradient, using the natural temperature gradient of the cooling curve of the system, or electronically moving the temperature gradient across a fixed crucible. These methods are illustrated in Figure 2.14.

Figure 2.14

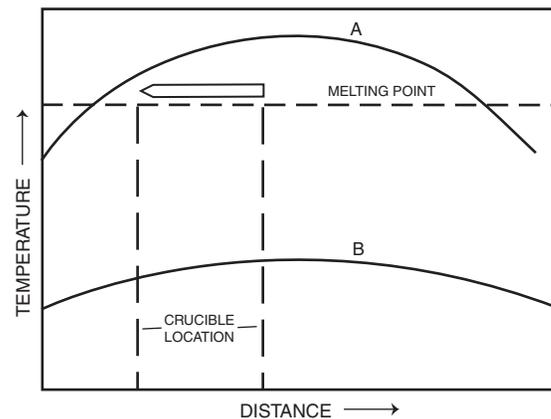
Vertical Gradient Freeze

Two-zone furnace used for growing crystals from the melt in a containing crucible.



Horizontal Gradient Freeze

Temperature gradient method for growing crystals from the melt. As the temperature is changed from curve A to curve B, the melt is progressively solidified from the tapered end of the crucible.



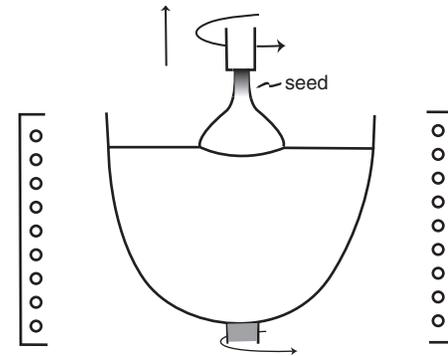
Crystal pulling or Czochralski growth utilizes a seed crystal to nucleate crystallization in the melt pool as shown in Figure 2.15. The crystal may have an arbitrary shape since it is not confined by the crucible walls. In this process, the components are melted, a seed is lowered into the center of the crucible, the temperature of the liquid/

solid interface is controlled near T_{MP} , and the seed is gradually pulled away from the melt. The growth rate and crystal shape are controlled by the heat input to the crucible, the temperature gradient at the S/L interface and the pull rate.

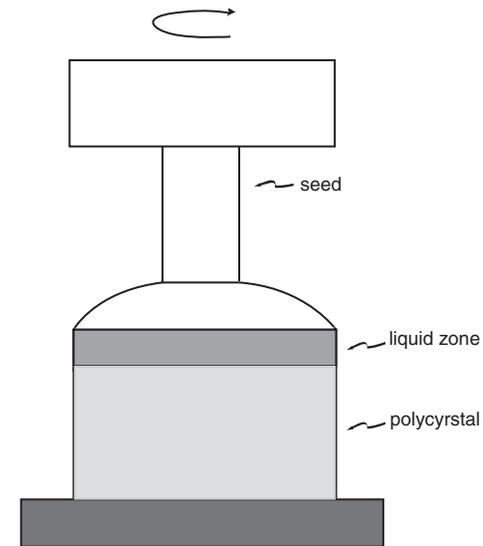
A disadvantage of this method is the resulting inhomogeneity of the impurity or dopant distribution

Figure 2.15

Czochralski Growth (Pulling)



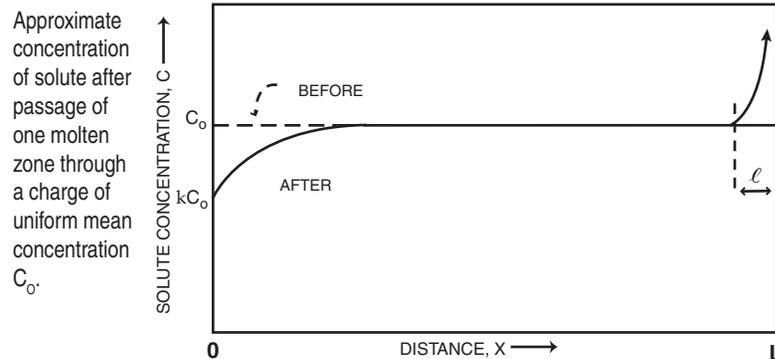
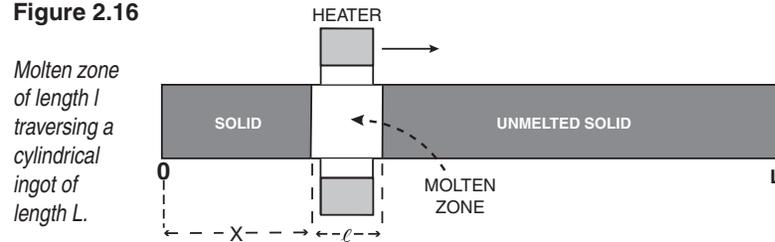
Float Zone Growth



along the boule. When the distribution coefficient of the impurity is less than unity, $k = \frac{C_S}{C_L} < 1$ the melt becomes richer in solute as the growth proceeds. In a closed system, therefore, one cannot maintain a constant impurity concentration over the length of the entire crystal boule. The chief advantages of crystal pulling are the absence of crucible restraint (and associated strain) and the convenient visibility of the liquid/solid interface for control of growth conditions.

