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.

This is a heterogeneous reaction involving 3 distinct pure phases. There is no equilibrium constant, but stability is determined by the overall lowest Gibbs free energy. Since $\Delta G° < 0$, $Mg_2TiO_4(s)$ will co-exist with *either* $MgO(s)$ or $TiO_2(s)$ unless there is an exact 2:1 molar ratio between MgO and TiO_2.

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

 # moles MgO = 0.9925 mol; #moles TiO_2 = 2.0039 mol

There is an excess of TiO_2. 0.9925 mol MgO will consume 0.4963 mol TiO_2 to form 0.4963 mol Mg_2TiO_4. Then, 1.5076 mol TiO_2 remains.

At equilibrium: 79.6 g Mg_2TiO_4 and 120.4 g TiO_2

(b) 80.0 g Mg_2TiO_4 and 20.0 g MgO

 # moles Mg_2TiO_4 = 0.4985 mol; #moles MgO = 0.4962 mol

Mg_2TiO_4 has a lower Gibbs free energy than a mixture of MgO and TiO_2. No reaction occurs.

At equilibrium: 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

 # moles Mg_2TiO_4 = 0.9971 mol; # moles MgO = 0.9925 mol; #moles TiO_2 = 1.0017 mol

Mg_2TiO_4 has a lower Gibbs free energy than a mixture of MgO and TiO_2. There is an excess of TiO_2. 0.9925 mol MgO will consume 0.4963 mol TiO_2 to form 0.4963 mol Mg_2TiO_4. Then, 0.5055 mol TiO_2 remains and there are 1.4934 mol Mg_2TiO_4.

At equilibrium: 239.6 g Mg_2TiO_4 and 40.4 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.

This is a heterogeneous reaction involving 3 distinct pure phases. There is no equilibrium constant, but stability is determined by the overall lowest Gibbs free energy. Since $\Delta G° > 0$, $FeCl_2(s)$ will co-exist with *either* $Fe(s)$ or $FeCl_3(s)$ unless there is an exact 1:2 molar ratio between Fe and $FeCl_3$.

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

 # moles $FeCl_2$ = 0.9862 mol; #moles Fe = 1.0028 mol

$FeCl_2$ has a lower Gibbs free energy than a mixture of Fe and $FeCl_3$. No reaction occurs.

At equilibrium: 125.0 g $FeCl_2$ and 56.0 g Fe

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

 # moles $FeCl_3$ = 0.9865 mol; #moles Fe = 1.0028 mol

There is an excess of Fe. 0.9865 mol $FeCl_3$ will consume 0.4933 mol Fe to form 1.4798 mol $FeCl_2$. Then, 0.5095 mol Fe remains.

At equilibrium: 187.5 g $FeCl_2$ and 28.5 g Fe

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

#moles Fe = 2.0056 mol # moles $FeCl_3$ = 0.9865 mol; # moles $FeCl_2$ = 0.4931 mol

$FeCl_2$ has a lower Gibbs free energy than a mixture of Fe and $FeCl_3$. There is an excess of Fe. 0.9865 mol $FeCl_3$ will consume 0.4933 mol Fe to form 1.4798 mol $FeCl_2$. Then, 1.5123 mol Fe remains and there are 1.9729 mol $FeCl_2$.

At equilibrium: 250.1 g $FeCl_2$ and 84.4 g Fe

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

This is a homogeneous reaction involving 1 distinct phase and 3 species. The equilibrium constant is

$$K_p(500\ K) = e^{-(-7388)/(4157)} = e^{1.777} = 5.914 = \frac{p^2_{BrCl}}{p_{Br_2}p_{Cl_2}}.$$

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

To achieve equilibrium, Br_2 and Cl_2 react to form BrCl. Therefore, the initial partial pressures of Br_2 and Cl_2 will be reduced by the same value x. As a result, $2x$ will be the equilibrium partial pressure of BrCl at equilibrium. Then, we need to solve $\frac{(2x)^2}{(2-x)(1-x)} = 5.914$. After a little algebra, the quadratic equation to solve is $1.914x^2 - 17.742x + 11.828 = 0$. The solutions are $x = 8.547$ and $x = 0.723$. Only the second solution is chemically valid.

At equilibrium: 1.277 atm Br_2, 0.277 atm Cl_2, and 1.446 atm BrCl.

(b) 2.00 atm BrCl

To achieve equilibrium, BrCl reacts to form Br_2 and Cl_2. Therefore, the partial pressures of Br_2 and Cl_2 will be grow to the same value x. As a result, in initial pressure of BrCl will be reduced by $2x$. Then, we need to solve $\frac{(2-2x)^2}{(x)(x)} = 5.914$. After a little algebra, the quadratic equation to solve is $1.914x^2 + 8x - 4 = 0$. The solutions are $x = -4.631$ and $x = 0.451$. Only the second solution is chemically valid.

At equilibrium: 0.451 atm Br_2, 0.451 atm Cl_2, and 1.098 atm BrCl.

(c) 2.00 atm BrCl and 1.00 atm Cl_2

To achieve equilibrium, BrCl reacts to form Br_2 and Cl_2. Therefore, the initial partial pressures of Br_2 and Cl_2 will be grow by the same value x. As a result, in initial pressure of BrCl will be reduced by $2x$. Then, we need to solve $\frac{(2-2x)^2}{(x)(1+x)} = 5.914$. After a little algebra, the quadratic equation to solve is $1.914x^2 + 13.914x - 4 = 0$. The solutions are $x = -7.547$ and $x = 0.277$. Only the second solution is chemically valid.

At equilibrium: 0.277 atm Br_2, 1.277 atm Cl_2, and 1.446 atm BrCl.

(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.

Use the Arrhenius-type expression: $D(T) = D_0 e^{-Q/RT}$

$$D(500°C) = D(773.15\ K) = (2.8\ cm^2/sec)e^{-39.048} = 3.1 \times 10^{-17}\ cm^2/sec$$

$$D(900°C) = D(1173.15\ K) = (2.8\ cm^2/sec)e^{-25.734} = 1.9 \times 10^{-11}\ cm^2/sec$$

Both temperatures are below the melting temperature of iron. The self-diffusion coefficient increases over this 400 K range by a factor of ~600,000. The BCC structure is not the densest packing of atoms, but it is denser than network structures.

(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.

$$\boldsymbol{D_\alpha(910°\mathrm{C}) = D_\alpha(1183.15\ \mathrm{K}) = (2.8\ \mathrm{cm^2/sec})e^{-25.517} = 2.3\times 10^{-11}\ \mathrm{cm^2/sec}}$$
$$\boldsymbol{D_\gamma(910°\mathrm{C}) = D_\gamma(1183.15\ \mathrm{K}) = (0.49\ \mathrm{cm^2/sec})e^{-28.871} = 1.4\times 10^{-13}\ \mathrm{cm^2/sec}}$$

The self-diffusion coefficient for BCC Fe is ~160× or 0.6% larger than that for FCC Fe. The change arising from the different D_0 values accounts for a factor of 5.7; the change arising from the different activation energies Q accounts for a factor of 28.6.

The BCC structure is ~0.9% less dense than the FCC structure. Therefore, movement of atoms through the more densely packed structure manifests a larger diffusion coefficient.

(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.

$$\boldsymbol{D_{\mathrm{Cu}}(300\ \mathrm{K}) = (1.64\ \mathrm{cm^2/sec})e^{-87.403} = 1.80\times 10^{-38}\ \mathrm{cm^2/sec}}$$
$$\boldsymbol{D_{\mathrm{Zn}}(300\ \mathrm{K}) = (0.24\ \mathrm{cm^2/sec})e^{-75.776} = 2.96\times 10^{-34}\ \mathrm{cm^2/sec}}$$

The diffusion coefficient for Zn in FCC Cu is ~16000× larger than that for Cu in FCC Cu, and this outcome arises largely from the differences in activation energies for substitutional diffusion. According to the unit cell information, the volumes of Cu and Zn atoms are, respectively, ~11.8 Å^3 and ~15.2 Å^3. Although Zn atoms are larger than Cu atoms, in the FCC Cu "matrix" and according to these results, Zn atoms will tend to move faster and farther, on average, than Cu atoms in FCC Cu. Perhaps there is an electronic rationale: Zn is more electropositive than Cu. In a FCC Cu matrix, Zn atoms may appear smaller from a small degree of electron transfer into the Cu-rich conduction band. However, this assessment is speculative.

(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?

$$\boldsymbol{\frac{D(350°\mathrm{C})}{D(300°\mathrm{C})} = \frac{D(623\ \mathrm{K})}{D(573\ \mathrm{K})} = \frac{e^{-8.012}}{e^{-8.711}} = 2.012}$$
$$\boldsymbol{D(350°\mathrm{C}) = (2.012)(7.8\times 10^{-11}\ \mathrm{m^2/sec}) = 1.6\times 10^{-10}\ \mathrm{m^2/sec}}$$

(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.

$$\boldsymbol{\frac{D(1000°\mathrm{C})}{D(500°\mathrm{C})} = \frac{D(1273\ \mathrm{K})}{D(773\ \mathrm{K})} = \frac{7.0\times10^{-13}}{1.0\times10^{-17}} = 70{,}000 = \frac{e^{-Q/10583.7}}{e^{-Q/6426.7}} = e^{Q/16362.3}}$$
$$\boldsymbol{Q = (16{,}362.3\ \mathrm{J/mol})(\ln 70{,}000) = 182{,}542\ \mathrm{J/mol} = 183\ \mathrm{kJ/mol}}$$

(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.

Cr atoms diffuse via vacancies in BCC Fe whereas N atoms diffuse interstitially. As a result, N atoms should have larger diffusion coefficients than Cr, which is largely represented by a much lower activation energy *Q*. The temperature differences are related by a factor ~1.2, which will probably cause a smaller change than the differences in *Q*. Using these arguments, the following trend for diffusion coefficients is expected:

$$\boldsymbol{D_{\mathrm{N}}(900°\mathrm{C}) > D_{\mathrm{N}}(700°\mathrm{C}) > D_{\mathrm{Cr}}(900°\mathrm{C}) > D_{\mathrm{Cr}}(700°\mathrm{C}).}$$

(**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.

$$\boldsymbol{D_{\mathrm{Ge\ in\ Ge}}(500\ \mathrm{K}) = (13.6\ \mathrm{cm^2/sec})e^{-71.686} = 1.00 \times 10^{-30}\ \mathrm{cm^2/sec}}$$

$$\boldsymbol{D_{\mathrm{Ge\ in\ Cu}}(500\ \mathrm{K}) = (0.40\ \mathrm{cm^2/sec})e^{-44.984} = 1.16 \times 10^{-20}\ \mathrm{cm^2/sec}}$$

$$\boldsymbol{D_{\mathrm{Ge\ in\ Al}}(500\ \mathrm{K}) = (0.48\ \mathrm{cm^2/sec})e^{-29.108} = 1.10 \times 10^{-13}\ \mathrm{cm^2/sec}}$$

The diamond-type structure is a 3-d, 4-connected tetrahedral network, whereas FCC is a dense packing of atomic spheres. Ge will diffuse through these structures via the substitutional or vacancy diffusion mechanism.

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

$$\boldsymbol{R_c} \sim \frac{\mathbf{2(0.178)(7.114)(1357)}}{\mathbf{(236)(13260)}} \cdot \frac{\mathbf{1}}{\mathbf{10^6}} = \mathbf{1.098 \times 10^{-9}\ m = 10.98}\ \text{Å}$$

For FCC Cu, the volume per Cu atom = (3.615 Å)^3/4 = 11.81 Å^3.

Volume of the spherical nucleus with critical radius = (4π/3)(10.98 Å)^3 = 5544.9 Å^3

 # atoms in the spherical nucleus with critical radius = (5544.9) / (11.81) ~ 470 Cu atoms.

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

$$\boldsymbol{R_c} \sim \frac{\mathbf{2(0.069)(18.268)(600)}}{\mathbf{(80)(4770)}} \cdot \frac{\mathbf{1}}{\mathbf{10^6}} = \mathbf{3.964 \times 10^{-9}\ m = 39.64}\ \text{Å}$$

For FCC Pb, the volume per Pb atom = (4.951 Å)^3/4 = 30.34 Å^3.

Volume of the spherical nucleus with critical radius = (4π/3)(39.64 Å)^3 = 260909.3 Å^3

 # atoms in the spherical nucleus with critical radius = (260909.3) / (30.34) ~ 8600 Pb atoms.

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

For Sn: $\Delta T_{\max} = 191$ 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

$$\boldsymbol{R_c} \sim \frac{2(0.075)(16.291)(505)}{(191)(7030)} \cdot \frac{1}{10^6} = \mathbf{9.191 \times 10^{-10}\ m = 9.19\ \text{Å}}$$

Since 8.00 Å < 9.19 Å, this nucleus will dissolve in the supercooled liquid.

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

For Cu: $\Delta T_{\max} = 236$ 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

$$\boldsymbol{R_c} \sim \frac{2(0.178)(7.114)(1357)}{(236)(13260)} \cdot \frac{1}{10^6} = \mathbf{1.098 \times 10^{-9}\ m = 10.98\ \text{Å}}$$

Since 15.00 Å > 10.98 Å, this nucleus will continue to grow.

(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

For 15.0 Å radius sphere:
Volume = $(4\pi/3)(15.0\ \text{Å})^3 = 14137.2\ \text{Å}^3 = 1.414 \times 10^{-20}$ cm^3.
Surface Area = $(4\pi)(15.0\ \text{Å})^2 = 2827.4\ \text{Å}^2 = 2.827 \times 10^{-17}$ m^2
Surface Free Energy = $(0.178)(2.827 \times 10^{-17}) = 5.033 \times 10^{-18}$ J
Volume Free Energy = $-(2308)(1.414 \times 10^{-20})/(7.114) = -4.587 \times 10^{-18}$ J

For 10.0 Å radius sphere:
Volume = $(4\pi/3)(10.0\ \text{Å})^3 = 4188.8\ \text{Å}^3 = 4.189 \times 10^{-21}$ cm^3.
Surface Area = $(4\pi)(15.0\ \text{Å})^2 = 1256.6\ \text{Å}^2 = 1.257 \times 10^{-17}$ m^2
Surface Free Energy = $(0.178)(1.257 \times 10^{-17}) = 2.237 \times 10^{-18}$ J
Volume Free Energy = $-(2308)(4.189 \times 10^{-21})/(7.114) = -1.359 \times 10^{-18}$ J

For 20.0 Å radius sphere:
Volume = $(4\pi/3)(20.0\ \text{Å})^3 = 33510.3\ \text{Å}^3 = 3.351 \times 10^{-20}$ cm^3.
Surface Area = $(4\pi)(20.0\ \text{Å})^2 = 5026.5\ \text{Å}^2 = 5.027 \times 10^{-17}$ m^2
Surface Free Energy = $(0.178)(5.027 \times 10^{-17}) = 8.948 \times 10^{-18}$ J
Volume Free Energy = $-(2308)(3.351 \times 10^{-20})/(7.114) = -1.087 \times 10^{-17}$ J

Changing from 15.0 Å to 20.0 Å:
ΔG(surface) = $+3.915 \times 10^{-18}$ J; **ΔG(volume) = -6.283×10^{-18} J**

Changing from 15.0 Å to 10.0 Å:
ΔG(surface) = -2.796×10^{-18} J; **ΔG(volume) = $+3.228 \times 10^{-18}$ J**

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).

