Sources

H.F. Franzen, *Physical Chemistry of Inorganic Crystalline Solids*, Springer-Verlag, New York, 1986
H.F. Franzen, *J. Chem. Educ.* **1988**, *65*, 146-147
D.R. Gaskell, *Introduction to Metallurgical Thermodynamics*, 2nd Ed., Taylor and Francis, USA, 1983
A.R. West, *Solid State Chemistry and Its Applications*, John Wiley & Sons, New York, 1984

Useful resources for some of the following problems include:

- NIST-JANAF Thermochemical Tables at https://janaf.nist.gov/
- ACERS – NIST Phase Equilibria Diagrams Online Search Database, *NIST Standard Reference Database 31* at https://phaseonline.ceramics.org/ped_figure_search
- ASM Handbooks Online: https://dl.asminternational.org/handbooks

Fundamentals (Stability; Diffusion; Nucleation)

(1) For the solid-state reaction, $2\ MgO(s) + TiO_2(s) \rightarrow Mg_2TiO_4(s)$, $\Delta G°(1000\ K) = -27.62$ kJ/mol.

Determine the compounds and their quantities that exist when thermodynamic equilibrium is established at 1000 K for the following initial conditions:

(a) 40.0 g MgO and 160.0 g TiO_2

(b) 80.0 g Mg_2TiO_4 and 20.0 g MgO

(c) 160.0 g Mg_2TiO_4, 40.0 g MgO, and 80.0 g TiO_2

(2) For the solid-state reaction, $3\ FeCl_2(s) \rightarrow Fe(s) + 2\ FeCl_3(s)$, $\Delta G°(500\ K) = +247.82$ kJ/mol.

Determine the compounds and their quantities that exist when thermodynamic equilibrium is established at 500 K for the following initial conditions:

(a) 125.0 g $FeCl_2$ and 56.0 g Fe

(b) 160.0 g $FeCl_3$ and 56.0 g Fe

(c) 112.0 g Fe, 160.0 $FeCl_3$, and 62.5 g $FeCl_2$

(3) For the gas-phase reaction, $Br_2(g) + Cl_2(g) \rightarrow 2\ BrCl(g)$, $\Delta G°(500\ K) = -7.388$ kJ/mol.

Determine the species and their partial pressures that exist when thermodynamic equilibrium is established at 500 K for the following initial conditions:

(a) 2.00 atm Br_2 and 1.00 atm Cl_2

(b) 2.00 atm BrCl

(c) 2.00 atm BrCl and 1.00 atm Cl_2

(4) Evaluate the change in self-diffusion coefficient (in cm^2/sec) for Fe atoms in α-Fe from 500°C to 900°C.

D_0(α-Fe) = 2.8 cm^2/sec; Q(α-Fe) = 251 kJ/mol.

(5) α-Fe (BCC) and γ-Fe (FCC) coexist at ~910°C. Their densities at this coexistence temperature are, respectively, 7.63 g/cm^3 and 7.70 g/cm^3. Evaluate the self-diffusion coefficients (in cm^2/sec) for the two forms of iron at their coexistence temperature and briefly discuss implications of the difference.

D_0(α-Fe) = 2.8 cm^2/sec; Q(α-Fe) = 251 kJ/mol.
D_0(γ-Fe) = 0.49 cm^2/sec; Q(γ-Fe) = 284 kJ/mol.

(6) Compare the diffusion coefficients for Cu atoms and Zn atoms in FCC Cu at 300 K. FCC Cu has a cell constant 3.615 Å and distorted HCP Zn has cell constants *a* = 2.665 Å, *c* = 4.947 Å. Discuss the difference.

Cu in FCC Cu(*s*): D_0 = 1.64 cm^2/sec; Q = 218 kJ/mol.
Zn in FCC Cu(*s*): D_0 = 0.24 cm^2/sec; Q = 189 kJ/mol.

(7) At 300°C, the diffusion coefficient and activation energy for Cu atoms in Si(*s*) are $D = 7.8 \times 10^{-11}$ m^2/sec and Q = 41.5 kJ/mol. What is the diffusion coefficient for this system at 350°C assuming no change in activation energy?

(8) The self-diffusion coefficient of Ag atoms in solid silver metal is 1.0×10^{-17} m^2/sec at 500°C and 7.0×10^{-13} m^2/sec at 1000°C. Estimate the activation energy for self-diffusion of Ag in this temperature range.

(9) Rank the magnitudes of the diffusion coefficients from greatest to least for:

(i) N atoms in α-Fe at 700°C,

(ii) N atoms in α-Fe at 900°C,

(iii) Cr atoms in α-Fe at 700°C,

(iv) Cr atoms in α-Fe at 900°C.

(**10)** Compare the diffusion coefficients for Ge atoms in (i) diamond-type Ge, (ii) FCC Cu, and (iii) FCC Al at 500 K. Discuss the differences.

Ge in diamond-type Ge(*s*): D_0 = 13.6 cm^2/sec; Q = 298 kJ/mol.
Ge in FCC Cu(*s*): D_0 = 0.40 cm^2/sec; Q = 187 kJ/mol.
Ge in FCC Al(*s*): D_0 = 0.48 cm^2/sec; Q = 121 kJ/mol.

(11) Estimate the radius (in Å) and the number of Cu atoms in the critical spherical nucleus when solid copper forms by homogeneous nucleation from a maximally supercooled liquid. Copper is FCC with lattice parameter of 3.615 Å.

For Cu: $\Delta T_{\text{max}} = 236$ K; $T_m = 1357$ K
$\Delta h_{\text{fus}} = 13.26$ kJ/mol $\gamma = 0.178$ J/m^2 $v^{(s)} = 7.114$ cm^3/mol

(12) Estimate the radius (in Å) and the number of Pb atoms in the critical spherical nucleus when solid lead forms by homogeneous nucleation from a maximally supercooled liquid. Lead is FCC with lattice parameter of 4.951 Å.

For Pb: $\Delta T_{\text{max}} = 80$ K; $T_m = 600$ K
$\Delta h_{\text{fus}} = 4.77$ kJ/mol $\gamma = 0.069$ J/m^2 $v^{(s)} = 18.268$ cm^3/mol

(13) What happens to a spherical nucleus of tin that has a diameter of 8.00 Å in the maximally supercooled liquid?

For Sn: $\Delta T_{\text{max}} = 191$ K; $T_m = 505$ K
$\Delta h_{\text{fus}} = 7.03$ kJ/mol $\gamma = 0.075$ J/m^2 $v^{(s)} = 16.291$ cm^3/mol

(14) What happens to a spherical nucleus of copper that has a diameter of 15.0 Å in the maximally supercooled liquid?

For Cu: $\Delta T_{\text{max}} = 236$ K; $T_m = 1357$ K
$\Delta h_{\text{fus}} = 13.26$ kJ/mol $\gamma = 0.178$ J/m^2 $v^{(s)} = 7.114$ cm^3/mol

(15) Consider a spherical nucleus of copper with a diameter of 15.0 Å in the maximally supercooled liquid. What are the changes in surface free energy (in J) and bulk free energy (in J) if the diameter is increased to 20.0 Å? If the diameter is decreased to 10.0 Å?

For Cu: $\Delta T_{\max} = 236$ K; $T_m = 1357$ K
$\Delta h_{\text{fus}} = 13.26$ kJ/mol $\gamma = 0.178$ J/m^2 $v^{(s)} = 7.114$ cm^3/mol

Phase Diagrams: Gibbs Phase Rule and Heterogeneous Equilibria

(16) A metal oxychloride, $MOCl_2(s)$ is heated to high temperatures and allowed to reach equilibrium at which the vapor contains $O_2(g)$, $OCl(g)$, and $Cl_2(g)$ and the condensed phase consists of only M with a small amount of O in solid solution, i.e., $MO_x(ss)$. (Franzen)

(a) Construct the species-by-element matrix for this system using $MO_x(ss)$, $O_2(g)$, and $Cl_2(g)$ in the first 3 columns to determine a set of independent net reactions (balanced chemical equilibria).

(b) What restraint, if any, is placed on the system by the experimental procedure?

(c) How many components and how many independent intensive variables are there? Briefly explain the significance of the outcome.

(17) Consider a system containing the species $La_2O_3(s)$, $La_2S_3(s)$, $La_2O_2S(s)$, $SO(g)$, $SO_2(g)$, and $O_2(g)$. (Franzen)

(a) Construct the species-by-element matrix for this system using $La_2O_3(s)$, $SO(g)$, and $O_2(g)$ in the first 3 columns to determine a set of independent net reactions (balanced chemical equilibria).

(b) Write distinct balanced chemical heterogeneous equilibria containing $SO_2(g)$ and $O_2(g)$ as gas phase species. NOTE: these are not independent reactions because they can be derived from the ones you obtain in (a).

(c) Determine the number of degrees of freedom and discuss the implications of the result.

(18) The solid solution $TiO_xC_{1-x}(ss)$, when heated in an evacuated container, establishes equilibrium with $O_2(g)$, $CO(g)$, TiO(g), and Ti(g). (Franzen)

(a) Construct the species-by-element matrix for this system using the elements of the solid solution Ti(*ss*), O(*ss*), and C(*ss*) as distinct species. To build the matrix, use Ti(*g*), CO(*g*), and $O_2(g)$ as the first 3 columns. Determine a set of independent net reactions (balanced chemical equilibria).

(b) Construct the species-by-element matrix for this system using TiO(*ss*) and TiC(*ss*) as different species of the solid solution. To build this matrix, use Ti(*g*), CO(*g*), and $O_2(g)$ as the first 3 columns. Determine a set of independent net reactions (balanced chemical equilibria).

(c) For (a) and (b), determine the number of components (considering any restraints), the number of phases, and the number of degrees of freedom. Discuss and compare the two outcomes.

(19) Estimate the temperature at which $Ag_2O(s)$ decomposes into Ag(*s*) and $O_2(g)$ on heating in (Gaskell)

(a) pure oxygen at 1 atm;

(b) air at 1 atm.

$\Delta G_f^0(Ag_2O, s) = -30{,}540 + 66.11T$ J/mol

(20) 1.00 g $CaCO_3(s)$ is placed in an evacuated rigid 1.00 L container at room temperature and the system is heated. Calculate (Gaskell)

(a) the highest temperature at which $CaCO_3(s)$ is present in the container;

(b) the pressure (atm) in the vessel at 1000 K;

(c) the pressure (atm) in the vessel at 1500 K.

$CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s)$, $\Delta G°(T) = -168{,}400 + 144\,T$ J/mol

(21) A Cu-Zn alloy is placed in one end of an evacuated, closed tube, and is heated to 900°C. When the other end of the tube is cooled to 740°C, Zn vapor begins to condense. Calculate the activity of Zn in the alloy relative to pure zinc. (Gaskell)

Vapor pressure Zn: $\ln p\ (\text{atm}) = -\frac{15{,}250}{T} - 1.255\ \ln T + 21.79$

(22) A mixture of NiO(*s*) and H_2(*g*) is sealed in a 10.0 L closed container and heated to 500 K. Analysis of the container identified Ni(*s*), NiO(*s*), H_2(*g*), and H_2O(*g*) coexisting at equilibrium.

(a) How many independent intensive variables does this system have as described?

(b) What are the independent intensive variables in this system?

(c) Using the following thermodynamic information, calculate the ratio $p(H_2O) / p(H_2)$.

$H_2(g) + \frac{1}{2} O_2(g) \rightleftharpoons H_2O(g)$ $\Delta G° = –246{,}000 + 54.8\ T$ (J/mol)
$Ni(s) + \frac{1}{2} O_2(g) \rightleftharpoons NiO(s)$ $\Delta G° = –244{,}550 + 98.5\ T$ (J/mol)

(d) If 0.500 mol H_2(*g*) is placed in the container, what is the minimum number of moles of NiO(*s*) that must be added to ensure equilibrium among Ni(*s*), NiO(*s*), H_2(*g*), and H_2O(*g*) at 500 K?

(23) Consider a system containing the species $CoSO_4$(*s*), CoO(*s*), SO_2(*g*), SO_3(*g*), and O_2(*g*).

(a) Determine the number of degrees of freedom and its implications for this system.

(b) If equilibrium is achieved by decomposition of $CoSO_4$(*s*) at 1223 K, determine the number of degrees of freedom for the system.

(c) Using the following information, calculate the total pressure exerted by this system at equilibrium at 1223 K in a closed container.

$CoO(s) + SO_3(g) \rightleftharpoons CoSO_4(s)$ $\Delta G°(T) = –227{,}860 + 165.3T$ J/mol
$SO_2(g) + \frac{1}{2} O_2(g) \rightleftharpoons SO_3(g)$ $\Delta G°(T) = –94{,}560 + 89.37T$ J/mol

(d) What is the minimum amount of $CoSO_4$(*s*) needed (in g) to achieve equilibrium among these 5 species at 1223 K in a 10.00 L closed container?

(24) Zinc oxide ZnO(*s*) is heated in a sealed, evacuated container with graphite. At equilibrium, in addition to ZnO(*s*) and C(*s*), there also exist Zn(*g*), CO(*g*) and CO_2(*g*). (Gaskell)

(a) Construct the species-by-element matrix using Zn(*g*), C(*s*), and CO(*g*) as the first 3 columns and provide a set of independent net reactions (balanced chemical equilibria) for this system.

(b) There is one restraint created by the synthetic procedure as described. What is this equation among the intensive variables? (HINT: Consider mass balance for the various elements.)

(c) How many degrees of freedom does this system have as described? Discuss the significance of the outcome.

(d) List the intensive variables and the restraints for this system.

(e) Assuming there are sufficient ZnO(*s*) and C(*s*) to establish equilibrium at 1223 K, calculate the partial pressures of Zn(*g*), CO(*g*), and CO_2(*g*) in the container at equilibrium.

$C(s) + \frac{1}{2} O_2(g) \rightleftharpoons CO(g)$ $\Delta G°(T) = –111{,}700 – 87.65\ T$ J/mol
$C(s) + O_2(g) \rightleftharpoons CO_2(g)$ $\Delta G°(T) = –394{,}700 – 0.84\ T$ J/mol
$Zn(g) + \frac{1}{2} O_2(g) \rightleftharpoons ZnO(s)$ $\Delta G°(T) = –460{,}200 – 198\ T$ J/mol

(25) The Th-N system contains Th(*s*), N_2(*g*), ThN(*s*), and Th_3N_4(*s*) at 1 atm. (Franzen)

(a) According to the Gibbs phase rule, what is the maximum number of phases that can coexist at equilibrium?

(b) Can Th(*s*), ThN(*s*), and Th_3N_4(*s*) all coexist in equilibrium at 2000 K and 1 atm? Explain your choice and discuss the significance of your answer.

At 2000 K, $\Delta G_f^0(Th_3N_4, s) = –630.0$ kJ/mol and $\Delta G_f^0(ThN, s) = –206.4$ kJ/mol.

(c) Determine what phases are present and their expected quantities (in grams) at equilibrium if 16.0 g of Th(*s*) and 1.00 g of N_2(*g*) are mixed in an inert 0.500 L container at 2000 K.

(d) Determine what phases are present and their expected quantities (in grams) at equilibrium if 18.0 g of Th(*s*) and 1.00 g of N_2(*g*) are mixed in an inert 0.500 L container at 2000 K.

(26) 100.0 grams of SiO_2(*s*) and 100.0 grams of graphite are placed in a rigid 20.0 liter vessel, which is evacuated at room temperature and then heated to high temperature at which point silica and graphite react to form SiC(*s*). The vapor contains CO(*g*) and SiO(*g*). (Gaskell)

(a) Construct the species-by-element matrix for the system at equilibrium using SiO_2(*s*), C(*s*), and CO(*g*) as the first 3 columns. Determine the independent net reactions (balanced chemical equilibria).

(b) How many independent intensive variables are there in this system?

(c) At 1500°C, calculate

(i) the equilibrium partial pressures (in atm) of CO(*g*) and SiO(*g*) in the vessel;

(ii) the mass (in g) of SiC(*s*) formed; and

(iii) the mass (in g) of graphite consumed.

At 1500°C: ΔG_f^0(SiC, *s*) = –56.99 kJ/mol, ΔG_f^0(SiO_2, *s*) = –595.9 kJ/mol

ΔG_f^0(SiO, *g*) = –246.1 kJ/mol, ΔG_f^0(CO, *g*) = –266.9 kJ/mol

(27) Pure Si(*s*), SiO_2(*s*), and Si_3N_4(*s*) are equilibrated with an N_2-O_2 gas mixture at high temperature. (Gaskell)

(a) How many degrees of freedom does this system have?

(b) Write all balanced chemical equilibria involving two condensed phases.

(c) What is the composition of the gas mixture at equilibrium at 1000 K?

Si(*s*) + O_2(*g*) = SiO_2(*s*) $\Delta G°(T) = –902{,}000 + 174T$ J/mol

3 Si(*s*) + 2 N_2(*g*) = Si_3N_4(*s*) $\Delta G°(T) = –741{,}000 + 332T$ J/mol

(d) If an equilibrium mixture of Si(*s*), SiO_2(*s*), and Si_3N_4(*s*) at 1000 K is then exposed to air at 1 atm pressure, what is the expected outcome?

(28) $FeSO_4$(*s*) is heated to 929 K in a 10.0 L evacuated container such that $FeSO_4$(*s*), Fe_2O_3(*s*), SO_2(*g*), SO_3(*g*) and O_2(*g*) are present at equilibrium. (Franzen)

At 929 K: ΔG_f^0($FeSO_4$, *s*) = –640 kJ/mol; ΔG_f^0(SO_2, *g*) = –294 kJ/mol

ΔG_f^0(Fe_2O_3, *s*) = –577 kJ/mol; ΔG_f^0(SO_3, *g*) = –305 kJ/mol

(a) Write the possible 3-phase chemical equilibria in this system.

(b) What is the equilibrium total pressure (in atm)?

(c) What is the minimum amount of $FeSO_4$(*s*) (in g) needed for these 5 species to be at equilibrium?

(29) 1.0 μmol CuO(*s*) and 0.1 μmol Cu(*s*) are placed in a 1.00 L container at 1000 K. Determine the identity and quantity (in μmol) of each phase present at equilibrium. (Franzen)

At 1000 K: ΔG_f^0(CuO, *s*) = –66.66 kJ/mol; ΔG_f^0(Cu_2O, *s*) = –77.94 kJ/mol

(30) $CdSO_4$ exists in the solid as an anhydrous form and two distinct hydrates. Determine the phases present and number of moles of each phase at equilibrium if 1.0 mmol $CdSO_4$(*s*) and 3.0 mmol H_2O(*g*) are placed in a 2.00 L container at 298 K. Assume the vapor behaves ideally. (Franzen)

At 298 K: ΔG_f^0($CdSO_4$, *s*) = –823.2 kJ/mol; ΔG_f^0(H_2O, *g*) = –228.7 kJ/mol

ΔG_f^0($CdSO_4 \cdot H_2O$, *s*) = –1069.4 kJ/mol; ΔG_f^0($CdSO_4 \cdot 8/3\ H_2O$, *s*) = –1466.1 kJ/mol

(31) Determine the phases and their quantities (in moles and grams) at equilibrium if 1.00 g of a Zr-Al mixture with overall mole fraction of Zr = 0.55 is heated to 1500 K in an inert 1.00 L container. (Franzen)

$Zr_2Al_3(s) \rightleftharpoons 2\ ZrAl(s) + Al(g)$: $\Delta G°(T) \sim 372{,}800 - 118.4\,T$ (J/mol)

$5/7\ Zr_2Al_3(s) = 2/7\ Zr_5Al_4(s) + Al(g)$: $\Delta G°(T) \sim 369{,}700 - 115.5\,T$ (J/mol)

(32) Consider a system containing the species Cu(*s*), $Cu_2O(s)$, CuO(*s*), and $O_2(g)$. Using $\log p_{O_2}$ and T as axes, construct the phase diagram for the temperature range 700–1100 K:

$\Delta G_f^0(Cu_2O, s) = -168{,}300 + 72.79T$ J/mol

$\Delta G_f^0(CuO, s) = -151{,}450 + 85.05T$ J/mol

(33) ZnO(*s*) and ZnS(*s*) are loaded into a closed container with an $H_2S(g)$-$H_2O(g)$-$H_2(g)$ atmosphere. When equilibrium is reached at 2000 K, the gas phase contains $H_2S(g)$, $H_2O(g)$, $H_2(g)$, $O_2(g)$, $S_2(g)$, and Zn(*g*). (Gaskell)

(a) Determine the number of components and number of degrees of freedom for this system.

(b) If $p_{H_2O} = 0.500$ atm and $p_{H_2} = 0.0421$ atm, what is the total pressure (in atm) in the chamber?

At 2000 K $Zn(g) + ½\ O_2(g) \rightleftharpoons ZnO(s)$, $\Delta G° = -79{,}460$ J/mol

$Zn(g) + ½\ S_2(g) \rightleftharpoons ZnS(s)$, $\Delta G° = +7{,}210$ J/mol

$H_2(g) + ½\ O_2(g) \rightleftharpoons H_2O(g)$, $\Delta G° = -136{,}820$ J/mol

$H_2(g) + ½\ S_2(g) \rightleftharpoons H_2S(g)$, $\Delta G° = +8{,}490$ J/mol

(34) A metal M(*s*) can form an oxide MO(*s*) and a carbide MC(*s*). A mixture of MO(*s*) and excess C(s) is heated in a closed container. At equilibrium, C(*s*) is present in the container, and the gas phase contains CO(*g*), $CO_2(g)$, and $O_2(g)$.