The *zone melting* method employs localized heating to produce a molten zone in the solid charge as shown in Figure 2.16. The zone is passed along the entire charge until all solid material has been melted and resolidified. The moving zone removes the closed system constraint and

Figure 2.16



homogeneity in solute distribution results. In the float zoning method, no containing vessel is employed, and high purity is possible. A chief limitation of the process is the difficulty in controlling heat input and outflow over a small slab section in a large diameter charge. Only materials that possess a high surface tension in the liquid state will support a stable floating zone.

Growth from Solution

Solution growth is most appropriate for materials which decompose at the melting point. By moving down the liquidus to a low temperature (lower vapor pressure), the growth process can take place under more controlled conditions. For most semiconductor materials the solvent is a metal and the crystal is a compound or alloy containing the metal (e.g. Ga or In) or an elemental lattice in which the metal has very low solubility.

The low temperature of growth slows all kinetic processes and the growth rates are usually slower than for growth from the melt. The critical factors are:

- 1) diffusion of solute to the S/L interface
- 2) attachment of the solute to the crystal
- 3) dissipation of the latent heat of fusion, ΔH_f

The second factor plays a key role in the anisotropic growth behavior for different III-V compound crystal surfaces. In particular, the (111)B face is rougher than (111)A (i.e., has more surface steps or solute attachment sites) and displays faster growth kinetics when the chemical potential of the A species is higher. These conditions are typical for the liquid phase epitaxial (LPE) process, an application of solution growth that is preponderant for compound semiconductor materials.

EXAMPLE 2.1

What is the influence of a temperature gradient on a system consisting of a solid solute in contact with a liquid solvent?

A temperature gradient $\Delta T = (T_1 - T_2)$ results in the conditions shown in the phase diagram of Figure 2.17. In general, the addition of solute lowers the melting point of the solid. Liquid of composition C_1 is formed by melting at the interface at X_1 . A higher solute concentration is required to produce equilibrium at T_2 , the cold end of the liquid zone. Solute will, therefore, diffuse from region X_1 to region X_2 . Equilibrium is maintained by melting (dissolving more solute) at $X_1(T_1)$ and solidification (when $C < C_2$) at $X_2(T_2)$. The zone of liquid solvent will, thus, migrate through the rod toward the hot end. This process, known as temperature gradient zone melting (TGZM) has been employed to produce aluminum doped isolation grids for silicon TRIAC devices.

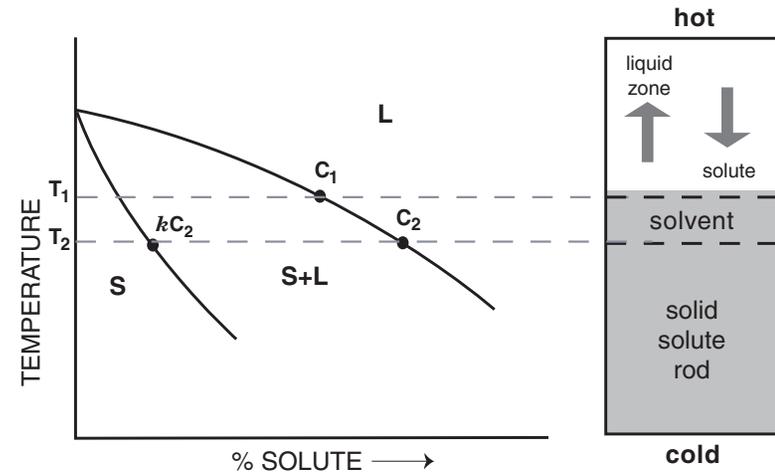


Figure 2.17

Temperature gradient zone melting. The liquid solvent zone will migrate from cold to hot regions because solute is more soluble in the cold liquid.

- *Chemical Vapor Deposition (CVD)*, the chemical reaction of molecular species in the gas phase or at the substrate.

The primary determinants in both are transport of the vapor to the crystal surface, nucleation and growth of surface layers, and dissipation of the latent heat. The key, controllable growth parameters are the temperatures of the substrate (and, hence, the vapor pressure of the substrate during growth) and the flux of reactants.

Vapor phase equilibria are of concern during crystal growth and during simple heat treatment of volatile components. At equilibrium the chemical potential of a constituent in the solid phase, μ_i , is directly proportional to the logarithm of the partial pressure, $\ln(p_i)$, in the vapor phase. Vapor phase equilibria are usually plotted as μ_i vs.

Vapor Phase Growth

Vapor phase growth is the most effective means of producing thin layers of material ($<1000\text{\AA}$). Two methods are generally available:

- *Molecular Beam Epitaxy (MBE)*, the controlled evaporation of one or more components onto a substrate.

