

Phase Diagrams

Much of solid-state chemistry is governed by the thermodynamics of heterogeneous equilibria. Understanding such equilibria can be important to optimize any solid-state synthetic strategy. Furthermore, thermodynamic factors can influence the occurrence of nonstoichiometry in solids and procedures for growing crystals. To utilize thermodynamics effectively, it is important to assess the factors that lead to a minimum Gibbs free energy for any pure substance or mixture. An appendix to this unit summarizes useful thermodynamic relationships for solid-state systems.

READING: H.F. Franzen, *Physical Chemistry of Solids*, Ch. 7

H.F. Franzen, *Physical Chemistry of Inorganic Crystalline Solids*, Ch. V

A.R. West, *Solid State Chemistry and Its Applications*, Ch. 11

(19) A *phase diagram* is a map of the equilibrium states for a system. Therefore, the diagram summarizes in graphical form the minima of the Gibbs free energy with respect to temperature, pressure, and composition for the system in question. Learning how to read a phase diagram and how to extract important information are important when planning any synthetic procedure or for growing crystals from liquids.

(20) Gibbs Phase Rule: All features and interpretations of phase diagrams are based upon application of the Gibbs phase rule,

$$F = C - P + 2.$$

According to H.F. Franzen, “this rule is a basis of, rather than a result of, the laws of thermodynamics.” The equation relates the intensive variables of the Gibbs free energy function with the chemical make-up and existing phases for any system at equilibrium. For any phase φ , the Gibbs free energy $G^{(\varphi)}(T, p, n_i)$ is a function of temperature, pressure, and the numbers of moles of each component and is an extensive property of the system. Dividing $G^{(\varphi)}$ by the total number of moles N gives the *molar Gibbs energy* $g^{(\varphi)}(T, p, x_i)$, in which x_i is the mole fraction of component i .

$$g^{(\varphi)}(T, p, x_i) = \frac{1}{N} G^{(\varphi)}(T, p, n_i) = g^{(\varphi)}\left(T, p, \frac{n_i}{N}\right).$$

The variables of $g^{(\varphi)}$ are *intensive variables* of the system. The Gibbs phase rule holds when the molar Gibbs free energy over all phases is a minimum value, i.e., when the system is at equilibrium. The different terms in the expression are:

$F =$ # *degrees of freedom* = # *independent* intensive variables, which means the number of intensive variables that can be freely changed while retaining the same equilibrium state. Alternatively, F is the number of intensive variables that must be specified for the state of the system to be completely defined. Therefore, $F \geq 0$.

$P =$ # *phases* φ present at equilibrium. Phases are physically distinct and, in principle, mechanically separable portions of a sample. A mixture of different solid-state phases may not be distinguished by visual inspection but, rather, using X-ray diffraction or electron microscopy. According to Gibbs, a phase is uniform throughout, both in chemical composition as well as physical state. Therefore, phases can be either pure substances or homogeneous mixtures, i.e., solutions. Distinct pure substances (phases) include different:

- physical states, e.g., $\text{H}_2\text{O}(s)$ and $\text{H}_2\text{O}(l)$;
- chemical compositions; e.g., $\text{MgSiO}_3(s)$ and $\text{Mg}_2\text{SiO}_4(s)$;
- atomic structures, e.g., $\alpha\text{-Fe}(s)$ (BCC) and $\gamma\text{-Fe}(s)$ (FCC).

Solutions can be gases, liquids, or solids. Every mixture of gases is homogeneous and a single phase, i.e., $P = 1$. Examples of liquid-phase solutions include $\text{NaCl}(aq) = \text{Na}^+(aq) + \text{Cl}^-(aq)$ and the homogeneous mixture $\text{Si}_x\text{Ge}_{1-x}(l)$ for $0 < x < 1$. *Solid solutions* are also homogeneous mixtures, such as $\text{Si}_x\text{Ge}_{1-x}(s)$ and $(\text{Al}_{1-x}\text{Cr}_x)_2\text{O}_3$ ($0 \leq x \leq 1$). They can form between elements with similar sizes and electronegativities while also adopting the same structure type. For the oxide $(\text{Al}_{1-x}\text{Cr}_x)_2\text{O}_3$, Al^{3+} and Cr^{3+} ions have similar sizes and prefer octahedral coordination. Other formulations include $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$ ($0 \leq x \leq 2$) and $(\text{Al}_2\text{O}_3)_{1-x}(\text{Cr}_2\text{O}_3)_x$. $P > 1$ for all heterogeneous mixtures.

$C =$ # *components* or constituents that can undergo independent variation in different phases. Alternatively, C is the minimum number of constituents needed to completely describe the composition of all phases present. Often, C is the number of different elements in the system, but not always. For example, $\text{Ca}_3\text{SiO}_5(s)$ and $\text{Ca}_3\text{Si}_2\text{O}_7(s)$ are distinct phases in the 2-component system between CaO and SiO_2 , although there are 3 elements. In pure CaO and SiO_2 , the $\text{Ca}:\text{O}$ and $\text{Si}:\text{O}$ molar ratios are both fixed values. In the literature, “composition” can be used to describe different aspects of a system:

- the *chemical* composition of a single phase;
- the relative amounts of different phases in a mixture, called *phase* composition;
- the *overall* composition of a mixture, irrespective of phase component compositions.

The value of C in the Gibbs phase rule refers to the overall chemical composition.

Determining the number of components in a complex system is extremely important for proper application of the Gibbs phase rule. A general approach involves:

- (1) Identifying the number of possible different chemical species (S) in the equilibrium state. There are no general restrictions on S , but you may apply specific criteria to decide whether a species is observable in the equilibrium state or not. For example, if the partial pressure of a gas-phase species is below some threshold value, that gas species may be neglected. You can never select too many species, but you must be careful not to utilize too few. Here are some guidelines for selecting chemical species:
 - Each pure element or compound is a distinct chemical species such as $\text{N}_2(g)$, $\text{Si}(s)$, $\text{H}_2\text{O}(g)$, and $\text{SiO}_2(s)$.
 - Each constituent of a solution is a distinct chemical species. Examples of liquid solutions include $\text{NaCl}(aq) = \text{Na}^+(aq)$, $\text{Cl}^-(aq)$, and $\text{H}_2\text{O}(l)$ and $\text{Si}_{1-x}\text{Ge}_x(l) = \text{Si}(ls)$ and $\text{Ge}(ls)$. The designation “ ls ” stands for “liquid solution”, which means that neither Si nor Ge exist in their pure liquid state. Examples of solid solutions include $\text{Si}_{1-x}\text{Ge}_x(s) = \text{Si}(ss)$ and $\text{Ge}(ss)$ and $(\text{Al}_{1-x}\text{Cr}_x)_2\text{O}_3 = \text{Al}_2\text{O}_3(ss)$ and $\text{Cr}_2\text{O}_3(ss)$. Likewise, the designation “ ss ” stands for “solid solution”.
- (2) Determining the number of *independent* net chemical equations (R) among the different species (S) existing at equilibrium. In fact, these equations represent possible chemical equilibria in the system. The more species selected to exist in the equilibrium state, the more independent chemical equations result.
- (3) Identifying the number of external chemical restraints (ρ) imposed by the synthetic procedure leading to the equilibrium state. This value can take any of three forms:
 - fixing the temperature;
 - fixing the total pressure;
 - stoichiometric restrictions on mole fractions within homogeneous solutions.

Therefore, the number of independent components C are evaluated from the number of chemical species S with the numbers of independent net chemical equations R and external restraints ρ acting as restraints:

$$C = S - R - \rho.$$

As mentioned above, in the absence of any externally imposed restraints by the synthetic procedure, the number of components $C = S - R$ often equals the number of elements making up all the chemical species at equilibrium.

(21) The Gibbs phase rule is completely general for any chemical system at equilibrium, and a short derivation provides some insights about how it works. For a system of variables and linear equations relating these variables, the number of *degrees of freedom* F is the difference:

$$F = (\# \text{ variables}) - (\# \text{ equations}),$$

which corresponds to the number of variables that can be independently changed. A system is *precisely determined* if $F = 0$, i.e., each variable must adopt a certain value to satisfy the different equations. If $F > 0$, the system is *under-determined* so that F variables are not precisely restricted. On the other hand, if $F < 0$, then the system is *over-determined*, and there may be no solution because the variables may not simultaneously satisfy all equations. Therefore, in the Gibbs phase rule, F will control how many different phases P can coexist at equilibrium.

For any phase diagram, the underlying equation(s) are the molar Gibbs free energy functions for every possible phase. For any phase φ containing mole fraction x_i of component i , the molar Gibbs free energy $g^{(\varphi)}(T, p, x_i)$ is a function of the $C + 2$ intensive variables, T , p , and the mole fractions x_i ($i = 1, \dots, C$). The differential of the molar Gibbs free energy is

$$\begin{aligned} dg^{(\varphi)} &= \left(\frac{\partial g^{(\varphi)}}{\partial T} \right)_{p, x_i} dT + \left(\frac{\partial g^{(\varphi)}}{\partial p} \right)_{T, x_i} dp + \sum_{i=1}^C \left(\frac{\partial g^{(\varphi)}}{\partial x_i^{(\varphi)}} \right)_{T, p} dx_i^{(\varphi)} \\ &= -s^{(\varphi)} dT + v^{(\varphi)} dp + \sum_{i=1}^C \mu_i^{(\varphi)} dx_i^{(\varphi)}, \end{aligned}$$

in which $s^{(\varphi)}$ = molar entropy of phase φ , $v^{(\varphi)}$ = molar volume of phase φ , and $\mu_i^{(\varphi)}$ = chemical potential or partial molar Gibbs free energy of component i in phase φ . Therefore, the function $g^{(\varphi)}(T, p, x_i)$ has $C + 2$ variables. If there are P phases in the system, then each phase φ will have its own composition, given by the mole fractions $x_i^{(\varphi)}$ ($i = 1, \dots, C$; $\varphi = 1, \dots, P$). Therefore, the total number of variables in the system is $P(C + 2)$.

One set of restraints involves the composition of each phase:

$$x_1^{(\varphi)} + x_2^{(\varphi)} + \dots + x_C^{(\varphi)} = 1.$$

Other restraints arise from the equilibrium conditions. At thermodynamic equilibrium, each of the P phases must be at the same temperature (thermal equilibrium), the same total pressure (mechanical equilibrium), and the chemical potential of each component must be the same value in each of the P phases (chemical equilibrium). Thus, there are $P - 1$ equations for temperature, $P - 1$ equations for pressure, and $C(P - 1)$ equations among the chemical potentials, for a total number of $(C + 2)(P - 1) + P$ equations. Then,

$$F = (\# \text{ variables}) - (\# \text{ equations}) = P(C + 2) - [(P - 1)(C + 2) + P] = C - P + 2.$$

We will now apply the Gibbs phase rule to different cases of heterogeneous equilibria to see how this equation is applied to problems in solid-state chemistry.

(22) Heterogeneous Equilibria involve mixtures of different phases, which may involve pure compounds or solutions. Calculations of equilibrium states require using relationships among intensive variables and rely on the equations appropriate for equilibrium thermodynamics. For a brief summary of important fundamental definitions and relationships in thermodynamics, please see the Appendix at the end of this unit. We will examine equilibrium for a solid-gas mixture and a multiple solid-state mixture.

Solid-Gas Equilibria: Consider a mixture of $\text{Cu}(\text{OH})_2(\text{s})$, $\text{CuO}(\text{s})$, and $\text{H}_2\text{O}(\text{g})$ at equilibrium in a closed container. How many *independent intensive variables* F are there for this system?

Identifying F for a given chemical system can tell you whether equilibrium can be achieved or not and how much control you, as the experimentalist, have over achieving an equilibrium state. A chemical system typically allows control when there is one degree of freedom ($F = 1$) because there is one variable, often temperature, that can be changed (controlled) and the other variables will follow suit from the Gibbs phase rule for equilibrium to exist. Therefore, answering this question will tell you how much freedom exists to control the equilibrium state of this mixture.

To evaluate F , we must identify the number of phases P and the number of components C . Phase identification is generally straightforward, whereas determination of C , especially for complex systems, can be challenging. So, a general strategy will be described.

$P = 3$: There are 2 distinct solids, $\text{Cu}(\text{OH})_2(\text{s})$ and $\text{CuO}(\text{s})$, and a gaseous species, $\text{H}_2\text{O}(\text{g})$.

$C = S - R - \rho$: In general, the most challenging aspect of determining C is to identify the number of independent net chemical reactions R among the different species in the system. Although you may be able to accomplish this by sight for many problems, if there are several species present at equilibrium, then this step is more difficult. A general method to obtain R is to set up a *species-by-element matrix*, in which the different species label the columns and the different elements label the rows. The matrix elements in a given column correspond to the number of atoms of each element in that species. In setting up the species-by-element matrix, it is advantageous to order the species by increasing complexity from left-to-right, but also to account for all elements in the early columns. Once this matrix is set up, use *matrix row-reduction* to achieve a unit matrix at the left-hand side of this species-by-element matrix, i.e., 1's along the diagonal from upper left to the right and 0's below and above each of these diagonal members. Row-reduction operations include

- multiplying or dividing a row by any number;
- adding or subtracting one row from another.

At the end of matrix row-reduction, the *rank* of the “row-reduced” matrix is the number of “1”s along the diagonal, also called the dimension of the unit matrix. Therefore, the rank is a value no larger than the number of different elements in the system and the number of independent net chemical reactions is

$$R = S - \text{rank}.$$

In the absence of any other restraints, then

$$\text{rank} = S - R = C.$$

The row-reduced matrix also allows a change of basis between elements and the subset of chemical species determining the rank of the matrix. By changing the basis, the independent net chemical equations can be written down from the R right-hand columns of the row-reduced matrix.

For the current problem, $S = 3$ consisting of $\text{Cu}(\text{OH})_2(\text{s})$, $\text{CuO}(\text{s})$, and $\text{H}_2\text{O}(\text{g})$ and there are 3 elements Cu, H, and O, so a 3×3 species-by-element matrix is set up:

(1) Set up Species-by-Element Matrix:

	CuO	H ₂ O	Cu(OH) ₂
Cu	1	0	1
H	0	2	2
O	1	1	2

(2) Subtract Row #1 from Row #3:

	CuO	H ₂ O	Cu(OH) ₂
Cu	1	0	1
H	0	2	2
O	0	1	1

(3) Divide Row #2 by 2:

	CuO	H ₂ O	Cu(OH) ₂
Cu	1	0	1
H	0	1	1
O	0	1	1

(4) Subtract Row #2 from Row #3:

	CuO	H ₂ O	Cu(OH) ₂
Cu	1	0	1
H	0	1	1
O	0	0	0

After Step (4), the matrix is row-reduced. As identified by the shading, the row-reduced matrix has rank = 2. Therefore, since $R = 3 - 2 = 1$, there is *one independent chemical equation* relating the three species with each other. To write down this chemical equation, the unit matrix allows a “change of basis”, which means that element Cu can be switched with species CuO and element H can be switched with species H₂O:

	Cu	H	Cu(OH) ₂
CuO	1	0	1
H ₂ O	0	1	1
O	0	0	0

Now, take each species in the column(s) beyond the rank value of the matrix and set it equal, using the chemical equilibrium sign “ \rightleftharpoons ”, to the sum of each row basis multiplied by the numerical factor in the row. In this case, we obtain:



Therefore, the 3 species in this system are related to each other by one chemical equilibrium.

Finally, are there any externally imposed restraints ρ ? The way the question is posed, there is no description of the initial conditions that were used to establish equilibrium. Therefore, $\rho = 0$. Since $S = 3$, $R = 1$, and $\rho = 0$, then $C = 3 - 1 - 0 = 2$.

$F = 2 - 3 + 2 = 1$: There is one independent intensive variable for this system. As a result, this system is called *univariant*. What does this result mean and what can be learned from it?

(23) For this *univariant* system, there is *one intensive variable* that can be freely set to any reasonable experimental value. In other words, if one of these independent intensive variables is set, then the equilibrium state of the system is uniquely defined. For the system consisting of the 3 phases Cu(OH)₂(s), CuO(s), and H₂O(g), there are five intensive variables:

(1) Temperature T (2) Total pressure $p_{\text{TOT}} = p_{\text{H}_2\text{O}}$ because there is only water vapor in the gas phase(3) Mole fraction of H₂O in the gas phase, $x_{\text{H}_2\text{O}}^{(g)}$ (4) Mole fraction of CuO in the solid CuO, $x_{\text{CuO}}^{(\text{CuO},s)}$ (5) Mole fraction of Cu(OH)₂ in the solid Cu(OH)₂, $x_{\text{Cu(OH)}_2}^{(\text{Cu(OH)}_2,s)}$.

At chemical equilibrium, there are four equations (restraints):

- (1) $x_{\text{Cu(OH)}_2}^{(\text{Cu(OH)}_2, s)} = 1$ (pure, solid phase Cu(OH)_2)
- (2) $x_{\text{CuO}}^{(\text{CuO}, s)} = 1$ (pure, solid phase CuO)
- (3) $x_{\text{H}_2\text{O}}^{(g)} = 1$ (H_2O is the only gaseous species)
- (4) $\mu_{\text{Cu(OH)}_2}^{(\text{Cu(OH)}_2, s)} = \mu_{\text{CuO}}^{(\text{CuO}, s)} + \mu_{\text{H}_2\text{O}}^{(g)}$ (equal chemical potentials required for equilibrium).