(a) What is the maximum number of degrees of freedom for this system? Identify the intensive variables that can be freely varied.

(b) What is the maximum number of phases that can co-exist? What are the implications of this conclusion?

(c) What is the maximum number of phases that can co-exist at some fixed temperature and total pressure? What are the implications of this conclusion?

(d) Given the following thermodynamic information:

$\Delta G_f^0(MO, s) = -529{,}300 + 125.5T$ J/mol, $\Delta G_f^0(MC, s) = -12{,}550 + 8.368T$ J/mol

$\Delta G_f^0(CO, g) = -111{,}800 - 87.70T$ J/mol, $\Delta G_f^0(CO_2, g) = -394{,}300 - 0.84T$ J/mol

determine the solid phases present and gas-phase composition for the conditions:

(i) 800 K and 1 atm total pressure;

(ii) 1200 K and 1 atm total pressure;

(iii) 1600 K and 1 atm total pressure.

(35) At high temperatures, metal oxides can be reduced using solid carbon to give either the metal carbide or the metallic element.

(a) At 1500 K and 1 atm total pressure, the gas phase mixture in equilibrium with C(*s*) is mostly CO(*g*) and CO_2(*g*). What are the equilibrium partial pressures (in atm) of CO(*g*) and CO_2(*g*) with C(*s*) at these conditions?

ΔG_f^0(CO, *g*) = –243.3 kJ/mol ΔG_f^0(CO_2, *g*) = –395.6 kJ/mol

(b) At 1500 K and 1 atm total pressure, is Cr_2O_3(*s*) reduced to Cr(*s*) or $Cr_{23}C_6$(*s*)?

ΔG_f^0(Cr_2O_3, *s*) = –730.9 kJ/mol ΔG_f^0($Cr_{23}C_6$, *s*) = –469.5 kJ/mol

(c) At 1500 K and 1 atm total pressure, is MnO(*s*) reduced to Mn(*s*) or Mn_3C(*s*)?

ΔG_f^0(MnO, *s*) = –275.6 kJ/mol ΔG_f^0(Mn_3C, *s*) = –15.6 kJ/mol

(36) A metal M(*s*) can form the oxides MO(*s*) and M_3O_4(*s*).

ΔG_f^0(MO, *s*) = –259,741 + 62.58 T J/mol ΔG_f^0(M_3O_4, *s*) = –1,091,290 + 312.90 T J/mol

(a) Write out all possible 3-phase equilibria for this system. For each chemical equation, determine the expression for $\Delta G°(T)$ and discuss the implications of the result.

(b) What is the maximum number of independent intensive variables available to this system? Discuss the implications of this result.

(c) What is the maximum number of phases that can coexist at equilibrium in this system? Discuss the implications of this result.

(37) Consider a system containing the species V_2O_4(*s*), V_2O_5(*s*), $VOSO_4$(*s*), SO_2(*g*), and SO_3(*g*). (See H. Flood, O.J. Kleppa, *J. Am. Chem. Soc.* **1947**, *69*, 998-1002.)

(a) Write the balanced chemical equations for all possible 3-phase equilibria. For each equation, write expressions for the equilibrium constants.

(b) How many *independent* net reactions (balanced chemical equilibria) are there? Show the implications of your answer.

(c) How many degrees of freedom are there for this heterogeneous mixture at equilibrium? Discuss the implications of this value.

(d) Construct a qualitative phase diagram for this system at any fixed temperature using *p*(SO_2) and *p*(SO_3) as axes.

(e) Determine the partial pressures of SO_2(*g*) and SO_3(*g*) at 850 K for all phases to coexist at equilibrium.

ΔG_f^0(V_2O_5, *s*) = –1184.48 kJ/mol ΔG_f^0(SO_2, *g*) = –297.21 kJ/mol

ΔG_f^0(V_2O_4, *s*) = –1138.19 kJ/mol ΔG_f^0(SO_3, *g*) = –316.09 kJ/mol

ΔG_f^0($VOSO_4$, *s*) = –914.14 kJ/mol

(38) When CuS(*s*) is heated in air, $CuSO_4$(*s*) forms. On further heating, $CuSO_4$(*s*) decomposes to CuO(*s*) with SO_2(*g*) and O_2(*g*) being the major reactive gases present. Above ~660ºC, CuO(*s*) is the only condensed phase product; but below ~660ºC, increasing amounts of $CuSO_4$(*s*) are found mixed with CuO(*s*).

ΔG_f^0(CuO, *s*) = –153,500 + 87.46 T J/mol

ΔG_f^0(CuS, *s*) = –56,370 + 7.02 T J/mol

ΔG_f^0($CuSO_4$, *s*) = –775,300 + 377.8 T J/mol

ΔG_f^0(SO_2, *g*) = –314,100 + 21.83 T J/mol

ΔG_f^0(SO_3, *g*) = –408,700 + 111.2 T J/mol

(a) Verify that CuS(*s*), $CuSO_4$(*s*), and CuO(*s*) can all coexist with the gas phase mixture SO_2-SO_3-O_2 for a fixed temperature.

(b) Evaluate the equilibrium partial pressures of the gases SO_2(*g*), SO_3(*g*), and O_2(*g*) as a function of temperature between 400 K and 1000 K. Plot the results as $\log p_{\text{gas}}$ vs. T.

(c) Construct a phase diagram of the condensed phases for $T = 800$ K, plotted with $\log p_{O_2}$ as the *x*-axis and $\log p_{SO_2}$ as the *y*-axis.

(d) Construct a phase diagram of the condensed phases for $T = 1000$ K, plotted with $\log p_{O_2}$ as the *x*-axis and $\log p_{SO_2}$ as the *y*-axis.

(e) From your answers, rationalize the chemistry described above.

NOTE: The description is a significant simplification of the numerous steps that occur. For further information, see Sararzadeh, M.S.; Howard, S.M. "Solid State Phase Transformations during the Oxidation of Copper Sulfides: Roaster Diagrams for the Cu-S-O System," *Solid State Sci.* **2018**, *83*, 65-69.

Phase Diagrams: One-Component Diagrams

(39) The temperature dependences of the vapor pressures of Zn(*s*) and Zn(*l*) are:

Zn(*s*): $\ln p$ (atm) = $-15{,}775/T - 0.755 \ln T + 19.25$

Zn(*l*): $\ln p$ (atm) = $-15{,}246/T - 1.255 \ln T + 21.79$.

Calculate:

(a) the normal boiling point of Zn;
(b) the triple point temperature;
(c) the heat of vaporization of Zn at the normal boiling point;
(d) the heat of fusion of Zn at the triple point.

(40) Carbon has two allotropes, graphite and diamond. At 25°C and 1 atm, graphite is the stable allotrope. Estimate the pressure (in atm) needed to convert graphite at 25°C to diamond.

	ΔH_f^0 (kJ/mol)	$S°$ (J/mol·K)	ρ (g/cm^3)
Graphite	---	5.74	2.22
Diamond	1.90	2.37	3.52

(41) The densities of solid and liquid lead at the normal melting temperature of 327°C are 10.94 and 10.65 g/cm^3, respectively. Estimate the pressure (in atm) which must be applied to increase the melting point of lead by 20°C. (Gaskell)

AW(Pb) = 207 g/mol ΔH_{fus}(Pb) = 4.810 kJ/mol

(42) A quantity of supercooled liquid tin is adiabatically contained at 495 K. Calculate the mole fraction of tin which spontaneously freezes. The normal melting point of tin is 505 K. (Gaskell)

ΔH_{fus} = 7.029 kJ/mol

$C_p(l) = 34.7 - 0.0092\ T$ J/mol·K $C_p(s) = 18.5 + 0.026\ T$ J/mol·K

(43) When ferromagnetic BCC α-Fe(*s*) is heated at ambient pressure, it transforms to FCC γ-Fe(s) at 1180 K, and then to paramagnetic BCC δ-Fe(*s*) at 1670 K before melting at 1810 K. Estimate the hypothetical melting point of γ-Fe and its heat of fusion (in J/mol) from the following data. (Gaskell)

γ-Fe → δ-Fe: ΔH = 880 J/mol $C_p(\gamma) = 7.70 + 0.0195\ T$ J/mol·K

δ-Fe → Fe(*l*): ΔH_{fus} = 13,800 J/mol $C_p(\delta)$ = 43.9 J/mol·K

$C_p(l)$ = 41.8 J/mol·K

(44) α-Sn(*s*) transforms on heating to β-Sn(*s*) at 286 K. β-Sn(*s*) then melts at 505 K.

α-Sn → β-Sn: ΔH = 2,095 J/mol $C_p(\alpha)$ = 25.3 J/mol·K $\rho(\alpha)$ = 5.77 g/cm^3

β-Sn → Sn(*l*): ΔH_{fus} = 7,029 J/mol $C_p(\beta)$ = 30.4 J/mol·K $\rho(\beta)$ = 7.265 g/cm^3

$C_p(l)$ = 28.5 J/mol·K $\rho(l)$ = 6.97 g/cm^3

(a) What is the slope of the $p(T)$ curve between α-Sn(*s*) and β-Sn(*s*) near 286 K?
(b) At what temperature (in K) does the transition α-Sn(*s*) → β-Sn(*s*) occur under 50.0 atm?
(c) At what pressure is the transition temperature for α-Sn(*s*) → β-Sn(*s*) lower by 25 K?
(d) What is the slope of the $p(T)$ curve between β-Sn(*s*) and Sn(*l*) near 505 K?
(e) Estimate the hypothetical melting point of α-Sn(*s*) and its heat of fusion (in J/mol).

Phase Diagrams: Two-Component Diagrams

(45) What are mole and mass percents of

(a) Al_2O_3 in $Al_6Si_2O_{13}$;

(b) Y_2O_3 in yttrium iron garnet $Y_3Fe_5O_{12}$;

(c) SiO_2 in each phase of the CaO-SiO_2 system: Ca_3SiO_5, Ca_2SiO_4, $Ca_3Si_2O_7$, and $CaSiO_3$;

(d) P_2O_5 in each phase of the Na_2O-P_2O_5 system: Na_3PO_4, $Na_4P_2O_7$, $Na_5P_3O_{10}$, and $NaPO_3$.