***S* = 4**	**$MO_x(ss)$**	**$O_2(g)$**	**$Cl_2(g)$**	**$OCl(g)$**
M	**1**	**0**	**0**	**0**
O	***x***	**2**	**0**	**1**
Cl	**0**	**0**	**2**	**1**

To determine independent net reactions, this matrix must be row-reduced:

***S* = 4**	**$MO_x(ss)$**	**$O_2(g)$**	**$Cl_2(g)$**	**$OCl(g)$**
M	**1**	**0**	**0**	**0**
O	**0**	**1**	**0**	**1/2**
Cl	**0**	**0**	**1**	**1/2**

Then follow by a "change of basis" by switching the first 3 column headings with the row headings:

***S* = 4**	**M**	**O**	**Cl**	**$OCl(g)$**
$MO_x(ss)$	**1**	**0**	**0**	**0**
$O_2(g)$	**0**	**1**	**0**	**1/2**
$Cl_2(g)$	**0**	**0**	**1**	**1/2**

There is 1 independent net reaction:

$$OCl(g) \rightleftharpoons \frac{1}{2} O_2(g) + \frac{1}{2} Cl_2(g)$$

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

All species originate from $MOCl_2(s)$. Let n_0 = # moles $MOCl_2$ introduced into the chamber. Then, at equilibrium:

 # moles M = (# moles MO_x) = n_0

 # moles O = x(# moles MO_x) + 2(# moles O_2) = n_0

 # moles Cl = 2(# moles Cl_2) + (# moles OCl) = $2n_0$

Then,

$(1 - x)$(# moles MO_x) = 2(# moles O_2) and

2(# moles MO_x) = 2(# moles Cl_2) + (# moles OCl).

Therefore, $\frac{2}{1-x}$(# moles O_2) = 2(# moles Cl_2) + (# moles OCl), which is 1 restraint among partial pressures (mole fractions) of the gas phase species: $\frac{2}{1-x} p_{O_2} = 2p_{Cl_2} + p_{OCl}$.

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

 # components C = 3; # phases P = 2 = $MO_x(ss)$ and gas mixture; # additional restraints ρ = 1

 # degrees of freedom $F = C - P + 2 - \rho = 3 - 2 + 2 - 1 = 2$.

Two degrees of freedom mean there are two independent intensive variables for this system. For example, if the total pressure and temperature are both fixed, then the solubility of O in M, $MO_x(ss)$ will adopt a certain value.

(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).

***S* = 6**	**La_2O_3(*s*)**	**SO(*g*)**	**O_2(*g*)**	**La_2S_3(*s*)**	**La_2O_2S(*s*)**	**SO_2(*g*)**
La	**2**	**0**	**0**	**2**	**2**	**0**
S	**0**	**1**	**0**	**3**	**1**	**1**
O	**3**	**1**	**2**	**0**	**2**	**2**

To determine independent net reactions, this matrix must be row-reduced:

***S* = 6**	**La_2O_3(*s*)**	**SO(*g*)**	**O_2(*g*)**	**La_2S_3(*s*)**	**La_2O_2S(*s*)**	**SO_2(*g*)**
La	**1**	**0**	**0**	**1**	**1**	**0**
S	**0**	**1**	**0**	**3**	**1**	**1**
O	**0**	**0**	**1**	**–3**	**–1**	**1/2**

Then follow by a "change of basis" by switching the first 3 column headings with the row headings:

***S* = 6**	**La**	**S**	**O**	**La_2S_3(*s*)**	**La_2O_2S(*s*)**	**SO_2(*g*)**
La_2O_3(*s*)	**1**	**0**	**0**	**1**	**1**	**0**
SO(*g*)	**0**	**1**	**0**	**3**	**1**	**1**
O_2(*g*)	**0**	**0**	**1**	**–3**	**–1**	**1/2**

There are 3 independent net reactions:

$$La_2S_3(s) + 3\,O_2(g) \rightleftharpoons La_2O_3(s) + 3\,SO(g)$$

$$La_2O_2S(s) + O_2(g) \rightleftharpoons La_2O_3(s) + SO(g)$$

$$SO_2(g) \rightleftharpoons SO(g) + \tfrac{1}{2}\,O_2(g)$$

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

$$La_2S_3(s) + \tfrac{9}{2}\,O_2(g) \rightleftharpoons La_2O_3(s) + 3\,SO_2(g)$$

$$La_2O_2S(s) + \tfrac{3}{2}\,O_2(g) \rightleftharpoons La_2O_3(s) + SO_2(g)$$

$$La_2S_3(s) + 3\,O_2(g) \rightleftharpoons La_2O_2S(s) + 2\,SO_2(g)$$

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

 # components *C* = 3; # phases *P* = 4 = La_2O_3(*s*), La_2S_3(*s*), La_2O_2S(*s*), and gas mixture.

 # degrees of freedom $F = C - P + 2 = 3 - 4 + 2 = 1$.

One degree of freedom implies that if any intensive variable is fixed, all others must adopt certain values. The most convenient intensive variables to fix are either temperature or total pressure.

(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).

***S* = 7**	**Ti(*g*)**	**CO(*g*)**	**$O_2(g)$**	**TiO(*g*)**	**Ti(*ss*)**	**O(*ss*)**	**C(*ss*)**
Ti	**1**	**0**	**0**	**1**	**1**	**0**	**0**
C	**0**	**1**	**0**	**0**	**0**	**0**	**1**
O	**0**	**1**	**2**	**1**	**0**	**1**	**0**

To determine independent net reactions, this matrix must be row-reduced:

***S* = 7**	**Ti(*g*)**	**CO(*g*)**	**$O_2(g)$**	**TiO(*g*)**	**Ti(*ss*)**	**O(*ss*)**	**C(*ss*)**
Ti	**1**	**0**	**0**	**1**	**1**	**0**	**0**
C	**0**	**1**	**0**	**0**	**0**	**0**	**1**
O	**0**	**0**	**1**	**1/2**	**0**	**1/2**	**–1/2**

Then follow by a "change of basis" by switching the first 3 column headings with the row headings:

***S* = 7**	**Ti**	**C**	**O**	**TiO(*g*)**	**Ti(*ss*)**	**O(*ss*)**	**C(*ss*)**
Ti(*g*)	**1**	**0**	**0**	**1**	**1**	**0**	**0**
CO(*g*)	**0**	**1**	**0**	**0**	**0**	**0**	**1**
$O_2(g)$	**0**	**0**	**1**	**1/2**	**0**	**1/2**	**–1/2**

There are 4 independent net reactions:

$$TiO(g) \rightleftharpoons Ti(g) + \frac{1}{2} O_2(g)$$

$$Ti(ss) \rightleftharpoons Ti(g)$$

$$O(ss) \rightleftharpoons \frac{1}{2} O_2(g)$$

$$C(ss) + \frac{1}{2} O_2(g) \rightleftharpoons CO(g)$$

(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).

***S* = 6**	**Ti(*g*)**	**CO(*g*)**	**$O_2(g)$**	**TiO(*g*)**	**TiO(*ss*)**	**TiC(*ss*)**
Ti	**1**	**0**	**0**	**1**	**1**	**1**
C	**0**	**1**	**0**	**0**	**0**	**1**
O	**0**	**1**	**2**	**1**	**1**	**0**

To determine independent net reactions, this matrix must be row-reduced:

***S* = 6**	**Ti(*g*)**	**CO(*g*)**	**$O_2(g)$**	**TiO(*g*)**	**TiO(*ss*)**	**TiC(*ss*)**
Ti	**1**	**0**	**0**	**1**	**1**	**1**
C	**0**	**1**	**0**	**0**	**0**	**1**
O	**0**	**0**	**1**	**1/2**	**1/2**	**–1/2**

Then follow by a "change of basis" by switching the first 3 column headings with the row headings:

***S* = 6**	**Ti**	**C**	**O**	**TiO(*g*)**	**TiO(*ss*)**	**TiC(*ss*)**
Ti(*g*)	**1**	**0**	**0**	**1**	**1**	**1**
CO(*g*)	**0**	**1**	**0**	**0**	**0**	**1**
O_2(*g*)	**0**	**0**	**1**	**1/2**	**1/2**	**–1/2**

There are 3 independent net reactions:

$TiO(g) \rightleftharpoons Ti(g) + \frac{1}{2} O_2(g)$

$TiO(ss) \rightleftharpoons Ti(g) + \frac{1}{2} O_2(g)$

$TiC(ss) + \frac{1}{2} O_2(g) \rightleftharpoons Ti(g) + CO(g)$

(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.

 # components *C* = 3; # phases *P* = 2 = $TiO_xC_{1-x}(ss)$ solid solution and gas mixture.

There is one restraint set by the experimental procedure: Let n_0 = # moles $TiO_xC_{1-x}(ss)$. At equilibrium and using the atomic solid solution components,

 # moles Ti = (# moles Ti(*ss*)) + (# moles TiO(*g*)) + (# moles Ti(*g*)) = n_0

 # moles O = *x*(# moles O(*ss*)) + (# moles TiO(*g*)) + 2(# moles O_2(*g*)) = xn_0

 # moles C = (1–*x*)(# moles C(*ss*)) + (# moles CO(*g*)) = $(1-x)n_0$

Since (# moles Ti(*ss*)) = *x*(# moles O(*ss*)) + (1–*x*)(# moles C(*ss*)), then

(# moles Ti(*g*)) – (# moles CO(*g*)) – 2(# moles O_2(*g*)) = 0 or $p_{Ti} - p_{CO} - 2p_{O_2} = 0$.

 # degrees of freedom *F* = *C* – *P* + 2 – 1 = 3 – 2 + 2 – 1 = 2.

If we formulate the solid solution using TiO(*ss*) and TiC(*ss*), then the same restraint arises:

 # moles Ti = *x*(# moles TiO(*ss*)) + (1–*x*)(# moles TiC(*ss*)) + (# moles TiO(*g*)) + (# moles Ti(*g*)) = n_0

 # moles O = *x*(# moles TiO(*ss*)) + (# moles TiO(*g*)) + 2(# moles O_2(*g*)) = xn_0

 # moles C = (1–*x*)(# moles TiC(*ss*)) + (# moles CO(*g*)) = $(1-x)n_0$

(# moles Ti(*g*)) – (# moles CO(*g*)) – 2(# moles O_2(*g*)) = 0 or $p_{Ti} - p_{CO} - 2p_{O_2} = 0$.

Therefore, the two descriptions of the system yield the same # degrees of freedom. Therefore, any 2 intensive variables are freely varying. Two convenient variables to consider are temperature and total pressure.

(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

The reaction is $Ag_2O(s) \longrightarrow 2\,Ag(s) + ½\,O_2(g)$; $K = p_{O_2}^{1/2}$ and $\Delta G° = 30,540 - 66.11T = -8.314T \ln p_{O_2}^{1/2}$.

(a) In pure oxygen at 1 atm, decomposition occurs when $30,540 - 66.11T < 0$, or $T > 462$ K.

(b) In air at 1 atm, $p_{O_2} = 0.2$ atm. Decomposition occurs when $30,540 - 66.11T < 6.69T$, or $T > 420$ K.

(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;

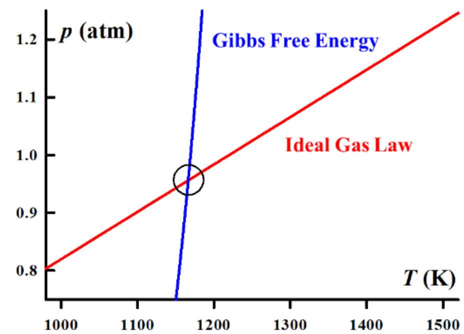
(b) the pressure (atm) in the vessel at 1000 K;

(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

The reaction is $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$; $K = p_{CO_2} = \exp(17.32 - (20{,}255/T))$

(a) When $CaCO_3(s)$ is completely consumed, the number of moles of $CO_2(g)$ = number of moles of $CaCO_3(s)$ placed into the container. FW($CaCO_3$) = 100.08 g/mol. Therefore, 1.00 g $CaCO_3$ = 9.99×10^{-3} mole $CaCO_3(s)$. The temperature at which $CaCO_3(s)$ is consumed is determined by plotting p_{CO_2} vs. T in two different ways: (1) using the ideal gas law based upon 9.99×10^{-3} mole $CO_2(g)$; and (2) using the Gibbs free energy of decomposition (shown to the right). The highest temperature is the intersection of these two curves, which is ~1167 K.



(b) At 1000 K, p_{CO_2} is determined by the extent of decomposition of $CaCO_3(s)$, which is given by the expression from the Gibbs free energy: $p_{CO_2} = \exp(-2.935) = 0.0531$ atm.

(c) At 1500 K, p_{CO_2} is determined by the ideal gas law because $CaCO_3(s)$ is fully decomposed: $p_{CO_2} = (8.1978 \times 10^{-4})(1500\text{ K}) = 1.230$ atm.

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

Vapor pressure of Zn(*g*) for the Cu-Zn alloy at 900°C = $a_{Zn}p^0_{Zn}$, where p^0_{Zn} = vapor pressure of Zn(*s*) at the same temperature. $p^0_{Zn}(1173.15\text{ K}) = 0.9242$ atm.

Since Zn(*s*) begins to condense at 740°C, then the pressure of Zn(*g*) must be $p^0_{Zn}(740°C) = 0.1426$ atm.

Therefore, $a_{Zn} = \frac{0.1426}{0.9242} = 0.154$.

(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?

Construct the species-by-element matrix:

***S* = 4**	**Ni(*s*)**	**H_2(*g*)**	**H_2O(*g*)**	**NiO(*s*)**
Ni	**1**	**0**	**0**	**1**
H	**0**	**2**	**2**	**0**
O	**0**	**0**	**1**	**1**

After row-reduction:

***S* = 4**	**Ni(*s*)**	**H_2(*g*)**	**H_2O(*g*)**	**NiO(*s*)**
Ni	**1**	**0**	**0**	**1**
H	**0**	**1**	**0**	**–1**
O	**0**	**0**	**1**	**1**

 # components *C* = 3; # phases *P* = 3 = Ni(*s*), NiO(*s*), and gas mixture

 # degrees of freedom *F* = *C* – *P* + 2 = 3 – 3 + 2 = 2.

According to the experimental procedure, temperature is set at 500 K, which is one restraint.

Therefore, *F* = 1, that is, a *univariant system*.

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

There are 6 intensive variables:

Temperature *T*, total pressure p_{TOT},

mole fraction of Ni in Ni(*s*) $x_{Ni}^{(Ni,s)}$, mole fraction of NiO in NiO(*s*) $x_{NiO}^{(NiO,s)}$,

mole fraction of H_2(*g*) in the gas $x_{H_2}^{(g)}$, and mole fraction of H_2O(*g*) in the gas $x_{H_2O}^{(g)}$.

There are the following 5 restraints:

$T = 500$ K, $x_{Ni}^{(Ni,s)} = 1$, $x_{NiO}^{(NiO,s)} = 1$, $x_{H_2}^{(g)} + x_{H_2O}^{(g)} = 1$, and $K_p(500\text{ K}) = \frac{p_{H_2O}}{p_{H_2}} = \frac{x_{H_2O}}{x_{H_2}}$.

Therefore, there is one independent intensive variable, which is the total pressure.

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

$H_2(g) + ½ O_2(g) \rightleftharpoons H_2O(g)$ $\Delta G° = –246{,}000 + 54.8\ T$ (J/mol)
$Ni(s) + ½ O_2(g) \rightleftharpoons NiO(s)$ $\Delta G° = –244{,}550 + 98.5\ T$ (J/mol)

$NiO(s) + H_2(g) \rightleftharpoons Ni(s) + H_2O(g)$ $\Delta G° = –1{,}450 – 43.7\ T$

$K_p = p(H_2O) / p(H_2) = \exp(–\Delta G°/RT)$

At *T* = 500 K, $\Delta G°$ = –23,300 J/mol

$p(H_2O) / p(H_2) = K_p = \exp(5.605) = 272$.

(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?

At *T* = 500 K, $p_{TOT} = n_{TOT}RT/V$ = 2.05 atm.

Then, $x_{H_2}^{(g)} = 3.66 \times 10^{-3}$ and $x_{H_2O}^{(g)} = 0.996$, which means there are 0.498 mol H_2O(*g*) and 0.002 mol H_2(*g*) in the gas mixture. Therefore, slightly more than 0.498 mol NiO(*s*) must be placed in the chamber to ensure that all four species will co-exist 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.