The chemical potential for each species S in phase φ is related to its activity $a_S^{(\varphi)}$:

$$\mu_{\text{Cu(OH)}_2}^{(\text{Cu(OH)}_2, s)} = \mu_{\text{Cu(OH)}_2}^{(\text{Cu(OH)}_2, s)^\circ} + RT \ln \left(a_{\text{Cu(OH)}_2}^{(\text{Cu(OH)}_2, s)} \right) = \mu_{\text{Cu(OH)}_2}^{(\text{Cu(OH)}_2, s)^\circ}$$

$$\mu_{\text{CuO}}^{(\text{CuO}, s)} = \mu_{\text{CuO}}^{(\text{CuO}, s)^\circ} + RT \ln \left(a_{\text{CuO}}^{(\text{CuO}, s)} \right) = \mu_{\text{CuO}}^{(\text{CuO}, s)^\circ}$$

$$\mu_{\text{H}_2\text{O}}^{(g)} = \mu_{\text{H}_2\text{O}}^{(g)^\circ} + RT \ln \left(a_{\text{H}_2\text{O}}^{(g)} \right) = \mu_{\text{H}_2\text{O}}^{(g)^\circ} + RT \ln p_{\text{H}_2\text{O}}$$

In these expressions, $\mu_S^{(\varphi)^\circ}$ is the chemical potential of species S in phase φ for its standard or reference state. For every pure substance in a condensed state, liquid or solid, $a_S^{(\varphi)} = 1$. Now, the equation between chemical potentials means that $\Delta G = 0$ for the heterogeneous equilibrium among $\text{Cu(OH)}_2(s)$, $\text{CuO}(s)$, and $\text{H}_2\text{O}(l)$. Therefore,

$$\begin{aligned} \Delta G = 0 &= \mu_{\text{Cu(OH)}_2}^{(\text{Cu(OH)}_2, s)} - \mu_{\text{CuO}}^{(\text{CuO}, s)} - \mu_{\text{H}_2\text{O}}^{(g)} \\ &= \left(\mu_{\text{Cu(OH)}_2}^{(\text{Cu(OH)}_2, s)^\circ} - \mu_{\text{CuO}}^{(\text{CuO}, s)^\circ} - \mu_{\text{H}_2\text{O}}^{(g)^\circ} \right) + RT \ln p_{\text{H}_2\text{O}} = \Delta G^\circ + RT \ln K(T) \end{aligned}$$

from which we can write an expression for the equilibrium constant

$$K_p(T) = p_{\text{H}_2\text{O}}(T) = p_{\text{TOT}}(T) = e^{(-\Delta G^\circ/RT)}.$$

ΔG° is the standard Gibbs free energy difference for the balanced chemical equation. Since $p_{\text{H}_2\text{O}}$ is a function of T only, then either T or $p_{\text{H}_2\text{O}}$ can be independently varied as long as $\text{Cu(OH)}_2(s)$, $\text{CuO}(s)$, and $\text{H}_2\text{O}(g)$ coexist. If temperature is fixed, then equilibrium demands a specific $p_{\text{H}_2\text{O}}$; if $p_{\text{H}_2\text{O}}$ is adjusted to some fixed value, then equilibrium among the 3 phases will only occur for a specific temperature. Therefore, this system is *univariant* as described.

To calculate the equilibrium states for this 3-phase system, we need an expression for ΔG° of the equilibrium $\text{Cu(OH)}_2(s) \rightleftharpoons \text{CuO}(s) + \text{H}_2\text{O}(g)$:

$$\Delta G^\circ(\text{J/mol}) \approx 52,500 - 123 T = (6,315 - 14.8 T)R,$$

so that the expression between $p_{\text{H}_2\text{O}}$ and temperature is:

$$K_p(T) = p_{\text{H}_2\text{O}}(T) = e^{(14.8 - 6,315/T)}.$$

Plotting this equation using $p_{\text{H}_2\text{O}}$ as one axis and temperature as the other axis creates a *phase diagram* for this system. There are two regions separated by the curve $K_p(T)$. Therefore, the equilibrium state for this system is determined by $p_{\text{H}_2\text{O}}(T)$:

$p_{\text{H}_2\text{O}}(T) = K(T)$: This equality identifies the conditions of pressure and temperature at which three phases coexist: $\text{Cu(OH)}_2(s)$, $\text{CuO}(s)$, and $\text{H}_2\text{O}(g)$ and $F = 1$. Because this line represents a univariant system, if either T or $p_{\text{H}_2\text{O}}$ is set, the other variable is also fixed for the 3 phases to coexist.

$p_{\text{H}_2\text{O}} > K(T)$: If the three species occur in the chamber, then $\text{CuO}(s)$ and $\text{H}_2\text{O}(g)$ are thermodynamically driven to form $\text{Cu}(\text{OH})_2(s)$. This process will occur until either the 3-phase equilibrium is established or $\text{CuO}(s)$ is consumed. As a result, this region of the diagram allows for the coexistence of $\text{Cu}(\text{OH})_2(s)$ and $\text{H}_2\text{O}(g)$. This is a 2-phase region ($P = 2$) and, according to the Gibbs phase rule, there are 2 independent intensive variables ($F = 2$), $p_{\text{H}_2\text{O}}$ and T .

$p_{\text{H}_2\text{O}} < K(T)$: If the three species occur in the chamber, then $\text{Cu}(\text{OH})_2(s)$ is thermodynamically driven to form $\text{CuO}(s)$ and $\text{H}_2\text{O}(g)$. This process will occur until either the 3-phase equilibrium is established or $\text{Cu}(\text{OH})_2(s)$ is consumed. As a result, this region of the diagram allows for the coexistence of $\text{CuO}(s)$ and $\text{H}_2\text{O}(g)$ and is also a 2-phase region with 2 independent intensive variables, $p_{\text{H}_2\text{O}}$ and T .

(24) Now, consider some *restraints* placed on the system by the initial conditions to establish equilibrium to see how they affect the # degrees of freedom F :

How many *degrees of freedom* F are there for an equilibrium mixture of $\text{Cu}(\text{OH})_2(s)$, $\text{CuO}(s)$, and $\text{H}_2\text{O}(g)$ in a closed 1.00 L container if equilibrium is established by decomposition of 0.050 mole $\text{Cu}(\text{OH})_2$?

With respect to the Gibbs phase rule, then we need to evaluate whether the synthetic conditions create any additional restraints on the *intensive variables*, which are T , $p_{\text{H}_2\text{O}}$, $x_{\text{H}_2\text{O}}^{(g)}$, $x_{\text{CuO}}^{(\text{CuO},s)}$, and $x_{\text{Cu}(\text{OH})_2}^{(\text{Cu}(\text{OH})_2,s)}$. The procedure specifies the initial number of moles of $\text{Cu}(\text{OH})_2(s)$ and the volume of the container. How do these affect F ? Here, I'll answer this question using n_0 moles $\text{Cu}(\text{OH})_2(s)$ and volume V_0 for the container:

The initial number of moles of $\text{Cu}(\text{OH})_2$ places constraints on the numbers of moles of Cu, H and O atoms in the container (using mass balance). At equilibrium

$$n_{\text{eq}}(\text{Cu}) = n_{\text{eq}}(\text{Cu}(\text{OH})_2) + n_{\text{eq}}(\text{CuO}) = n_0$$

$$n_{\text{eq}}(\text{H}) = 2n_{\text{eq}}(\text{Cu}(\text{OH})_2) + 2n_{\text{eq}}(\text{H}_2\text{O}) = 2n_0$$

$$n_{\text{eq}}(\text{O}) = 2n_{\text{eq}}(\text{Cu}(\text{OH})_2) + n_{\text{eq}}(\text{CuO}) + n_{\text{eq}}(\text{H}_2\text{O}) = 2n_0$$

These three equations lead to

$$n_{\text{eq}}(\text{CuO}) = n_{\text{eq}}(\text{H}_2\text{O})$$

$$n_{\text{eq}}(\text{Cu}(\text{OH})_2) = n_0 - n_{\text{eq}}(\text{CuO}) = n_0 - n_{\text{eq}}(\text{H}_2\text{O}) \geq 0.$$

The container volume together with $n_{\text{eq}}(\text{H}_2\text{O})$ will determine $p_{\text{H}_2\text{O}}$. If water vapor is treated as an ideal gas, then

$$p_{\text{H}_2\text{O}} = \frac{n_{\text{eq}}(\text{H}_2\text{O})RT}{V_0} = \left(\frac{n_{\text{eq}}(\text{H}_2\text{O})R}{V_0} \right) T,$$

which indicates that the pressure of water vapor is a function of temperature. Since the initial conditions do not affect the mole fractions of the components of each phase, then among the 5 intensive variables, there are 4 restraints and the number of degrees of freedom $F = 1$. Therefore, the imposed conditions are not any additional restraints on the intensive variables.

How do the conditions affect the equilibrium state of the mixture? The initial number of moles of $\text{Cu}(\text{OH})_2(s)$ restricts the *maximum pressure* of $\text{H}_2\text{O}(g)$ in the gas phase according to

$$p_{\text{max H}_2\text{O}} = \left(\frac{n_0 R}{V_0} \right) T.$$

By graphing $p_{\max \text{H}_2\text{O}}(T)$ and $p_{\text{H}_2\text{O}}(T) = K(T)$ from the 3-phase equilibrium, there are three situations to consider:

(1) Maximum $p_{\text{H}_2\text{O}}$ will be *larger* than $p_{\text{H}_2\text{O}}$ demanded by the 3-phase equilibrium:

$$p_{\max \text{H}_2\text{O}} > p_{\text{H}_2\text{O}}(T): \left(\frac{n_0 R}{V_0}\right) T > e^{(14.8-6,315/T)}.$$

$\text{Cu}(\text{OH})_2(s)$ will decompose to form $\text{CuO}(s)$ and $\text{H}_2\text{O}(g)$ until the total pressure equals $p_{\text{H}_2\text{O}}$ for the 3-phase equilibrium to occur. That is, not all of the initial n_0 moles $\text{Cu}(\text{OH})_2(s)$ will decompose. This situation occurs below some specific temperature T_0 .

(2) Maximum $p_{\text{H}_2\text{O}}$ will *equal* $p_{\text{H}_2\text{O}}$ demanded by the 3-phase equilibrium:

$$p_{\max \text{H}_2\text{O}} = p_{\text{H}_2\text{O}}(T): \left(\frac{n_0 R}{V_0}\right) T = e^{(14.8-6,315/T)}.$$

There is a specific temperature T_0 where this outcome occurs. At this point, all $\text{Cu}(\text{OH})_2(s)$ will be just consumed and only $\text{CuO}(s)$ and $\text{H}_2\text{O}(g)$ will remain in the chamber.

(3) Maximum $p_{\text{H}_2\text{O}}$ will be *smaller* than $p_{\text{H}_2\text{O}}$ demanded by the 3-phase equilibrium:

$$p_{\max \text{H}_2\text{O}} < p_{\text{H}_2\text{O}}(T): \left(\frac{n_0 R}{V_0}\right) T < e^{(14.8-6,315/T)}.$$

All n_0 moles $\text{Cu}(\text{OH})_2(s)$ will have decomposed to form n_0 moles $\text{CuO}(s)$ and n_0 moles $\text{H}_2\text{O}(g)$. The pressure in the container will be controlled by the ideal gas law $p_{\max \text{H}_2\text{O}}(T)$.

For the specific conditions stated in the problem, the maximum pressure of $\text{H}_2\text{O}(g)$ follows:

$$p_{\max \text{H}_2\text{O}}(\text{atm}) = \left(\frac{(0.050 \text{ mol})(0.08206 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K})}{1.00 \text{ L}}\right) T = 0.0041 T.$$

The temperature at which $p_{\max \text{H}_2\text{O}}(T)$ and $p_{\text{H}_2\text{O}}(T) = K(T)$ cross is 445 K. Therefore, below 445 K, the 3 phases $\text{Cu}(\text{OH})_2(s)$, $\text{CuO}(s)$, and $\text{H}_2\text{O}(g)$ coexist in equilibrium, whereas at and above 445 K, the 2 phases $\text{CuO}(s)$, and $\text{H}_2\text{O}(g)$ coexist.

(25) How many *degrees of freedom* F are there for an equilibrium mixture of $\text{Cu}(\text{OH})_2(s)$, $\text{CuO}(s)$, and $\text{H}_2\text{O}(g)$ in a closed 1.00 L container if equilibrium is established by decomposition of 0.050 mole $\text{Cu}(\text{OH})_2$ at 420 K?

By specifying the temperature, this condition is an additional restraint and $F = 0$, i.e., there are no degrees of freedom. Using the results from slide **(24)**, the pressure of $\text{H}_2\text{O}(g)$ in the 1.00 L container will be:

$$p_{\text{H}_2\text{O}}(T < 445 \text{ K}) = e^{(14.8-6,315/T)} \text{ and } p_{\text{H}_2\text{O}}(T > 445 \text{ K}) = 0.0041 T.$$

The temperature is below 445 K, so we use the expression for the 3-phase equilibrium and

$$p_{\text{H}_2\text{O}}(420 \text{ K}) = e^{(14.8-6,315/420)} = e^{-0.236} = 0.79 \text{ atm}.$$

To summarize, what can be learned from the problem in slides **(22)-(25)** regarding preparative solid-state chemistry? The problem involved the heterogeneous chemical equilibrium:



- The Gibbs phase rule provides the relationship between the number of phases that can coexist when the system *is at equilibrium*, and the number of intensive variables that can be controlled.

- The equilibrium mixture of the three phases $\text{Cu}(\text{OH})_2(s)$, $\text{CuO}(s)$, and $\text{H}_2\text{O}(g)$ is a *univariant* system. Because each solid is a pure phase and there is a single gaseous species, there must be a relationship between temperature and the pressure of water vapor at equilibrium.
- If 3-phase equilibrium is established by decomposing $\text{Cu}(\text{OH})_2(s)$ in a sealed, evacuated chamber, there *must be a sufficient amount* of the hydroxide to yield the appropriate equilibrium number of moles of water vapor for the temperature of the system. If this amount is too small, then $\text{Cu}(\text{OH})_2(s)$ will completely decompose. The chamber will only contain $\text{CuO}(s)$ and $\text{H}_2\text{O}(g)$ and $p_{\text{H}_2\text{O}}$ is too low to “drive” the reaction that would reform $\text{Cu}(\text{OH})_2(s)$.
- If a sealed chamber contains $\text{Cu}(\text{OH})_2(s)$, but the atmosphere has a (partial) pressure of water vapor that exceeds its equilibrium value, then no decomposition of the hydroxide will occur.

PROBLEM 1: *Solid-Gas Equilibrium with restraint imposed by the synthetic procedure.* $\text{FeSO}_4(s)$ is heated to high temperature in an evacuated container. At equilibrium, $\text{FeSO}_4(s)$, $\text{Fe}_2\text{O}_3(s)$, $\text{SO}_2(g)$, $\text{SO}_3(g)$ and $\text{O}_2(g)$ are present.

- How many independent intensive variables are there for this system as described? What are the implications of this result?
- Write down the different heterogeneous equilibria that can occur in this system and expressions for their equilibrium constants.

This is a more complicated problem than was covered during lecture. As a prelude to the solution, it does show how a specific initial condition can lead to a restraint among intensive composition variables. This problem also illustrates how heterogeneous equilibria can affect stoichiometry.

SOLUTION: There are two distinct solids, $\text{FeSO}_4(s)$ and $\text{Fe}_2\text{O}_3(s)$, and one gaseous mixture, $\text{SO}_2(g)$, $\text{SO}_3(g)$ and $\text{O}_2(g)$, so $P = 3$. The number of components $C = S - R - \rho$ is determined by matrix row-reduction of the species-by-element matrix:

	Fe_2O_3	SO_2	O_2	SO_3	FeSO_4
Fe	2	0	0	0	1
S	0	1	0	1	1
O	3	2	2	3	4

(1) Divide 1st row by 2

	Fe_2O_3	SO_2	O_2	SO_3	FeSO_4
Fe	1	0	0	0	1/2
S	0	1	0	1	1
O	3	2	2	3	4

(2) Multiply 1st row by 3; subtract from 3rd row

Fe	1	0	0	0	1/2
S	0	1	0	1	1
O	0	2	2	3	5/2

(3) Multiply 2nd row by 2; subtract from 3rd row

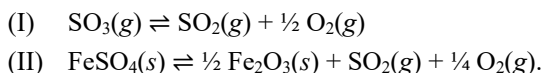
(4) Divide 3rd row by 2

Fe	1	0	0	0	1/2
S	0	1	0	1	1
O	0	0	1	1/2	1/4

The row-reduced matrix has rank 3 and there are $R = 2$ independent chemical equations relating the 5 species. Now, make the change of basis from (Fe, S, O) to (Fe_2O_3 , SO_2 , O_2):

	Fe	S	O	SO_3	FeSO_4
Fe_2O_3	1	0	0	0	1/2
SO_2	0	1	0	1	1
O_2	0	0	1	1/2	1/4

The last two columns give the independent net reactions for this construction:



NOTE: The order of column species is not unique, although judiciously choosing the order of species makes row-reduction straightforward. As an alternative option, consider the following species-by-element matrix and its solution – intermediate steps are deleted:

	FeSO ₄	SO ₃	O ₂	SO ₂	Fe ₂ O ₃
Fe	1	0	0	0	2
S	1	1	0	1	0
O	4	3	2	2	3

After complete row-reduction and basis change:

	Fe	S	O	SO ₂	Fe ₂ O ₃
FeSO ₄	1	0	0	0	2
SO ₃	0	1	0	1	-2
O ₂	0	0	1	-1/2	1/2

The 2 independent net chemical equations are



Now, $S = 5$ and $R = 2$. Are there any additional restraints ρ among the intensive variables imposed by the synthetic procedure? According to the problem, all elements in the container at equilibrium arise from $\text{FeSO}_4(\text{s})$, so we must look for any restrictions just among the mole fractions of the gas-phase species.

Let n_0 = number of moles of $\text{FeSO}_4(\text{s})$ placed in the container. Then,

$$\begin{aligned} n(\text{Fe}) &= n_0 = n(\text{FeSO}_4) + 2n(\text{Fe}_2\text{O}_3) \\ n(\text{S}) &= n_0 = n(\text{FeSO}_4) + n(\text{SO}_2) + n(\text{SO}_3) \\ n(\text{O}) &= 4n_0 = 4n(\text{FeSO}_4) + 2n(\text{SO}_2) + 3n(\text{SO}_3) + 2n(\text{O}_2) + 3n(\text{Fe}_2\text{O}_3) \end{aligned}$$

It is possible to eliminate $n(\text{FeSO}_4)$ and $n(\text{Fe}_2\text{O}_3)$, and obtain a relationship among the moles of gas:

$$n(\text{SO}_2) = n(\text{SO}_3) + 4n(\text{O}_2) \quad \text{-or-} \quad x(\text{SO}_2) = x(\text{SO}_3) + 4x(\text{O}_2)$$

So, there is one restriction among the mole fractions of the three gases by the initial conditions to establish equilibrium: $\rho = 1$. Therefore, $C = S - R - \rho = 5 - 2 - 1 = 2$; this is a 2-component system.