(46) Sketch the T-x_{SiO_2} phase diagram between 1450°C and 2150°C for the Al_2O_3-SiO_2 system using the following information:

- Al_2O_3 melts at 2060°C and SiO_2 melts at 1720°C
- One compound, $Al_6Si_2O_{13}$, melts congruently at 1850°C
- Eutectics occur at ~5 mole percent Al_2O_3 and 1595°C and at ~67 mole percent Al_2O_3 and 1840°C.

Label the stable phase(s) for all regions in the diagram.

(47) Sketch the T-$x_{Nb_2O_5}$ phase diagram between 550°C and 1550°C for the Na_2O-Nb_2O_5 system using the following information:

- Na_2O melts at ~1200°C and Nb_2O_5 melts at 1485°C
- There are two congruently melting compounds, Na_3NbO_4 at 992°C and $NaNbO_3$ at 1412°C
- There are two incongruently melting compounds, $Na_2Nb_8O_{21}$ at 1265°C to $Na_2Nb_{20}O_{51}$ and liquid, and $Na_2Nb_{20}O_{51}$ at 1290°C to Nb_2O_5 and liquid
- Eutectics occur at ~10 mole percent Nb_2O_5 and 830°C, ~31 mole percent Nb_2O_5 and 975°C, and ~68 mole percent Nb_2O_5 and 1220°C
- $NaNbO_3$ undergoes a polymorphic transition at 640°C.

(48) Sketch a qualitative T-$x_{\mathbf{B}}$ phase diagram for a system **A-B** that has the following features:

- $\mathbf{A_2B}$ and $\mathbf{AB_2}$ are congruently melting compounds with melting points above those of **A** and **B**
- **AB** melts incongruently to give $\mathbf{A_2B}$ and a liquid and has a lower limit of stability with respect to $\mathbf{A_2B}$ and $\mathbf{AB_2}$

(49) The KCl-$FeCl_2$ pseudobinary system has the following characteristics:

- KCl melts at 776°C; $FeCl_2$ melts at 677°C.
- There are two compounds, $KFeCl_3$ and K_2FeCl_4. $KFeCl_3$ melts congruently at 400°C, whereas K_2FeCl_4 melts incongruently at 385°C. Also, $KFeCl_3$ and K_2FeCl_4 undergo polymorphic transformations at, respectively, 290°C and 255°C.
- There are two eutectic points: (1) at 38 mole percent $FeCl_2$ and 355°C; and (2) at 54 mole percent $FeCl_2$ and 390°C.
- The solubility of $FeCl_2$ in KCl(*l*) reaches the peritectic melting temperature of K_2FeCl_4 at 34 mole percent $FeCl_2$.

(a) Sketch the T-x_{FeCl_2} phase diagram between 150°C and 850°C for this system. Identify the stable phases in each region of the diagram.

(b) Write the chemical equations for the equilibria at each eutectic point.

(c) For a specimen prepared at 42 mole percent $FeCl_2$, describe the equilibrium phases that will exist as the liquid mixture is cooled slowly from 500°C to 200°C.

(50) The KCl-$MnCl_2$ pseudobinary system has the following characteristics:

- KCl melts at 776°C; $MnCl_2$ melts at 652°C.
- There are three compounds, $KMnCl_3$, $K_3Mn_2Cl_7$, and K_4MnCl_6. $KMnCl_3$ melts congruently at 490°C, whereas K_4MnCl_6 and $K_3Mn_2Cl_7$ melt peritectically at, respectively, 448°C and 437°C. Also, $KMnCl_3$ undergoes a polymorphic transformation at 386°C.
- There are two eutectic points: (1) at 33 mole percent $MnCl_2$ and 420°C; and (2) at 63 mole percent $MnCl_2$ and 448°C.
- The solubility of $MnCl_2$ in KCl(*l*) reaches the peritectic melting temperature of K_4MnCl_6 at 29 mole percent $MnCl_2$.

(a) Sketch the T-$x_{\mathrm{MnCl_2}}$ phase diagram between 300°C and 800°C for this system. Identify the stable phases in each region of the diagram.

(b) Write the chemical equations for the equilibria at each eutectic point.

(c) For a specimen prepared at 37.5 mole percent $MnCl_2$, describe the equilibrium phases that will exist as the liquid mixture is slowly cooled from 600°C to 300°C.

(51) The NaCl-$MnCl_2$ pseudobinary system has the following characteristics:

- NaCl melts at 801°C; $MnCl_2$ melts at 652°C.
- There are four compounds, $NaMn_2Cl_5$, $NaMnCl_3$, Na_2MnCl_4, and Na_4MnCl_6. $NaMnCl_3$ melts congruently at 428°C, whereas Na_4MnCl_6, Na_2MnCl_4, and $NaMn_2Cl_5$ melt peritectically at, respectively, 458°C, 437°C, and 428°C. Also, $NaMn_2Cl_5$ undergoes a polymorphic transformation at 381°C.
- There is one clear eutectic point at 47 mole percent $MnCl_2$ and 420°C. There is a second eutectic point very close to the melting point of $NaMnCl_3$.
- The solubility of $MnCl_2$ in KCl(*l*) reaches the peritectic melting temperatures of Na_4MnCl_6 and Na_2MnCl_4 at, respectively, 38 and 41 mole percent $MnCl_2$.
- The solubility of NaCl in $MnCl_2$(*l*) reaches the peritectic melting temperature of $NaMn_2Cl_5$ at 47 mole percent NaCl.

(a) Sketch the T-$x_{\mathrm{MnCl_2}}$ phase diagram between 300°C and 550°C for this system. Identify the stable phases in each region of the diagram.

(b) Write the chemical equation for the equilibrium at the clear eutectic point.

(c) For a specimen prepared at 45 mole percent $MnCl_2$, describe the equilibrium phases that will exist as the liquid mixture is slowly cooled from 550°C to 300°C.

(d) For a specimen prepared at 60 mole percent $MnCl_2$, describe the equilibrium phases that will exist as the liquid mixture is slowly cooled from 550°C to 300°C.

(52) According to the Sr-Al phase diagram:

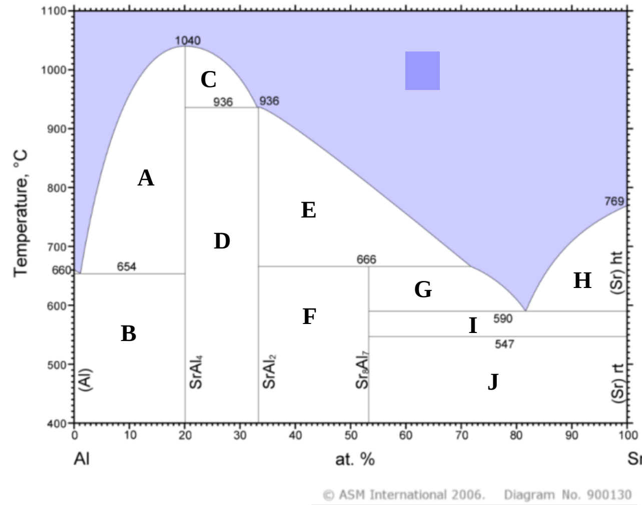
(a) Identify the equilibrium phases existing in each region **A-J**. For any liquid phase, specify the range in chemical composition.

(b) What is the meaning of the horizontal line at 547°C between **I** and **J**?

(c) Identify the temperatures where 3 phases coexist and write the balanced chemical equilibria.

(d) Describe a method to prepare single crystals of $Sr_8Al_7(s)$. Be specific.

(e) Describe what happens if a 10.00-gram sample of pure Sr_8Al_7 is slowly heated from 25°C to just above 666°C. What are the phase(s) and amounts?



(f) A sample of pure Sr_8Al_7 is heated to 1000°C. After the sample is completely molten, it is rapidly cooled to 25°C. What phases are likely to occur when the sample is analyzed at 25°C?

(53) According to the Gd-Al phase diagram:

(a) Determine the phase compositions for the following points:

(i) $800°\text{C}, x_{\text{Al}} = 0.85$;

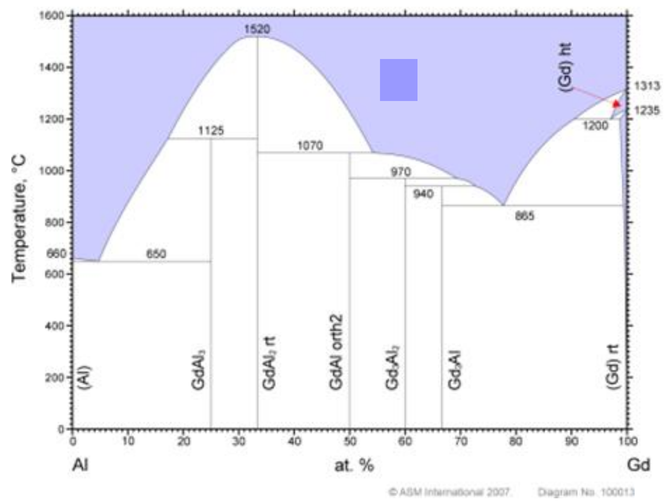
(ii) $400°\text{C}, x_{\text{Gd}} = 0.62$;

(iii) $1070°\text{C}, x_{\text{Gd}} = 0.50$;

(iv) $1400°\text{C}, x_{\text{Al}} = 0.30$.

(b) Write the *balanced chemical equilibria* that occur at: 650°C, 865°C, 940°C, 970°C, 1070°C, 1125°C, 1200°C, and 1520°C.

(c) Describe how you would prepare crystals of $GdAl_2$ if you only had access to a furnace that could achieve 1200°C as its highest temperature?



(54) According to the Sr-Cu phase diagram:

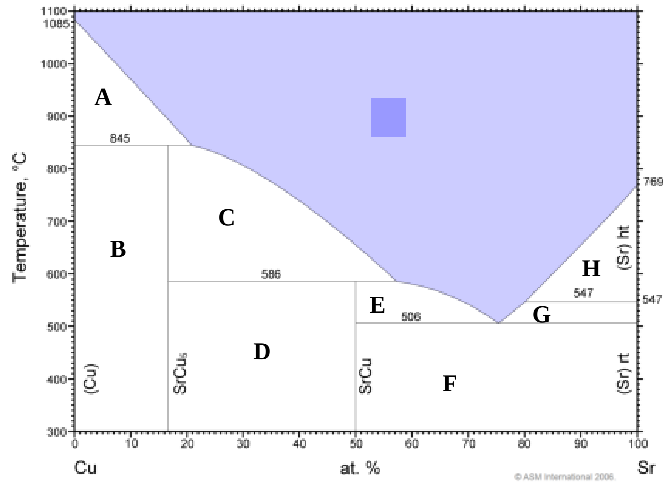
(a) Identify the equilibrium phases existing in each region **A-H**. For any liquid phase, specify the range in chemical composition.

(b) What is the meaning of the horizontal line at 547°C between **G** and **H**?