Construct the species-by-element matrix:

***S* = 5**	**CoO(*s*)**	**$SO_3(g)$**	**$O_2(g)$**	**$CoSO_4(s)$**	**$SO_2(g)$**
Co	**1**	**0**	**0**	**1**	**0**
S	**0**	**1**	**0**	**1**	**1**
O	**1**	**3**	**2**	**4**	**2**

After row-reduction:

***S* = 5**	**CoO(*s*)**	**$SO_3(g)$**	**$O_2(g)$**	**$CoSO_4(s)$**	**$SO_2(g)$**
Co	**1**	**0**	**0**	**1**	**0**
S	**0**	**1**	**0**	**1**	**1**
O	**0**	**0**	**1**	**0**	**–1/2**

 # components *C* = 3; # phases *P* = 3 = $CoSO_4(s)$, CoO(*s*), and gas mixture

 # degrees of freedom *F* = *C* – *P* + 2 = 3 – 3 + 2 = 2.

With two degrees of freedom, there are two independent intensive variables among T, p_{TOT}, p_{SO_2}, p_{O_2}, and p_{SO_3}. It is most convenient to consider *T* and p_{TOT}. If the synthetic procedure introduces any additional restraint(s), then either one or both of these variables may no longer be independent.

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

***T* = 1223 K fixes the temperature. We must examine if starting with only $CoSO_4(s)$ provides another restraint. Let n_0 = initial # moles $CoSO_4(s)$. Then**

 # moles Co = n_0 = (# moles $CoSO_4$) + (# moles CoO)

 # moles S = n_0 = (# moles $CoSO_4$) + (# moles SO_2) + (# moles SO_3)

 # moles O = $4n_0$ = 4(# moles $CoSO_4$) + (# moles CoO) + 2(# moles SO_2) + 3(# moles SO_3) + 2(# moles O_2)

These equations can be manipulated to give: (# moles SO_2) = 2(# moles O_2), or $p_{SO_2} = 2p_{O_2}$.

Therefore, there are 2 restraints from the experimental procedure. As a result, *F* = 0, which means that the total gas pressure must adopt a fixed value for equilibrium among the 5 species.

(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

$SO_2(g) + ½ O_2(g) \rightleftharpoons SO_3(g)$ $\Delta G°(T) = –94{,}560 + 89.37T$ J/mol

Use the following two equilibria:

$CoSO_4(s) \rightleftharpoons CoO(s) + SO_3(g)$; $\Delta G°(1223\text{ K}) = +25{,}698.1\text{ J/mol}$

$K_1 = p_{SO_3} = \exp(-2.5273) = 0.07987$

$SO_2(g) + ½ O_2(g) \rightleftharpoons SO_3(g)$; $\Delta G°(1223\text{ K}) = +14{,}739.5\text{ J/mol}$

$$K_2 = \frac{p_{SO_3}}{p_{SO_2}p_{O_2}^{1/2}} = \exp(-1.4496) = 0.23467$$

Since $p_{SO_2} = 2p_{O_2}$, then the equations for K_1 and K_2 give

$p_{SO_3} = 0.0799$ **atm,** $p_{SO_2} = 0.6142$ **atm, and** $p_{O_2} = 0.3071$ **atm, and**

p_{TOT} = (0.0799 + 0.6142 + 0.3071) atm = 1.0012 atm.

(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?

The minimum amount of $CoSO_4$(*s*) would be *just consumed* under these conditions. Therefore, we need to obtain n_0 = initial # moles $CoSO_4$(*s*) such that

 # moles Co = n_0 = (# moles CoO)

 # moles S = n_0 = (# moles SO_2) + (# moles SO_3)

 # moles O = $4n_0$ = (# moles CoO) + 2(# moles SO_2) + 3(# moles SO_3) + 2(# moles O_2)

The # moles of different gas species are determined from their partial pressures:

 # moles SO_2 = $\frac{(0.6142)(10.00)}{(0.08206)(1223)} = 0.06120$ mole # moles SO_3 = $\frac{(0.0799)(10.00)}{(0.08206)(1223)} = 0.00796$ mole

Therefore, n_0 = (0.06120) + (000796) = 0.06916 mole $CoSO_4$ needed. FW($CoSO_4$) = 154.989 g/mol.

Then, at least 10.72 g $CoSO_4$(*s*) needed.

(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.

Construct the species-by-element matrix:

***S* = 5**	**Zn(*g*)**	**C(*s*)**	**CO(*g*)**	**ZnO(*s*)**	**CO_2(*g*)**
Zn	**1**	**0**	**0**	**1**	**0**
C	**0**	**1**	**1**	**0**	**1**
O	**0**	**0**	**1**	**1**	**2**

After row-reduction and basis switch:

***S* = 5**	**Zn**	**C**	**O**	**ZnO(*s*)**	**CO_2(*g*)**
Zn(*g*)	**1**	**0**	**0**	**1**	**0**
C(*s*)	**0**	**1**	**0**	**–1**	**–1**
CO(*g*)	**0**	**0**	**1**	**1**	**2**

There are 2 independent net reactions:

ZnO(*s*) + C(*s*) ⇌ Zn(*g*) + CO(*g*)

C(*s*) + CO_2(*g*) ⇌ 2 CO(*g*)

(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.)

Let n_{01} = # moles ZnO and n_{02} = # moles C introduced into the chamber. Then, at equilibrium:

 # moles Zn = n_{01} = (# moles ZnO(*s*)) + (# moles Zn(*g*))

 # moles O = n_{01} = (# moles ZnO(*s*)) + (# moles CO(*g*)) + 2(# moles CO_2(*g*))

 # moles C = n_{02} = (# moles C(*s*)) + (# moles CO(*g*)) + (# moles CO_2(*g*))

Then, (# moles Zn(*g*)) = (# moles CO(*g*)) + 2(# moles CO_2(*g*)) or $p_{Zn} = p_{CO} + 2p_{CO_2}$.

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

 # components *C* = 3; # phases *P* = 3 = ZnO(*s*), C(*s*), and gas mixture; # additional restraints ρ = 1

 # degrees of freedom $F = C – P + 2 – \rho = 3 – 3 + 2 – 1 = 1$.

With one degrees of freedom, there is one independent intensive variable among T, p_{TOT}, p_{Zn}, p_{CO}, and p_{CO_2}. Perhaps the most convenient variable to consider as independent is temperature.

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

There are 7 intensive variables: $T,\ p_{TOT},\ x_{ZnO}^{(ZnO,s)},\ x_C^{(C,s)},\ x_{Zn}^{(g)},\ x_{CO}^{(g)},\ x_{CO_2}^{(g)}$.

There are 6 restraints on these variables:

In solids: $x_{ZnO}^{(ZnO,s)} = 1;\ x_C^{(C,s)} = 1;$

In gas: $x_{Zn}^{(g)} + x_{CO}^{(g)} + x_{CO_2}^{(g)} = 1;\ x_{Zn}^{(g)} = x_{CO}^{(g)} + 2x_{CO_2}^{(g)};$

Equilibria: $K_1(T) = p_{Zn}p_{CO} = x_{Zn}\,x_{CO}\,p_{TOT}^2;\qquad K_2(T) = \frac{p_{CO}^2}{p_{CO_2}} = \frac{x_{CO}^2}{x_{CO_2}}\,p_{TOT}$

(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*) + ½ O_2(*g*) ⇌ CO(*g*) $\Delta G°(T) = –111{,}700 – 87.65T$ J/mol

C(*s*) + O_2(*g*) ⇌ CO_2(*g*) $\Delta G°(T) = –394{,}700 – 0.84T$ J/mol

Zn(*g*) + ½ O_2(*g*) ⇌ ZnO(*s*) $\Delta G°(T) = –460{,}200 – 198\,T$ J/mol

Using this information:

ZnO(*s*) + C(*s*) ⇌ Zn(*g*) + CO(*g*): $\Delta G° = 348{,}500 – 285.65\,T;$ $K_1 = p_{Zn}p_{CO}$

C(*s*) + CO_2(*g*) ⇌ 2 CO(*g*): $\Delta G° = 171{,}300 – 176.14\,T;$ $K_2 = \frac{p_{CO}^2}{p_{CO_2}}$

At 1000 K, K_1 = 1.087 and K_2 = 76.632.

Using $p_{Zn} = p_{CO} + 2p_{CO_2}$, we obtain the equation $\frac{K_1}{p_{CO}} = p_{CO} + \frac{2}{K_2}p_{CO}^2$. Solving this equation (graphically) gives:

$p_{Zn} = 0.0162$ **atm,** $p_{CO} = 0.0158$ **atm,** $p_{CO_2} = 0.000171$ **atm.**

(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?

Set up the species-by-element matrix and apply row-reduction:

***S* = 4**	**Th(*s*)**	**N_2(*g*)**	**ThN(*s*)**	**Th_3N_4(*s*)**
Th	**1**	**0**	**1**	**3**
N	**0**	**1**	**1/2**	**2**

Therefore, *C* = 2; a two-component system. There are 2 independent net reactions:

ThN(*s*) ⇌ Th(*s*) + ½ N_2(*g*)

Th_3N_4(*s*) ⇌ 3 Th(*s*) + 2 N_2(*g*)

 # degrees of freedom *F* = *C* – *P* + 2 = 2 – *P* + 2 = 4 – *P*.

The Gibbs phase rule allows at most 4 phases to coexist in this two-component system, which occurs for fixed values of temperature and total pressure.

(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, ΔG_f^0(Th_3N_4, *s*) = –630.0 kJ/mol and ΔG_f^0(ThN, *s*) = –206.4 kJ/mol.

For the three solid phases to coexist, then *F* = 1. Therefore, both temperature and pressure cannot be simultaneously. For the following equilibrium:

4 ThN(*s*) ⇌ Th(*s*) + Th_3N_4(*s*);   ΔG°(2000 K) = (–630.0 kJ) – 4(–206.4 kJ) = +195.6 kJ.

Therefore, ThN(*s*) is *stable* with respect to disproportionation into Th(*s*) and Th_3N_4(*s*) at 2000 K, and all three solids *cannot* coexist at equilibrium.

Depending on the overall Th:N molar ratio, there are three possible equilibrium states:

(1) Th:N < 1:   ThN(*s*) and Th_3N_4(*s*) coexist;

(2) Tb:N = 1: ThN(*s*) exists as a single solid phase; or

(3) Th:N > 1: ThN(*s*) and Th(*s*) coexist.

(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.

 # moles Th = 16.0g / 232.04g/mol = 0.06895 mol Th
 # moles N = 2 (1.00g / 28.02g/mol) = 0.07139 mole N

Therefore, Th:N molar ratio = 0.966. With excess N, we conclude that ThN(*s*) and $Th_3N_4(s)$ coexist with $N_2(g)$ in the container:

$Th_3N_4\,(s) \rightleftharpoons 3\,ThN\,(s) + \frac{1}{2}\,N_2\,(g)$; $\Delta G°(2000\text{ K}) = 3(-206.4\text{ kJ}) - (-630.0\text{ kJ}) = +10.8\text{ kJ/mol}$
$K_p\,(2000\text{ K}) = \exp[-10800/(8.314)(2000)] = 0.522$

$K_p = p_{N_2}^{1/2} = 0.522$. Therefore, $p_{N_2} = 0.2725$ atm, and for $V = 0.500$ L and $T = 2000$ K,

$n(N_2) = p_{N_2}V/RT = 8.30 \times 10^{-4}$ mole $N_2(g) = 0.0233$ g $N_2(g)$.

Using conservation of mass: Then,

$n(Th) = 0.06895\text{ mol} = 3n(Th_3N_4) + n(ThN)$

$n(N) = 0.07139\text{ mole} = 4n(Th_3N_4) + n(ThN) + 2n(N_2) = 4n(Th_3N_4) + n(ThN) + 0.00166$

Solving these two linear equations with two unknowns yields

$n(Th_3N_4) = 0.00074$ mol = 0.557 g and $n(ThN) = 0.0668$ mol = 16.431 g

NOTE: the total mass of products is 17.0 g, in agreement with the total mass at the start. Also, ThN (*s*) is the most abundant phase in the mixture.

(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.

 # moles Th = 18.0g / 232.04g/mol = 0.07757 mol Th
 # moles N = 2 (1.00g / 28.02g/mol) = 0.07139 mole N

Therefore, Th:N molar ratio = 1.087. With excess Th, we conclude that ThN(*s*) and Th(*s*) coexist with $N_2(g)$ in the container:

$ThN\,(s) \rightleftharpoons Th\,(s) + \frac{1}{2}\,N_2\,(g)$; $\Delta G°(2000\text{ K}) = +206.4\text{ kJ/mol}$
$K_p\,(2000\text{ K}) = \exp[-206400/(8.314)(2000)] = 4.066 \times 10^{-6}$

Since $K_p = p_{N_2}^{1/2}$, then $p_{N_2} = 1.653 \times 10^{-11}$ atm, and for $V = 0.500$ L and $T = 2000$ K,

$n(N_2) = p_{N_2}V/RT = 5.04 \times 10^{-14}$ mole $N_2(g) = 1.41 \times 10^{-12}$ g $N_2(g)$.

Using conservation of mass: Then,

$n(Th) = 0.07757\text{ mol} = n(Th) + n(ThN)$

$n(N) = 0.07139\text{ mole} = n(ThN) + 2n(N_2) \sim n(ThN)$

Solving these two linear equations with two unknowns yields

$n(ThN) = 0.07139$ mol = 17.565 g and $n(Th) = 0.00618$ mol = 1.434 g

NOTE: the total mass of products is 19.0 g, in agreement with the total mass at the start. Also, ThN (*s*) is the most abundant phase in the mixture.

(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 a set of independent net reactions (balanced chemical equilibria).

Construct the species-by-element matrix:

***S* = 5**	**SiO_2(*s*)**	**C(*s*)**	**CO(*g*)**	**SiC(*s*)**	**SiO(*g*)**
Si	**1**	**0**	**0**	**1**	**1**
C	**0**	**1**	**1**	**1**	**0**
O	**2**	**0**	**1**	**0**	**1**

After row-reduction and basis switch:

***S* = 5**	**Si**	**C**	**O**	**SiC(*s*)**	**SiO(*g*)**
SiO_2(*s*)	**1**	**0**	**0**	**1**	**1**
C(*s*)	**0**	**1**	**0**	**3**	**1**
CO(*g*)	**0**	**0**	**1**	**–2**	**–1**

There are 2 independent net reactions:

SiO_2(*s*) + 3 C(*s*) ⇌ SiC(*s*) + 2 CO(*g*)

SiO_2(*s*) + C(*s*) ⇌ SiO(*g*) + CO(*g*)

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

 # components *C* = 3; # phases *P* = 4 = SiO_2(*s*), C(*s*), SiC(s), and gas mixture.

There are no restraints established by the synthetic procedure.

 # degrees of freedom *F* = *C* – *P* + 2 = 3 – 4 + 2 = 1.

With one degree of freedom, there is one independent intensive variable among T, p_{TOT}, p_{CO}, and p_{SiO}. Perhaps the most convenient variable to consider as independent is temperature.

(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

SiO_2(*s*) + 3 C(*s*) ⇌ SiC(*s*) + 2 CO(*g*): **Δ*G*°(1773 K) = +5.11 kJ/mol**
$K_p = 0.7070 = p_{CO}^2$

SiO_2(*s*) + C(*s*) ⇌ SiO(*g*) + CO(*g*): **Δ*G*°(1773 K) = +82.9 kJ/mol**
$K_p = 0.003611 = p_{SiO}\, p_{CO}$

10.0 g SiO_2(*s*) = 1.6644 mol SiO_2

10.0 g C(*s*) = 8.3257 mol C

 # mol Si = 1.6644 mol = *n*(SiO_2) + *n*(SiC) + *n*(SiO)

 # mol O = 3.3288 mol = 2*n*(SiO_2) + *n*(SiO) + *n*(CO)

 # mol C = 8.3257 mol = *n*(C) + *n*(SiC) + *n*(CO)

(i) From the equilibrium constants, $p_{CO} = 0.841$ **atm;** $p_{SiO} = 0.00429$ **atm**

Therefore, n**(CO) =** $p_{CO}V/RT$ **= 0.1156 mol and** n**(SiO) =** $p_{SiO}V/RT$ **= 0.0005897 mol.**

$n(SiO_2)$ **= ½ (3.3288 – 0.0005897 – 0.1156) = 1.6063 mol.**

(ii) n**(SiC) = 1.6644 – 1.6063 – 0.0005897 = 0.05751 mol SiC = 2.306 g (formed)**

(iii) n**(C) = 8.3257 – 0.05751 – 0.1156 = 8.1526 mol C = 97.921 g (remains); 2.079 g consumed.**

(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?