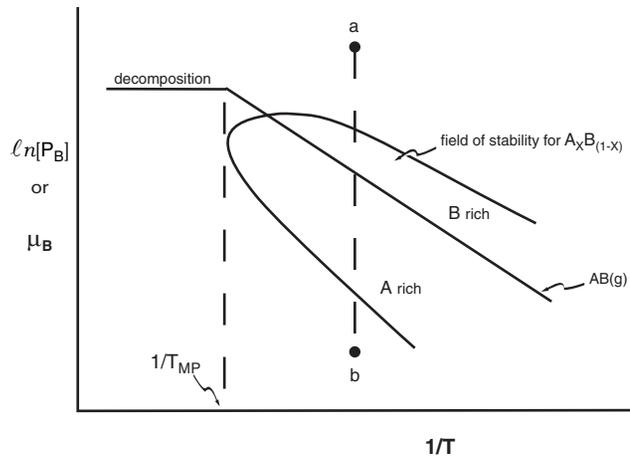


Figure 2.18
Equilibrium vapor pressure above an AB compound. The straight line gives the heat of vaporization for compound AB. The curved line gives the phase field (vapor pressure variations) for the nonstoichiometric solid.

$1/T$ as shown in Figure 2.18. The diagram plots the allowed chemical potentials of component B in the vapor above an AB compound. An existence region is shown as a range of allowed chemical potentials in the solid phase, $T < T_{MP}$.

In Figure 2.19 the constraint of *congruent sublimation* is illustrated. As shown *PbTe* has a narrow range of compositions in which *Pb(g)* and *Te₂(g)* are in equilibrium with the solid phase. This equilibrium does not necessarily relate to a stoichiometric *PbTe* compound. It describes, however, conditions under which the solid phase can be heated without decomposition. Note that no such region exists for *HgTe*. This result expresses the fact that no *HgTe* vapor can exist.

Thin film growth from the vapor phase may be achieved under conditions far from the equilibrium determined by the system intensive variables. These processes employ high rates and/or energy assisted pathways that utilize external plasmas, photons, electrons or short time heat pulses. This

approach is used to minimize interactions among fabrication steps of a complicated structure and to produce new metastable solid state materials.

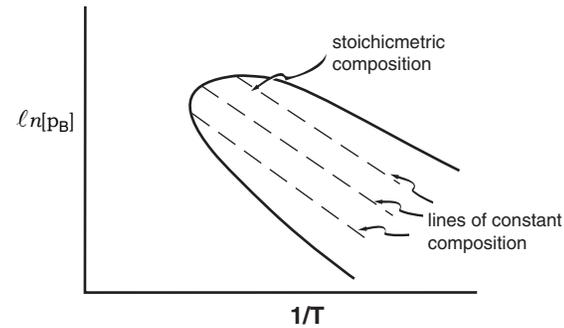
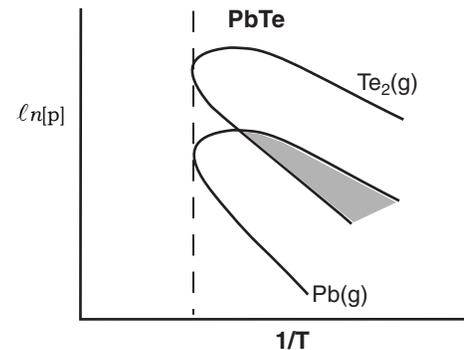
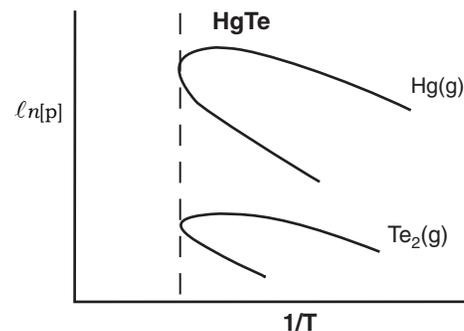


Figure 2.19
Sublimation of an AB compound.

a) Vapor pressure for specific compositions within the existence region of a compound AB.



b) Partial congruent sublimation; hashed area = congruent sublimation range



c) No congruent sublimation

QUESTIONS

1. When a supercooled liquid freezes, a latent heat of fusion ΔH_f is evolved. What is the thermodynamic and atomistic basis of this heat?
 2. A solid state reaction proceeds with an activation energy of 1 electron volt. What is the ratio of the reaction rates at 1000°K and at room temperature?
 3. When viewing a slightly oxidized polycrystalline metal one notices that different grains show different colors. What aspect of solid state reactivity is the basis of this phenomenon?
 4. Identify a solid state reaction which is central to your research interests.
 - a) What is the rate-limiting step?
 - b) How is the reaction rate controlled?
 - c) How are the reaction products controlled?
 - d) Why is this reaction important?
 5. The magnitudes of the distribution coefficient and maximum solubility of a foreign metal in silicon or germanium are determined primarily by the covalent radius of the substituent and secondarily by the periodic table group to which the element belongs. What factors would you expect to be important in determining the solubility and distribution coefficient of foreign ions in an ionic material such as MgO? CaWO_4 ?
 6. MgO has the NaCl structure and melts at 2800°C. BeO has the wurtzite structure and melts at 2400°C. Draw a reasonable phase diagram for the system MgO-BeO and label the areas and lines. (There is no intermediate compound formed.)
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