(a) Therefore, the # of independent variables is $F = C - P + 2 = 2 - 3 + 2 = 1$; this is a *univariant* system. Let's now explain this outcome by identifying the intensive variables and the chemical restraints. There are 7 intensive variables:

$$T \quad p_{\text{TOT}} \quad \text{FeSO}_4(\text{s}): x_{\text{FeSO}_4}^{(\text{FeSO}_4, \text{s})} \quad \text{Fe}_2\text{O}_3(\text{s}): x_{\text{Fe}_2\text{O}_3}^{(\text{Fe}_2\text{O}_3, \text{s})} \quad \text{Gas: } x_{\text{SO}_3}^{(\text{g})} \quad x_{\text{SO}_2}^{(\text{g})} \quad x_{\text{O}_2}^{(\text{g})}$$

and 6 restraints:

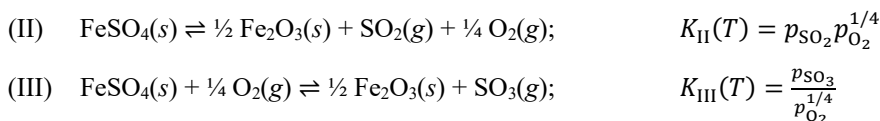
$$\begin{aligned} \text{Composition:} \quad & x_{\text{FeSO}_4}^{(\text{FeSO}_4, \text{s})} = 1 && x_{\text{Fe}_2\text{O}_3}^{(\text{Fe}_2\text{O}_3, \text{s})} = 1 && x_{\text{SO}_3}^{(\text{g})} + x_{\text{SO}_2}^{(\text{g})} + x_{\text{O}_2}^{(\text{g})} = 1 \\ \text{Initial Conditions:} \quad & x_{\text{SO}_2}^{(\text{g})} = x_{\text{SO}_3}^{(\text{g})} + 4x_{\text{O}_2}^{(\text{g})} \\ \text{Chemical Equilibria:} \quad & \mu_{\text{SO}_3}^{(\text{g})} = \mu_{\text{SO}_2}^{(\text{g})} + \frac{1}{2}\mu_{\text{O}_2}^{(\text{g})} && \mu_{\text{FeSO}_4}^{(\text{FeSO}_4, \text{s})} = \frac{1}{2}\mu_{\text{Fe}_2\text{O}_3}^{(\text{Fe}_2\text{O}_3, \text{s})} + \mu_{\text{SO}_2}^{(\text{g})} + \frac{1}{4}\mu_{\text{O}_2}^{(\text{g})}. \end{aligned}$$

The restraints arising from the chemical equilibria may be rewritten using equilibrium constants:

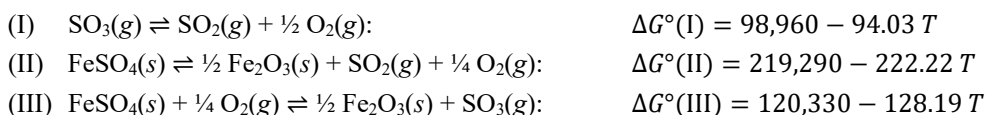
$$K_{\text{I}}(T) = \frac{p_{\text{SO}_2} p_{\text{O}_2}^{1/2}}{p_{\text{SO}_3}} = \left(\frac{x_{\text{SO}_2} x_{\text{O}_2}^{1/2}}{x_{\text{SO}_3}} \right) p_{\text{TOT}}^{1/2} \quad K_{\text{II}}(T) = p_{\text{SO}_2} p_{\text{O}_2}^{1/4} = (x_{\text{SO}_2} x_{\text{O}_2}^{1/4}) p_{\text{TOT}}^{5/4}$$

Therefore, an equation of state for this 3-phase equilibrium can be expressed by $p_{\text{TOT}}(T)$.

(b) The different heterogeneous equilibria that can occur in this system must involve the 3 phases. Since there are 2 sulfur oxides, there are 2 heterogeneous equilibria:

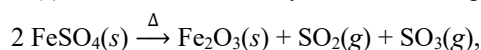


Calculations of equilibrium states require knowledge of the standard Gibbs free energy differences for the various equilibria in this system. These data are provided below and the results for this problem, i.e., the temperature-dependent total pressure along with the partial pressures of the gaseous components, are graphed:



Only 2 of these equilibria are *independent net chemical equations* that provide restraints on the intensive variables.

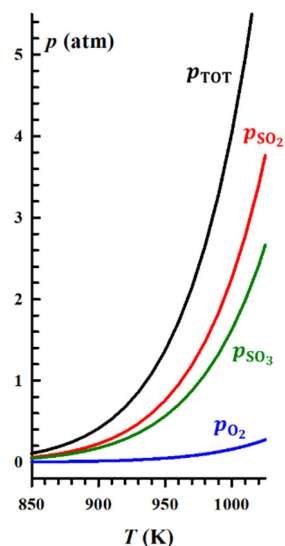
The equilibrium partial pressure of $\text{O}_2(\text{g})$ is significantly smaller than those of $\text{SO}_2(\text{g})$ and $\text{SO}_3(\text{g})$. In fact, the thermal decomposition of $\text{FeSO}_4(\text{s})$ can also be written by the chemical equation:



which is the sum of equilibria (II) and (III) above. However, this “reaction” ignores the presence of $\text{O}_2(\text{g})$ and suggests that the equilibrium partial pressures of $\text{SO}_2(\text{g})$ and $\text{SO}_3(\text{g})$ should be equal. Although their values are close to each other, $p_{\text{SO}_2} > p_{\text{SO}_3}$. As $\text{SO}_3(\text{g})$ is reduced, Fe(II) and oxide are oxidized, respectively, to Fe(III) and $\text{O}_2(\text{g})$. For this thermal decomposition process,

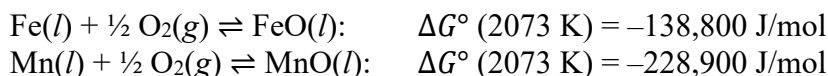
$$\Delta G^\circ = 339,620 - 350.41 T.$$

Thermal decomposition becomes observable about 950 K; the standard Gibbs free energy predicts a value between 940 K (from III) and 985 K (from II).



PROBLEM 2: Liquid solution-Gas Equilibria. Consider a liquid Mn-Fe alloy and a liquid MnO-FeO solution in equilibrium with an O_2 atmosphere at high temperature.

- Construct a species-by-element matrix and determine a set of independent net reactions (chemical equilibria) for this system.
- Using these equilibria, write down other heterogeneous equilibria for this system?
- How many degrees of freedom does this system have? Explain the result.
- Both liquid solutions behave ideally, so that the activities of solution components equal their mole fractions. If the Mn-Fe alloy is an equimolar mixture and the temperature is 2073 K, can the equilibrium state of this system be determined? If ‘yes’, what is the concentration of FeO in the liquid oxide solution and what is the $\text{O}_2(\text{g})$ pressure?



SOLUTION: The liquid phases in this system are (i) the Mn-Fe alloy = $\text{Mn}_{1-x}\text{Fe}_x(l) = (1-x) \text{Mn}(ls) + x \text{Fe}(ls)$, and (ii) the MnO-FeO liquid solution = $\text{MnO}_{1-y}\text{FeO}_y(l) = (1-y) \text{MnO}(ls) + y \text{FeO}(ls)$.

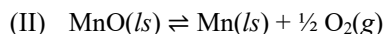
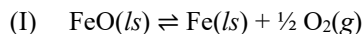
- The species are the different components in each solution plus O_2 :

(1) Divide 3rd row by 2

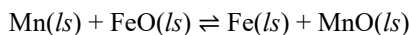
	Mn	Fe	O_2	MnO	FeO
Mn	1	0	0	1	0
Fe	0	1	0	0	1
O	0	0	2	1	1

	Mn	Fe	O_2	MnO	FeO
Mn	1	0	0	1	0
Fe	0	1	0	0	1
O	0	0	0	$\frac{1}{2}$	$\frac{1}{2}$

The row-reduced matrix has rank 3 and there are $R = 2$ independent chemical equations relating the 5 species:



(b) By “subtracting” (I) from (II), a heterogeneous equilibrium arises among components of the two liquid solutions:



(c) To get the number of degrees of freedom, apply the Gibbs Phase Rule:

$P = 3$: There are two distinct liquids, the Mn-Fe alloy and the MnO-FeO liquid solution, and one gaseous component, $\text{O}_2(g)$.

$C = 5 - 2 - 0 = 3$: There are 5 species and 2 independent net reactions from part (a). As stated, there are no additional restraints.

$F = 3 - 3 + 2 = 2$. This system is *bivariant*, which means that two intensive variables must be specified so that a unique determination of the equilibrium state can be determined. There are 7 intensive variables for this system: $T, p_{\text{TOT}} = p_{\text{O}_2}, x_{\text{Mn}}^{(l1)}, x_{\text{Fe}}^{(l1)}, x_{\text{MnO}}^{(l2)}, x_{\text{FeO}}^{(l2)}, x_{\text{O}_2}^{(g)}$; and 5 restraints:

$$\text{Compositions:} \quad x_{\text{O}_2}^{(g)} = 1, \quad x_{\text{Mn}}^{(l1)} + x_{\text{Fe}}^{(l1)} = 1, \quad x_{\text{MnO}}^{(l2)} + x_{\text{FeO}}^{(l2)} = 1,$$

$$\text{Equilibria:} \quad K_I(T) = \frac{a_{\text{Fe}}^{(l1)}}{a_{\text{FeO}}^{(l2)}} p_{\text{O}_2}^{(g)} = \frac{x_{\text{Fe}}^{(l1)}}{x_{\text{FeO}}^{(l2)}} p_{\text{O}_2}^{(g)} \quad K_{II}(T) = \frac{a_{\text{Mn}}^{(l1)}}{a_{\text{MnO}}^{(l2)}} p_{\text{O}_2}^{(g)} = \frac{x_{\text{Mn}}^{(l1)}}{x_{\text{MnO}}^{(l2)}} p_{\text{O}_2}^{(g)}$$

The expressions for the equilibrium constants utilize the ideal behavior of these solutions and provide restrictions on the values of the mole fractions of the solution constituents.

(d) By setting the temperature at 2073 K, the equilibrium constants K_I and K_{II} can be calculated. Setting the mole fractions for the alloy allows determination of the mole fractions for the oxide solution from the heterogeneous equilibrium in (b). Then, the O_2 pressure can be calculated.

$$K_I(2073 \text{ K}) = e^{-138,800/8.314 \cdot 2073} = e^{-8.0534} = 3.18 \times 10^{-4} = \frac{x_{\text{Fe}}^{(l1)}}{x_{\text{FeO}}^{(l2)}} p_{\text{O}_2}^{(g)}$$

$$K_{II}(2073 \text{ K}) = e^{-228,900/8.314 \cdot 2073} = e^{-13.2812} = 1.71 \times 10^{-6} = \frac{x_{\text{Mn}}^{(l1)}}{x_{\text{MnO}}^{(l2)}} p_{\text{O}_2}^{(g)}$$

In the alloy, $x_{\text{Fe}}^{(l1)} = x_{\text{Mn}}^{(l1)} = 0.5$, so that the equilibrium constant of the heterogeneous equilibrium between the two liquid solutions is:

$$K(T) = \frac{x_{\text{Fe}}^{(l1)} x_{\text{MnO}}^{(l2)}}{x_{\text{Mn}}^{(l1)} x_{\text{FeO}}^{(l2)}} = \left(\frac{0.5}{0.5} \right) \frac{x_{\text{MnO}}^{(l2)}}{x_{\text{FeO}}^{(l2)}} = \frac{1 - x_{\text{FeO}}^{(l2)}}{x_{\text{FeO}}^{(l2)}} = \frac{K_I(T)}{K_{II}(T)}$$

At 2073 K this equation (restraint) is

$$\frac{1 - x_{\text{FeO}}^{(l2)}}{x_{\text{FeO}}^{(l2)}} = \frac{3.18 \times 10^{-4}}{1.71 \times 10^{-6}} = 186, \text{ so that } x_{\text{FeO}}^{(l2)} = 5.35 \times 10^{-3}.$$

Using the values of $x_{\text{Fe}}^{(l1)} = 0.5$ and $x_{\text{FeO}}^{(l2)} = 5.35 \times 10^{-3}$ in the expression for $K_I(2073 \text{ K})$ gives $p_{\text{O}_2}^{(g)}$:

$$p_{\text{O}_2}^{(g)} = \left(\frac{x_{\text{FeO}}^{(l2)}}{x_{\text{Fe}}^{(l1)}} \right) K_I(2073 \text{ K}) = \left(\frac{5.35 \times 10^{-3}}{0.5} \right) 3.18 \times 10^{-4} = 3.40 \times 10^{-6} \text{ atm.}$$

Then, the oxide solution is very rich in $\text{MnO}(l)$. You can check these results by using the equation for $K_{II}(2073 \text{ K})$.

(26) Solid-Solid Equilibria: When all the species in a system are pure condensed phases, then equilibrium must be considered from the Gibbs free energy difference because an equilibrium constant is no longer meaningful. Equilibrium is established when $\Delta G = 0$ between the two sides of the balanced chemical equation. Therefore, as chemical equilibrium among pure condensed phases is established, one of the reaction components is totally depleted, a situation which differs from gas-phase or solution-phase equilibria.

PROBLEM: Under what conditions can $\text{Cu}(s)$, $\text{Cu}_2\text{O}(s)$, and $\text{CuO}(s)$ *all* co-exist at equilibrium? Start by using the Gibbs phase rule to determine F . There are three distinct solid phases, $P = 3$. From the species-by-element matrix, $S = 3$ and $R = 1$:

(1) Set up Species-by-Element Matrix:

	Cu	CuO	Cu ₂ O
Cu	1	1	2
O	0	1	1

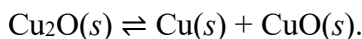
(2) Subtract Row #1 from Row #2

	Cu	CuO	Cu ₂ O
Cu	1	0	1
O	0	1	1

(3) Change Basis

	Cu	O	Cu ₂ O
Cu	1	0	1
CuO	0	1	1

The independent net chemical equation is



There are no arbitrary restraints, $\rho = 0$, and $C = S - R - \rho = 2$, which corresponds to the number of different elements. Therefore, the number of degrees of freedom

$$F = C - P + 2 = 2 - 3 + 2 = 1,$$

i.e., this is a *univariant* system. There are 5 intensive variables: T , p , $x_{\text{Cu}}^{(\text{Cu},s)}$, $x_{\text{Cu}_2\text{O}}^{(\text{Cu}_2\text{O},s)}$, $x_{\text{CuO}}^{(\text{CuO},s)}$. Since all chemical species in the system are pure solids, each mole fraction is unity, which gives 3 restraints. The 4th restraint must be a relationship between temperature and total pressure. At 1 atm pressure, chemical equilibrium will occur among the 3 pure condensed phases $\text{Cu}(s)$, $\text{Cu}_2\text{O}(s)$, and $\text{CuO}(s)$ only if

$$\Delta G = 0 = \Delta G^\circ(T).$$

Now, ΔG° can adopt one of three values with the associated outcomes:

- $\Delta G^\circ(T) = 0$: All three solids can coexist.
- $\Delta G^\circ(T) < 0$: The right-hand side of the chemical equation is favored. In this case, only $\text{Cu}(s)$ and $\text{CuO}(s)$ can coexist at equilibrium because any $\text{Cu}_2\text{O}(s)$ will completely react.
- $\Delta G^\circ(T) > 0$: The left-hand side of the chemical equation is favored, so $\text{Cu}(s)$ and $\text{CuO}(s)$ will not coexist. The equilibrium state depends on the total mole fraction of O (x_{O}) in the system:
 - If $x_{\text{O}} = 0.33$, only $\text{Cu}_2\text{O}(s)$ can exist as the equilibrium phase. This is an example of a line compound, and it melts at 1230°C.
 - If $x_{\text{O}} < 0.33$, $\text{Cu}_2\text{O}(s)$ and $\text{Cu}(s)$ can coexist; no $\text{CuO}(s)$ will occur at equilibrium.
 - If $x_{\text{O}} > 0.33$, $\text{Cu}_2\text{O}(s)$ and $\text{CuO}(s)$ can coexist; no $\text{Cu}(s)$ will occur at equilibrium.

According to thermodynamic data for the Cu-O system,

$$\Delta G^\circ(T) = 14,600 + 16.47 T \text{ (J/mol)} \text{ for } \text{Cu}_2\text{O}(s) \rightleftharpoons \text{Cu}(s) + \text{CuO}(s).$$

Therefore, since $\Delta G^\circ(T) > 0$, $\text{Cu}(s)$, $\text{Cu}_2\text{O}(s)$, and $\text{CuO}(s)$ cannot all coexist at equilibrium for any temperature at 1 atm total pressure. Depending on the total mole fraction of O in the system, then either one solid phase (Cu_2O) or two solid phases (Cu and Cu_2O or CuO and Cu_2O) can coexist. We can see this in the Cu-O phase diagram from 0–50 atomic percent O ($0 \leq x_{\text{O}} \leq 0.50$).

Since the one degree of freedom for this system as described implies a relationship between temperature and total pressure, then we must examine the relationship between ΔG and pressure:

$$\Delta G(T, p) = 0 = \Delta G^\circ(T) + \int_1^p \Delta V dp.$$

ΔV is the difference in molar volumes between the two sides of the chemical equation. Although molar volumes vary with temperature by thermal expansion coefficients, these changes are usually small for solids and may be ignored. For this equilibrium, $\Delta V = -6.71 \times 10^{-6} \text{ m}^3/\text{mol}$. Then

$$14,600 + 16.47 T - (6.71 \times 10^{-6})(p - 1) \sim 14,600 + 16.47 T - (6.71 \times 10^{-6})p = 0,$$

which provides the relationship between temperature and total pressure. For example, at $T = 1000 \text{ K}$, $\Delta G(1000 \text{ K}, p) = 0$ for $4.63 \times 10^9 \text{ J/m}^3 = 4.63 \text{ GPa}$.

Phase diagrams map out the equilibrium phases in a system for conditions of temperature, pressure, and chemical composition. The most commonly used phase diagrams for synthesis and crystal growing involve one component, two components, and three components. Since phases at equilibrium correspond to an overall minimum Gibbs free energy, there are two important relationships among the differentials of the intensive variables for a phase φ :

$$(1) \text{ Molar Gibbs free energy: } dg^{(\varphi)} = -s^{(\varphi)} dT + v^{(\varphi)} dp + \sum_{i=1}^C \mu_i^{(\varphi)} dx_i^{(\varphi)}.$$

$$(2) \text{ The Gibbs-Duhem equation: } \sum_{i=1}^C x_i^{(\varphi)} d\mu_i^{(\varphi)} + s^{(\varphi)} dT - v^{(\varphi)} dp = 0.$$

These equations are important for understanding features of phase diagrams.