This system contains 5 species: Si(*s*), SiO_2(*s*), Si_3N_4(*s*), N_2(*g*), and O_2(*g*). Construct the species-by-element matrix using the 3 elements as the first 3 columns:

S = 5	Si(*s*)	N_2(*g*)	O_2(*g*)	SiO_2(*s*)	Si_3N_4(*s*)
Si	1	0	0	1	3
N	0	2	0	0	4
O	0	0	2	2	0

After row-reduction and basis switch:

S = 5	Si	C	O	SiO_2(*s*)	Si_3N_4(*s*)
Si(*s*)	1	0	0	1	3
N_2(*g*)	0	1	0	0	2
O_2(*g*)	0	0	1	1	0

 # components *C* = 3; # phases *P* = 4 = Si(*s*), SiO_2(*s*), Si_3N_4(*s*), and gas mixture.

There are no restraints established by the synthetic procedure.

 # degrees of freedom *F* = *C* – *P* + 2 = 3 – 4 + 2 = 1.

With one degree of freedom, there is one independent intensive variable.

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

From the species-by-element matrix, there are 2 net reactions involving 2 solid phases:

$SiO_2(s) \rightleftharpoons Si(s) + O_2(g)$

$Si_3N_4(s) \rightleftharpoons 3\ Si(s) + 2\ N_2(g)$

The third equilibrium involves SiO_2(*s*) and Si_3N_4(*s*):

$3\ SiO_2(s) + 2\ N_2(g) \rightleftharpoons Si_3N_4(s) + 3\ O_2(g)$

(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

By setting the temperature to a fixed value of 1000 K, the system is invariant, and all intensive variables are fixed. We can use the first two equilibria above to determine the equilibrium partial pressures of the gas:

$SiO_2(s) \rightleftharpoons Si(s) + O_2(g)$: $\Delta G°(1000\ K) = +728{,}000$ J/mol $K = p_{O_2} = 9.37 \times 10^{-37}$

$Si_3N_4(s) \rightleftharpoons 3\ Si(s) + 2\ N_2(g)$: $\Delta G°(1000\ K) = +409{,}000$ J/mol $K = p_{N_2}^2 = 4.32 \times 10^{-22}$

$p_{O_2} = 9.37 \times 10^{-37}$ **atm;** $p_{N_2} = 2.07 \times 10^{-11}$ **atm**

(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?

In air, p_{O_2}~ 0.2 atm and p_{N_2}~ 0.8 atm. Therefore, Si(*s*) is unstable relative to SiO_2(*s*) and Si_3N_4(*s*).

For 3 SiO_2(*s*) + 2 N_2(*g*) ⇌ Si_3N_4(*s*) + 3 O_2(*g*), Δ*G*°(1000 K) = +1,775,000 J/mol and $K = \frac{p_{O_2}^3}{p_{N_2}^2}$ = 4.41 × 10^{-66}. As a result, SiO_2(*s*) and Si_3N_4(*s*) cannot co-exist at equilibrium in air, but the nitride should react to form SiO_2(*s*).

(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.

$FeSO_4$(*s*) ⇌ ½ Fe_2O_3(*s*) + SO_2(*g*) + ¼ O_2(*g*)

$FeSO_4$(*s*) + ¼ O_2(*g*) ⇌ ½ Fe_2O_3(*s*) + SO_3(*g*)

$FeSO_4$(*s*) ⇌ ½ Fe_2O_3(*s*) + ½ SO_2(*g*) + ½ SO_3(*g*)

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

 # components *C* = 3; # phases *P* = 3 = $FeSO_4$(*s*), Fe_2O_3(*s*), and gas mixture; *T* = 929 K.

All elements originate from $FeSO_4$. Is there a restraint among the gas-phase variables?

Let n_0 = # moles $FeSO_4$(*s*) placed into the container. Then,

Fe: n_0 = (# mol $FeSO_4$, *s*) + 2(# mol Fe_2O_3, *s*)

S: n_0 = (# mol $FeSO_4$, *s*) + (# mol SO_2, *g*) + (# mol SO_3, *g*)

O 4n_0 = 4(# mol $FeSO_4$, *s*) + 3(# mol Fe_2O_3, *s*) + 2(# mol SO_2, *g*) + 3(# mol SO_3, *g*) + 2(# mol O_2, *g*)

From these 3 equations, we find: (# mol SO_2, *g*) = (# mol SO_3, *g*) + 4(# mol O_2, *g*) or

$$p_{SO_2} = p_{SO_3} + 4p_{O_2}$$

Since there is one restraint among the gas-phase partial pressures as well as a fixed temperature,

 # degrees of freedom *F* = *C* – *P* + 2 – 2 = 3 – 3 + 2 – 2 = 0.

Therefore, there is a unique solution. Using the restraint among partial pressures and the following two equilibria:

$FeSO_4$(*s*) ⇌ ½ Fe_2O_3(*s*) + SO_2(*g*) + ¼ O_2(*g*): $\Delta G°(929\text{ K}) = +57,500\text{ J/mol}$

$$K_1 = 5.8458 \times 10^{-4} = p_{SO_2} p_{O_2}^{1/4}$$

$FeSO_4$(*s*) ⇌ ½ Fe_2O_3(*s*) + ½ SO_2(*g*) + ½ SO_3(*g*): $\Delta G°(929\text{ K}) = +52,000\text{ J/mol}$

$$K_2 = 1.1915 \times 10^{-3} = p_{SO_2}^{1/2} p_{SO_3}^{1/2}$$

the following equation arises: $p_{SO_2} = \frac{1.4197\times10^{-6}}{p_{SO_2}} + 4\frac{1.1678\times10^{-13}}{p_{SO_2}^4}$**, which can be solved to give**

$p_{SO_2} = 3.504 \times 10^{-3}$ **atm;** $p_{SO_3} = 4.052 \times 10^{-4}$ **atm;** $p_{O_2} = 7.747 \times 10^{-4}$ **atm**

$p_{TOT} = 4.684 \times 10^{-3}$ **atm**

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

From the conservation of matter equations above, we use the S atom equation. The minimum # moles $FeSO_4$ needed means that there will be just above 0 moles $FeSO_4$ at equilibrium. The # moles of SO_2(*g*) and SO_3(*g*) are obtained from the ideal gas law using their respective partial pressures.

n_0(min) = (# mol SO_2, *g*) + (# mol SO_3, *g*) = $4.596 \times 10^{-4} + 5.315 \times 10^{-5} = 5.128 \times 10^{-4}$ **mol**

Therefore, at least 0.0778 g or 77.8 mg $FeSO_4$(*s*) must be introduced into the container.

(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 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

For this system, the possible species are CuO(*s*), Cu(*s*), Cu_2O(*s*), and O_2(*g*). The initial conditions set up 1.1 μmol Cu atoms and 1.0 μmol O atoms.

Let's first consider the possible equilibrium among the 3 solid phases:

Cu_2O(*s*) ⇌ Cu(*s*) + CuO(*s*), $\boldsymbol{\Delta G^\circ(1000\ \mathrm{K}) = +11,280\ \mathrm{J/mol}}$

Since the system contains 52.4 mole percent Cu, then Cu_2O(*s*) and CuO(*s*) co-exist at equilibrium. In the absence of any O_2(*g*), there will be 0.1μmol Cu_2O(*s*) and 0.9 μmol CuO(*s*).

Now we must consider the formation of O_2(*g*) by using the chemical equilibrium:

2 CuO(*s*) ⇌ Cu_2O(*s*) + ½ O_2(*g*), $\boldsymbol{\Delta G^\circ(1000\ \mathrm{K}) = +55,380\ \mathrm{J/mol}}$

$$\boldsymbol{K = 1.2798 \times 10^{-3} = p_{O_2}^{1/2}}$$

At equilibrium, $\boldsymbol{p_{O_2} = 1.638 \times 10^{-6}}$ atm, which, using the ideal gas law, means $\boldsymbol{1.996 \times 10^{-8}}$ mol O_2 or 0.02 μmol O_2. To achieve this result, 0.08 μmol CuO(*s*) are consumed and 0.04 μmol Cu_2O(*s*) are formed. The identity and quantity of each phase is:

0.82 μmol CuO(*s*), 0.14 μmol Cu_2O(*s*), and 0.02 μmol O_2(*g*).

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

For this system, the possible species are $CdSO_4$(*s*), $CdSO_4$·H_2O(*s*), $CdSO_4$·8/3 H_2O(*s*), and H_2O(*g*). The initial conditions set up 1.0 mmol $CdSO_4$ and 3.0 mmol H_2O.

Let's first consider the possible equilibrium among the 3 solid phases:

$CdSO_4$·H_2O(*s*) ⇌ $CdSO_4$(*s*) + $CdSO_4$·8/3 H_2O(*s*), $\boldsymbol{\Delta G^\circ(298\ \mathrm{K}) = +5,112.5\ \mathrm{J/mol}}$

Since the system contains 75 mole percent H_2O, then $CdSO_4$·H_2O(*s*) and $CdSO_4$·8/3 H_2O(*s*) co-exist at equilibrium. The following 3-phase chemical equilibrium is:

$CdSO_4$·8/3 H_2O(*s*) ⇌ $CdSO_4$·H_2O(*s*) + 5/3 H_2O(*g*), $\boldsymbol{\Delta G^\circ(298\ \mathrm{K}) = +15,533.3\ \mathrm{J/mol}}$

$$\boldsymbol{K = 1.8930 \times 10^{-3} = p_{H_2O}^{5/3}}$$

At equilibrium, $\boldsymbol{p_{H_2O} = 0.02324}$ atm, which, using the ideal gas law, means $\boldsymbol{1.901 \times 10^{-3}}$ mol H_2O or 1.9 mmol H_2O. Therefore, 1.1 mmol H_2O must be distributed between the two solids. To determine the molar distribution, set up two equations:

$CdSO_4$: ***x*** **$CdSO_4$·H_2O(*s*) + *y* $CdSO_4$·8/3 H_2O(*s*) = 1.0 mmol**

H_2O: ***x*** **$CdSO_4$·H_2O(*s*) + 8*y*/3 $CdSO_4$·8/3 H_2O(*s*) = 1.1 mmol**

Solving these equations gives *x* = 0.94 and *y* = 0.06. At equilibrium, there are

0.94 mmol $CdSO_4$·H_2O(*s*), 0.06 mmol $CdSO_4$·8/3 H_2O(*s*), and 1.9 mmol H_2O(*g*).

(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*) ⇌ 2 ZrAl(*s*) + Al(*g*): $\Delta G^\circ(T) \sim 372{,}800 - 118.4\,T$ (J/mol)

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

For this system, the possible species are ZrAl(*s*), Zr_2Al_3(*s*), Zr_5Al_4(*s*), and Al(*g*). The initial conditions set up 8.8275 mmol Zr atoms and 7.2225 mmol Al atoms.

Let's consider the possible equilibrium among the 3 solid phases:

ZrAl(*s*) ⇌ 1/7 Zr_2Al_3(*s*) + 1/7 Zr_5Al_4(*s*), $\boldsymbol{\Delta G^\circ(1500\ \mathrm{K}) = +625\ \mathrm{J/mol}}$

Since the system contains 55 mole percent Zr, then ZrAl(*s*) and Zr_5Al_4 (*s*) co-exist at equilibrium, but the solid will be mostly Zr_5Al_4. The following 3-phase chemical equilibrium is:

5 ZrAl(*s*) ⇌ Zr_5Al_4(*s*) + Al(*g*), $\Delta G°(1500\text{ K}) = +199,575\text{ J/mol}$

$K = 1.1218 \times 10^{-7} = p_{Al}$

Using the ideal gas law, there are 9.114×10^{-10} mol Al(*s*) or 0.91 nmol Al(*s*).

Zr atoms are distributed among ZrAl(*s*) and Zr_5Al_4(*s*); the amount of Al atoms in the gas phase is *negligible* as compared to what are in the solids. Let n_1 = # mmoles ZrAl(*s*) at equilibrium, and n_2 = # mmoles Zr_5Al_4(*s*) at equilibrium. There are two equations that allow us to solve for these quantities:

Zr atom balance: 8.8275 mmol Zr = $n_1 + 5n_2$

Al atom balance: 7.2225 mol Al = $n_1 + 4n_2$.

Then, n_1 = 0.803 mmol ZrAl(*s*) = 0.0949 g; n_2 = 1.605 mmol Zr_5Al_4(*s*) = 0.9051 g.

(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

For 3 solid phases, there are 3 possible equilibria between 2 solids and O_2(*g*):

2 Cu_2O(*s*) ⇌ 4 Cu(*s*) + O_2(*g*), $\Delta G° = +336,600 - 145.58T = -2.303RT\log p_{O_2}$

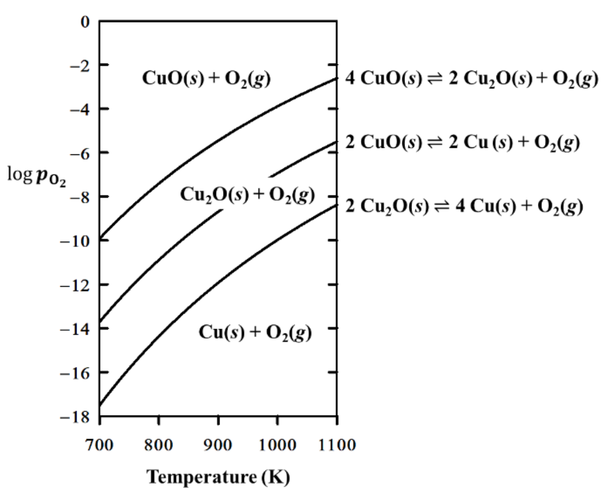
$\log p_{O_2} = 7.603 - \frac{17,580}{T}$: **(–17.51 to –8.31)**

2 CuO(*s*) ⇌ 2 Cu(*s*) + O_2(*g*), $\Delta G° = +302,900 - 170.10T = -2.303RT\log p_{O_2}$

$\log p_{O_2} = 8.884 - \frac{15,820}{T}$: **(–13.72 to –5.50)**

4 CuO(*s*) ⇌ 2 Cu_2O(*s*) + O_2(*g*), $\Delta G° = +269,200 - 194.70T = -2.303RT\log p_{O_2}$

$\log p_{O_2} = 10.169 - \frac{14,060}{T}$: **(–9.92 to –2.61)**



The lines identify equilibrium between 2 solid phases. If p_{O_2} is higher than the equilibrium value, then the solid on the reactant (left) side is thermodynamically stable; if p_{O_2} is lower than the equilibrium value, then the solid on the product (right) side is thermodynamically stable.

Therefore,

- **At low p_{O_2} (below the lowest line), Cu(*s*) is the stable solid relative to the oxides.**
- **At high p_{O_2} (above the highest line), CuO(*s*) is the stable solid relative to the others.**
- **At intermediate p_{O_2} (between the lowest and highest lines), Cu_2O(*s*) is the stable solid relative to the others.**

(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.