(c) Identify the temperatures where 3 phases coexist and write the balanced chemical equilibria.

(d) Describe a method to prepare single crystals of SrCu(*s*). Be specific.

(e) Describe what happens if a 5.00-gram sample of pure $SrCu_5$ is slowly heated from 25°C to just above 845°C. What are the phase(s) and amounts?



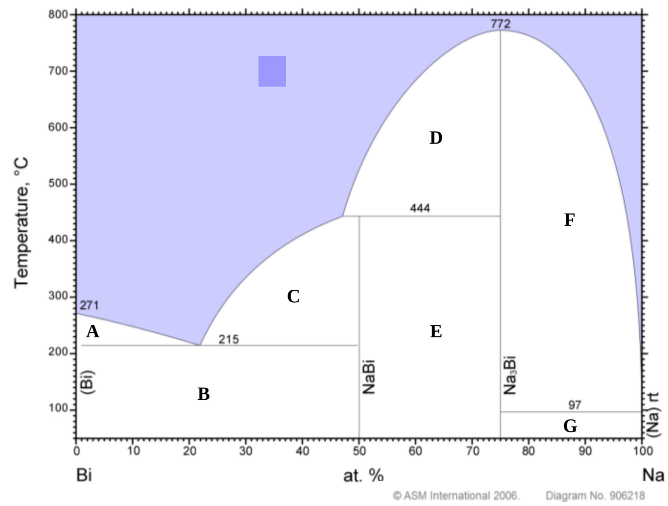
(55) According to the Bi-Na phase diagram:

(a) Identify the equilibrium phases existing in each region **A-G**. For any liquid phase, specify the range in chemical composition.

(b) Identify the temperatures where 3 phases coexist and write the balanced chemical equilibria.

(c) Describe a method to prepare single crystals of NaBi(*s*). Be specific.

(d) Describe what happens if a 5.00-gram sample of pure NaBi is slowly heated from 25°C to just above 444°C. What are the phase(s) and amounts?



(56) According to the InI-MnI_2 phase diagram:

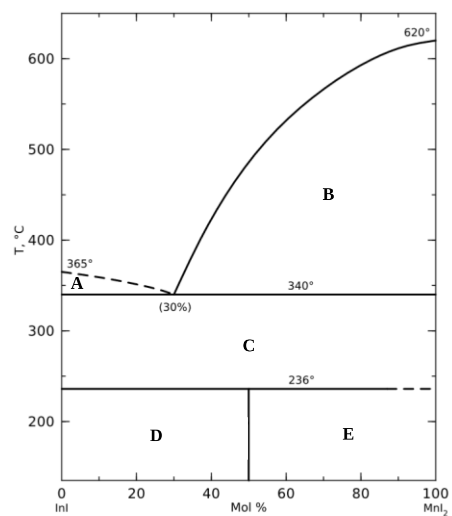
(a) Label each region of this InI-MnI_2 phase diagram.

(b) Identify the temperatures and balanced chemical equations of every 3-phase equilibrium.

(c) Describe the phase transitions that occur when a sample of $InMnI_3$(*s*) is heated from room temperature to 600°C.

(d) According to this diagram, how would you try to make $InMnI_3$?

(e) If a mixture containing 80 mole percent MnI_2 is used to grow crystals of MnI_2, what fraction of the melt can be converted to large MnI_2 crystals?

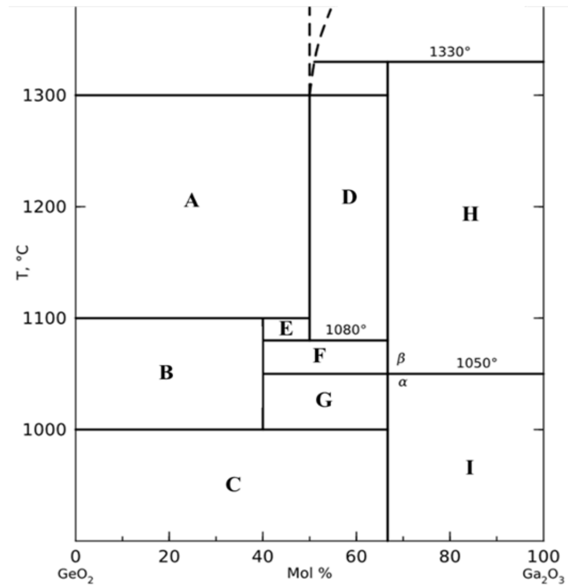


(57) For this GeO_2-Ga_2O_3 subsolidus phase diagram:

(a) Identify all ternary compounds in the diagram.

(b) Identify the phases existing in the 2-phase regions labeled **A**–**I**.

(c) Write the balanced chemical equations for all 3-phase equilibria and their temperatures.



(58) Consider a binary system **A-B** in which **A** melts at 150°C and **B** melts at 200°C. A careful examination of the system at 25°C reveals only one intermediate phase **X**. The following reactions are performed using different molar ratios with the results shown. All mixtures are first reacted in closed containers at 250°C, where the system is completely liquid, and slowly cooled to 25°C, where the system is completely solid. Thermal behavior on cooling is followed visually.

	Loaded	Thermal Behavior (Solidification)	Phases Observed at 25°C
(1)	1 **A**: 1 **B**	Starts at ~125°C; ends at ~90°C	Mostly **X** with a little **A** and **B**
(2)	1 **A**: 2 **B**	Starts at ~160°C; ends at ~90°C	Good crystals of **B**; some **X**
(3)	1 **A**: 5 **B**	Starts at ~185°C; ends at ~90°C	Good crystals of **B**; less **X** than in (2)
(4)	2 **A**: 1 **B**	Starts at ~75°C; ends at ~60°C	Good crystals of **X**; some **A**
(5)	5 **A**: 1 **B**	Starts at ~100°C; ends at ~60°C	Good crystals of **A**; some **X**

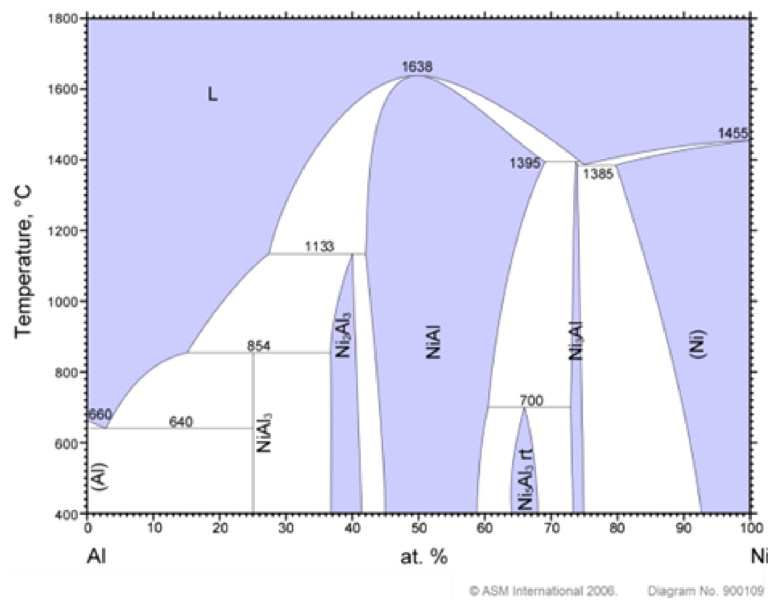
Sketch a T-$x_{\mathbf{B}}$ phase diagram for the **A-B** system consistent with these observations.

(59) Consider a binary system **A-B** in which **A** melts at 400°C and **B** melts at 600°C. A careful examination of the system at 25°C reveals only two intermediate phases **X** and **Y**, which is richer in **B** than **X**. The following reactions are performed using different molar ratios with the results shown. All mixtures are first reacted in closed containers at 850°C, where the system is completely liquid, and ended at 25°C.

	Loaded Composition	Reaction Conditions	Phases Observed
(1)	1 **A**: 2 **B**	Cool slowly	Good crystals of **Y**; **B**
(2)	2 **A**: 1 **B**	Cool slowly	**A**, **X**, and **Y**
(3)	1 **A**: 1 **B**	Quench to & anneal at 450°C, then cool rapidly	Only **X** and **Y**
(4)	3 **A**: 2 **B**	Quench to & anneal at 300°C, then cool rapidly	**A**, **X**, and **Y** (compared to (2), there is more **X**, less **A**)
(5)	3 **A**: 2 **B**	Quench to & anneal at 500°C, then cool rapidly	**A**, **X**, and **Y** (compared to (2), there is less **X**, more **A** and **Y**)
(6)	2 **A**: 3 **B**	Cool slowly	Only **Y**

Sketch a T-$x_{\mathbf{B}}$ phase diagram for the **A-B** system consistent with these observations.

(60) In the Al-Ni phase diagram:



(a) What is the maximum solubility of Al in fcc Ni(s)?

(b) What phases are in equilibrium at 800°C for an overall composition of:

15 mole percent Ni;
15 mole percent Al;
66.7 mole percent Ni;
66.7 mole percent Al.

(c) What occurs as a melt with 20 mole percent Ni is slowly cooled from 1800°C to 400°C?

(d) What are the minimum and maximum Ni contents and their corresponding temperatures for NiAl? NiAl(s) adopts the CsCl-type structure. For each case, determine the average coordination environment for every atom in NiAl(s).

(e) What is the Gibbs free energy of NiAl(s) at 1638°C relative to unmixed Al(l) and Ni(l) assuming that $Al_{1-x}Ni_x(l)$ forms an ideal solution?

(f) The cohesive energy of Ni(s) is larger than that of Al(s). Using this information and your answer to (e), provide a rationale for the shape of the NiAl homogeneity range below 1638°C.

(61) Under ambient pressure, the only compound in the Na-Cl binary system is NaCl, which is a *line compound* and has a very narrow width in composition. From the thermodynamic perspective, at ambient temperature NaCl(*s*) can exist in equilibrium when it is saturated either with Na(*s*) or Cl_2(*g*). Using the following thermodynamic information,

	ΔH_f^0(298 K) (kJ/mol)	S^0(298 K) (J/mol·K)		ΔH_f^0(298 K) (kJ/mol)	S^0(298 K) (J/mol·K)
Na(*s*)		51.2	Cl_2(g)		222.96
Na(*g*)	107.32	153.60	Cl(g)	121.68	165.09
NaCl(*s*)	–411.15	72.13			

calculate the partial pressures of Cl_2(*g*), Cl(*g*), and Na(*g*) over NaCl(*s*) at 298 K in equilibrium with

(a) Pure Na(*s*)

(b) Cl_2(*g*) at 1 atm.