(27) One-component phase diagrams ($C = 1$) identify the equilibrium phases for pure substances. Since $x_1^{(\varphi)} = 1$ for any phase φ , $dx_1^{(\varphi)} = 0$ and the molar Gibbs free energy $g^{(\varphi)}$ depends just on the two intensive variables T and p . By applying the Gibbs-Duhem relation,

$$dg^{(\varphi)} = -s^{(\varphi)} dT + v^{(\varphi)} dp = d\mu_1^{(\varphi)},$$

the molar Gibbs free energy for any phase in the system is its chemical potential.

As illustrated by the phase diagram for **iron**, there are four solid phase regions (α , ϵ , γ , and δ) and a liquid phase (L) region at higher temperatures.^{56,57} These regions are bordered by lines where two different phases meet. Lastly, there are two specific points where three boundary lines converge. What are the implications of the information in this diagram?

According to the Gibbs phase rule, the number of degrees of freedom is $F = 1 - P + 2 = 3 - P$, so that no more than 3 phases may coexist at equilibrium in a one component (unary) system.

$P = 1, F = 2$: The chemical potential $\mu_1^{(\alpha)}(T, p)$ for a single stable phase α has the lowest free energy value when compared with all other phases in the system. At a specific temperature and pressure where α is the equilibrium state, both temperature and pressure may be changed independently by dT and dp without changing the equilibrium state. In other words, there are no restraints on the intensive variables and single phases correspond to *regions* in the phase diagram.

α -Fe (bcc) is the stable form of the element at ambient temperature and pressure. At low temperatures and high pressures, hcp ϵ -Fe becomes stable. Heating bcc α -Fe or hcp ϵ -Fe leads to ccp γ -Fe. Lastly, just below the melting point and for relatively low pressures, bcc δ -Fe is the stable form. In fact, δ -Fe is the re-emergence of paramagnetic α -Fe.

⁵⁶ D.A. Young, *Phase Diagrams of the Elements*, University of California Press, Berkeley, **1991**.

⁵⁷ P.I. Dorogokupets, A.M. Dymshits, K.D. Litasov, T.S. Sokolova, *Sci. Rep.* **2017**, 7, 41863.

$P = 2, F = 1$: For two phases α and β to coexist at equilibrium, then $\mu_1^{(\alpha)}(T, p) = \mu_1^{(\beta)}(T, p)$, which is one restraint on the two intensive variables. To maintain the equilibrium $\alpha \rightleftharpoons \beta$, either temperature or pressure may be freely varied but not both simultaneously. Therefore, these equilibria correspond to $p(T)$ lines in the diagram. Phases α and β can be two different solid-state structures or one solid phase and the liquid phase. The change of pressure accompanying the change of temperature that maintains the equilibrium $\alpha \rightleftharpoons \beta$ is determined by setting the differentials of the two chemical potentials equal to each other:

$$\begin{aligned} \text{Phase } \alpha: \quad d\mu_1^{(\alpha)} &= -s^{(\alpha)}dT + v^{(\alpha)}dp; & \text{Phase } \beta: \quad d\mu_1^{(\beta)} &= -s^{(\beta)}dT + v^{(\beta)}dp. \\ d\mu_1^{(\alpha)} = d\mu_1^{(\beta)} &\Rightarrow -s^{(\alpha)}dT + v^{(\alpha)}dp = -s^{(\beta)}dT + v^{(\beta)}dp. \end{aligned}$$

Rearranging the second equation yields the *Clapeyron equation*, which expresses the slope of the $p(T)$ boundary between the regions for phases α and β :

$$\frac{dp}{dT} = \frac{s^{(\beta)} - s^{(\alpha)}}{v^{(\beta)} - v^{(\alpha)}} = \frac{\Delta s^{(\alpha\beta)}}{\Delta v^{(\alpha\beta)}} \text{ for } \alpha \rightleftharpoons \beta.$$

$\Delta s^{(\alpha\beta)}$ and $\Delta v^{(\alpha\beta)}$ are, respectively, the molar entropy and molar volume differences between the two phases. As a result, the slope of the $p(T)$ boundary between two coexisting phases depends on the relative signs of the entropy and volume differences between the two phases.

As a rule of thumb, as temperature increases and reaches a point where the equilibrium $\alpha \rightleftharpoons \beta$ occurs, then $\Delta s^{(\alpha\beta)} > 0$ and $\Delta v^{(\alpha\beta)} > 0$, so that the slope of the $p(T)$ boundary is positive. This occurs in the phase diagram for Fe except the boundary between the low-temperature bcc α -phase and the higher temperature ccp γ -phase. This behavior implies that $\Delta v^{(\alpha\gamma)} < 0$ from bcc to ccp at and near 1173 K. On the other hand, if a phase transition transpires with increasing pressure, usually $\Delta v^{(\alpha\beta)} < 0$ and the slopes of these boundaries are negative.

$P = 3, F = 0$: When three phases α , β , and γ coexist, then both temperature and pressure must be fixed because there are 2 restraints among the chemical potentials:

$$\mu_1^{(\alpha)}(T, p) = \mu_1^{(\beta)}(T, p) = \mu_1^{(\gamma)}(T, p).$$

The points (T_0, p_0) in the diagram where this condition holds are called *triple points*, and three different $p(T)$ curves converge at $p_0(T_0)$. Two triple points occur for iron: 757 K, 10.4 GPa for α - γ - ϵ ; and 1991 K, 5.3 GPa for δ - γ -liquid.

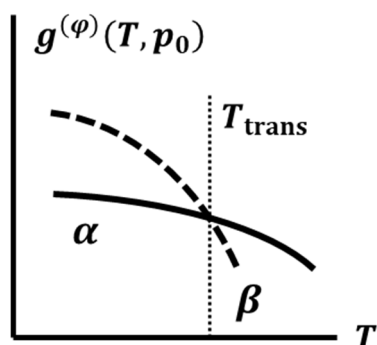
(28) Free Energies: These diagrams arise by comparing the Gibbs free energies for different phases in the system at various temperatures and pressures. It is perhaps easiest to follow these variations by restricting changes to a single intensive variable. At constant pressure,

$$\left(\frac{dg^{(\varphi)}}{dT}\right)_p = -s^{(\varphi)}(T) < 0 \text{ and } \left(\frac{d^2g^{(\varphi)}}{dT^2}\right)_p = -\left(\frac{ds^{(\varphi)}(T)}{dT}\right)_p < 0.$$

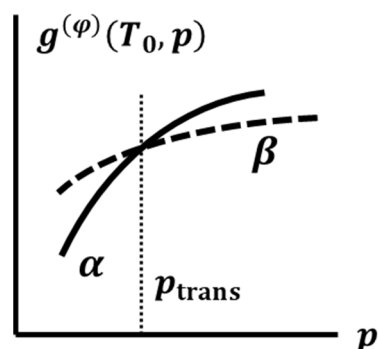
Since the molar entropy increases with increasing temperature, $g^{(\varphi)}(T, p)$ decreases with increasing temperature and the slope of $g^{(\varphi)}(T, p)$ becomes increasingly negative. On the other hand, at constant temperature

$$\left(\frac{dg^{(\varphi)}}{dp}\right)_T = v^{(\varphi)}(p) > 0 \text{ and } \left(\frac{d^2g^{(\varphi)}}{dp^2}\right)_T = \left(\frac{dv^{(\varphi)}(p)}{dp}\right)_T < 0,$$

and $g^{(\varphi)}(T, p)$ increases with increasing pressure. However, as pressure increases, the molar volume decreases. This qualitative analysis of the free energy function leads to the following two families of curves:



At constant pressure and increasing temperature, a phase transition from α to β occurs at T_{trans} where the free energy of β falls below that of α . Since phase α has the lower Gibbs free energy at lower temperatures, then $s^{(\beta)} > s^{(\alpha)}$. Phases α and β coexist at T_{trans} , $\alpha \rightleftharpoons \beta$ with $\Delta s^{(\alpha\beta)} = s^{(\beta)} - s^{(\alpha)}$.



At constant temperature and increasing pressure, a phase transition from α to β occurs at p_{trans} where the free energy of β falls below that of α . Since phase α has the lower Gibbs free energy at lower pressures, then $v^{(\beta)} < v^{(\alpha)}$. Phases α and β coexist at p_{trans} , $\alpha \rightleftharpoons \beta$ with $\Delta v^{(\alpha\beta)} = v^{(\beta)} - v^{(\alpha)}$.

In the phase diagram of Fe, the region below the melting point labeled as δ -Fe is the re-emergence of bcc paramagnetic α -Fe. This outcome implies that the curvature of the $g^{(\alpha)}(T, p_0 \sim 1 \text{ atm})$ with respect to temperature is larger than the curvature of $g^{(\gamma)}(T, p_0 \sim 1 \text{ atm})$. At the transition from α -Fe to γ -Fe at 1173 K, $s^{(\gamma)}(T) > s^{(\alpha)}(T)$, whereas at the transition from γ -Fe to δ -Fe at 1660 K, $s^{(\alpha)}(T) > s^{(\gamma)}(T)$.⁵⁸

(29) Two-component phase diagrams ($C = 2$) map the stable compounds, solutions, and mixtures for various temperatures and mole fractions (mole percentages) at a fixed pressure of 1 atm. For any phase φ in a binary system $x_1^{(\varphi)} + x_2^{(\varphi)} = 1$ and $dx_1^{(\varphi)} = -dx_2^{(\varphi)}$. Then, the differential of the molar Gibbs free energy $g^{(\varphi)}$ at constant pressure is:

$$\begin{aligned} dg^{(\varphi)} &= -s^{(\varphi)}dT + v^{(\varphi)}dp + \mu_1^{(\varphi)}dx_1^{(\varphi)} + \mu_2^{(\varphi)}dx_2^{(\varphi)} \\ &= -s^{(\varphi)}dT + (\mu_2^{(\varphi)} - \mu_1^{(\varphi)})dx_2^{(\varphi)}. \end{aligned}$$

Therefore, if P phases coexist at equilibrium, the molar Gibbs free energy has $P + 1$ independent intensive variables arising from temperature and P different mole fractions $x_2^{(\varphi)}$.

According to the Gibbs phase rule, the number of degrees of freedom for fixed pressure is

$$F = (C - 1) - P + 2 = C - P + 1 = 3 - P.$$

Therefore, no more than 3 phases can coexist at equilibrium in a binary system at fixed pressure. Like one-component (unary) diagrams, binary phase diagrams include regions, lines, and points but their interpretations are quite different. In particular, there are three distinct line types in two-component diagrams:

- (1) Vertical lines correspond to *stoichiometric (line) compounds*. These lines are projections of one-component p - T diagrams onto the fixed pressure of 1 atm.

⁵⁸ C.-P. Yap, "The Free Energy of Transition of Iron ($\alpha \rightleftharpoons \gamma$)", *Trans. Faraday Soc.* **1932**, 28, 781-788.

- (2) Horizontal lines indicate a fixed temperature and intersect 3 distinct phases. Therefore, $F = 0$. Two of these phases are at the limits of these lines.
- (3) Curved lines form boundaries between a single-phase region and a two-phase region.

The Mg-Sn diagram illustrates many important features of binary phase diagrams. The horizontal axis is the mole fraction (atomic percent) of Sn and the vertical axis is temperature. There is one compound Mg_2Sn identified by the vertical line at $x_{\text{Sn}} = 1/3$. Various slanted lines border the liquid region. There is also a small region at the left border for small values of x_{Sn} , and there are two horizontal lines where two curved lines converge on intermediate points.

$P = 1, F = 2$: The molar Gibbs free energy $g^{(\alpha)}(T, x_2)$ for a single stable phase α has the overall lowest value against all other possible phases or phase mixtures in the system. Temperature and mole fraction can be independently varied without changing the equilibrium state because there are no restraints on these intensive variables. Single phases with variable composition are either liquid or solid solutions and correspond to *regions* in the phase diagram. In the Mg-Sn diagram, the liquid solution $\text{Mg}_{1-x}\text{Sn}_x(l)$ extends over the entire composition range at high temperatures and there is a solid solution $\text{Mg}_{1-\delta}\text{Sn}_\delta(s)$ below the melting point of Mg.

Line compounds ($P = 1, F = 1$) are single phases with fixed composition, so $C = 1$ and T is the only degree of freedom. $\text{Mg}_2\text{Sn}(s)$ is represented by the vertical line below $T = 771^\circ\text{C}$.

$P = 2, F = 1$: Two coexisting phases α and β at equilibrium have different chemical compositions specified by $x_2^{(\alpha)}$ and $x_2^{(\beta)}$. Furthermore, the chemical potentials for each component in the two phases must be equal:

$$\mu_1^{(\alpha)}(T, x_2^{(\alpha)}) = \mu_1^{(\beta)}(T, x_2^{(\beta)}) \text{ and } \mu_2^{(\alpha)}(T, x_2^{(\alpha)}) = \mu_2^{(\beta)}(T, x_2^{(\beta)}),$$

which are two restraints on the three intensive variables $T, x_2^{(\alpha)}, x_2^{(\beta)}$. These conditions create *regions* with left and right boundaries at the different compositions. The slope $(dT/dx_2^{(\varphi)})$ of a specific boundary depends on the nature of the phase φ :

- If φ is a line compound, the boundary is vertical with infinite slope because $dx_2^{(\varphi)} = 0$.
- If φ is a solution, the boundary is slanted with a positive or negative slope.

Therefore, if the boundary phases α and β are both pure substances, then the mole fractions $x_2^{(\alpha)}$ and $x_2^{(\beta)}$ in each phase are fixed values and only temperature can be independently varied. This occurs between $\text{Mg}_2\text{Sn}(s)$ and $\text{Sn}(s)$ below 204°C .

On the other hand, if at least one of the boundary phases is a solution, say β , then either T or $x_2^{(\beta)}$ can be independently varied. The slope of this boundary is given by the *Gibbs-Konovalov equation*:^{59, 60}

$$\left(\frac{dT}{dx_2^{(\beta)}}\right)_p = \frac{-\left[\left(\frac{d\mu_1^{(\beta)}}{dx_1^{(\beta)}}\right)_{T,p} + \left(\frac{d\mu_2^{(\beta)}}{dx_2^{(\beta)}}\right)_{T,p}\right](x_2^{(\beta)} - x_2^{(\alpha)})}{(s^{(\beta)} - s^{(\alpha)}) + (s_2^{(\beta)} - s_1^{(\beta)})(x_2^{(\beta)} - x_2^{(\alpha)})}.$$

⁵⁹ H.F. Franzen, B.C. Gerstein, *A.I.Ch.E. Journal* **1966**, 12, 364-368.

⁶⁰ D. Goodman, J.W. Cahn, L.H. Bennett, *Bull. Alloy Phase Diag.* **1981**, 2, 29-34.

DERIVATION: The Gibbs-Duhem equation for each phase at fixed pressure gives

$$s^{(\alpha)}dT + x_1^{(\alpha)}d\mu_1^{(\alpha)} + x_2^{(\alpha)}d\mu_2^{(\alpha)} = s^{(\alpha)}dT + x_2^{(\alpha)}(d\mu_2^{(\alpha)} - d\mu_1^{(\alpha)}) + d\mu_1^{(\alpha)} = 0;$$

$$s^{(\beta)}dT + x_1^{(\beta)}d\mu_1^{(\beta)} + x_2^{(\beta)}d\mu_2^{(\beta)} = s^{(\beta)}dT + x_2^{(\beta)}(d\mu_2^{(\beta)} - d\mu_1^{(\beta)}) + d\mu_1^{(\beta)} = 0.$$

At equilibrium, $d\mu_1^{(\alpha)} = d\mu_1^{(\beta)} \equiv d\mu_1$ and $d\mu_2^{(\alpha)} = d\mu_2^{(\beta)} \equiv d\mu_2$, so take the difference between these two equations:

$$(s^{(\beta)} - s^{(\alpha)})dT + (x_2^{(\beta)} - x_2^{(\alpha)})(d\mu_2 - d\mu_1) = (\Delta s^{(\alpha\beta)})dT + (\Delta x_2^{(\alpha\beta)})(d\mu_2 - d\mu_1) = 0.$$

The differential of the chemical potential for each component in phase β can be related to temperature and mole fraction differentials as follows:

$$d\mu_1^{(\beta)} = -s_1^{(\beta)}dT + \left(\frac{\partial\mu_1^{(\beta)}}{\partial x_1^{(\beta)}}\right)_{T,p} dx_1^{(\beta)} \text{ and } d\mu_2^{(\beta)} = -s_2^{(\beta)}dT + \left(\frac{\partial\mu_2^{(\beta)}}{\partial x_2^{(\beta)}}\right)_{T,p} dx_2^{(\beta)}.$$

Then, substituting these expressions for $d\mu_1$ and $d\mu_2$ gives

$$\begin{aligned} d\mu_2 - d\mu_1 &= d\mu_2^{(\beta)} - d\mu_1^{(\beta)} = -\left(s_2^{(\beta)} - s_1^{(\beta)}\right)dT + \left(\frac{\partial\mu_2^{(\beta)}}{\partial x_2^{(\beta)}}\right)_{T,p} dx_2^{(\beta)} - \left(\frac{\partial\mu_1^{(\beta)}}{\partial x_1^{(\beta)}}\right)_{T,p} dx_1^{(\beta)} \\ &= \left(s_1^{(\beta)} - s_2^{(\beta)}\right)dT + \left[\left(\frac{\partial\mu_2^{(\beta)}}{\partial x_2^{(\beta)}}\right)_{T,p} + \left(\frac{\partial\mu_1^{(\beta)}}{\partial x_1^{(\beta)}}\right)_{T,p}\right] dx_2^{(\beta)} \end{aligned}$$

which replaces the chemical potential difference above:

$$(s^{(\beta)} - s^{(\alpha)})dT + (x_2^{(\beta)} - x_2^{(\alpha)})\left\{\left(s_1^{(\beta)} - s_2^{(\beta)}\right)dT + \left[\left(\frac{\partial\mu_2^{(\beta)}}{\partial x_2^{(\beta)}}\right)_{T,p} + \left(\frac{\partial\mu_1^{(\beta)}}{\partial x_1^{(\beta)}}\right)_{T,p}\right] dx_2^{(\beta)}\right\} = 0.$$

Combining terms and rearranging gives the Gibb-Konovalov equation stated above.