This system contains 8 species: 2 solids and a gas phase mixture of 6 species. Construct the species-by-element matrix using the 4 elemental gases as the first 4 columns:

S = 8	Zn(*g*)	H_2(*g*)	S_2(*g*)	O_2(*g*)	ZnO(*s*)	ZnS(*s*)	H_2S(*g*)	H_2O(*g*)
Zn	1	0	0	0	1	1	0	0
H	0	2	0	0	0	0	2	2
S	0	0	2	0	0	1	1	0
O	0	0	0	2	1	0	0	1

After row-reduction and basis switch:

S = 8	Zn	H	S	O	ZnO(*s*)	ZnS(*s*)	H_2S(*g*)	H_2O(*g*)
Zn(*g*)	1	0	0	0	1	1	0	0
H_2(*g*)	0	1	0	0	0	0	1	1
S_2(*g*)	0	0	1	0	0	1/2	1/2	0
O_2(*g*)	0	0	0	1	1/2	0	0	1/2

 # components *C* = 4; # phases *P* = 3 = ZnO(*s*), ZnS(*s*), and gas mixture.

There is <u>one</u> restraint: fixed temperature.

 # degrees of freedom $F = C - P + 2 - \rho = 4 - 3 + 2 - 1 = 2$.

Therefore, if 2 intensive variables have specific fixed values, then there is a unique equilibrium state. These 2 intensive variables can be the mole fractions or partial pressures of 2 gases in the mixture.

(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*) ⇌ ZnO(*s*), $\Delta G° = -79{,}460$ J/mol $\quad K_1 = \frac{1}{p_{Zn}p_{O_2}^{1/2}} = 118.9$

Zn(*g*) + ½ S_2(*g*) ⇌ ZnS(*s*), $\Delta G° = +7{,}210$ J/mol $\quad K_2 = \frac{1}{p_{Zn}p_{S_2}^{1/2}} = 0.6482$

H_2(*g*) + ½ O_2(*g*) ⇌ H_2O(*g*), $\Delta G° = -136{,}820$ J/mol $\quad K_3 = \frac{p_{H_2O}}{p_{H_2}p_{O_2}^{1/2}} = 3745$

H_2(*g*) + ½ S_2(*g*) ⇌ H_2S(*g*), $\Delta G° = +8{,}490$ J/mol $\quad K_4 = \frac{p_{H_2S}}{p_{H_2}p_{S_2}^{1/2}} = 0.6001$

From K_3, $p_{O_2} = \left(\frac{(0.500)}{(0.0421)(3745)}\right)^2 = 1.01 \times 10^{-5}$ atm.

From K_1, $p_{Zn} = \frac{1}{(118.9)(1.01\times10^{-5})^{1/2}} = 2.65$ atm.

From K_2, $p_{S_2} = \left(\frac{1}{(2.65)(0.6482)}\right)^2 = 0.339$ atm.

From K_4, $p_{H_2S} = (0.6001)(0.0421)(0.339)^{1/2} = 0.0147$ atm.

(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.

 # Components *C* = 3 (M, C, and O). According to the Gibbs phase rule, $F = 3 - P + 2 = 5 - P$.

Since there must be at least 1 phase in the system, the maximum *F* = 4.

The solids are pure, so the only variable compositions are any two of the three gas-phase components. Therefore, the free intensive variables are T, p_{TOT}, and any two of p_{CO}, p_{CO_2}, p_{O_2} because $p_{TOT} = p_{CO} + p_{CO_2} + p_{O_2}$.

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

At most, 5 phases can coexist. These are M(*s*), MO(s), C(s), MC(s), and the gas mixture. According to the conditions described above, all three metal-containing solids may coexist, but this occurs at an invariant point with fixed values of T, p_{TOT}, p_{CO}, p_{CO_2}, p_{O_2}.

(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?

Fixing the temperature and total pressure introduces 2 restraints. Therefore, $F = 5 – P – 2 = 3 – P$. Therefore, at most, 3 phases can coexist. According to the conditions described above, one metal-containing solid may coexist with C(*s*) and the gas mixture, which will have a fixed composition.

(d) Given the following thermodynamic information:

ΔG_f^0(MO, *s*) = –264,650 + 62.75 *T* J/mol, ΔG_f^0(MC, *s*) = –12,550 + 8.368 *T* J/mol

ΔG_f^0(CO, *g*) = –111,800 – 87.70 *T* J/mol, ΔG_f^0(CO_2, *g*) = –394,300 – 0.84 *T* 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.

According to the narrative, C(*s*) must be in equilibrium with CO(*g*), CO_2(*g*), and O_2(*g*). Therefore, the following 2 chemical equilibria must occur in the container:

C(*s*) + CO_2(*g*) ⇌ 2 CO(*g*), $\Delta G° = 170,700 - 174.56\,T$,

$$K_1 = \frac{p_{CO}^2}{p_{CO_2}} = \exp\left(21.00 - \frac{20,532}{T}\right)$$

2 CO_2(*g*) ⇌ 2 CO(*g*) + O_2(*g*), $\Delta G° = 565,000 - 173.72\,T$,

$$K_2 = \frac{p_{CO}^2 p_{O_2}}{p_{CO_2}^2} = \exp\left(20.89 - \frac{67,958}{T}\right)$$

With the restraint, $p_{CO} + p_{CO_2} + p_{O_2} = 1$ atm, specific values of the partial pressures of the gases can be evaluated for each temperature. Also, p_{O_2} is negligible when compared to p_{CO} and p_{CO_2}.

800 K: $K_1 = 0.009260$; $K_2 = 1.497 \times 10^{-28}$
$p_{CO} = 0.0917$ atm; $p_{CO_2} = 0.9083$ atm; $p_{O_2} = 1.469 \times 10^{-26}$ atm

1200 K: $K_1 = 48.29$; $K_2 = 2.986 \times 10^{-16}$
$p_{CO} = 0.9801$ atm; $p_{CO_2} = 0.0199$ atm; $p_{O_2} = 1.231 \times 10^{-19}$ atm

1600 K: $K_1 = 3488$; $K_2 = 4.216 \times 10^{-10}$
$p_{CO} = 0.9997$ atm; $p_{CO_2} = 0.0003$ atm; $p_{O_2} = 3.797 \times 10^{-17}$ atm

The three other solids in the system are M(*s*), MO(*s*), and MC(*s*). To identify which one of these solids also exists for the fixed temperature and pressure, it is best to consider the 3-phase chemical equilibria involving two of these solids and the gases CO(*g*) and CO_2(*g*):

M(*s*) + CO_2(*g*) ⇌ MO(*s*) + CO(*g*), $\Delta G° = 17,850 - 24.11\,T$,

$$K_3 = \frac{p_{CO}}{p_{CO_2}} = \exp\left(2.900 - \frac{2147}{T}\right)$$

MC(*s*) + CO_2(*g*) ⇌ M(*s*) + 2 CO(*g*), $\Delta G° = 183,250 - 182.93\,T$,

$$K_4 = \frac{p_{CO}^2}{p_{CO_2}} = \exp\left(22.00 - \frac{22,041}{T}\right)$$

MC(*s*) + 2 CO_2(*g*) ⇌ MO(*s*) + 3 CO(*g*), $\Delta G° = 201,100 - 206.20\,T$,

$$K_5 = \frac{p_{CO}^3}{p_{CO_2}^2} = \exp\left(24.80 - \frac{24,188}{T}\right)$$

800 K: $K_3 = 1.241$; $\frac{p_{CO}}{p_{CO_2}} = 0.1010 < K_3$: **MO(*s*) stable over M(*s*)**

$K_4 = 0.00388$; $\frac{p_{CO}^2}{p_{CO_2}} = 0.00926 > K_4$: **MC(*s*) stable over M(*s*)**

$\boldsymbol{K_5 = 0.00436;} \quad \frac{p_{CO}^3}{p_{CO_2}^2} = \mathbf{0.000934} < K_5$: **MO(*s*) stable over MC(*s*)**

Therefore, MO(*s*) exists with C(*s*) and the CO(*g*), CO_2(*g*), O_2(*g*), which is richest in CO_2(*g*).

1200 K: $\boldsymbol{K_3 = 3.037;} \quad \frac{p_{CO}}{p_{CO_2}} = \mathbf{3332} > K_3$: **M(*s*) stable over MO(*s*)**

$\boldsymbol{K_4 = 37.81;} \quad \frac{p_{CO}^2}{p_{CO_2}} = \mathbf{48.3} > K_4$: **MC(*s*) stable over M(*s*)**

$\boldsymbol{K_5 = 103.9;} \quad \frac{p_{CO}^3}{p_{CO_2}^2} = \mathbf{2377} > K_5$: **MC(*s*) stable over MO(*s*)**

Therefore, MC(*s*) exists with C(*s*) and the CO(*g*), CO_2(*g*), O_2(*g*), which is richest in CO(*g*).

1600 K: $\boldsymbol{K_3 = 4.750;} \quad \frac{p_{CO}}{p_{CO_2}} = \mathbf{49.3} > K_3$: **M(*s*) stable over MO(*s*)**

$\boldsymbol{K_4 = 3731;} \quad \frac{p_{CO}^2}{p_{CO_2}} = \mathbf{3331} < K_4$: **M(*s*) stable over MC(*s*)**

$\boldsymbol{K_5 = 16035;} \quad \frac{p_{CO}^3}{p_{CO_2}^2} = \mathbf{1.11 \times 10^7} > K_5$: **MC(*s*) stable over MO(*s*)**

Therefore, M(*s*) exists with C(*s*) and the CO(*g*), CO_2(*g*), O_2(*g*), which is richest in CO(*g*).

(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

C(*s*) + CO_2(*g*) ⇌ 2 CO(*g*), $\boldsymbol{\Delta G° = -91,000}$ **J/mol** $\boldsymbol{K = \frac{p_{CO}^2}{p_{CO_2}} = 1476}$

Since $\boldsymbol{p_{CO} + p_{CO_2} = 1}$ **atm, then** $\boldsymbol{p_{CO} = 0.9993}$ **atm and** $\boldsymbol{p_{CO_2} = 0.000677}$ **atm.**

(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

Cr_2O_3(*s*) + 3 CO(*g*) ⇌ 2 Cr(*s*) + 3 CO_2(*g*)

$\boldsymbol{\Delta G° = +274,000}$ **J/mol;** $\boldsymbol{K = 2.87 \times 10^{-10}}$

$$\boldsymbol{Q = \left(\frac{p_{CO_2}}{p_{CO}}\right)^3 = \left(\frac{0.000677}{0.9993}\right)^3 = 3.11 \times 10^{-10} > K}$$

23 Cr_2O_3(*s*) + 93 CO(*g*) ⇌ 2 $Cr_{23}C_6$(*s*) + 81 CO_2(*g*),

$\boldsymbol{\Delta G° = +6,455,000}$ **J/mol;** $\boldsymbol{\ln K = -517.6}$

$$\boldsymbol{\ln Q = \ln\left(\frac{p_{CO_2}^{81}}{p_{CO}^{93}}\right) = 81 \ln p_{CO_2} - 93 \ln p_{CO} = -591 < \ln K}$$

Therefore, $Cr_{23}C_6$(*s*) is stable over Cr_2O_3(*s*), which is stable over Cr(*s*). Cr_2O_3(*s*) is reduced to $Cr_{23}C_6$(*s*)

(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

MnO(*s*) + CO(*g*) ⇌ Mn(*s*) + CO_2(*g*)

$\boldsymbol{\Delta G° = +123,300}$ **J/mol;** $\boldsymbol{K = 5.08 \times 10^{-5}}$

$$\boldsymbol{Q = \frac{p_{CO_2}}{p_{CO}} = \frac{0.000677}{0.9993} = 6.77 \times 10^{-4} > K}$$

3 MnO(*s*) + 5 CO(*g*) ⇌ Mn_3C(*s*) + 4 CO_2(*g*),

$\boldsymbol{\Delta G° = +445,300}$ **J/mol;** $\boldsymbol{K = 3.11 \times 10^{-16}}$

$$Q = \frac{p_{CO_2}^4}{p_{CO}^5} = \frac{(0.000677)^4}{(0.9993)^5} = 2.11 \times 10^{-13} > K$$

Therefore, MnO(*s*) is stable over both Mn_3C(*s*) and Mn(*s*). Therefore, MnO(*s*) is not reduced to either Mn(*s*) or Mn_3C(*s*).

(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.

With 4 species M(*s*), MO(*s*), M_3O_4(*s*), and O_2(*g*), there are 4 possible 3-phase equilibria:

MO(*s*) ⇌ M(s) + ½ O_2(*g*), $\Delta G° = -\Delta G_f^0(\mathrm{MO}, s) = 259,741 - 62.58\,T = -9.57\,T \log p_{O_2}$

M_3O_4(*s*) ⇌ 3 M(s) + 2 O_2(*g*), $\Delta G° = -\Delta G_f^0(\mathrm{M_3O_4}, s) = 1,091,290 - 312.90\,T = -38.29\,T \log p_{O_2}$

M_3O_4(*s*) ⇌ 3 MO(s) + ½ O_2(*g*), $\Delta G° = 3\,\Delta G_f^0(\mathrm{MO}, s) - \Delta G_f^0(\mathrm{M_3O_4}, s) = 312,067 - 125.16\,T = -9.57\,T \log p_{O_2}$

M(s) + M_3O_4(*s*) ⇌ 4 MO(*s*), $\Delta G° = 4\,\Delta G_f^0(\mathrm{MO}, s) - \Delta G_f^0(\mathrm{M_3O_4}, s) = 52,326 - 62.58\,T$

The first three equilibria involve 2 solids and 1 gas-phase species. For each 3-phase equilibrium, $p_{O_2}(T)$ is a specific function of temperature. For some temperature T', then there are 3 possibilities:

- **$p_{O_2} = p_{O_2}(T')$: all three phases coexist**
- **$p_{O_2} > p_{O_2}(T')$: O_2(*g*) coexists with the solid phase on the left-side of the chemical equation**
- **$p_{O_2} < p_{O_2}(T')$: O_2(*g*) coexists with the solid phase on the right-side of the chemical equation**

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

There are 6 intensive variables: $T, p_{\mathrm{TOT}}, x_{O_2}^{(g)}, x_{\mathrm{M}}^{(\mathrm{M},s)}, x_{\mathrm{MO}}^{(\mathrm{MO},s)}, x_{\mathrm{M_3O_4}}^{(\mathrm{M_3O_4},s)}$.

There are 4 general restraints on composition:

$x_{O_2}^{(g)} = 1,\ x_{\mathrm{M}}^{(\mathrm{M},s)} = 1,\ x_{\mathrm{MO}}^{(\mathrm{MO},s)} = 1,\ x_{\mathrm{M_3O_4}}^{(\mathrm{M_3O_4},s)} = 1.$

Therefore, there are at most 2 independent intensive variables, which are T and p_{TOT}.

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

 # Components *C* = 2. So, *F* = 2 – *P* + 2 = 4 – *P*. For a uniquely defined system, no more than 4 phases can coexist at equilibrium.

For this system, it is possible for the 3 solids M(*s*), MO(*s*), and M_3O_4(*s*) and the gas O_2(*g*) to coexist, but that would require the three 3-phase equilibria involving O_2(*g*) to have coincidental p_{O_2} values for some specific temperature T_0. For this to be true, the 3-phase equilibrium among the 3 solids must occur at the same temperature. According to the Gibbs free energy expression, $T_0 = 836$ K.

(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.