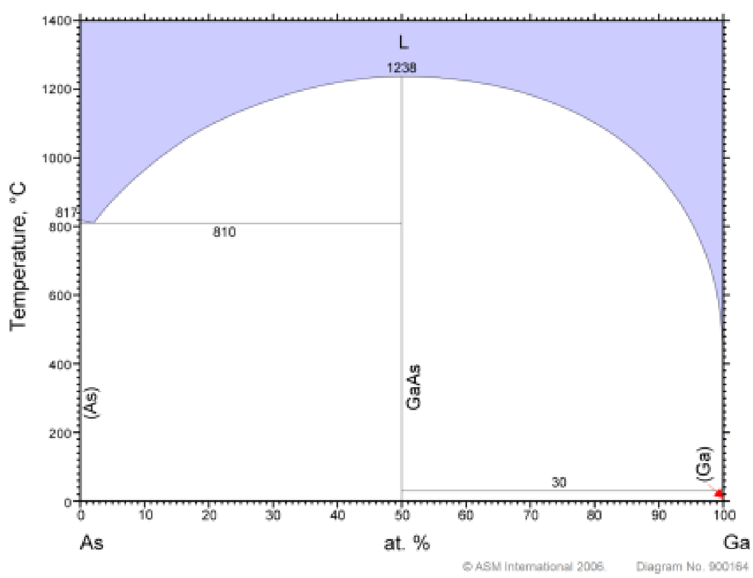
(62) According to the As-Ga phase diagram:

(a) What is the solubility of GaAs in Ga at 1000°C? How much Ga would be required to dissolve 1g of GaAs at 1000°C?

(b) What fraction of a mixture that is 30 mole percent As will be liquid at 1000°C?

(c) Arsenic sublimes at 614°C. What is the significance of the temperature 817°C at 0 at. % Ga?

(d) GaAs is the only line compound in this system. From a thermodynamic viewpoint, at ambient temperature GaAs(*s*) can exist in equilibrium when it is saturated either with Ga(*s*) or As(*s*). Using the following thermodynamic information,



	ΔH_f^0(298 K) (kJ/mol)	S^0(298 K) (J/mol·K)		ΔH_f^0(298 K) (kJ/mol)	S^0(298 K) (J/mol·K)
Ga(*s*)		40.8	As(*s*)		24.5
Ga(*g*)	272.0	169.0	As_4(*g*)	144.0	320.0
GaAs(*s*)	–67.8	64.2			

calculate the partial pressures of As_4(*g*) and Ga(*g*) over GaAs(*s*) at 298 K in equilibrium with

- Pure Ga(*s*)
- Pure As(*s*)

(63) Elements **A** and **B** form two stoichiometric compounds $\mathbf{A_2B}$ and $\mathbf{AB_2}$. The elements and the two compounds are solids up to at least 1000°C, and no solid solutions occur. **A**(*s*) is involatile, which means it has a very small vapor pressure, whereas **B**(*s*) has a measurable vapor pressure, which varies with temperature as

$$\log p_{\mathbf{B}}^{0} = -\frac{9{,}780}{T} + 5.683.$$

The vapor pressure exerted by the equilibrated mixture $\mathbf{A_2B}$-$\mathbf{AB_2}$ is $\log p_{\mathbf{B}} = -\frac{11{,}242}{T} + 6.53$ and the vapor pressure exerted by the equilibrated **A**-$\mathbf{A_2B}$ mixture is $\log p_{\mathbf{B}} = -\frac{12{,}603}{T} + 6.90$.

(a) Determine the heat of sublimation (in kJ/mol) of **B**(s).

(b) Determine $\Delta G_f^0(\mathbf{AB_2})$ and $\Delta G_f^0(\mathbf{A_2B})$ at 1000°C.

(c) Plot the activities of **A** and **B** vs. $x_{\mathbf{B}}$ for $0 \leq x_{\mathbf{B}} \leq 1$.

(64) FeO and MnO form ideal liquid and solid solutions.

FeO: $T_f = 1643$ K; $\Delta H_{\text{fus}} = 30{,}960$ J/mol

MnO: $T_f = 2148$ K; $\Delta H_{\text{fus}} = 54{,}400$ J/mol

When an equimolar solid solution is heated from room temperature,

(a) Estimate the temperature at which equilibrium melting begins.

(b) Estimate the composition of the first-formed liquid.

(c) Estimate the temperature at which the sample is completely melted.

You may assume that the molar heat capacity changes on melting for FeO and MnO is zero.

(65) MgO and NiO are both rocksalt-type solids that form complete homogeneous mixtures in the solid and liquid states.

MgO: $T_f = 2800$ K $\Delta H_{\text{fus}} = 77{,}400$ J

NiO: $T_f = 2000$ K $\Delta H_{\text{fus}} = 50{,}600$ J

Assuming that both solutions are ideal mixtures, predict:

(a) Temperature when an equimolar NiO:MgO mixture solidifies on cooling from the liquid;

(b) Composition of the first solid particles that form from the equimolar NiO:MgO mixture;

(c) Temperature when a 1:3 NiO:MgO molar mixture solidifies on cooling from the liquid;

(d) Composition of the first solid particles that form from the 1:3 NiO:MgO molar mixture;

(e) Temperature when a 2:1 NiO:MgO molar mixture solidifies on cooling from the liquid;

(f) Composition of the first solid particles that form from this 2:1 NiO:MgO molar mixture.

(66) UF_4 and ZrF_4 form continuous solid and liquid solutions. There is a eutectic point with a minimum melting temperature of 1038 K at 77 mole percent ZrF_4.

UF_4: $T_f = 1308$ K; $\Delta S_{\text{fus}} = 65.27\ \text{J/mol} \cdot \text{K}$

ZrF_4: $T_f = 1185$ K; $\Delta S_{\text{fus}} = 53.14\ \text{J/mol} \cdot \text{K}$

Assume the solid mixture is an ideal solution whereas the liquid mixture is a regular solution with the coefficient of the excess free energy term designated as Ω.

(a) Write the expression for the Gibbs free energy of the solid solution as a function of T and $x_s \equiv x_{\text{ZrF}_4,s}$ using $UF_4(s)$ and $ZrF_4(s)$ as the reference phases.

(b) Write the expression for the Gibbs free energy of the liquid solution as a function T, $x_l \equiv x_{\text{ZrF}_4,l}$, and Ω using $UF_4(s)$ and $ZrF_4(s)$ as the reference phases.

(c) At the eutectic point, $x_s = x_l \equiv x$. What are the relevant equations at this point among T, x, and Ω?

(d) If $T = 1038$ K, what does this model give for the values of x and Ω?

(e) If $x = 0.77$, what does this model give for the values of T and Ω?

(f) If $\Omega = -25{,}000$ J/mol, what does this model give for the values of T and x?

(g) Assess the usefulness of this model for the UF_4-ZrF_4 phase diagram.

(67) Cd is virtually insoluble in solid Bi, Bi is only slightly soluble in solid Cd, and the two elements are completely miscible in the liquid. They form a eutectic at 419 K and $x_{\text{Cd}} = 0.55$.

Bi: $T_f = 544$ K; $\Delta H_{\text{fus}} = 10{,}900$ J/mol

Cd: $T_f = 594$ K; $\Delta H_{\text{fus}} = 6{,}400$ J/mol

Assuming that the liquid mixture is an ideal solution, and the solids are mutually insoluble, then:

(a) Determine a relationship between T and x_{Cd} that describes the liquidus curve where Bi(s) is in equilibrium with the liquid.

(b) Determine a relationship between T and x_{Cd} that describes the liquidus curve where Cd(s) is in equilibrium with the liquid.

(c) From your answers to (a) and (b), estimate the eutectic temperature and composition. Assume the molar heat capacity change on melting is zero.

(d) Compare your answer in (c) to the experimental values. How would the ideal liquid solution be modified to account for the difference?

(68) Au and Si are mutually insoluble in the solid state and form a eutectic with eutectic temperature of 636 K and composition $x_{\text{Si}} = 0.186$.

Au: $T_f = 1336$ K; $\Delta H_{\text{fus}} = 12{,}700$ J/mol

Si: $T_f = 1683$ K; $\Delta H_{\text{fus}} = 50{,}630$ J/mol

(a) Determine a relationship between T and x_{Si} that describes the liquidus curve where Au(s) is in equilibrium with the liquid.

(b) Determine a relationship between T and x_{Si} that describes the liquidus curve where Si(s) is in equilibrium with the liquid.

(c) From your answers to (a) and (b), estimate the eutectic temperature and composition. Assume the molar heat capacity change on melting is zero.

(d) Calculate the free energy of the eutectic melt relative to unmixed Au(l) and Si(l) and unmixed Au(s) and Si(s).

(69) NaF and PbF_2 are mutually insoluble in the solid state, and they are completely miscible in the liquid.

NaF: $T_f = 1037°\text{C}$; $\Delta H_{\text{fus}} = 33{,}350\ \text{J/mol}$

PbF_2: $T_f = 851°\text{C}$; $\Delta H_{\text{fus}} = 14{,}730\ \text{J/mol}$

(a) Estimate the eutectic temperature and composition (as mole percent PbF_2) assuming that the liquid mixture is an ideal solution.

(b) According to the phase diagram, the eutectic point occurs at 542°C and 67 mole percent PbF_2. Assuming that the liquid mixture is a regular solution, deduce the interaction term in the Gibbs free energy expression of the liquid.

(70) **A** and **B** form two compounds **AB**(*s*) and $\mathbf{AB_3}$(*s*) with

A(*s*) + **B**(*s*) = **AB**(*s*): $\Delta G°(T) = -26{,}000 - 4.56T$ J/mol

A(*s*) + 3 **B**(*s*) = $\mathbf{AB_3}$(*s*): $\Delta G°(T) = -22{,}260 - 8.83T$ J/mol

A(*s*) and **B**(*s*) are mutually immiscible and both melt above 1200 K. The two compounds exist at fixed compositions. Construct the phase diagram for this system plotted as T vs. $x_{\mathbf{B}}$ for the temperature range 500 K to 1200 K.

(71) Elements **A** and **B** form three compounds $\mathbf{A_3B_2}$(*s*), **AB**(*s*), and $\mathbf{AB_2}$(*s*) which have the following Gibbs free energy of formation with respect to the solid elements:

$$\Delta G_f^0(\mathbf{A_3B_2}) = -135{,}900 + 51.20\,T$$

$$\Delta G_f^0(\mathbf{AB}) = -60{,}000 + 20.30\,T$$

$$\Delta G_f^0(\mathbf{AB_2}) = -150{,}000 + 65.31\,T$$

A(*s*) and **B**(*s*) are mutually immiscible and both melt above 3200 K. The three compounds exist at fixed compositions and no solid solutions occur. Construct the phase diagram for this system plotted as T vs. $x_{\mathbf{B}}$ for the temperature range 500 K to 3200 K.