The chemical potential of component i in solution β is related the component's activity $a_i^{(\beta)}$ by

$$\mu_i^{(\beta)} = \mu_i^{\circ(\beta)} + RT \ln a_i^{(\beta)} = \mu_i^{\circ(\beta)} + RT \ln \gamma_i^{(\beta)} x_i^{(\beta)}.$$

$\gamma_i^{(\beta)}$ is the activity coefficient of component i in solution β . For real solutions, this coefficient depends on mole fraction. For ideal solutions, $\gamma_i^{(\beta)} = 1$ so that activity is the mole fraction. If the solution phase β is assumed to behave ideally over the entire composition range, then

$$\frac{d\mu_i^{(\beta)}}{dx_i^{(\beta)}} \sim \frac{RT}{x_i^{(\beta)}} \text{ and } \left(\frac{dT}{dx_2^{(\beta)}}\right)_p \sim \frac{-RT \Delta x_2^{(\alpha\beta)}}{[\Delta s^{(\alpha\beta)} + (s_2^{(\beta)} - s_1^{(\beta)}) \Delta x_2^{(\alpha\beta)}] x_1^{(\beta)} x_2^{(\beta)}}.$$

For many cases, the slope of the boundary depends on the sign relationship between the molar entropy and mole fraction differences between phases α and β : $\Delta s^{(\alpha\beta)} = s^{(\beta)} - s^{(\alpha)}$ and $\Delta x_2^{(\alpha\beta)} = x_2^{(\beta)} - x_2^{(\alpha)}$.

From the Mg-Sn diagram, the region bounded by $\text{Mg}_2\text{Sn}(s)$ on the left and the sloped line from ($T = 204^\circ$, $x_{\text{Sn}} = 0.78$) to ($T = 771^\circ$, $x_{\text{Sn}} = 0.33$) on the right is a two-phase region with one degree of freedom. Points "inside" the region correspond to the two boundary phases at the specific temperature; these two points are "connected" by a *conode* or *tie line*. For points in this region, the composition of $\text{Mg}_2\text{Sn}(s)$ is fixed ($x_{\text{Sn}}^{(\alpha)} = 1/3$), but either temperature or mole fraction of the liquid solution $x_{\text{Sn}}^{(\beta)}$ can be independently varied.

Line compounds ($P = 2$, $F = 0$) undergo phase transitions at specified temperatures at which the two phases coexist. These changes are either *polymorphic transitions* between two different solid-

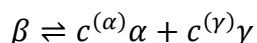
state structures or *melting/freezing*. For example, two phases coexist at 771°C, the melting point of Mg₂Sn: Mg₂Sn(s) ⇌ Mg₂Sn(l).

P = 3, F = 0: When three phases α , β , and γ coexist, the chemical potentials are related by:

$$\text{Component \#1: } \mu_1^{(\alpha)}(T, x_2^{(\alpha)}) = \mu_1^{(\beta)}(T, x_2^{(\beta)}) = \mu_1^{(\gamma)}(T, x_2^{(\gamma)}) \text{ and}$$

$$\text{Component \#2: } \mu_2^{(\alpha)}(T, x_2^{(\alpha)}) = \mu_2^{(\beta)}(T, x_2^{(\beta)}) = \mu_2^{(\gamma)}(T, x_2^{(\gamma)}).$$

With 4 restraints and 4 variables, temperature must also be fixed by this equilibrium. Therefore, three-phase equilibria are represented by *horizontal lines*. If the phases α and γ are, respectively, the left and right limits of a horizontal line and β falls between them in composition, then a chemical equilibrium can be written:



where $c^{(\alpha)}$ and $c^{(\gamma)}$ are numerical coefficients to create a balanced chemical equation. Such three-phase equilibria occur at 204° and 561°C in the Mg-Sn system. We will examine how to write the balanced chemical equations shortly.

(30) Free Energies: To understand the features of a two-component phase diagram, the general strategy is to plot the molar Gibbs free energies $g^{(\varphi)}(T_0, x_2)$ of each phase φ with respect to the mole fraction $x_2^{(\varphi)}$ for a specific temperature T_0 . Across the entire range $0 \leq x_2 \leq 1$, the lowest Gibbs free energies, which can occur for no more than three phases, are identified. This process is repeated for many different temperatures, and the phase diagram can be mapped out.

To construct these free energy plots, it is important to identify reference (standard) states and to understand the Gibbs free energies for pure compounds, solutions, and heterogeneous mixtures. Then, for a given temperature, *what are the conditions of the different free energies necessary for coexistence of two or three phases?* In other words, because the equilibrium state requires a minimum in the Gibbs free energy, *how do these minima emerge to allow multiple phases to be at equilibrium with each other?*

For this discussion, we limit the components to be elements designated **A** and **B**, but they can be pure compounds as well. Also, the reference states are the elements in their solid state, i.e., **A**(s) and **B**(s). Now, the phases formed by two components can be either pure solid compounds **A_mB_n**(s) or solutions **A_{1-x}B_x**(s) or **A_{1-x}B_x**(l). There are two different ways to express the molar Gibbs free energies with respect to the reference states for each type of phase:

$$\begin{aligned} \text{Compound } \mathbf{A}_m\mathbf{B}_n(s): \quad g^{(\varphi)}(T, x) &= g^{(\varphi)}\left(T, \frac{n}{m+n}\right) = \frac{1}{m+n} \Delta G_f^\circ(T) \\ &= \frac{m}{m+n} \mu_{\mathbf{A}}^{(\varphi)}(T) + \frac{n}{m+n} \mu_{\mathbf{B}}^{(\varphi)}(T) \end{aligned}$$

- $\Delta G_f^\circ(T)$ = Gibbs free energy of formation from $m \mathbf{A}(s) + n \mathbf{B}(s) \longrightarrow \mathbf{A}_m\mathbf{B}_n(s)$.
- $g^{(\varphi)}(T, x)$ is the Gibbs free energy per *one mole* of atoms.
- The second equation is the weighted average of the chemical potentials for each component.

$$\begin{aligned} \text{Solution } \mathbf{A}_{1-x}\mathbf{B}_x(s): \quad g^{(s)}(T, x) &= \Delta h_{\text{mix}}^{(s)}(T, x) - T\Delta s_{\text{mix}}^{(s)}(T, x) \\ &= (1-x)\mu_{\mathbf{A}}^{(s)}(T) + x\mu_{\mathbf{B}}^{(s)}(T) = \mu_{\mathbf{A}}^{(s)}(T) + \left(\mu_{\mathbf{B}}^{(s)}(T) - \mu_{\mathbf{A}}^{(s)}(T)\right)x \end{aligned}$$

$$\begin{aligned} \text{Solution } \mathbf{A}_{1-x}\mathbf{B}_x(l): \quad g^{(l)}(T, x) &= \Delta h_{\text{mix}}^{(l)}(T, x) - T\Delta s_{\text{mix}}^{(l)}(T, x) + (1-x)\Delta g_{\text{fus,A}}(T) + xg_{\text{fus,B}}(T) \\ &= (1-x)\mu_{\mathbf{A}}^{(l)}(T) + x\mu_{\mathbf{B}}^{(l)}(T) = \mu_{\mathbf{A}}^{(l)}(T) + \left(\mu_{\mathbf{B}}^{(l)}(T) - \mu_{\mathbf{A}}^{(l)}(T)\right)x \end{aligned}$$

- The Gibbs free energy of a solution involves both enthalpy and entropy of mixing.
- Because the reference states are chosen as solids, the molar Gibbs free energy of the liquid solution includes melting terms for the two components. In the limits of $x \rightarrow 0$ and $x \rightarrow 1$, the pure components converge to their liquid states, which are not the reference states.
- The second equation for each solution is the weighted average of the corresponding chemical potentials for each component in the solution. These equations are linear in the mole fraction $x^{(\varphi)}$ and the coefficient is the slope of the line.

For plots of the molar Gibbs free energies of the Mg-Sn system, Mg(s) and Sn(s) serve as the reference states. Throughout the entire diagram, there are three distinct phases: (i) the line compound Mg₂Sn(s); the solid solution Mg_{1-δ}Sn_δ(s) close to 561°C; and (iii) the liquid solution Mg_{1-x}Sn_x(l). The standard Gibbs free energy of Mg₂Sn(s) is

$$\Delta G_f^\circ(T) \sim -72,900 + 14.24 T \text{ (J/mol)}.$$

Since the liquid solution can exist over the entire range of $0 \leq x_{\text{Sn}} \leq 1$, the enthalpy of mixing is exothermic while the entropy of mixing arises mostly from configurational entropy. On the other hand, since the solid solution has a limited range of x_{Sn} , the enthalpy of mixing is endothermic. Now, let's examine three different temperature values in the $g^{(\varphi)}(T, x_{\text{Sn}})$ diagram and analyze the free energy curves, which are illustrated *qualitatively*:

$T = 150^\circ\text{C}$: The only stable phases are the pure elements Mg(s) and Sn(s) and the compound Mg₂Sn(s). We ignore the solid solution at this temperature because the mole fraction of Sn is negligibly small. The molar Gibbs free energies of the solids are

$$g^{(s)}(150^\circ\text{C}, x_{\text{Sn}} = 0) = 0 \text{ J/mol};$$

$$g^{(s)}(150^\circ\text{C}, x_{\text{Sn}} = 0.33) = \frac{1}{3}(-66,900 \text{ J/mol}) = -22,300 \text{ J/mol};$$

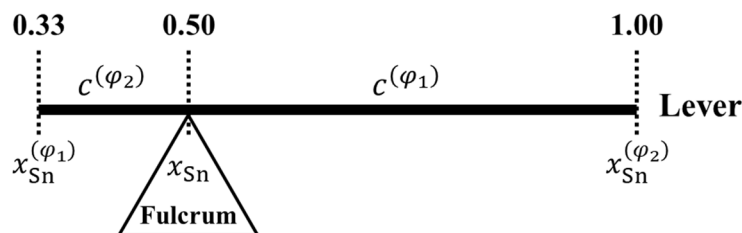
$$g^{(s)}(150^\circ\text{C}, x_{\text{Sn}} = 1) = 0 \text{ J/mol}.$$

These points are connected by the dotted line $g^{(s)}(T, x_{\text{Sn}})$. The molar Gibbs free energy of the liquid solution $g^{(l)}(T, x_{\text{Sn}})$ lies completely above $g^{(s)}(T, x_{\text{Sn}})$ because 150°C is below the melting points of Mg and Sn. Therefore, Mg(s) and Mg₂Sn(s) coexist for $0 < x_{\text{Sn}} < 0.33$, and Mg₂Sn(s) and Sn(s) coexist for $0.33 < x_{\text{Sn}} < 1$.

Phase Composition: The composition of a heterogeneous mixture for a specified overall mole fraction of Sn is provided by the *lever rule*. Consider $x_{\text{Sn}} = 0.50$. This composition point serves as a fulcrum for a lever bounded by $x_{\text{Sn}} = 0.33$ for Mg₂Sn(s) = Mg_{0.67}Sn_{0.33}(s) and $x_{\text{Sn}} = 1$ for Sn(s). The corresponding amounts of each phase are determined by the ratios:

$$c^{(\text{Mg}_{0.67}\text{Sn}_{0.33},s)} = \frac{1.00-0.50}{1.00-0.33} = 0.75; \quad c^{(\text{Sn},s)} = \frac{0.50-0.33}{1.00-0.33} = 0.25.$$

The denominators are the mole fraction differences between the phase boundaries $\varphi_1 = \text{Mg}_{0.67}\text{Sn}_{0.33}(s)$ and $\varphi_2 = \text{Sn}(s)$. The numerator for $c^{(\varphi_1)}$ is the mole fraction difference between $x_{\text{Sn}}^{(\varphi_2)}$ and the specified value x_{Sn} ; the numerator for $c^{(\varphi_2)}$ is the mole fraction difference between the specified value x_{Sn} and $x_{\text{Sn}}^{(\varphi_1)}$. The following sketch illustrates how the lever rule works:

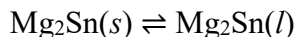


This calculation is carried out for Mg_2Sn specified as $\text{Mg}_{0.67}\text{Sn}_{0.33}$, i.e., for 1 mole total atoms. Using the usual chemical formulations,

$$c^{(\text{Mg}_2\text{Sn})} = \frac{1}{3}c^{(\text{Mg}_{0.67}\text{Sn}_{0.33})} = 0.25.$$

Therefore, the equilibrium phases of a 50:50 molar mixture of Mg:Sn at 150°C are an equal molar mixture of the phases $\text{Mg}_2\text{Sn}(s)$ and $\text{Sn}(s)$.

$T = 771^\circ\text{C}$: This temperature is the melting point of $\text{Mg}_2\text{Sn}(s)$ and exceeds the melting points of Mg and Sn. Liquids exist for x_{Sn} lower and higher than 0.33, while the two-phase equilibrium,



occurs for $x_{\text{Sn}} = 0.33$, so that the only solid at this temperature is $\text{Mg}_2\text{Sn}(s)$. The solid phase molar Gibbs free energy curve is a dotted line connecting the reference states with $g^{(s)}(771^\circ\text{C}, x_{\text{Sn}} = 0.33) = -19,340 \text{ J/mol}$. The liquid phase curve $g^{(l)}(771^\circ\text{C}, x_{\text{Sn}})$ lies below $g^{(s)}(771^\circ\text{C}, x_{\text{Sn}})$ except for $x_{\text{Sn}} = 0.33$, where they intersect:

$$g^{(s)}(771^\circ\text{C}, x_{\text{Sn}} = 0.33) = g^{(l)}(771^\circ\text{C}, x_{\text{Sn}} = 0.33).$$

$T = 350^\circ\text{C}$: This temperature is below the melting point of Mg but above the melting point of Sn. The stable phases are $\text{Mg}(s)$ (ignoring any dissolved Sn), $\text{Mg}_2\text{Sn}(s)$, and $\text{Mg}_{1-x}\text{Sn}_x(l)$ for $0.78 \leq x_{\text{Sn}} \leq 1$. Therefore, $g^{(s)}(350^\circ\text{C}, x_{\text{Sn}})$ is the dotted line connecting the two reference states with $g^{(s)}(350^\circ\text{C}, x_{\text{Sn}} = 0.33) = -21,340 \text{ J/mol}$. On the other hand, $g^{(l)}(350^\circ\text{C}, x_{\text{Sn}})$ is above $g^{(s)}$ at lower values of x_{Sn} and is below $g^{(s)}$ at higher values of x_{Sn} with the crossing point falling in the range $0.33 < x_{\text{Sn}} < 0.78$. Then, for mole fractions $0 < x_{\text{Sn}} < 0.33$, $\text{Mg}(s)$ and $\text{Mg}_2\text{Sn}(s)$ are the two equilibrium phases. For $0.33 < x_{\text{Sn}} < 0.78$, the straight line connecting the molar Gibbs free energies for $\text{Mg}_2\text{Sn}(s)$ and $\text{Mg}_{0.22}\text{Sn}_{0.78}(l)$ falls below both free energy curves. Therefore, a mixture of the two border phases has an overall lower Gibbs free energy than either phase. This straight line corresponds to the tangent of the continuous curve $g^{(l)}(350^\circ\text{C}, x_{\text{Sn}})$ at $x_{\text{Sn}} = 0.78$, and this construction is called the *common tangent rule*, although $g^{(s)}(T, x_{\text{Sn}})$ strictly does not have a defined slope at $x_{\text{Sn}} = 0.33$. The common tangent is a straight line that can be expressed as

$$\text{Tangent of } g^{(s)}(T, x_{\text{Sn}} = 0.33) = \text{Tangent of } g^{(l)}(T, x_{\text{Sn}} = 0.78):$$

$$\mu_{\text{Mg}}^{(s)}(T) + \left(\mu_{\text{Sn}}^{(s)}(T) - \mu_{\text{Mg}}^{(s)}(T) \right) x_{\text{Sn}} = \mu_{\text{Mg}}^{(l)}(T) + \left(\mu_{\text{Sn}}^{(l)}(T) - \mu_{\text{Mg}}^{(l)}(T) \right) x_{\text{Sn}}.$$

As a result, the coexistence of the solid and liquid phases gives rise to the restraints for the chemical potentials of each component:

$$\mu_{\text{Mg}}^{(s)}(T) = \mu_{\text{Mg}}^{(l)}(T) \equiv \mu_{\text{Mg}}(T) \text{ and } \mu_{\text{Sn}}^{(s)}(T) = \mu_{\text{Sn}}^{(l)}(T) \equiv \mu_{\text{Sn}}(T).$$

Lastly, $g^{(l)}(771^\circ\text{C}, x_{\text{Sn}})$ for $0.78 < x_{\text{Sn}} \leq 1$ is the overall minimum and the liquid solution $\text{Mg}_{1-x}\text{Sn}_x(l)$ is the only stable phase for this region.

We can apply the *lever rule* to determine the phase composition for any point on the tie line in the two-phase region. For example, consider again a 50:50 molar mixture of Mg:Sn. Then the phase composition is

$$c^{(\text{Mg}_2\text{Sn},s)} = \frac{1}{3}c^{(\text{Mg}_{0.67}\text{Sn}_{0.33})} = \frac{1}{3}\left(\frac{0.78-0.50}{0.78-0.33}\right) = \frac{1}{3}(0.622) = 0.207$$

$$c^{(l)} = \frac{0.50-0.33}{0.78-0.33} = 0.378.$$

Therefore, an equimolar mixture of Mg and Sn at 350°C exists as 35.4 mole percent $\text{Mg}_2\text{Sn}(s)$ and 64.6 mole percent $\text{Mg}_{0.22}\text{Sn}_{0.78}(l)$ because

$$35.4 \text{ mole percent} = \frac{0.207}{0.207+0.378} \times 100\% \quad \text{and} \quad 64.6 \text{ mole percent} = \frac{0.378}{0.207+0.378} \times 100\%.$$

(31) A three-phase equilibrium occurs at...

$T = 561^\circ\text{C}$: Let's start for compositions $0.33 \leq x_{\text{Sn}} \leq 1$, where there is a two-phase region $0.33 < x_{\text{Sn}} < 0.58$ and a single-phase liquid solution for $0.58 \leq x_{\text{Sn}} \leq 1$. At this temperature, Mg exists as a solid; Sn as a liquid. Therefore, $g^{(l)}(561^\circ\text{C}, x_{\text{Sn}})$ crosses $g^{(s)}(561^\circ\text{C}, x_{\text{Sn}})$ for the pure solids at some point $0.33 < x_{\text{Sn}} < 0.58$. A common tangent occurs through the two points $g^{(l)}(561^\circ\text{C}, x_{\text{Sn}} = 0.58)$ and $g^{(s)}(561^\circ\text{C}, x_{\text{Sn}} = 0.33)$, which explains the two-phase region. For x_{Sn} below 0.33, there is a three-phase equilibrium consisting of the line compound $\text{Mg}_2\text{Sn}(s)$, the liquid solution $\text{Mg}_{0.89}\text{Sn}_{0.11}(l)$, and the solid solution $\text{Mg}_{0.97}\text{Sn}_{0.03}(s)$. For these three phases to coexist at equilibrium, there must be a *common tangent* line for the three molar Gibbs free energy curves. On the scale of this diagram, this effect is difficult to see, so let's magnify these curves...