There are 4 distinct phases: V_2O_4(*s*), V_2O_5(*s*), $VOSO_4$(*s*), and a SO_2(*g*)/SO_3(*g*) gas mixture. As a result, there are 3 possible 3-phase equilibria:

V_2O_5(*s*) + SO_2(*g*) ⇌ V_2O_4(*s*) + SO_3(*g*), $K_1 = \frac{p_{SO_3}}{p_{SO_2}}$

$VOSO_4$(*s*) ⇌ ½ V_2O_4(*s*) + SO_3(*g*), $K_2 = p_{SO_3}$

2 $VOSO_4(s) \rightleftharpoons V_2O_5(s) + SO_2(g) + SO_3(g)$, $\quad K_3 = p_{SO_2}\, p_{SO_3}$

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

To determine independent net reactions, construct the species-by-element matrix:

S = 5	$V_2O_4(s)$	$SO_2(g)$	$SO_3(g)$	$V_2O_5(s)$	$VOSO_4(s)$
V	2	0	0	2	1
S	0	1	1	0	1
O	4	2	3	5	5

Following row-reduction and a "change of basis", we obtain:

S = 5	V	S	O	$V_2O_5(s)$	$VOSO_4(s)$
$V_2O_4(s)$	1	0	0	1	1/2
$SO_2(g)$	0	1	0	–1	0
$SO_3(g)$	0	0	1	1	1

There are 2 independent net reactions:

(I) $V_2O_5(s) + SO_2(g) \rightleftharpoons V_2O_4(s) + SO_3(g)$

(II) $VOSO_4(s) \rightleftharpoons ½\, V_2O_4(s) + SO_3(g)$

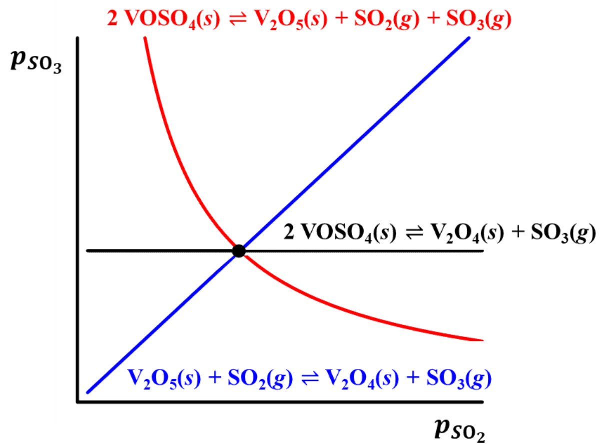
These are two of the three 3-phase equilibria written in (a). The remaining chemical equation can be obtained from 2 (II) – (I), which means that $K_3 = K_2^2/K_1$ and this expression agrees with the expressions for K_1, K_2, K_3.

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

 # Components *C* = 3; *P* = 4, which are the 3 solids and 1 gas-phase mixture. So, *F* = 3 – 4 + 2 = 1. Therefore, if all 4 phases coexist at equilibrium, then one intensive variable is freely variable.

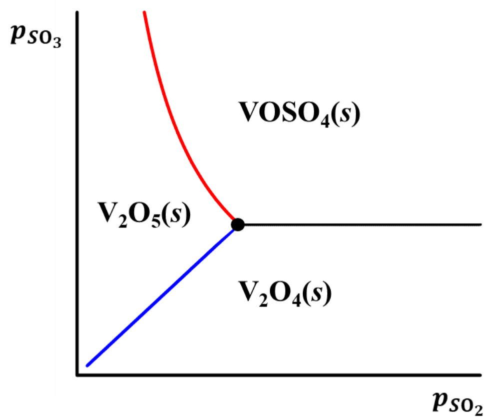
The intensive variables in this system that can be variable include $T, p_{TOT}, x_{SO_2}, x_{SO_3}$, but there is one restraint: $x_{SO_2} + x_{SO_3} = 1$. Therefore, among T, p_{TOT}, x_{SO_3}, if any two of these are fixed, then all 4 phases can coexist.

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



Using the 3 equilibria determined in (a), the relationships between p_{SO_2} and p_{SO_3} are given by the expressions for the equilibrium constants. They intersect at a single point.

Each curve represents a 3-phase equilibrium. Points above a curve favor the solid on the left-side (reactant-side) of the chemical equation; points below a curve favor the solid on the right-side (product-side) of the chemical equation:



Red curve: above – $VOSO_4(s)$ stable
below – $V_2O_5(s)$ stable
Black curve: above – $VOSO_4(s)$ stable
below – $V_2O_4(s)$ stable
Blue curve: above – $V_2O_5(s)$ stable
below – $V_2O_4(s)$ stable

As a result, there are three 2-phase regions, separated by three 3-phase curves, which meet at a single 4-phase point.

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

$\Delta G_f^0(V_2O_5, s) = -1184.48$ kJ/mol $\Delta G_f^0(SO_2, g) = -297.21$ kJ/mol

$\Delta G_f^0(V_2O_4, s) = -1138.19$ kJ/mol $\Delta G_f^0(SO_3, g) = -316.09$ kJ/mol

$\Delta G_f^0(VOSO_4, s) = -914.14$ kJ/mol

$V_2O_5(s) + SO_2(g) \rightleftharpoons V_2O_4(s) + SO_3(g)$, $\boldsymbol{\Delta G° = +27.41}$ **kJ/mol**

$\boldsymbol{K_1 = \frac{p_{SO_3}}{p_{SO_2}} = 0.02068}$

$VOSO_4(s) \rightleftharpoons ½\, V_2O_4(s) + SO_3(g)$, $\boldsymbol{\Delta G° = +28.96}$ **kJ/mol**

$\boldsymbol{K_2 = p_{SO_3} = 0.01662}$

$2\, VOSO_4(s) \rightleftharpoons V_2O_5(s) + SO_2(g) + SO_3(g)$, $\boldsymbol{\Delta G° = +30.50}$ **kJ/mol**

$\boldsymbol{K_3 = p_{SO_2}\, p_{SO_3} = 0.01335}$

Therefore, $p_{SO_3} = 0.0166$ atm and $p_{SO_2} = 0.803$ atm.

(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).

$\Delta G_f^0(CuO, s) = -153{,}500 + 87.46\, T$ J/mol

$\Delta G_f^0(CuS, s) = -56{,}370 + 7.02\, T$ J/mol

$\Delta G_f^0(CuSO_4, s) = -775{,}300 + 377.8\, T$ J/mol

$\Delta G_f^0(SO_2, g) = -314{,}100 + 21.83\, T$ J/mol

$\Delta G_f^0(SO_3, g) = -408{,}700 + 111.2\, T$ 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.

The system has 3 components: Cu, S, and O.

For fixed temperature, the # degrees of freedom $\boldsymbol{F = 3 - P + 1 = 4 - P}$.

Therefore, the maximum # phases that can coexist at equilibrium is 4, which are the 3 condensed phases and the gas mixture.

(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 $\log p_{gas}$ vs. T.

The equilibrium partial pressures of the gases can be determined by identifying important 3-phase equilibria:

(1) $CuSO_4(s) \rightleftharpoons CuS(s) + 2\ O_2(g)$ $\Delta G°(1) = 718,930 - 370.78\,T = -19.1437\,T \log K(1)$

$K(1) = p_{O_2}^2;\ \log K(1) = 2 \log p_{O_2}$

Therefore, $\log p_{O_2} = 9.684 - \frac{18,777.2}{T}$

(2) $CuSO_4(s) \rightleftharpoons CuO(s) + SO_3(g)$ $\Delta G°(2) = 213,100 - 179.14\,T = -19.1437\,T \log K(2)$

$K(2) = p_{SO_3};\ \log K(2) = \log p_{SO_3}$

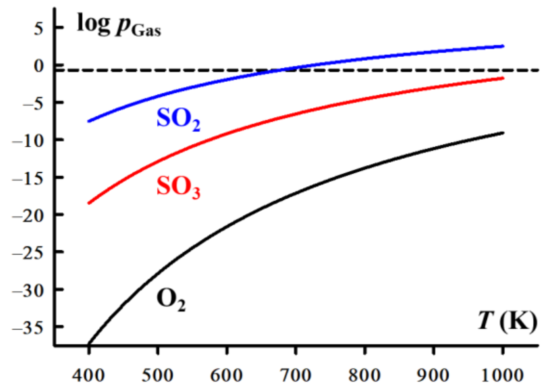
Therefore, $\log p_{SO_3} = 9.358 - \frac{11,131.6}{T}$

(3) $2\ CuS(s) + 3\ O_2(g) \rightleftharpoons 2\ CuO(s) + 2\ SO_2(g)$

$\Delta G°(3) = -822,460 + 204.54\,T = -19.1437\,T \log K(3)$

$K(3) = \frac{p_{SO_2}^2}{p_{O_2}^3};\ \log K(3) = 2 \log p_{SO_2} - 3 \log p_{O_2}$

Therefore, $\log p_{SO_2} = 9.184 - \frac{6684.6}{T}$



(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.

For a fixed temperature, there will be a single point where CuS(*s*), CuO(*s*), and CuSO4(*s*) coexist. To construct this phase diagram, we need to identify the 3 equilibria involving 2 distinct condensed phases with SO2(*g*) and/or O2(*g*).

(1) $CuSO_4(s) \rightleftharpoons CuS(s) + 2\ O_2(g)$ $\Delta G°(1) = 718,930 - 370.78\,T = 422,306$ **J/mol**

$K(1) = p_{O_2}^2 = 10^{-27.575}$

Therefore, $\log p_{O_2} = -13.787$ **at equilibrium.**

(2) $CuSO_4(s) \rightleftharpoons CuO(s) + SO_2(g) + ½\ O_2(g)$

$\Delta G°(2) = 307,700 - 268.51\,T = 92,892$ **J/mol**

$K(2) = p_{SO_2} p_{O_2}^{1/2} = 10^{-6.065}$

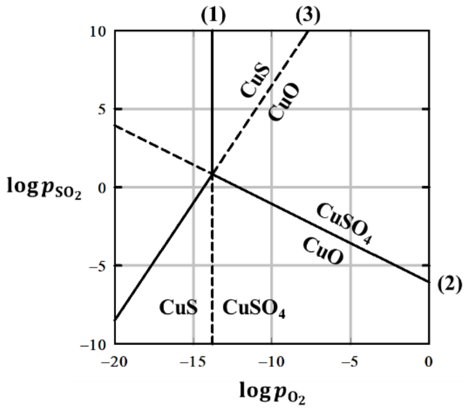
Therefore, $\log p_{SO_2} = -6.065 - 0.5 \log p_{O_2}$ **at equilibrium.**

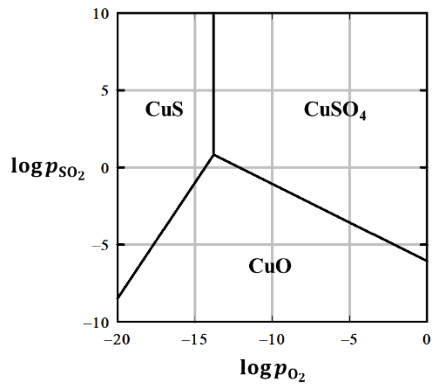
(3) $2\ CuS(s) + 3\ O_2(g) \rightleftharpoons 2\ CuO(s) + 2\ SO_2(g)$

$\Delta G°(3) = -822,460 + 204.54\,T = -658,828$ **J/mol**

$K(3) = \frac{p_{SO_2}^2}{p_{O_2}^3} = 10^{43.019}$

Therefore, $\log p_{SO_2} = 21.509 + 1.5 \log p_{O_2}$ **at equilibrium.**





The left-hand plot shows the three lines described by the 3-phase equilibria; they intersect at the single point where CuS(*s*), CuO(*s*), and CuSO4(*s*) can coexist at 800 K. For equilibrium (1), if $\log p_{O_2}$ exceeds –13.787, then CuSO4(*s*) is stable; if $\log p_{O_2}$ lies below –13.787, then CuS(*s*) is stable. For equilibria (2) and (3), if $\log p_{SO_2}$ exceeds each line, then the solid on the reactant-side is stable; if $\log p_{SO_2}$ lies below each line, then the solid on the product-side is stable. The phase diagram (right-hand plot) removes the dashed part of each line arising from the equilibrium constants.

(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.

Repeat the analysis in (c) for *T* = 1000 K:

(1) CuSO4(*s*) ⇌ CuS(*s*) + 2 O2(*g*) $\Delta G°(1) = 718,930 - 370.78\,T = 348,150$ **J/mol**

$$K(1) = p_{O_2}^2 = 10^{-18.186}$$

Therefore, $\log p_{O_2} = -9.093$ at equilibrium.

(2) CuSO4(*s*) ⇌ CuO(*s*) + SO2(*g*) + ½ O2(*g*)

$$\Delta G°(2) = 307,700 - 268.51\,T = 39,190 \text{ J/mol}$$

$$K(2) = p_{SO_2} p_{O_2}^{1/2} = 10^{-2.047}$$

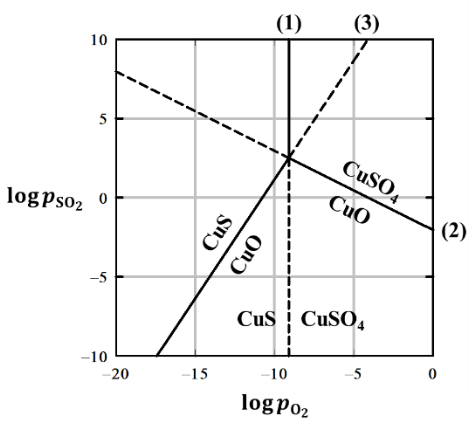
Therefore, $\log p_{SO_2} = -2.047 - 0.5 \log p_{O_2}$ at equilibrium.

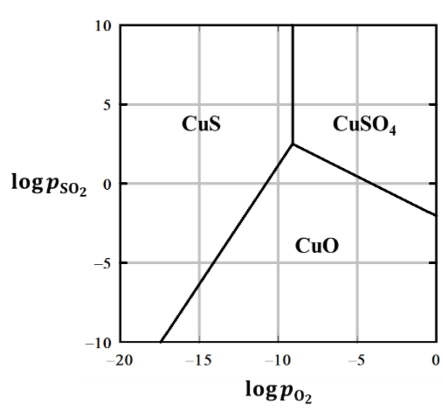
(3) 2 CuS(*s*) + 3 O2(*g*) ⇌ 2 CuO(*s*) + 2 SO2(*g*)

$$\Delta G°(3) = -822,460 + 204.54\,T = -617,920 \text{ J/mol}$$

$$K(3) = \frac{p_{SO_2}^2}{p_{O_2}^3} = 10^{32.278}$$

Therefore, $\log p_{SO_2} = 16.139 + 1.5 \log p_{O_2}$ at equilibrium.





The left-hand plot shows the three lines described by the 3-phase equilibria; they intersect at the single point where CuS(*s*), CuO(*s*), and $CuSO_4$(*s*) can coexist at 800 K. For equilibrium (1), if $\log p_{O_2}$ exceeds –9.093, then $CuSO_4$(*s*) is stable; if $\log p_{O_2}$ lies below –9.093, then CuS(*s*) is stable. For equilibria (2) and (3), if $\log p_{SO_2}$ exceeds each line, then the solid on the reactant-side is stable; if $\log p_{SO_2}$ lies below each line, then the solid on the product-side is stable. The phase diagram (right-hand plot) removes the dashed part of each line arising from the equilibrium constants.

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

The major gas from decomposition of CuS(*s*) is SO_2(*g*) in the temperature range 400 K to 1000 K. O_2(*g*) is present in air, at a partial pressure of 0.2 atm for 1 atm atmospheric pressure.

Decomposition of CuS(*s*) to $CuSO_4$(*s*) and CuO(*s*) are each enthalpy-driven, whereas the conversion of $CuSO_4$(*s*) into CuO(*s*) is entropy-driven. Therefore, at higher temperatures, CuO(*s*) is the only product.

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 (in K) of Zn;

This is the temperature at which this equilibrium occurs: Zn(*l*) ⇌ Zn(*g*), 1 atm

Solve: 0 = –15,246/*T* – 1.255 ln *T* + 21.79, which gives *T* = 1180 K.

(b) the triple point temperature (in K);

This is the temperature at which vapor pressures of the solid and liquid are equal.

Solve: 0 = 529/*T* – 0.5 ln *T* + 2.54, which gives *T* = 711 K.

(c) the heat of vaporization (in kJ/mol) of Zn at the normal boiling point;

For the equilibrium between liquid and vapor, Zn(*l*) ⇌ Zn(*g*), the Clausius equation gives

$$\frac{dp}{dT} = \frac{\Delta S_{\text{vap}}}{\Delta V} \sim \frac{\Delta H_{\text{vap}} p}{RT^2}\text{; or } \frac{dp}{pdT} = \frac{d\ln p}{dT} = \frac{\Delta H_{\text{vap}}}{RT^2}.$$

Since $\frac{d\ln p}{dT} = \frac{15{,}246}{T^2} - \frac{1.255}{T}$**, then for** $T_b = 1180$ **K,**

$$\Delta H_{\text{vap}}(T_b) = 15{,}246R - 1.255RT = 114{,}443\ \text{J/mol} = 114.4\ \text{kJ/mol}.$$

(c) the heat of fusion (in kJ/mol) of Zn at the triple point.