(72) MC_2(*s*) can be equilibrated with MC(*s*) and C(*s*) at high temperature and can be equilibrated with M_2C_3(*s*) and C(*s*) at lower temperature. Using the following information, construct the T-x_{C} phase diagram for the M-C carbide system in the 1000-2500 K range:

M(*s*) + C(*s*) = MC(*s*); $\Delta G°(T) = -105{,}000 + 6.28T$ J/mol

2 M(*s*) + 3 C(*s*) = M_2C_3(*s*); $\Delta G°(T) = -236{,}800 + 25.1T$ J/mol

M(*s*) + 2 C(*s*) = MC_2(*s*); $\Delta G°(T) = -115{,}900 + 10.9T$ J/mol

(73) For a regular solution with components **A** and **B**, show that the chemical potentials $\mu_{\mathbf{A}}$ and $\mu_{\mathbf{B}}$ are $\mu_{\mathbf{A}} = RT\ln x_{\mathbf{A}} + \Omega x_{\mathbf{B}}^2$ and $\mu_{\mathbf{B}} = RT\ln x_{\mathbf{B}} + \Omega x_{\mathbf{A}}^2$.

(74) In the Mg-Si phase diagram, Mg_2Si is the only line compound, and it melts congruently at 1358 K. Furthermore, there are eutectic points for Mg_2Si(*s*) with Mg(*s*) and Mg_2Si(*s*) with Si(*s*). Assuming all liquid mixtures exhibit regular solution behavior, and all solids are completely immiscible, evaluate the liquidus curve $T(x_{\text{Si}})$ and construct the Mg-Si phase diagram using the following information:

Mg: $T_f = 921$ K $\Delta G_{\text{fus}} = 8{,}790 - 9.54\,T$ (J/mol)

Si: $T_f = 1688$ K $\Delta G_{\text{fus}} = 50{,}630 - 30.0\,T$ (J/mol)

2 Mg(*l*) + Si(*s*) ⇌ Mg_2Si(*s*) $\Delta G° = -100{,}400 + 39.3\,T$ (J/mol)

(75) Construct a binary **A-B** phase diagram plotted as T vs x_B using the following information:

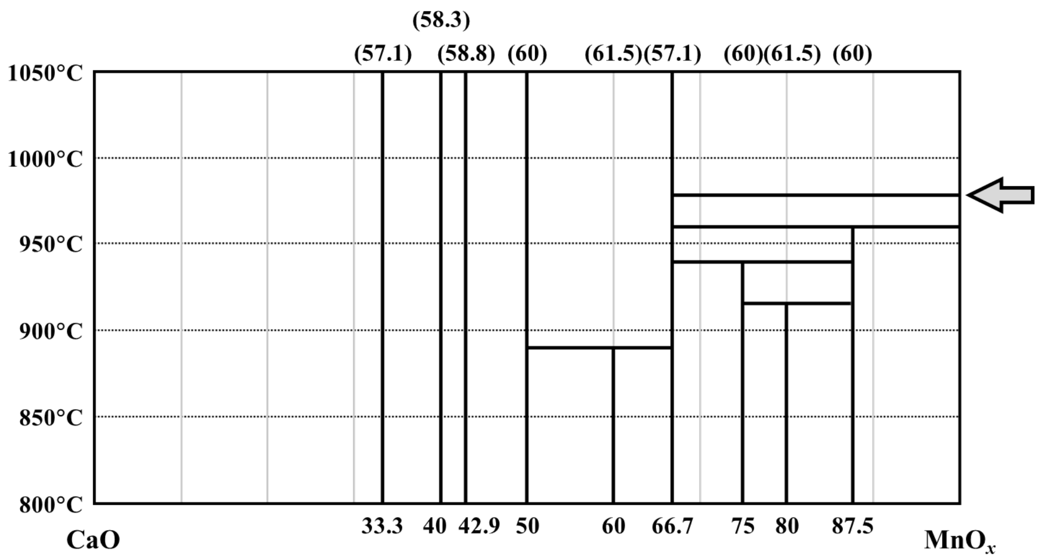
A: $T_f = 840°C$; $\Delta H_{fus} = 8{,}540$ J/mol

B: $T_f = 650°C$; $\Delta H_{fus} = 8{,}480$ J/mol

AB$_2$: $T_f = 710°C$; $\Delta G_f^0(\mathbf{AB}) = -13{,}400 - 8.37\,T$

Assume that the liquid mixture is a regular solution.

(76) Consider the following isobaric ($p_{O_2} = 1.00$ atm) subsolidus Ca-Mn-O phase diagram:



(See H.S. Horowitz, J.M. Longo, *Mat. Res. Bull.* **1978**, *13*, 1359-1369.)

(a) The right end is labeled as "MnO$_x$" because there are three possible manganese oxides: MnO_2, Mn_2O_3, and Mn_3O_4. According to the Gibbs phase rule, how many solid manganese oxide phases can coexist for $p_{O_2} = 1.00$ atm?

(b) Determine the stable manganese oxide phase(s) vs. temperature for $p_{O_2} = 1.00$ atm.

$\Delta G_f^0(MnO_2) = -520{,}600 + 182.2\,T$

$\Delta G_f^0(Mn_2O_3) = -959{,}050 + 252.2\,T$

$\Delta G_f^0(Mn_3O_4) = -1{,}383{,}990 + 334.7\,T$

From your results, explain the arrow at the MnO$_x$ axis.

(c) Identify all the compounds in this diagram. The values at the bottom of the diagram give the mole percent MnO$_x$ in the CaO-MnO$_x$ mixture; the values at the top of the diagram give the mole percent O. These compounds contain either isovalent Mn or mixed valent Mn. Write the formulas of these compounds using these oxidation states.

(d) Write the balanced chemical equation for every 3-solid phase equilibrium in the diagram.

Chemical Vapor Transport

(77) For the transport of ZnS(*s*) using I_2 from 900° C to 800°C, estimate the transport rate (mg ZnS/hour) if sufficient iodine is added to a 20.0 cm long tube with 1.0 cm inner diameter to give 2 mg iodine/cm^3. Assume $\Delta p(I_2)$ = 0.0050 atm between the opposite ends of the tube.

(78) Write two plausible balanced chemical equilibria for the transport of Nb_3SI_7(*s*) using I_2 as a transport reagent near 800°C. Possible gas phase species include NbI_5(*g*), NbI_4(*g*), or S_2(*g*).

The solid forms in the high temperature end of the reaction tube. Using the rules for chemical transport, by which of the two reactions do you expect transport to occur? Explain your choice.

(79) Iron silicides can be transported using iodine, but, in some cases, it is not iodine that serves as the transport agent but silicon(IV) iodide. Studies of the gas phase species reveal the following possible species: FeI_2(*g*), FeI_3(*g*), SiI_2(*g*), and SiI_4(*g*).

(a) Write balanced chemical equations for the possible transport equilibria of FeSi(*s*) and $FeSi_2$(*s*) with I_2(*g*) as the transport agent.

(b) Write balanced chemical equations for the possible transport equilibria of FeSi(*s*) and $FeSi_2$(*s*) with SiI_4(*g*) as the transport agent.

(c) Experiments show that FeSi(*s*) transports from cold-to-hot whereas $FeSi_2$(*s*) transports from hot-to-cold. Which modes of chemical transport are effective for each case?

(80) Crude MCl_3(*s*) can be prepared by reacting M(*s*) with MCl_5 at 300°C. Purification of MCl_3(*s*) arises using chemical transport with MCl_5(*g*) as the transport agent, with the other gas phase species being MCl_4(*g*). FW(MCl_3) = 150.0 g/mol.

	MCl_3(*s*)	**MCl_4(*g*)**	**MCl_5(*g*)**
ΔH_f^0 (kJ/mol)	–538.1	–571.8	–710.9
$S°$ (J/K·mol)	137.2	355.6	397.5

(a) Determine the optimum median temperature (in °C) for transport.

(b) What is the direction of transport?

(c) Estimate high and low temperatures around the median temperature that would create a pressure difference of 0.2 atm in the transport tube. Assume that sufficient MCl_5 is loaded into the transport tube for an initial pressure of 1.0 atm.

(d) A transport experiment is set up using a 20.0 cm long silica tube with 1.0 cm inner diameter. Sufficient MCl_5 is loaded to create a total pressure of 1.0 atm and the temperature differential around the median transport temperature provides a pressure difference of 0.2 atm across the tube. Approximately how long would it take to transport 1.0 g MCl_3(*s*)?

(81) Consider the transport of Si(*s*) using $SiCl_4$(*g*) as the transport agent between 800ºC and 1000ºC in a tube of length 18.0 cm and 9.0 mm cross sectional diameter.

ΔG_f^0($SiCl_4$, *g*) = –659,690 + 128.5 *T* J/mol

ΔG_f^0($SiCl_2$, *g*) = –171,820 – 33.9 *T* J/mol

(a) Write the balanced chemical transport equilibrium.

(b) Determine $\Delta H°$ and $\Delta S°$ for this equilibrium. What is the direction of Si(*s*) transport?

(c) Evaluate $K(800°C)$ and $K(1000°C)$ for this equilibrium.

(d) How many moles of $SiCl_4$ are needed for a total pressure of 0.100 atm in the transport tube?

(e) Evaluate the partial pressures (in atm) of the gases in each end of the transport tube for the condition in (d).

(f) Estimate the mass (in mg) of Si(*s*) transported over 24 hours.

(82) Iron(III) oxide can be transported using HCl(*g*) and involves the gaseous species $FeCl_3$(*g*) and H_2O(*g*). (See *Z. Anorg. Allg. Chem.* **1956**, *286*, 27.) For 300–1500 K,

ΔG_f^0($FeCl_3$, *g*) = –255,890 + 23.1 *T* (J/mol) ΔG_f^0(HCl, *g*) = –93,540 – 7.1 *T* (J/mol)

ΔG_f^0(Fe_2O_3, *s*) = –816,440 + 253.5 *T* (J/mol) ΔG_f^0(H_2O, *g*) = –245,520 + 53.5 *T* (J/mol)

(a) Write the balanced chemical equilibrium describing the transport of iron(III) oxide.

(b) In what direction would iron(III) oxide be transported?

(c) A transport experiment is carried out in a 180 mm long tube, inner diameter 9 mm between 1000° and 800°C. If 4.6 μmol HCl is placed into the transport container, then

- Evaluate the initial pressure (in atm) of HCl(*g*) in each end of the transport tube. You may assume one-half the volume of the whole tube for each end.
- Estimate the difference in partial pressures of HCl(*g*) from one end of the tube to the other.
- Estimate how many grams of iron(III) oxide will be transported during 10 hours.