(32) The liquid solution curve $g^{(l)}(561^\circ\text{C}, x_{\text{Sn}})$ is above 0 for $x_{\text{Sn}} = 0$ because $\text{Mg}(s)$ is the stable state. However, the curve drops below $g^{(s)}(561^\circ\text{C}, x_{\text{Sn}})$ for the pure solids, which is the dotted line connecting $g^{(s)}(561^\circ\text{C}, x_{\text{Sn}} = 0) = 0$ with $g^{(s)}(561^\circ\text{C}, x_{\text{Sn}} = 0.33) = -21,640 \text{ J/mol}$. To ensure that $\text{Mg}_2\text{Sn}(s)$ is an equilibrium phase at this temperature, $g^{(l)}(561^\circ\text{C}, x_{\text{Sn}})$ must intersect $g^{(s)}(561^\circ\text{C}, x_{\text{Sn}})$ again and rise above it. Lastly, the solid solution curve $g^{(ss)}(561^\circ\text{C}, x_{\text{Sn}})$ drops rapidly from 0 and then quickly rises above all other molar Gibbs free energy curves. This behavior of the Gibbs free energy of the solid solution suggests that entropy and not enthalpy drives the dissolution of Sn into $\text{Mg}(s)$. For this three-phase equilibrium, the common tangent rule is

$$\text{Tangent of } g^{(ss)}(561^\circ\text{C}, x_{\text{Sn}} = 0.03) = \text{Tangent of } g^{(l)}(561^\circ\text{C}, x_{\text{Sn}} = 0.11) = \text{Tangent of } g^{(s)}(561^\circ\text{C}, x_{\text{Sn}} = 0.33):$$

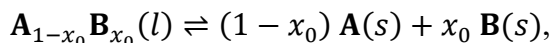
$$\mu_{\text{Mg}}^{(s)}(T) + \left(\mu_{\text{Sn}}^{(s)}(T) - \mu_{\text{Mg}}^{(s)}(T)\right)x_{\text{Sn}} = \mu_{\text{Mg}}^{(l)}(T) + \left(\mu_{\text{Sn}}^{(l)}(T) - \mu_{\text{Mg}}^{(l)}(T)\right)x_{\text{Sn}} = \mu_{\text{Mg}}^{(ss)}(T) + \left(\mu_{\text{Sn}}^{(ss)}(T) - \mu_{\text{Mg}}^{(ss)}(T)\right)x_{\text{Sn}}$$

These relationships establish the four restraints that are responsible for three-phase equilibria having 0 degrees of freedom:

$$\mu_{\text{Mg}}^{(s)}(T) = \mu_{\text{Mg}}^{(l)}(T) = \mu_{\text{Mg}}^{(ss)}(T) \equiv \mu_{\text{Mg}}(T)$$

$$\mu_{\text{Sn}}^{(s)}(T) = \mu_{\text{Sn}}^{(l)}(T) = \mu_{\text{Sn}}^{(ss)}(T) \equiv \mu_{\text{Sn}}(T).$$

(33) *Eutectics*: In a two-component **A-B** system, a *eutectic* is a mixture at some fixed composition that melts at a temperature below the melting points for each pure component. A simple example where a eutectic occurs is if **A** and **B** form a *homogeneous mixture* in the liquid state and a *heterogeneous mixture* in the solid state for all mole fractions x_{B} . For this case, the eutectic is a liquid solution in equilibrium with the two pure phases:



which is a three-phase equilibrium at a specific temperature T_0 . In the phase diagram for this system, the horizontal line connecting these three phases at T_0 is called the *solidus line* because all stable phases below this line are solids. The melting points of each pure component are connected to the eutectic point at T_0, x_0 forming two connected curves called the *liquidus line* because the stable phase above this curve is liquid. The solidus and liquidus curves divide the T - x_B diagram into 4 regions and the presence of the 3-phase eutectic equilibrium naturally arises from the molar Gibbs free energy curves for the homogeneous liquid solution and the heterogeneous solid mixture.

For the following discussion, $\mathbf{A}(s)$ and $\mathbf{B}(s)$ are chosen to be the reference states, so $g_{\mathbf{A}}^{(s)} = 0$, $g_{\mathbf{B}}^{(s)} = 0$, and the line connecting them is $g^{(s)}(T, x_B) = 0$ for the entire heterogeneous mixture. The homogeneous liquid solution $\mathbf{A}_{1-x}\mathbf{B}_x(l)$ is stable relative to the corresponding mixture of the pure liquids $(1-x)\mathbf{A}(l) + x\mathbf{B}(l)$ so that the $g^{(l)}(T, x_B)$ curve is U-shaped between the two pure liquid components. Then, the important parts of this phase diagram are:

- a one-phase $\mathbf{A}_{1-x}\mathbf{B}_x(l)$ liquid region ($P = 1, F = 2$) above the liquidus curve. Temperature and mole fraction can be independently varied in this region. For temperatures above the higher melting component \mathbf{B} , $g^{(l)}(T, x) < g^{(s)}(T, x)$ for all mole fractions.
- a two-phase $\mathbf{A}(s) + \mathbf{B}(s)$ solid region ($P = 2, F = 1$) below the solidus curve. Variation in temperature is the only degree of freedom. For temperatures below the lower melting component \mathbf{A} , $g^{(l)}(T, x_B) > g^{(s)}(T, x_B)$ for all mole fractions.
- a two-phase $\mathbf{A}(s) + \mathbf{A}_{1-x}\mathbf{B}_x(l)$ mixed region ($P = 2, F = 1$) above the solidus curve and below the liquidus curve for compositions $0 < x < x_0$.
- a two-phase $\mathbf{B}(s) + \mathbf{A}_{1-x}\mathbf{B}_x(l)$ mixed region ($P = 2, F = 1$) above the solidus curve and below the liquidus curve for compositions $x_0 < x < 1$.

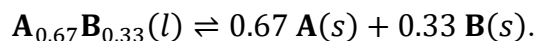
For a temperature T' above the melting point of the lower melting \mathbf{A} and below the melting point of the higher melting \mathbf{B} , the stable phases are liquid $\mathbf{A}_{1-x}\mathbf{B}_x(l)$ for compositions left of the liquidus line ($0 < x \leq x'$) and a mixture of $\mathbf{B}(s)$ and $\mathbf{A}_{1-x'}\mathbf{B}_{x'}(l)$ for $x' < x < 1$. The $g^{(l)}(T', x)$ curve for $\mathbf{A}_{1-x}\mathbf{B}_x(l)$ is below $g^{(s)}(T', 0)$ for $\mathbf{A}(s)$ and is above $g^{(s)}(T', 1)$ for $\mathbf{B}(s)$, so that $g^{(l)}(T', x)$ crosses $g^{(s)}(T', x) = 0$ once. The tangent of the $g^{(l)}(T', x)$ curve at x' intersects $g^{(s)}(T, 1)$, which explains the occurrence of two phases.

For a temperature T'' above the solidus line and below the melting point of the lower melting \mathbf{A} , there are 3 stability regions. The $g^{(l)}(T'', x)$ curve is above both $g^{(s)}(T', 0)$ for $\mathbf{A}(s)$ and $g^{(s)}(T', 1)$ for $\mathbf{B}(s)$. Therefore, $g^{(l)}(T'', x)$ crosses $g^{(s)}(T'', x) = 0$ twice and there are two “common tangents”, one intersecting $g^{(s)}(T, 0)$ and the other intersecting $g^{(s)}(T, 1)$.

- a three-phase eutectic equilibrium at T_0 among the liquid $\mathbf{A}_{1-x_0}\mathbf{B}_{x_0}(l)$, $\mathbf{A}(s)$, and $\mathbf{B}(s)$. For this unique situation, $g^{(l)}(T_0, x)$ just touches $g^{(s)}(T_0, x) = 0$ at the eutectic composition x_0 to rationalize the coexistence of three distinct phases. In the diagram, the eutectic composition is $x_0 = 0.33$. The relative amounts of $\mathbf{A}(s)$ and $\mathbf{B}(s)$ in the eutectic equilibrium are given by the lever rule:

$$c_{\mathbf{A}}^{(s)} = \frac{1.00-0.33}{1.00-0.00} = 0.67, \quad c_{\mathbf{B}}^{(s)} = \frac{0.33-0.00}{1.00-0.00} = 0.33,$$

so that the eutectic equilibrium is:



Mixtures of **A** and **B** near 33 mole percent **B** have a melting point that is lower than the melting points of pure **A** and pure **B**. In fact, this outcome will be observed on freezing rather than on melting because the solids do not form a homogeneous mixture.

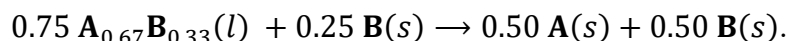
In two-component phase diagrams, eutectic points occur on cooling for four different cases. For the following examples, the composition of the β phase is between that of phases α and γ :

- (1) $\beta(l) \rightleftharpoons \alpha(s) + \gamma(s)$: a liquid phase disproportionates into two solid phases, called a *eutectic* decomposition. This equilibrium occurs for many alloy systems and salt mixtures. An example is in the Cd-Bi system at 146°C: $\text{Cd}_{0.55}\text{Bi}_{0.45}(l) \rightleftharpoons 0.55 \text{Cd}(s) + 0.45 \text{Bi}(s)$.
- (2) $\beta(l) \rightleftharpoons \alpha(l) + \gamma(s)$ or $\beta(l) \rightleftharpoons \alpha(s) + \gamma(l)$: a liquid phase disproportionates into a liquid and a solid phase, called a *monotectic* decomposition. An example of this equilibrium occurs in the Cu-Pb system at 955°C: $\text{Cu}_{0.84}\text{Pb}_{0.16}(l) \rightleftharpoons 0.75 \text{Cu}(s) + 0.25 \text{Cu}_{0.35}\text{Pb}_{0.65}(l)$.
- (3) $\beta(s) \rightleftharpoons \alpha(s) + \gamma(s)$: a solid phase disproportionates into two solid phases, called a *eutectoid* decomposition such as the austenite (Fe with 0.8 weight percent C) to ferrite (Fe) and cementite (Fe_3C) at 723°C.
- (4) $\beta(s) \rightleftharpoons \alpha(l) + \gamma(s)$ or $\beta(s) \rightleftharpoons \alpha(s) + \gamma(l)$: a solid phase disproportionates into a liquid and a solid phase, called a *catatectic* decomposition. The Cu-Sn diagram contains an example at 640°C: $\text{Cu}_{0.72}\text{Sn}_{0.28}(s) \rightleftharpoons 0.88 \text{Cu}_{0.74}\text{Sn}_{0.26}(s) + 0.12 \text{Cu}_{0.57}\text{Sn}_{0.43}(l)$.

(34) To understand the information in this phase diagram, heat a 50% **A**:50% **B** molar mixture, i.e., $x_{\text{B}} = 0.50$, above the melting point of the higher melting component **B** into the *liquid* region. At equilibrium, this process creates one liquid phase $\text{A}_{0.50}\text{B}_{0.50}(l)$. On cooling while maintaining equilibrium, $\text{B}(s)$ begins to precipitate when the temperature reaches the liquidus curve at T_1 . On further slow cooling of the mixture, $\text{B}(s)$ continues to solidify while the liquid phase composition follows the liquidus curve, becoming richer in **A** until the *eutectic temperature* T_0 is reached. If this process occurs sufficiently slowly, then large crystals of $\text{B}(s)$ will grow in the liquid. At the eutectic temperature, $\text{A}(s)$ begins to form. Just before this happens, the phase composition of the mixture of $\text{A}_{0.67}\text{B}_{0.33}(l)$ and $\text{B}(s)$ is determined by the lever rule:

$$c^{(l)} = \frac{0.50 - 0.33}{1.00 - 0.33} = 0.25, \quad c^{(s)} = \frac{1.00 - 0.50}{1.00 - 0.33} = 0.75.$$

Just below the eutectic temperature, the process that occurs is:



Further cooling of the system does not change phase composition of the mixture $\text{A}(s)$ and $\text{B}(s)$.

If a 67% **A**:33% **B** molar mixture is heated above $T_f(\text{B})$ and is then allowed to cool slowly, the mixture will remain liquid until the eutectic point is reached. Then, $\text{A}(s)$ and $\text{B}(s)$ will co-precipitate and be in equilibrium with $\text{A}_{0.67}\text{B}_{0.33}(l)$. As long as thermodynamic equilibrium is maintained, no two-phase solid-liquid mixture will occur at this composition.

(35) PRACTICE QUESTIONS: The Cd-Bi system shows general features of this simple eutectic. According to the diagram,

(a) Identify the phases existing in regions **1**, **2**, and **3**.

- 1:** two-phase region Bi(*s*) and Bi_{1-x}Cd_x(*l*) for 0 < *x* < 0.55.
2: two-phase region Bi(*s*) and Cd(*s*) for 0 < *x* < 1.
3: two-phase region Cd(*s*) and Bi_{1-x}Cd_x(*l*) for 0.55 < *x* < 1.

(b) What is the equilibrium at 146°C?

The eutectic temperature which occurs at the composition $x_{\text{Cd}} = 0.55$. The three-phase equilibrium relates the liquid at intermediate composition with the two end phases:

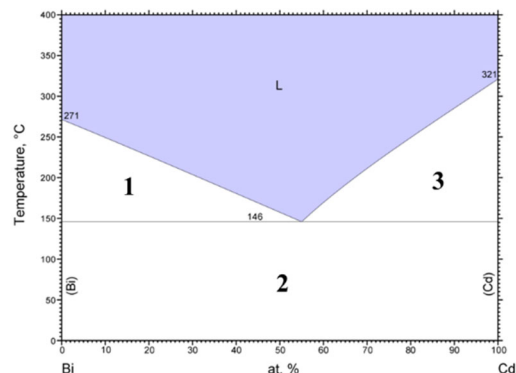


(c) What phases exist at 20 atomic percent Cd and 200°C?

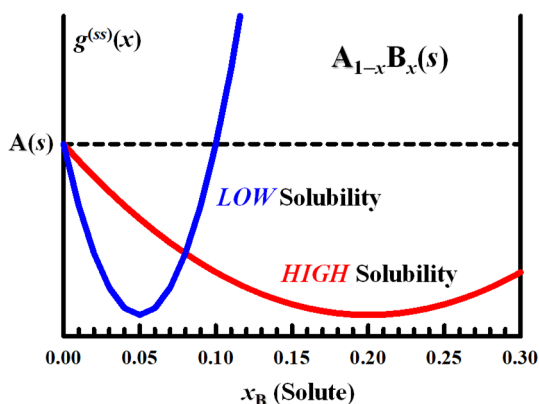
This point falls in the two-phase region **1**. The tie-line connects Bi(*s*) and Bi_{0.68}Cd_{0.32}(*l*)

(d) What phases exist at 10 atomic percent Bi and 250°C?

10 atomic percent Bi = 90 atomic percent Cd. Therefore, this point falls in the two-phase region **2**. The tie-line connects Cd(*s*) and Bi_{0.20}Cd_{0.80}(*l*)



(36) *Solid solutions* are an important part of solid-state chemistry because every solid-state compound shows some phase width. When this width is immeasurably small, the material is called a *line compound*. The accompanying diagram illustrates qualitatively how the molar Gibbs free energy of a solid solution $\text{A}_{1-x}\text{B}_x(s)$ varies with mole fraction of the solute component **B**. For these figures, **A**(*s*) is the solvent component and **B**(*s*) is the solute. If the solubility is high, then the Gibbs free energy remains less than the free energy of the pure mixed solids for larger values of x_{B} . Low solubility has a much narrower Gibbs free energy curve with composition.



For any solution, the Gibbs free energy has contributions from the enthalpy and entropy of mixing. Since the entropy of mixing is always favorable relative to that of the separate components, variations in solid solubility arise primarily from differences in enthalpies of mixing.

A solid solution can be *substitutional*, in which an element replaces another element such as Zn atoms replacing some Cu atoms in fcc Cu to give α -brass, or *interstitial*, in which a small atom occupies voids in the packing arrangement of another larger element such as C atoms occupying tetrahedral or octahedral voids in bcc Fe to give steel. In both cases, the lattice constants of the majority component (solvent) changes, but the overall structure remains unchanged. Hume-Rothery proposed the following rules for substitutional solid solutions:⁶¹ atoms forming the solution have similar metallic radii within 15% of each other, adopt the same or very similar crystal

⁶¹ See A. Martin, M. Thuo, *Acc. Mater. Res.* **2023**, *4*, 809-813.

structures, and have similar electronegativities. In addition, the solute atoms of the solution (minority component) have a higher valence than the solvent atoms (majority component)

A phase diagram shows a solid solution as a one-phase region with composition varying with temperature. The phase for **B** dissolved in **A**(s) is denoted as “**A(ss)**” and the maximum solubility of **B** in **A(ss)** occurs at T_0 and 23 mole percent **B**, $\mathbf{A}_{0.77}\mathbf{B}_{0.23}(ss)$. Also, the phase for **A** dissolved in **B**(s) is denoted as “**B(ss)**”, and its maximum solubility also occurs at T_0 but 16 mole percent **A** (84 mole percent **B**), $\mathbf{A}_{0.16}\mathbf{B}_{0.84}(ss)$. Both solid solution regions are bivariant, i.e., with $P = 1$, $F = 2$, allowing independent variation of temperature and composition. The phase diagram also shows a eutectic point at temperature T_0 and $x_B = 0.63$. On cooling the eutectic composition from the liquid phase, the following three-phase equilibrium occurs at T_0 :



in which the stoichiometric coefficients are determined by the lever rule.

(37) PRACTICE PROBLEM: The Pb-Sn system has a eutectic that also involves substitutional solid solutions. According to the phase diagram

(a) What is the maximum solubility of Sn in Pb(s)?

At 183°C, the composition of Pb(ss) is 29.5 atomic percent Sn, i.e., $x_{\text{Sn}} = 0.295$.

(b) What is the maximum solubility of Pb in Sn(s)?