For any temperature, $\Delta H_{\text{fus}}(T) = \Delta H_{\text{sub}}(T) - \Delta H_{\text{vap}}(T)$.

Applying the Clausius equation,

$$\Delta H_{\text{vap}}(711\ \text{K}) = 119.3\ \text{kJ/mol},$$

$$\Delta H_{\text{sub}}(711\ \text{K}) = 15{,}775R - 0.755RT = 126{,}690\ \text{J/mol} = 126.7\ \text{kJ/mol}.$$

$$\Delta H_{\text{fus}}(T) = 126.7 - 119.3 = 7.40\ \text{kJ/mol}.$$

***** This problem can be generalized to many different elements using the fitting parameters for vapor pressures of the metallic elements attached at the end of this file. Reference: Alcock, C.B., Itkin, V.P., Horrigan, M.K. *Can. Metallurg. Quart.* 1984, *23*, p. 309. *****

(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

Δ*G*°(Graphite → Diamond; 298 K) = 1,900 – (298)(2.37 – 5.74) = 2,904.26 J/mol

Under pressure: $\Delta G°(p) = 2{,}904.26 + V_{\text{Diamond}}(p-1) - V_{\text{Graphite}}(p-1)$

$$V_{\text{Graphite}} = \frac{1\ \text{cm}^3}{2.22\ \text{g}} \cdot \frac{12.011\ \text{g}}{1\ \text{mol}} \cdot \frac{1\ \text{L}}{1000\ \text{cm}^3} = 0.00541\ \text{L/mol}$$

$$V_{\text{Diamond}} = \frac{1\ \text{cm}^3}{3.52\ \text{g}} \cdot \frac{12.011\ \text{g}}{1\ \text{mol}} \cdot \frac{1\ \text{L}}{1000\ \text{cm}^3} = 0.00341\ \text{L/mol}$$

Then, graphite will convert diamond when $\Delta G°(p) = 0$:

2,904.26 J/mol = (0.00541 – 0.00341)(*p* – 1)(101.32 J/L·atm) = 0.2026(*p* – 1)

***p* ~ 14,300 atm is required to enact the transition. This is a thermodynamic conclusion and ignores kinetic factors.**

(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

$\Delta G°$(solid → liquid; 600 K) = 4,810 – (600)ΔS_{fus} = 0 J/mol; ΔS_{fus} = 8.017 J/mol·K

Assuming that ΔH_{fus} and ΔS_{fus} remain constant near the normal melting point of lead, then

$\Delta G°$(solid → liquid; 620 K) = 4,810 – (620)(8.017) = –160.5 J/mol

To estimate the pressure *p* that increases the melting point, then

$V_{\text{Solid}}(p-1) = -160.5 + V_{\text{Liquid}}(p-1)$

$$V_{\text{Solid}} = \frac{1\ \text{cm}^3}{10.94\ \text{g}} \cdot \frac{207\ \text{g}}{1\ \text{mol}} \cdot \frac{1\ \text{L}}{1000\ \text{cm}^3} = 0.0189\ \text{L/mol}$$

$$V_{\text{Liquid}} = \frac{1\ \text{cm}^3}{10.65\ \text{g}} \cdot \frac{207\ \text{g}}{1\ \text{mol}} \cdot \frac{1\ \text{L}}{1000\ \text{cm}^3} = 0.0194\ \text{L/mol}$$

Then, lead will melt at 620 K when:

160.5 J/mol = (0.0194 – 0.0189)(p – 1)(101.32 J/L·atm) = 0.05066 (p – 1)

***p* ~ 3170 atm is required to enact the transition. This is a thermodynamic conclusion and ignores kinetic factors.**

(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

When Sn(*l*) spontaneously freezes, heat is released. To address this question, since Sn(*l*) is adiabatically contained, then no heat is added or released during the process. Therefore, we can consider 2 steps:

(1) 1 mole supercooled Sn(*l*) at 495 K raises its temperature to 505 K, the normal melting point.

(2) Fraction *x* mole Sn(*l*) spontaneously freezes to Sn(*s*).

The sum of the enthalpies of these two steps adds to 0 (adiabatically enclosed Sn). Therefore,

$$\Delta H_1 = \int_{495\ \text{K}}^{505\ \text{K}} (34.7 - 0.0092\,T)\,dT = 34.7(10) - 0.0046(505^2 - 495^2) = +301\ \text{J/mol}$$

$$\Delta H_2 = x(-7029)\ \text{J/mol}$$

Since $\Delta H_1 + \Delta H_2 = 0$, then $x = \frac{301}{7029} = 0.0428$.

(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

BCC δ-Fe(*s*) must have a lower Gibbs free energy than both FCC γ-Fe(*s*) and Fe(*l*) between 1670 K and 1810 K. That means, by extending the Gibbs free energy curve for FCC γ-Fe(*s*) above 1670 K and the Gibbs free energy curve for Fe(*l*) below 1810 K, the two curves will intersect, which gives the hypothetical melting point of FCC γ-Fe(*s*). Therefore, at this hypothetical melting point T_m,

$$\Delta G(\delta \to \gamma) = \Delta G(\delta \to l).$$

$$\Delta H(\delta \to \gamma) = -880 + \int_{1670\ \text{K}}^{T_m} (7.70 + 0.0195T - 43.9)\,dT = 32,382 - 36.2T_m + 0.00975T_m^2$$

$$\Delta S(\delta \to \gamma) = -\frac{880}{1670} + \int_{1670\ \text{K}}^{T_m} \frac{(7.70 + 0.0195T - 43.9)}{T}\,dT = 235.53 + 0.0195T_m - 36.2\ln T_m$$

$$\Delta G(\delta \to \gamma) = \Delta H(\delta \to \gamma) - T_m\Delta S(\delta \to \gamma) = 32,382 - 271.73T_m - 0.00975T_m^2 + 36.2T_m \ln T_m$$

$$\Delta H(\delta \to l) = 13{,}800 + \int_{1810\text{ K}}^{T_m} (41.8 - 43.9)dT = 17{,}601 - 2.1T_m$$
$$\Delta S(\delta \to l) = \frac{13{,}800}{1810} + \int_{1810\text{ K}}^{T_m} \frac{(41.8-43.9)}{T} dT = 23.38 - 2.1\ln T_m$$
$$\Delta G(\delta \to l) = \Delta H(\delta \to l) - T_m\Delta S(\delta \to l) = 17{,}601 - 25.48T_m + 2.1T_m \ln T_m$$

The hypothetical melting point of FCC γ-Fe(*s*) is determined by solving the equation:

$$14{,}781 - 246.25T_m - 0.00975T_m^2 + 34.1T_m \ln T_m = 0,$$

which is perhaps most easily solved graphically (using a spreadsheet in Excel) by evaluating the expression for T_m between 1670 K and 1810 K. From this exercise, T_m = 1798 K.

The heat of fusion for the process FCC γ-Fe(*s*) → Fe(*l*) at 1798 K is:

$$\Delta H_{\text{fus}} = T_m\Delta S_{\text{fus}} = T_m\big(\Delta S(\delta \to l) - \Delta S(\delta \to \gamma)\big) = T_m(-212.15 - 0.0195T_m + 34.1\ln T_m)$$
$$= (1798\text{ K})(8.349\text{ J/mol}\cdot\text{K}) = 15{,}010\text{ J/mol.}$$

(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	ρ(α) = 5.77 g/cm^3
β-Sn → Sn(*l*):	ΔH_{fus} = 7,029 J/mol	$C_p(\beta)$ = 30.4 J/mol·K	ρ(β) = 7.265 g/cm^3
		$C_p(l)$ = 28.5 J/mol·K	ρ(*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?

$$\frac{dp}{dT} = \frac{\Delta S(\alpha\to\beta)}{\Delta V(\alpha\to\beta)};\ \Delta S(\alpha \to \beta) = \frac{\Delta H(\alpha\to\beta)}{T_t} = \frac{2{,}095\text{ J/mol}}{286\text{ K}} = 7.325\text{ J/mol·K}$$

$$\Delta V(\alpha \to \beta) = V_\beta - V_\alpha = \left(\frac{1\text{ cm}^3}{7.265\text{ g}} - \frac{1\text{ cm}^3}{5.77\text{ g}}\right)\left(\frac{118.71\text{ g}}{1\text{ mol}}\right)\left(\frac{101.32\frac{\text{J}}{\text{mol}}}{1\text{ L·atm}}\right) = -0.4286\text{ J/mol·atm}$$

Therefore, $\frac{dp}{dT} = \frac{7.325\text{ J/mol·K}}{-0.4286\text{ J/mol·atm}} = -17.09$ **atm/K**

(b) At what temperature (in K) does the transition α-Sn(*s*) → β-Sn(*s*) occur under 50.0 atm?

$\frac{49.0\text{ atm}}{T-286\text{ K}} = -17.09$: **$T$ = 283 K**

(c) At what pressure is the transition temperature for α-Sn(*s*) → β-Sn(*s*) lower by 25 K?

$\frac{p-1}{-25} = -17.09$: **p = 428 atm**

(d) What is the slope of the $p(T)$ curve between β-Sn(*s*) and Sn(*l*) near 505 K?

$$\frac{dp}{dT} = \frac{\Delta S(\beta\to l)}{\Delta V(\beta\to l)};\ \Delta S(\beta \to l) = \frac{\Delta H(\beta\to l)}{T_f} = \frac{7{,}029\text{ J/mol}}{505\text{ K}} = 13.9188\text{ J/mol·K}$$

$$\Delta V(\beta \to l) = V_l - V_\beta = \left(\frac{1\text{ cm}^3}{6.97\text{ g}} - \frac{1\text{ cm}^3}{7.265\text{ g}}\right)\left(\frac{118.71\text{ g}}{1\text{ mol}}\right)\left(\frac{101.32\frac{\text{J}}{\text{mol}}}{1\text{ L·atm}}\right) = 0.06991\text{ J/mol·atm}$$

Therefore, $\frac{dp}{dT} = \frac{13.9188\text{ J/mol·K}}{0.06991\text{ J/mol·atm}} = +199.1$ **atm/K**

(e) Estimate the hypothetical melting point of α-Sn(*s*) and its heat of fusion (in J/mol).

β-Sn(*s*) must have a lower Gibbs free energy than both α-Sn(*s*) and Sn(*l*) between 286 K and 505 K. That means, by extending the Gibbs free energy curve for α-Sn(*s*) above 286 K and the Gibbs free energy curve for Sn(*l*) below 505 K, the two curves will intersect, which gives the hypothetical melting point of α-Sn(*s*). Therefore, at this hypothetical melting point T_m,

$$\Delta G(\beta \to \alpha) = \Delta G(\beta \to l).$$

$$\Delta H(\beta \to \alpha) = -2{,}095 + \int_{286\text{ K}}^{T_m} (25.3 - 30.4)dT = -636.4 - 5.1T_m$$
$$\Delta S(\beta \to \alpha) = -\frac{2095}{286} + \int_{286\text{ K}}^{T_m} \frac{(25.3-30.4)}{T} dT = 21.52 - 5.1\ln T_m$$
$$\Delta G(\beta \to \alpha) = \Delta H(\beta \to \alpha) - T_m\Delta S(\beta \to \alpha) = -636.4 - 26.62T_m + 5.1T_m \ln T_m$$

$$\Delta H(\beta \to l) = 7{,}029 + \int_{505\text{ K}}^{T_m} (28.5 - 30.4)dT = 7{,}988.5 - 1.9T_m$$

$$\Delta S(\beta \rightarrow l) = \frac{7029}{505} + \int_{505\text{ K}}^{T_m} \frac{(28.5-30.4)}{T} dT = 25.75 - 1.9 \ln T_m$$

$$\Delta G(\beta \rightarrow l) = \Delta H(\delta \rightarrow l) - T_m \Delta S(\delta \rightarrow l) = 7,988.5 - 27.65 T_m + 1.9 \ln T_m$$

The hypothetical melting point of α-Sn(*s*) is determined by solving the equation:

$$8,624.9 - 1.03 T_m - 3.2 T_m \ln T_m = 0,$$

which is perhaps most easily solved graphically (using a spreadsheet in Excel) by evaluating the expression for T_m between 286 K and 505 K. From this exercise, $T_m = 423$ K.

The heat of fusion for the process α-Sn(*s*) → Sn(*l*) at 423 K is:

$$\Delta H_{\text{fus}} = T_m \Delta S_{\text{fus}} = T_m\big(\Delta S(\beta \rightarrow l) - \Delta S(\beta \rightarrow \gamma)\big) = T_m(4.23 + 3.2 \ln T_m)$$

$$= (423\text{ K})(23.58\text{ J/mol}\cdot\text{K}) = 9,980\text{ J/mol.}$$

Phase Diagrams: Two-Component Diagrams

(45) What are mole and mass percents of

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

$Al_6Si_2O_{13}$ = $(Al_2O_3)_3$ $(SiO_2)_2$

Mole percent Al_2O_3 = $\frac{3}{5} \times 100\% = 60\%$

Mass percent Al_2O_3 = $\frac{3(101.961)}{426.049} \times 100\% = 71.8\%$

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

$Y_3Fe_5O_{12}$ = $(Y_2O_3)_{3/2}$ $(Fe_2O_3)_{5/2}$

Mole percent Y_2O_3 = $\frac{3/2}{4} \times 100\% = 37.5\%$

Mass percent Y_2O_3 = $\frac{1.5(225.809)}{737.931} \times 100\% = 45.9\%$

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

Ca_3SiO_5 = $(CaO)_3$ $(SiO_2)_1$

Mole percent SiO_2 = $\frac{1}{4} \times 100\% = 25\%$

Mass percent SiO_2 = $\frac{1(60.083)}{228.314} \times 100\% = 26.3\%$

Ca_2SiO_4 = $(CaO)_2$ $(SiO_2)_1$

Mole percent SiO_2 = $\frac{1}{3} \times 100\% = 33.3\%$

Mass percent SiO_2 = $\frac{1(60.083)}{172.237} \times 100\% = 34.9\%$

$Ca_3Si_2O_7$ = $(CaO)_3$ $(SiO_2)_2$

Mole percent SiO_2 = $\frac{2}{5} \times 100\% = 40\%$

Mass percent SiO_2 = $\frac{2(60.083)}{288.397} \times 100\% = 41.7\%$

$CaSiO_3$ = $(CaO)_1$ $(SiO_2)_1$

Mole percent SiO_2 = $\frac{1}{2} \times 100\% = 50\%$

Mass percent SiO_2 = $\frac{1(60.083)}{116.160} \times 100\% = 51.7\%$

(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 $NaPO_3$.

Na_3PO_4 = $(Na_2O)_{3/2}$ $(P_2O_5)_{1/2}$

Mole percent P_2O_5 = $\frac{1/2}{2} \times 100\% = 25\%$

Mass percent P_2O_5 = $\frac{0.5(141.943)}{163.940} \times 100\% = 43.3\%$

$Na_4P_2O_7$ = $(Na_2O)_2$ $(P_2O_5)_1$

Mole percent P_2O_5 = $\frac{1}{3} \times 100\% = 33.3\%$

Mass percent P_2O_5 = $\frac{1(141.943)}{265.901} \times 100\% = 53.4\%$

$Na_5P_3O_{10}$ = $(Na_2O)_{5/2}$ $(P_2O_5)_{3/2}$

Mole percent P_2O_5 = $\frac{3/2}{4} \times 100\% = 37.5\%$

Mass percent P_2O_5 = $\frac{1.5(141.943)}{367.862} \times 100\% = 57.9\%$

$NaPO_3$ = $(Na_2O)_{1/2}$ $(P_2O_5)_{1/2}$

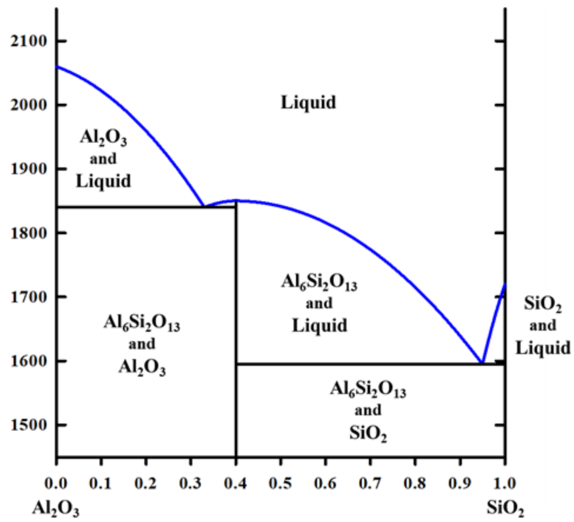
Mole percent P_2O_5 = $\frac{1/2}{1} \times 100\% = 50\%$

Mass percent P_2O_5 = $\frac{0.5(141.943)}{101.961} \times 100\% = 69.6\%$

(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.