(83) Titanium nitride TiN(*s*) has numerous important uses due to its corrosion resistance, low toxicity, and golden color. Its melting point is 2930°C. Pure TiN(*s*) can be obtained by chemical transport at temperatures near 1200 K using HCl(*g*). Using the following thermochemical information for 300–2500 K,

ΔG_f^0(TiN, *s*) = –337,170 + 94.5 *T* (J/mol) ΔG_f^0(HCl, *g*) = –94,170 – 6.3 *T* (J/mol)

ΔG_f^0($TiCl_3$, *g*) = –543,550 + 54.4 *T* (J/mol) ΔG_f^0(NH_3, *g*) = –53,240 + 116.2 *T* (J/mol)

ΔG_f^0($TiCl_4$, *g*) = –764,990 + 123.1 *T* (J/mol)

(a) Identify four potential chemical transport equilibria. Write the balanced chemical equations.

(b) Evaluate the optimum transport temperature (in K) for each equilibrium. Explain the results.

(c) For your equilibria in (a) that support transport, determine the direction of transport (hot-to-cold or cold-to-hot)

(d) Which equilibrium will be the most influential to control transport near and just above 1200 K. Discuss your reasoning.

(84) β-ZrNCl is a surprising material because on doping with small amounts of lithium, it shows superconductivity. β-ZrNCl(s) can be prepared by subjecting ZrH_2(s) to a gaseous stream of ammonium chloride, NH_4Cl, in ammonia at 923 K.

(a) Write this balanced chemical reaction. Identify the oxidation states of all elements in both reactants and products and discuss why this reaction proceeds spontaneously at high temperatures.

Sealing ca. 0.5 g. of as-prepared β-ZrNCl(s) in an evacuated fused silica tube (8 mm diameter, 150 mm length) placed in a furnace with a temperature gradient of 1023-1123 K produces highly crystalline β-ZrNCl in the higher temperature zone. Careful analysis suggests that small amounts of ammonium chloride were present in the as-prepared sample.

(b) To understand the observed chemical transport, β-ZrNCl was combined with an excess of ammonium chloride in an evacuated glass tube and heated gently (T < 600 K). The white solid, $(NH_4)_2ZrCl_6$, forms. Write the balanced chemical equation for this reaction.

(c) Vapor pressure measurements as a function of temperature for $(NH_4)_2ZrCl_6$ show that decomposition begins just above 600 K and is complete just above 700 K with the formation of ca. 4.9 molecules of gas per mole of $(NH_4)_2ZrCl_6$. A mass spectrum shows peaks with mass numbers near 17 amu, 36 amu, 91 amu, 126 amu, 162 amu, 197 amu and 233 amu.

- What are the likely species observed in the mass spectrum?
- Write the balanced chemical reaction for the decomposition of $(NH_4)_2ZrCl_6$ above 700 K.

(d) Combine the two reactions in parts (b) and (c) to produce a net reaction that represents a proper description of the chemical transport. Is this reaction consistent with the observation that β-ZrNCl forms in the high-temperature zone via a transport mechanism? What represents the transport agent for this reaction? Estimate the time needed to transport 0.5 g of β-ZrNCl assuming 1.0 atm total pressure.

(e) Further study of $(NH_4)_2ZrCl_6$ shows that between 823 and 1173 K, it decomposes into β-ZrNCl. Above 1323 K, $(NH_4)_2ZrCl_6$ decomposes into ZrN. Write balanced chemical equations for these two decomposition reactions.

(85) Elemental silicon Si(*s*), which melts at 1414°C, can be obtained in high purity using chemical transport reactions and various transport agents. Their standard Gibbs free energies of formation between 500 K and 1600 K are listed here:

$\Delta G_f^0(SiCl_2, g) = -171{,}820 - 33.9\,T$ (J/mol)

$\Delta G_f^0(HCl, g) = -94{,}180 - 6.5\,T$ (J/mol)

$\Delta G_f^0(SiCl_4, g) = -659{,}690 + 128.5\,T$ (J/mol)

$\Delta G_f^0(HI, g) = -6{,}570 - 7.4\,T$ (J/mol)

$\Delta G_f^0(SiH_4, g) = 24{,}060 + 98.3\,T$ (J/mol)

$\Delta G_f^0(SiI_4, g) = -231{,}340 + 116.1\,T$ (J/mol)

$\Delta G_f^0(SiH_2I_2, g) = -104{,}200 + 92.3\,T$ (J/mol)

For each of the following transport agents and associated gas-phase species listed below

- Write the balanced chemical transport equilibrium and its expression for ΔG^o;
- Determine the direction of transport of Si(*s*); and
- Determine the optimal median transport temperature.

(a) Transport agent: $SiCl_4(g)$, Gas-phase species: $SiCl_2(g)$

(b) Transport agent: $HCl(g)$, Gas-phase species: $SiH_4(g)$ and $SiCl_4(g)$

(c) Transport agent: $I_2(g)$, Gas-phase species: $SiI_4(g)$

(d) Transport agent: $HI(g)$, Gas-phase species: $SiH_2I_2(g)$

(86) Si(*s*) can be transported below its melting point of 1414°C using iodine. Transport agents for this system include $I_2(g)$ or $SiI_4(g)$, and species in the gas phase include I(*g*) and $SiI_2(g)$. The reference states for the following thermodynamic information for 500−1600 K are Si(*s*) and $I_2(g)$:

$$\Delta G_f^0(\text{I}, g) = 76{,}840 - 52.9\ T\ \text{(J/mol)}$$

$$\Delta G_f^0(\text{SiI}_2, g) = 26{,}840 - 36.0\ T\ \text{(J/mol)}$$

$$\Delta G_f^0(\text{SiI}_4, g) = -231{,}340 + 116.1\ T\ \text{(J/mol)}$$

(a) Write possible transport equilibria for Si(*s*) with either $I_2(g)$ or $SiI_4(g)$ as the transport agent. For each equilibrium, determine the optimum temperature for transport and the direction of transport. Discuss the implications of your answer with respect to effective transport of Si(*s*) using iodine.

(b) Sufficient $I_2(s)$ is added to the transport tube to achieve 1.00 atm total gas pressure at 800°C. What are the approximate partial pressures of I(*g*), $I_2(g)$, $SiI_2(g)$, and $SiI_4(g)$ in the container? How many moles/cm^3 of I_2 are needed to achieve this outcome?

(87) The van Arkel-de Boer process uses iodine as a transport agent to purify transition metals well below the melting points of the metals, i.e., typically below 1000°C.

(a) As temperature increases, the tendency for gaseous halogen molecules to form halogen atoms increases. Explain this phenomenon.

(b) Given $\Delta G_f^0(\text{I}, g) = 76{,}840 - 52.9\ T$ (in J/mol), what is the dominant iodine species for temperatures below 1000°C?

(c) Fe(*s*) is transported from 800°C to 1000°C using the van Arkel-de Boer process. A study of the iron-iodine system in the gas phase identifies $FeI_2(g)$ and $Fe_2I_4(g)$ as additional prominent gas phase species. Explain the observed transport behavior of iron.

$$\Delta G_f^0(\text{FeI}_2, g) = 18{,}500 - 50.8\ T\ \text{(in J/mol)}$$

$$\Delta G_f^0(\text{Fe}_2\text{I}_4, g) = -124{,}800 + 43.6\ T\ \text{(in J/mol)}$$

(d) Evaluate the equilibrium constants at 800°C and 1000°C for the chemical equilibrium between $FeI_2(g)$ and $Fe_2I_4(g)$. Which species dominates at each temperature? Propose molecular structures for each molecule.

(88) Vanadium and silica glass react ~1000°C to form V_3Si(*s*) and VO(*s*) using iodine or vanadium chlorides as transport agents. See K.E. Spear, P.W. Gilles, H. Schäfer, *J. Less-Common Met.* **1968**, *14*, 69-75.

(a) Write the balanced chemical equation for the process described.

(b) During transport experiments using iodine, analysis of the reaction tubes indicated that V_4O(*s*) and V_2O(*s*) are solid-state intermediates during the ultimate formation of VO(*s*). Vanadium metal is activated by forming vanadium(II) iodide, which transports vanadium throughout the reaction tubes. Write the balanced chemical equations for the following reactions that may occur:

(i) The transport equilibrium for vanadium metal by iodine.

(ii) Vanadium(II) iodide reacts with silica glass in the hot end of the tube to form the vanadium silicide and V_4O(*s*) while releasing iodine vapor.

(iii) V_4O(*s*) reacts with silica glass to give the vanadium silicide and the other intermediate V_2O(*s*).

(iv) V_2O(*s*) reacts with silica glass to give the vanadium silicide and vanadium(II) oxide.

(c) During transport experiments using vanadium chlorides, vanadium(II) chloride was introduced into the reaction tube. Calculations of pressures suggested that the primary chlorinating (transport) agents are vanadium(III) chloride and silicon tetrachloride. Other gas species include silicon dichloride, vanadium dichloride, and vanadyl trichloride $VOCl_3$(*g*). Write the balanced chemical equations for the following reactions that may occur:

(i) The transport equilibrium for the vanadium silicide by vanadium(III) chloride.

(ii) The transport equilibrium for the vanadium silicide by silicon tetrachloride.

(iii) The transport equilibrium for vanadium monoxide by vanadium(III) chloride.

(iv) The transport equilibrium for vanadium monoxide by silicon tetrachloride.

(89) Aluminum melts at 660°C and can be transported using aluminum trichloride, which sublimes at 180°C, as the transport agent. In $AlCl_3$(*g*), monomers and Al_2Cl_6(*g*) exist. During transport of Al(*s*), AlCl(*g*) and $AlCl_2$(*g*) are possible gas phase species. The Gibbs free energies of formation for various important species between 300 K and 900 K are:

ΔG_f^0(AlCl, *g*) = –53,260 – 83.1 T (J/mol) ΔG_f^0($AlCl_2$, *g*) = –281,960 – 33.4 T (J/mol)

ΔG_f^0($AlCl_3$, *g*) = –585,250 + 50.3 T (J/mol) ΔG_f^0(Al_2Cl_6, *g*) = –1,293,510 + 244.4 T (J/mol)

(a) 15.0 mg $AlCl_3$(*g*) is loaded into a sealed tube of volume 15.7 cm^3. Plot the partial pressures of $AlCl_3$(*g*) and Al_2Cl_6(*g*) and the total pressure (in atm) as a function of temperature between 180°C and 650°C. Discuss the implications of these results for transport of Al(*s*).

(b) Write the balanced chemical equations for the possible transport equilibria. For each equilibrium that supports transport, what is the direction of transport of aluminum and the optimum median transport temperature?

(c) $AlCl_2$(*g*) can disproportionate into $AlCl_3$(*g*) and AlCl(*g*). For what temperatures, is this reaction favored? What are the implications of this outcome for transporting Al?