At 183°C, the composition of Sn(ss) is 97 atomic percent Sn, i.e., $x_{\text{Sn}} = 0.97$ so that $x_{\text{Pb}} = 0.03$.

(c) What is the chemical equilibrium at 183°C?

This temperature is the eutectic temperature where the liquid solution with $x_{\text{Sn}} = 0.75$ is in equilibrium with the solid solutions Pb(ss) and Sn(ss) where maximum solubilities occur. The equilibrium is

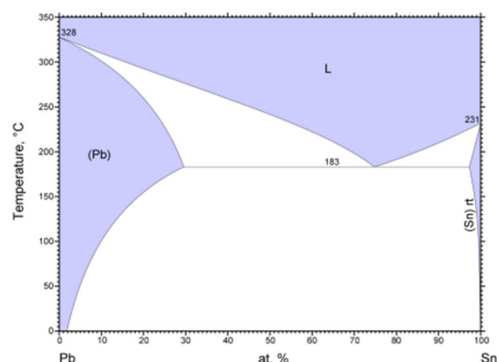


The stoichiometric coefficients are determined by the lever rule:

$$c^{(\text{Pb},ss)} = \frac{0.97-0.75}{0.97-0.295} = 0.326 \quad c^{(\text{Sn},ss)} = \frac{0.75-0.295}{0.97-0.295} = 0.674.$$

(38) Solutions – Regular Solution Model: Solutions play a very important role in multi-component phase diagrams. As mentioned above, the molar Gibbs free energy of any solution involves both an enthalpy and an entropy of mixing. To understand the features of binary phase diagrams, the molar Gibbs free energies of different phases must be evaluated and compared to assess whether one, two, or three different phases can coexist. An important model to analyze mixtures of two components is the *regular solution model*. In the simplest application, only solid and liquid solutions exist for a two-component **A-B** system. Then, the **A-B** phase diagram is constructed by comparing the molar Gibbs free energy curves for the solid solution $\mathbf{A}_{1-x}\mathbf{B}_x(s)$ and liquid solution $\mathbf{A}_{1-x}\mathbf{B}_x(l)$, i.e., $g^{(s)}(T, x)$ and $g^{(l)}(T, x)$, at various temperatures. If the two solid-state components **A**(s) and **B**(s) are the reference states, then $g^{(s)}(T, x)$ of the solid solution is just the free energy of mixing $g_{\text{mix}}^{(s)}(T, x)$, whereas $g^{(l)}(T, x)$ of the liquid solution includes the free energy of mixing $g_{\text{mix}}^{(l)}(T, x)$ and a melting term $g_{\text{fus}}(T, x)$.

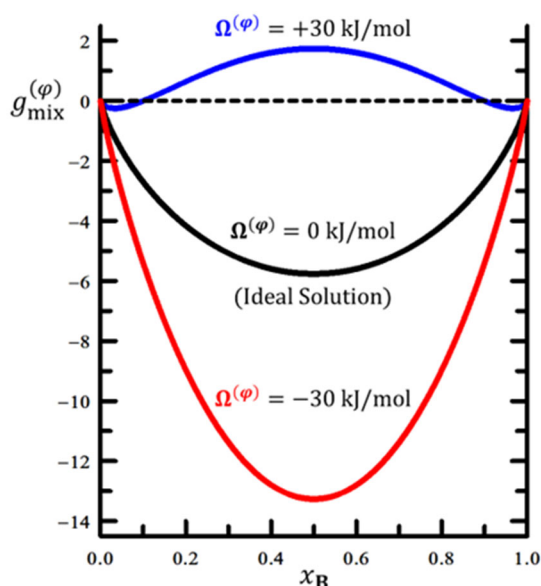
The molar Gibbs free energy of mixing for a *regular solution* $\mathbf{A}_{1-x}\mathbf{B}_x(\varphi)$ includes an enthalpy and entropy of mixing that depends only on concentration:



$$h_{\text{mix}}^{(\varphi)} = \Omega^{(\varphi)} x_{\text{A}} x_{\text{B}} = \Omega^{(\varphi)} x(1-x),$$

$$s_{\text{mix}}^{(\varphi)} = -R[x_{\text{A}} \ln x_{\text{A}} + x_{\text{B}} \ln x_{\text{B}}] = -R[(1-x) \ln(1-x) + x \ln x].$$

The entropy of mixing is entirely configurational entropy and corresponds to the entropy of mixing for an *ideal solution*. In the enthalpy of mixing expression, $\Omega^{(\varphi)}$ is an adjustable parameter that reflects the relative heteroatomic interactions vs. homoatomic interactions. If $\Omega^{(\varphi)} = 0$, the regular solution is an ideal solution. If $\Omega^{(\varphi)} < 0$, then heteroatomic **A–B** interactions are more favorable than homoatomic **A–A** and **B–B** interactions and mixing of **A** and **B** in the solution is effective. However, if $|\Omega^{(\varphi)}|$ is very large, then compound formation may occur rather than solution behavior. If $\Omega^{(\varphi)} > 0$, then homoatomic **A–A** and **B–B** interactions are more favorable than heteroatomic **A–B** interactions and each component has limited solubility in the other. Furthermore, if $|\Omega^{(\varphi)}|$ is very large, then phase segregation into **A**(φ) and **B**(φ) will occur. The molar Gibbs free energy of mixing curves $g_{\text{mix}}^{(\varphi)}(T, x) = h_{\text{mix}}^{(\varphi)} - T s_{\text{mix}}^{(\varphi)}$ for three different values of $\Omega^{(\varphi)}$ at $T = 1000$ K are shown here:



$\Omega^{(\varphi)} = +30$ kJ/mol: A repulsive interaction parameter between **A** and **B**. Therefore, component **A** tends to be surrounded by **A**, and **B** by **B**. $g_{\text{mix}}^{(\varphi)}(x) < 0$ for small and large x and reaches a maximum value for $x = 0.5$.

$\Omega^{(\varphi)} = 0$ kJ/mol: Mixing is completely random so that **A** and **B** do not exhibit any electronic or chemical differences in the solution. $g_{\text{mix}}^{(\varphi)}(x)$ is determined entirely by the configurational entropy of mixing.

$\Omega^{(\varphi)} = -30$ kJ/mol: An attractive interaction parameter between **A** and **B**. Therefore, component **A** tends to be surrounded by **B**, and **B** by **A**. $g_{\text{mix}}^{(\varphi)}(x)$ is more deeply curved than $g_{\text{mix}}^{(\varphi)}(x)$ for an ideal solution near $x = 0.5$ because the probability of heteroatomic contacts is greater with this interaction parameter.

Finally, we must include the molar Gibbs free energy of fusion for the liquid solution $\mathbf{A}_{1-x}\mathbf{B}_x(l)$, which is approximated as the weighted average of the two component terms.

$$g_{\text{fus}}(T, x) = (1-x)g_{\text{fus}}(\mathbf{A}) + xg_{\text{fus}}(\mathbf{B}).$$

A further simplification is to treat the enthalpy and entropy of fusion of each component as constants. Then, for any component **X**

$$g_{\text{fus}}(\mathbf{X}) = h_{\text{fus}}(\mathbf{X}) - T s_{\text{fus}}(\mathbf{X}) = T_f(\mathbf{X}) s_{\text{fus}}(\mathbf{X}) - T s_{\text{fus}}(\mathbf{X}) = (T_f(\mathbf{X}) - T) s_{\text{fus}}(\mathbf{X}).$$

Combining these two equations gives the *melting term* for the molar Gibbs free energy of the liquid solution:

$$g_{\text{fus}}(T, x) = (1-x)(T_f(\mathbf{A}) - T) s_{\text{fus}}(\mathbf{A}) + x(T_f(\mathbf{B}) - T) s_{\text{fus}}(\mathbf{B}).$$

According to this analysis, the expressions for the molar Gibbs free energies of the solid and liquid solutions $\mathbf{A}_{1-x}\mathbf{B}_x(\varphi)$ in the regular solution model are:

$$\begin{aligned} \text{Solid (s): } g^{(s)}(T, x) &= g_{\text{mix}}^{(s)}(T, x) \\ &= RT[x \ln x + (1 - x) \ln(1 - x)] + \Omega^{(s)}x(1 - x) \end{aligned}$$

$$\begin{aligned} \text{Liquid (l): } g^{(l)}(T, x) &= g_{\text{mix}}^{(l)}(T, x) + g_{\text{fus}}(T, x) \\ &= RT[x \ln x + (1 - x) \ln(1 - x)] + \Omega^{(l)}x(1 - x) \\ &\quad + (1 - x)(T_f(\mathbf{A}) - T)s_{\text{fus}}(\mathbf{A}) + x(T_f(\mathbf{B}) - T)s_{\text{fus}}(\mathbf{B}). \end{aligned}$$

This relatively simple solution model can generate numerous key types of binary phase diagrams because the model captures essential aspects of solution behavior. To construct a phase diagram, the molar Gibbs free energies of the liquid and solid solutions for a given temperature are analyzed for the stable phases, i.e., seeing if the common tangent rule must be applied or not. The procedure is repeated for numerous other temperatures to generate the complete diagram. As a specific application of this model, let the melting points of **A** and **B** be $T_f(\mathbf{A}) = 800$ K and $T_f(\mathbf{B}) = 1200$ K, and the entropies of fusion for both components be $s_{\text{fus}}(\mathbf{A}) = s_{\text{fus}}(\mathbf{B}) = +10$ J/mol · K. This value is a good approximation for many pure solids according to *Richard's rule*, which states that entropies of fusion are 8-15 J/mol·K. In this case, the corresponding enthalpies of fusion are $h_{\text{fus}}(\mathbf{A}) = 8.0$ kJ/mol and $h_{\text{fus}}(\mathbf{B}) = 12.0$ kJ/mol.

Various phase diagrams arise from the relative magnitudes and signs of the enthalpy of mixing parameters $\Omega^{(s)}$ and $\Omega^{(l)}$ in the molar Gibbs free energy expressions.⁶² The different binary phase diagrams are ordered according to $\Omega^{(s)}$ increasing from -15 kJ/mol in the bottom row to $+30$ kJ/mol in the top row, and $\Omega^{(l)}$ increasing from -20 kJ/mol in the left column to $+30$ kJ/mol in the right column. For $\Omega^{(s)} = \Omega^{(l)} = 0$, the solid and liquid states are both ideal solutions, and the corresponding phase diagram shows a lens shape. For $\Omega^{(s)} \leq 0$, the solid solution is more stable than the separated components over the entire composition range. For $\Omega^{(s)} > 0$, the two components prefer to segregate into two phases and the diagrams become more complicated. Eutectic diagrams emerge in this array for $\Omega^{(s)} > 0$ and $\Omega^{(l)} \leq 0$.

(39) *Ideal Solutions* are called Raoultian because the activities of every component in an ideal solution are equal to their mole fractions: $a_i^{(\varphi)} = x_i^{(\varphi)}$. As a result, the enthalpies of mixing of ideal solutions are 0 and the only contribution to the molar Gibbs free energy is configurational entropy. Therefore, the two components of an ideal solution $\mathbf{A}_{1-x}\mathbf{B}_x(\varphi)$ form a homogeneous mixture over the entire composition range from pure **A** to pure **B**.

An example of a binary system where both the solid and liquid states are ideal solutions is the Ge-Si system. Both elements adopt the same diamond-type structure, and their atomic sizes differ by less than 15%: $R_{\text{Si}} \sim 111$ pm; $R_{\text{Ge}} \sim 125$ pm. As a result, Si and Ge form homogeneous mixtures in both the solid and liquid states. Also, Si is the higher melting component of the system: $T_f(\text{Si}) = 1414^\circ\text{C}$; $T_f(\text{Ge}) = 938^\circ\text{C}$. The lens-shaped Ge-Si phase diagram has three distinct regions separated by the upper, liquidus curve and the lower, solidus curve of the lens:

- (1) One-phase, liquid solution region above the liquidus curve. With two intensive variables, T and $x_{\text{Si}}^{(l)}$, and no restraints, there are two degrees of freedom;
- (2) One-phase, solid solution region below the solidus curve. With two intensive variables, T and $x_{\text{Si}}^{(s)}$, and no restraints, there are two degrees of freedom.

⁶² A.D. Pelton, W.T. Thompson, *Prog. Solid State Chem.* **1975**, *10*, 119-155.

- (3) Two-phase mixture of liquid and solid solutions. For a given temperature, the tie line connects a liquid solution at lower Si content with a solid solution at higher Si content. The corresponding equilibria are:

$$\text{Si}(s) \rightleftharpoons \text{Si}(l): \Delta g_{\text{fus}}^{\circ}(T) = -RT \ln \frac{a_{\text{Si}}^{(l)}}{a_{\text{Si}}^{(s)}} = -RT \ln \frac{x_{\text{Si}}^{(l)}}{x_{\text{Si}}^{(s)}} = 50,200 - 29.824 T \text{ (J/mol)}$$

$$\text{Ge}(s) \rightleftharpoons \text{Ge}(l): \Delta g_{\text{fus}}^{\circ}(T) = -RT \ln \frac{a_{\text{Ge}}^{(l)}}{a_{\text{Ge}}^{(s)}} = -RT \ln \frac{x_{\text{Ge}}^{(l)}}{x_{\text{Ge}}^{(s)}} = 36,940 - 30.494 T \text{ (J/mol)}$$

Following each chemical equilibrium is the equation arising from the equality of chemical potentials, i.e., $\mu_{\text{Si}}^{(s)} = \mu_{\text{Si}}^{(l)}$ and $\mu_{\text{Ge}}^{(s)} = \mu_{\text{Ge}}^{(l)}$. Therefore, with three intensive variables, T , $x_{\text{Si}}^{(l)}$, and $x_{\text{Si}}^{(s)}$, and two restraints, there is one degree of freedom. As a result, setting the temperature allows determination of the compositions of the coexisting solid and liquid solutions.

EXAMPLE: Determine the Ge-Si solution compositions at 1450 K assuming ideal solution behavior in both the solid and liquid solutions.

Substituting 1450 K into the free energy expressions gives

$$\ln \frac{x_{\text{Si}}^{(l)}}{x_{\text{Si}}^{(s)}} = -0.5770 \text{ or } \frac{x_{\text{Si}}^{(l)}}{x_{\text{Si}}^{(s)}} = 0.5616; \quad \ln \frac{x_{\text{Ge}}^{(l)}}{x_{\text{Ge}}^{(s)}} = 0.6036 \text{ or } \frac{x_{\text{Ge}}^{(l)}}{x_{\text{Ge}}^{(s)}} = \frac{1-x_{\text{Si}}^{(l)}}{1-x_{\text{Si}}^{(s)}} = 1.8286.$$

There are two linear equation with two unknowns, a pair of equations that can be solved:

$$x_{\text{Si}}^{(l)} = 0.3673, x_{\text{Ge}}^{(l)} = 0.6327; \quad x_{\text{Si}}^{(s)} = 0.6540, x_{\text{Ge}}^{(s)} = 0.3460.$$

The liquid solution is richer in Ge and the solid solution is richer in Si because the temperature is near the average of the melting points of Ge and Si.

The Ge-Si phase diagram is explained by comparing the molar Gibbs free energy curves over the entire range of mole fraction for the solid and liquid solutions at specific temperatures. For $T > T_f(\text{Si})$, $g^{(l)}(T, x) < g^{(s)}(T, x)$ for all concentration values x and only the liquid-phase solution is stable. At temperatures just below $T_f(\text{Si})$, the $g^{(l)}(T, x)$ and $g^{(s)}(T, x)$ curves intersect at a large mole fraction x . Therefore, the common tangent rule yields two stable phases that are both Si-rich. For temperatures just above $T_f(\text{Ge})$, the $g^{(l)}(T, x)$ and $g^{(s)}(T, x)$ curves intersect at a small mole fraction x , and the common tangent rule yields two stable phases that are both Ge-rich. Lastly, for $T < T_f(\text{Ge})$, $g^{(l)}(T, x) > g^{(s)}(T, x)$ for all concentration values x and only the solid-phase solution is stable.

To understand the information of this phase diagram, consider a 50%:50% molar mixture of Ge and Si heated above the melting point of Si (1414°C) so that the mixture becomes liquid. On slow cooling, so that equilibrium can be maintained, the liquid phase remains until the temperature reaches the liquidus curve (~1270°C). At this point, the solid solution that is ~79% Si forms. As long as equilibrium is maintained by continued slow cooling, the composition of the liquid follows the liquidus curve and the composition of the solid follows the solidus curve until composition reaches 50% Si in the solid (~1110°C). Notice that both the equilibrium liquid and equilibrium solid increase their Ge content on cooling. Further cooling yields just the equimolar solid solution.

(40) Melting Behavior (Congruent vs. Incongruent): Melting is a phase transition from the solid state to the liquid state. Any pure solid-state compound will melt either congruently or incongruently, unless the compound becomes unstable with respect to two other solids. A *congruently* melting solid-state compound has a two-phase equilibrium at its melting point between the pure solid and the pure liquid. An *incongruently* melting solid-state compound has a three-phase equilibrium involving two solids and one liquid; the process is also called *peritectic*

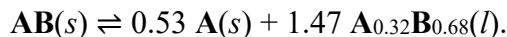
decomposition because the original solid compound transforms into a different solid and liquid. Let's examine how these two melting processes are revealed on model two-component **A-B** phase diagrams, each of which contains a line compound **AB**.

In the system where **AB(s)** melts *congruently*, the phase diagram consists of two contiguous eutectic mixtures: (i) **A** with **AB**; and (ii) **AB** with **B**. The diagram is divided into 1 single-phase liquid region at temperatures above the liquidus curve, 4 two-phase liquid-solid regions, and 2 two-phase heterogeneous solid-solid regions below the eutectic temperatures for each side. The three solids **A(s)**, **AB(s)**, and **B(s)** do not simultaneously coexist at equilibrium.

On heating, **AB(s)** will melt according to the equilibrium $\text{AB}(s) \rightleftharpoons \text{AB}(l)$ at its melting point T_f . Further heating sends **AB** into the liquid state. On cooling, when the temperature reaches T_f , **AB(s)** will precipitate from the melt and form the pure solid. The point ($x_B = 0.5, T = T_f$) is invariant ($F = 0$) because there is a single component ($C = 1$) with two coexisting phases ($P = 2$). Further cooling yields pure **AB(s)**.

In the system where **AB(s)** melts *incongruently*, in addition to the single-phase liquid region and 2 two-phase solid-solid **A(s)/AB(s)** and **AB(s)/B(s)** regions, there are 3 two-phase liquid-solid regions involving each of the three pure solids in this system. There is also one eutectic point.

On heating, **AB(s)** will melt by decomposition into **A(s)** and a liquid that is rich in **B**; its composition is read from the diagram to be $\text{A}_{0.32}\text{B}_{0.68}(l)$. This process is called *peritectic decomposition* and is represented by the chemical equilibrium at T_f :



The coefficients in the chemical equation are determined by the lever rule. Now, if the system is slowly heated so that equilibrium is maintained, **AB(s)** will “dissolve” in the liquid. As the temperature increases, the liquid will become richer in **A** along the liquidus curve. Once the liquidus curve reaches $x_B = 0.5$ at temperature T_4 , then the sample is completely melted. Further heating keeps a one-phase liquid mixture $\text{A}_{0.50}\text{B}_{0.50}(l) = \text{AB}(l)$. On cooling this liquid mixture, once the temperature reaches the liquidus curve, **A(s)** precipitates and the liquid that gets richer in **B** as further cooling ensues. At T_f , **AB(s)** forms, establishing a three-phase equilibrium with **A(s)** and $\text{A}_{0.32}\text{B}_{0.68}(l)$. If equilibrium can be achieved by a sufficiently slow cooling rate, then **A(s)** will react with the liquid to form **AB(s)**. However, if the time to establish this peritectic equilibrium is long compared to the rate of cooling, then on further cooling, **A(s)** may not completely react with the liquid to form **AB(s)**. Then, as the mixture cools, **AB(s)** continues to precipitate until the eutectic temperature T_3 is achieved, at which point **B(s)** will form. The resulting solid will be a heterogeneous mixture of **A(s)**, **AB(s)**, and **B(s)**. Complete peritectic recombinations do occur, for example, in geologically relevant phase spaces. However, for many experimental (synthetic) situations, it is often difficult to cool a liquid with a composition that matches an incongruently melting solid and form the solid exclusively without introducing other solid-state products.

Thus, if **AB(s)** melts *congruently*, then on heating into the liquid and subsequent cooling, pure **AB(s)** reforms. If **AB(s)** melts *incongruently*, then on heating into the liquid and subsequent cooling, **AB(s)** reforms, but it is possible that **A(s)** and **B(s)** may form as well. There are a couple of strategies to optimize the yield of **AB(s)** for this second case: (i) heat a 50:50 mixture of **A** and **B** into the liquid state and rapidly quench the mixture to a temperature just below the peritectic temperature T_f , followed by annealing, which may require long times; or (ii) heat a mixture of **A** and **B** that is sufficiently rich in **B**, so that on cooling, **AB(s)** will precipitate first. Then, separating **AB(s)** from the liquid by filtration or centrifugation is necessary to isolate crystals.

Peritectic temperatures in two-component phase diagrams occur for three different cases ($x_B^{(\alpha)} < x_B^{(\beta)} < x_B^{(\gamma)}$):

- $\beta(s) \rightleftharpoons \alpha(s) + \gamma(l)$ or $\beta(s) \rightleftharpoons \alpha(l) + \gamma(s)$: *Peritectic* decomposition, in which a solid phase disproportionates into a liquid phase and a solid phase;
- $\beta(s) \rightleftharpoons \alpha(l) + \gamma(l)$: *Syntectic* decomposition, in which a solid phase disproportionates into two liquid phases;
- $\beta(s) \rightleftharpoons \alpha(s) + \gamma(s)$: *Peritectoid* decomposition, in which a solid phase disproportionates into two other solid phases.

Two-component phase diagrams vary in complexity, but it is important to learn to read and use these diagrams for potential use during synthesis. They are compiled by the American Society for Metals (ASM), the National Institute of Standards and Technology (NIST), and the American Ceramics Society (ACerS). ASM International's Binary Alloy Phase Diagrams,⁶³ or In many phase diagrams, solid lines have been determined by experiments or thermodynamic calculations, whereas dashed lines refer to estimated curves. Programs, such as *CALPHAD* (*CAL*culat*ion of PH*ase *D*iagrams),⁶⁴ are used to calculate phase diagrams based on thermodynamic information of various components and phases.

(41) Reading Phase Diagrams: From the Mg-Sn phase diagram, (a) Identify all regions below the liquidus line; and (b) identify all 2-phase and 3-phase equilibria.

In the diagram, the minimum temperature is 100°C, which is above ambient temperature and the $\alpha \rightleftharpoons \beta$ transition temperature of 13.2°C for tin (α -Sn is semiconducting gray tin; β -Sn is metallic white tin). Therefore, Sn(s, rt) designates the room temperature form of white tin on the diagram. Up to 3.4 atomic percent Sn dissolves in Mg(s), but Mg is essentially insoluble in Sn(s, rt). At 33.3 atomic percent Sn, Mg₂Sn(s) is a line phase, and is displayed as a vertical line.

(a) The regions below the liquidus line as the mole fraction (atomic percent) Sn increases are:

- | | |
|--|---|
| $0 \leq x_{\text{Sn}} \leq 0.034, 100^\circ\text{C} \leq T \leq 650^\circ\text{C}$: | Mg _{1-x} Sn _x (s), solid solution of Sn dissolved in Mg(s). |
| $0 \leq x_{\text{Sn}} \leq 0.333, 100^\circ\text{C} \leq T \leq 561^\circ\text{C}$: | Mg _{1-x} Sn _x (s), $x_{\text{Sn}} \leq 0.034$; and Mg ₂ Sn(s). |
| $0 \leq x_{\text{Sn}} \leq 0.107, 561^\circ\text{C} \leq T \leq 650^\circ\text{C}$: | Mg _{1-x} Sn _x (s), $x_{\text{Sn}} \leq 0.034$; and Mg _{1-x} Sn _x (l), $x_{\text{Sn}} \leq 0.107$. |
| $0.107 \leq x_{\text{Sn}} \leq 0.333, 561^\circ\text{C} \leq T \leq 771^\circ\text{C}$: | Mg _{1-x} Sn _x (l), $0.107 \leq x_{\text{Sn}} \leq 0.333$; and Mg ₂ Sn(s). |
| $0.333 \leq x_{\text{Sn}} \leq 1, 100^\circ\text{C} \leq T \leq 204^\circ\text{C}$: | Mg ₂ Sn(s); and Sn(s, rt). |
| $0.333 \leq x_{\text{Sn}} \leq 0.904, 204^\circ\text{C} \leq T \leq 771^\circ\text{C}$: | Mg ₂ Sn(s); and Mg _{1-x} Sn _x (l), $0.333 \leq x_{\text{Sn}} \leq 0.904$. |
| $0.904 \leq x_{\text{Sn}} \leq 1, 204^\circ\text{C} \leq T \leq 232^\circ\text{C}$: | Mg _{1-x} Sn _x (l), $0.904 \leq x_{\text{Sn}} \leq 1$; and Sn(s, rt). |

(b) The 2-phase equilibria are congruent melting points of three pure species:

- | | |
|---------------------------|---|
| $T = 650^\circ\text{C}$: | Mg(s) \rightleftharpoons Mg(l). |
| $T = 771^\circ\text{C}$: | Mg ₂ Sn(s) \rightleftharpoons Mg ₂ Sn(l). |
| $T = 232^\circ\text{C}$: | Sn(s, rt) \rightleftharpoons Sn(l). |

The 3-phase equilibria are eutectic points involving 1 liquid phase and 2 solid phases:

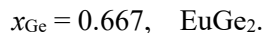
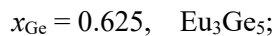
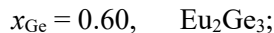
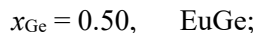
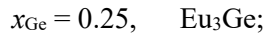
- | | |
|---------------------------|--|
| $T = 561^\circ\text{C}$: | Mg _{0.893} Sn _{0.107} (l) \rightleftharpoons 0.76 Mg _{0.966} Sn _{0.034} (ss) + 0.08 Mg ₂ Sn(s). |
| $T = 204^\circ\text{C}$: | Mg _{0.096} Sn _{0.904} (l) \rightleftharpoons 0.05 Mg ₂ Sn(s) + 0.85 Sn(s, rt). |

⁶³ ASM Alloy Phase Diagram Database, P. Villars, Ed.-in-chief: <https://matdata.asminternational.org/apd/index.aspx>

⁶⁴ P.J. Spencer, *Calphad*, **2008**, 32, 1-8.

(42) The Eu-Ge diagram is more complex than the Mg-Sn diagram because there are more line compounds and some interesting solid-state transformations above $\sim 750^\circ\text{C}$. From this diagram (a) how many different compounds are depicted, and (b) what happens to each of these compounds on heating?

(a) Compounds are depicted as vertical lines on the diagram. These occur for:



Therefore, there are 5 compounds in the Eu-Ge diagram.

(b) On heating:

Eu₃Ge: Congruently melts at 1215°C;

EuGe: Congruently melts at 1220°C;

Eu₂Ge₃: Peritectoidally decomposes into two solids, EuGe(s) and Eu₃Ge₅(s), at 916°C;

Eu₃Ge₅: Structural transformation at 870°C,
Peritectically decomposes (incongruently melts) at 1011°C;

EuGe₂: Structural transformation at 810°C,
Congruently melts at 1030°C.

(43) Write the 2-phase and 3-phase equilibria that occur in this system:

$T = 810^\circ\text{C}$: $\text{EuGe}_2(s, \text{rt}) \rightleftharpoons \text{EuGe}_2(s, \text{ht})$, polymorphic transition.

$T = 822^\circ\text{C}$: $\text{Eu}(s) \rightleftharpoons \text{Eu}(l)$, congruent melting.

$T = 870^\circ\text{C}$: $\text{Eu}_3\text{Ge}_5(s, \text{ht1}) \rightleftharpoons \text{Eu}_3\text{Ge}_5(s, \text{ht2})$, polymorphic transition.

$T = 938^\circ\text{C}$: $\text{Ge}(s) \rightleftharpoons \text{Ge}(l)$, congruent melting.

$T = 1030^\circ\text{C}$: $\text{EuGe}_2(s, \text{ht}) \rightleftharpoons \text{EuGe}_2(l)$, congruent melting.

$T = 1215^\circ\text{C}$: $\text{Eu}_3\text{Ge}(s) \rightleftharpoons \text{Eu}_3\text{Ge}(l)$, congruent melting.

$T = 1220^\circ\text{C}$: $\text{EuGe}(s) \rightleftharpoons \text{EuGe}(l)$, congruent melting.

$T = 723^\circ\text{C}$: $\text{Eu}_{0.19}\text{Ge}_{0.81}(l) \rightleftharpoons 0.19 \text{EuGe}_2(s, \text{rt}) + 0.43 \text{Ge}(s)$, eutectic temperature.

$T = 755^\circ\text{C}$: $\text{Eu}_3\text{Ge}_5(s, \text{ht1}) \rightleftharpoons \text{Eu}_2\text{Ge}_3(s) + \text{EuGe}_2(s, \text{rt})$, eutectoid temperature.

$T = 758^\circ\text{C}$: $\text{Eu}_{0.92}\text{Ge}_{0.08}(l) \rightleftharpoons 0.68 \text{Eu}(s) + 0.08 \text{Eu}_3\text{Ge}(s)$, eutectic temperature.

$T = 916^\circ\text{C}$: $\text{Eu}_2\text{Ge}_3(s) \rightleftharpoons 0.50 \text{EuGe}(s) + 0.50 \text{Eu}_3\text{Ge}_5(s, \text{ht2})$, peritectoid temperature.

$T = 966^\circ\text{C}$: $\text{Eu}_{0.42}\text{Ge}_{0.58}(l) \rightleftharpoons 0.18 \text{EuGe}(s) + 0.08 \text{Eu}_3\text{Ge}_5(s, \text{ht2})$, eutectic temperature.

$T = 1011^\circ\text{C}$: $\text{Eu}_3\text{Ge}_5(s, \text{ht2}) \rightleftharpoons 5.41 \text{Eu}_{0.40}\text{Ge}_{0.60}(l) + 0.86 \text{EuGe}_2(s, \text{ht})$, peritectic temperature.

$T = 1145^\circ\text{C}$: $\text{Eu}_{0.52}\text{Ge}_{0.48}(l) \rightleftharpoons 0.02 \text{Eu}_3\text{Ge}(s) + 0.46 \text{EuGe}(s)$, eutectic temperature.

(44) *Fluxes*: Phase diagrams are useful to assist in planning a synthetic procedure for growing single crystals of a known compound by using a *flux*, which is a liquid phase solvent that provides a mechanism to nucleate and grow target compounds into crystalline specimens. Fluxes can be reactive, which will incorporate into the products, or unreactive. Moreover, eutectic mixtures can be effective fluxes because their melting points are lower than those of each component, although these temperatures can still be quite high. For such conditions, special container materials and

clever means to separate the desired product from the flux material are necessary. It is important to choose a container material that is inert to the melt.

Container Material	$T_{\text{Soft}} (^{\circ}\text{C})$	$T_{\text{Soft}} (^{\circ}\text{C})$
Borosilicate glass (Pyrex)	515	820
Gold		1064
Silica (SiO_2)	1200	1853
Platinum		1770
Alumina (Al_2O_3)	1900	2072
Zirconia (ZrO_2)	2000	2700
Magnesia (MgO)	2400	2852
Tantalum		3017
Graphite		3600 (sublimes)

To assist in sufficiently slow crystal growth, the higher melting material should be placed on the bottom of the container. Often, the crucible needs to be enclosed in a secondary container, which is often fused silica or alumina. Because there may be different expansion coefficients between the crucible material and the secondary silica container, the crucible should be raised off the bottom of the silica tube with shards of silica.

Important characteristics of elements that form fluxes include: (i) low melting temperature; (ii) can be readily separated from reaction products; (iii) forms very few, if any, compounds with reactants (appropriate for *unreactive* fluxes); and (iv) a moderate vapor pressure, which implies a significant difference between its boiling and melting temperatures. Various examples of fluxes and containers are listed in the table below. Among these examples, Ga is effective due to its wide liquid range although it wets many solids. Bi is another effective flux element because it does not form compounds with many elements. However, the density of Bi(*s*) is lower than the density of Bi(*l*). Therefore, upon solidification, Bi fluxes can crack containers and lead to oxidation problems. Al is a low melting metal that can be an effective flux, but it attacks silica.

Element Flux	Container Choices	Crystals
Al	Alumina, Magnesia	Borides: TiB_2 , LnB_4 , LnB_6 (Ln = rare-earth) Aluminides: LnAl_3
Ga	Alumina, Magnesia	Si (amorphous), Ge (amorphous) GaSb (amorphous), LnSb
In	Alumina, Ta	ThCr_2Si_2 -types
Sn	Alumina, Silica, Graphite	Pnictides: LnSb , $\text{LnFe}_4\text{P}_{12}$ Heusler Alloys: TiNiSn
Bi	Alumina, Silica, Graphite	Phosphides: GaP (amorphous), ZnSiP_2 Uranium Compounds: UPt_3 , UAl_3
Zn	Alumina	Si, Ge GaSb, InAs, InSb
Cu	Graphite, Alumina, Magnesia, Ta	LnRh_4B_4 , LnCu_2Si_2 , V_3Si

To separate the flux from the product, chemical etching or centrifuging are the two principal strategies. When centrifuging, a plug of silica wool placed above the crucible can help filter the liquid flux and leave the crystalline product behind. Another option is the “Canfield crucible”, which includes a frit disc that allows separation of the liquid flux from the solid crystals. Chemical etching can be accomplished using NaOH(aq) for Al(l), HCl(aq) for Ga(l) and In(l), and dilute HCl(aq) for Sn(l).

(45) The quaternary *borocarbides* LnNi₂B₂C (Ln = Gd-Lu, Y) were discovered in the 1990s by researchers at AT&T Laboratories to show unusual superconducting behavior with T_c values between ~6 K and 19 K, which is unusual because many of these rare earth compounds also display spontaneous magnetization. The structure of these compounds involves a network of Ni atoms tetrahedrally surrounded by linear B–C–B units and Ln atoms in the large voids. Careful measurements of physical properties such as magnetization demand high quality single crystals. These compounds are a spectacular example of using a reactive flux to grow high quality crystals for such physical property measurements.⁶⁵ An excellent strategy is to try binary mixtures of elements contained in the complex quaternary material, for example, Ln-Ni and Ni-B. Canfield et al. achieved the best results using Ni₂B fluxes, which demonstrate eutectic-type behavior in the Ni-B system. Flux growth can yield penny-sized crystals.

READING:

- Z. Fisk, J.P. Remeika, *Handbook on the Chemistry and Physics of Rare Earths*, vol. 12, Eds. K.A. Gschneidner, Jr., L. Eyring, Elsevier, Amsterdam, 1989, pp. 53-70
- P.C. Canfield, Z. Fisk, *Phil. Mag. B* **1992**, *B65*, 1117-1123
- M. Kanatzidis, R. Pöttgen, W. Jeitschko, *Angew. Chem. Int. Ed. Engl.* **2005**, *44*, 6996-7023

(46) DISCUSSION QUESTIONS: Using the Ce-Sb phase diagram, how would you prepare high quality crystals of some different antimonides? What are the particular challenges and concerns?

CeSb₂ melts peritectically at 1130°C. It is difficult to avoid CeSb(s) by cooling a stoichiometric mixture of Ce and Sb from the melt, which must achieve a temperature of at least 1600°C. The reaction container can be a refractory metal, although Sb reacts with Nb or Ta. Using a Ce-Sb mixture greater than 85 mole percent Sb, CeSb₂ will precipitate from the liquid at temperatures below ~1050°C. This procedure allows alumina or even silica containers, and any remaining liquid can be separated by centrifugation at ~750°C.

CeSb melts congruently but at high temperature (1820°C) and can be grown using either excess Ce or excess Sb above 1500°C. To lower the reaction temperature, a Sn metal flux may prove effective. However, Ce forms CeSn₃ below ~1150°C, so a significant excess of Sn will be necessary to lower the precipitation temperature of CeSn₃ compared to CeSb.

Ce₂Sb melts peritectically at 1330°C. Therefore, melting, rapid quenching and annealing must be carried out in a refractory metal. An excess of Ce, i.e, more than 76 mole percent Ce, will lower the temperature for growing crystals; however, Ce(l) is aggressive and will attack silica and alumina, so it should be performed in Ta ampoules using silica as a secondary container. To work at temperatures less than 1100°C, there must be 80-90 mole percent Ce.

⁶⁵ P.C. Canfield, P.L. Gammel, D.J. Bishop, *Physics Today*, **1998**, *51*, 40-46.