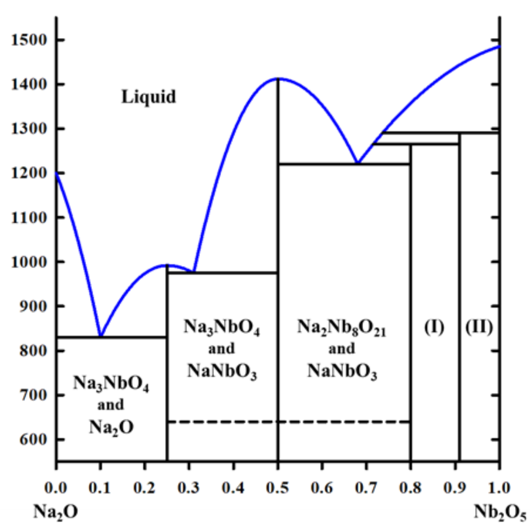
Label the stable phase(s) for all regions in the diagram.



- **$Al_6Si_2O_{13}$ = $(Al_2O_3)_3(SiO_2)_2$, so this compound occurs at x = 0.4.**
- **There is a small two-phase region involving $Al_6Si_2O_{13}$ and Liquid for 0.33 < x < 0.40.**

(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:

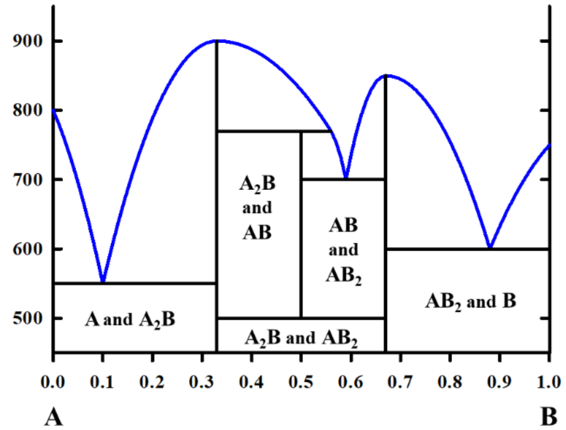
- Na_2O melts at ~1200°C and Nb_2O_5 melts at 1485°C
- There are two congruently melting compounds, Na_3NbO_4 at 992°C and $NaNbO_3$ at 1412°C
- There are two incongruently melting compounds, $Na_2Nb_8O_{21}$ at 1265°C to $Na_2Nb_{20}O_{51}$ and liquid, and $Na_2Nb_{20}O_{51}$ at 1290°C to Nb_2O_5 and 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.



- **Na_3NbO_4 occurs at x = 0.25; $NaNbO_3$ occurs at x = 0.50.**
- **$Na_2Nb_8O_{21}$ occurs at x = 0.80; $Na_2Nb_{20}O_{51}$ occurs at x = 0.91**
- **(I) = coexistence of $Na_2Nb_8O_{21}$ and $Na_2Nb_{20}O_{51}$.**
- **(II) = coexistence of $Na_2Nb_{20}O_{51}$ and Nb_2O_5.**
- **The dashed line indicates the polymorphic transition of $NaNbO_3$.**

(48) Sketch a qualitative T-x_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 $\mathbf{AB_2}$.

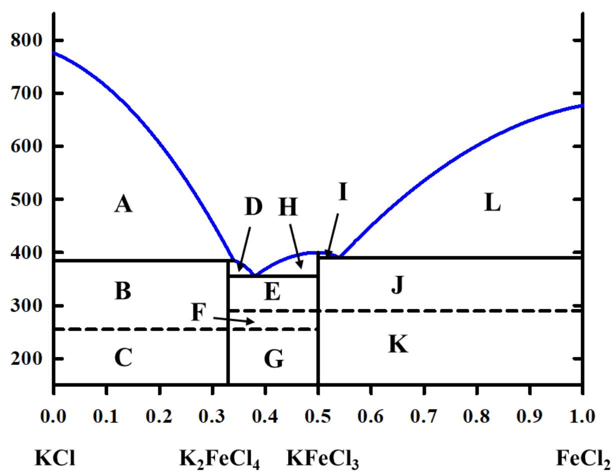


- **x_B = 0.33 for A_2B; x_B = 0.67 for AB_2.**
- **The eutectic features at low and high values of x_B are necessary because A_2B and AB_2 are congruently melting solids. The position of each eutectic point was not specified.**

(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.



A: **KCl(s) and $(KCl)_{1-x}(FeCl_2)_x(l)$, $0 \le x \le 0.34$**
B: **KCl(s) and $K_2FeCl_4(s)$-HT**
C: **KCl(s) and $K_2FeCl_4(s)$-LT**
D: **$K_2FeCl_4(s)$ and $(KCl)_{1-x}(FeCl_2)_x(l)$, $0.34 \le x \le 0.38$**
E: **$K_2FeCl_4(s)$-HT and $KFeCl_3(s)$-HT**
F: **$K_2FeCl_4(s)$-HT and $KFeCl_3(s)$-LT**
G: **$K_2FeCl_4(s)$-LT and $KFeCl_3(s)$-LT**
H: **$KFeCl_3(s)$ and $(KCl)_{1-x}(FeCl_2)_x(l)$, $0.38 \le x \le 0.50$**
I: **$KFeCl_3(s)$ and $(KCl)_{1-x}(FeCl_2)_x(l)$, $0.50 \le x \le 0.54$**
J: **$KFeCl_3(s)$-HT and $FeCl_2(s)$**
K: **$KFeCl_3(s)$-LT and $FeCl_2(s)$**
L: **$FeCl_2(s)$ and $(KCl)_{1-x}(FeCl_2)_x(l)$, $0.54 \le x \le 1.00$**

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

355°C: $(KCl)_{0.62}(FeCl_2)_{0.38}(l) \rightleftharpoons 0.24\ K_2FeCl_4(s) + 0.14\ KFeCl_3(s)$

390°C: $(KCl)_{0.46}(FeCl_2)_{0.54}(l) \rightleftharpoons 0.46\ KFeCl_3(s) + 0.08\ FeCl_2(s)$

(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.

500°C to ~385°C: **$(KCl)_{0.58}(FeCl_2)_{0.42}(l)$**

~385°C to 355°C: **$KFeCl_3(s)$-HT and $(KCl)_{1-x}(FeCl_2)_x(l)$, $0.42 \geq x \geq 0.38$. $KFeCl_3(s)$ precipitates when the temperature reaches the liquidus curve at ~385°C. On cooling, the composition of the liquid gets richer in KCl as more $KFeCl_3(s)$ forms.**

355°C to 290°C: **$K_2FeCl_4(s)$ forms at 355°C as part of a 3-phase eutectic equilibrium with $KFeCl_3(s)$-HT and $(KCl)_{0.62}(FeCl_2)_{0.38}(l)$. On cooling, the liquid solution condenses into $K_2FeCl_4(s)$-HT and $KFeCl_3(s)$-HT. At 290°C, $KFeCl_3(s)$ transforms to the LT form**

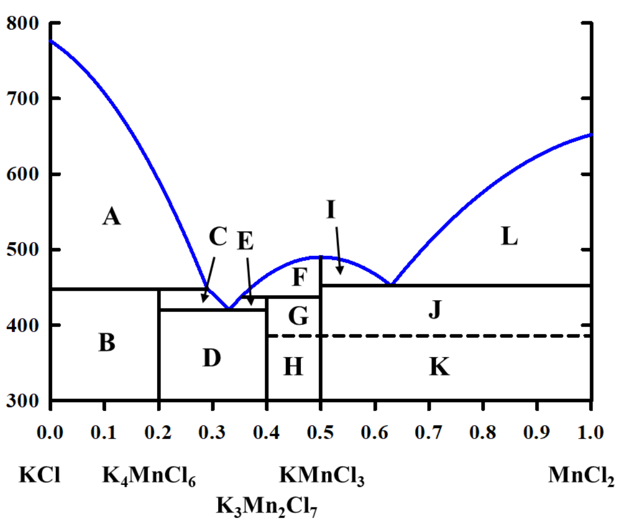
290°C to 255°C: **$K_2FeCl_4(s)$-HT and $KFeCl_3(s)$-LT coexist. At 255°C, $K_2FeCl_4(s)$ transforms to the LT form.**

255°C to 25°C: **$K_2FeCl_4(s)$-LT and $KFeCl_3(s)$-LT coexist. The mole percent of $K_2FeCl_4(s)$ is 38.1% and the mole percent of $KFeCl_3(s)$ is 61.9%.**

(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_{MnCl_2} phase diagram between 300°C and 800°C for this system. Identify the stable phases in each region of the diagram.



A: **KCl(s) and $(KCl)_{1-x}(FeCl_2)_x(l)$, $0 \leq x \leq 0.34$**
B: **KCl(s) and $K_2FeCl_4(s)$-HT**
C: **KCl(s) and $K_2FeCl_4(s)$-LT**
D: **$K_2FeCl_4(s)$ and $(KCl)_{1-x}(FeCl_2)_x(l)$, $0.34 \leq x \leq 0.38$**
E: **$K_2FeCl_4(s)$-HT and $KFeCl_3(s)$-HT**
F: **$K_2FeCl_4(s)$-HT and $KFeCl_3(s)$-LT**
G: **$K_2FeCl_4(s)$-LT and $KFeCl_3(s)$-LT**
H: **$KFeCl_3(s)$ and $(KCl)_{1-x}(FeCl_2)_x(l)$, $0.38 \leq x \leq 0.50$**
I: **$KFeCl_3(s)$ and $(KCl)_{1-x}(FeCl_2)_x(l)$, $0.50 \leq x \leq 0.54$**
J: **$KFeCl_3(s)$-HT and $FeCl_2(s)$**
K: **$KFeCl_3(s)$-LT and $FeCl_2(s)$**
L: **$FeCl_2(s)$ and $(KCl)_{1-x}(FeCl_2)_x(l)$, $0.54 \leq x \leq 1.00$**

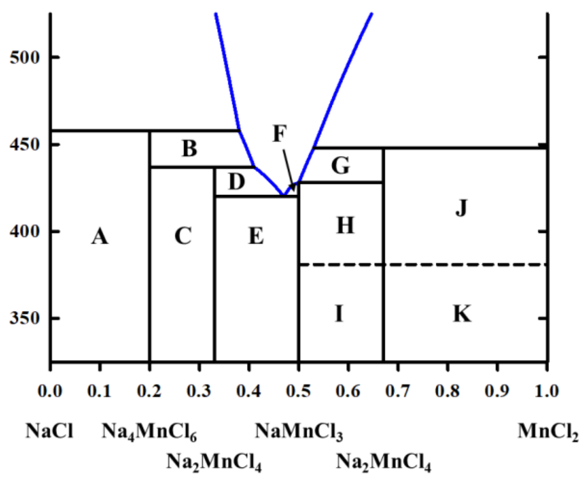
(b) Write the chemical equations for the equilibria at each eutectic point.

(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_{MnCl_2} phase diagram between 300°C and 550°C for this system. Identify the stable phases in each region of the diagram.



A: **NaCl(*s*) and Na_4MnCl_6(*s*)**
B: **Na_4MnCl_6(*s*) and $(NaCl)_{1-x}(MnCl_2)_x$(*l*), $0.38 \le x \le 0.41$**
C: **Na_4MnCl_6(*s*) and Na_2MnCl_4(*s*)**
D: **Na_2MnCl_4(*s*) and $(NaCl)_{1-x}(MnCl_2)_x$(*l*), $0.41 \le x \le 0.47$**
E: **Na_2MnCl_4(*s*) and $NaMnCl_3$(*s*)**
F: **$NaMnCl_3$(*s*) and $(NaCl)_{1-x}(MnCl_2)_x$(*l*), $0.47 \le x \le 0.50$**
G: **$NaMn_2Cl_5$(*s*) and $(NaCl)_{1-x}(MnCl_2)_x$(*l*), $0.50 \le x \le 0.53$**
H: **$NaMnCl_3$(*s*) and $NaMn_2Cl_5$(*s*)-HT**
I: **$NaMnCl_3$(*s*) and $NaMn_2Cl_5$(*s*)-LT**
J: **$NaMn_2Cl_5$(*s*)-HT and $MnCl_2$(*s*)**
K: **$NaMn_2Cl_5$(*s*)-LT and $MnCl_2$(*s*)**

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

420°C: **$(NaCl)_{0.53}(MnCl_2)_{0.47}(l) \rightleftharpoons 0.06\ Na_2MnCl_4(s) + 0.41\ NaMnCl_3(s)$**

(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.

550°C to ~430°C: **$(NaCl)_{0.55}(MnCl_2)_{0.45}$(*l*)**

~430°C to 420°C: **Na_2MnCl_4(*s*) and $(NaCl)_{1-x}(MnCl_2)_x$(*l*), $0.41 \le x \le 0.47$. Na_2MnCl_4(*s*) precipitates when the temperature reaches the liquidus curve at ~430°C. On cooling, the composition of the liquid gets richer in $MnCl_2$ as more Na_2MnCl_4(*s*) forms.**

420°C to 300°C: **$NaMnCl_3$(*s*) forms at 420°C as part of a 3-phase eutectic equilibrium with Na_2MnCl_4(*s*) and $(NaCl)_{0.53}(MnCl_2)_{0.47}$(*l*). On cooling, the liquid solution condenses into Na_2MnCl_4(*s*) and $NaMnCl_3$(*s*). At 290°C, $KFeCl_3$(*s*) transforms to the LT form.**

(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.

550°C to ~500°C: **$(NaCl)_{0.40}(MnCl_2)_{0.60}$(*l*)**

~500°C to 448°C: **$MnCl_2$(*s*) and $(NaCl)_{1-x}(MnCl_2)_x$(*l*), $0.60 \ge x \ge 0.53$. $MnCl_2$(*s*) precipitates when the temperature reaches the liquidus curve at ~500°C. On cooling, the composition of the liquid gets richer in NaCl as more $MnCl_2$(*s*) forms.**

448°C to 428°C:	**$NaMn_2Cl_5$(*s*) forms at 448°C as part of a 3-phase peritectic equilibrium with $MnCl_2$(*s*) and $(NaCl)_{0.47}(MnCl_2)_{0.53}$(*l*). On cooling, $MnCl_2$ dissolves leaving $NaMn_2Cl_5$(*s*)-HT and $(NaCl)_{1-x}(MnCl_2)_x$(*l*), $0.53 \geq x \geq 0.50$. At 428°C, the liquid condenses to $NaMnCl_3$(*s*).**
428°C to 381°C:	**$NaMnCl_3$(*s*) and $NaMn_2Cl_5$(*s*)-HT coexist. At 381°C, $NaMn_2Cl_5$(*s*) transforms to the LT form.**
381°C to 300°C:	**$NaMnCl_3$(*s*) and $NaMn_2Cl_5$(*s*)-LT coexist.**

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

(a) Identify the equilibrium phases existing in each region **A-K**.

A: $SrAl_4$ (*s*) + Sr_xAl_{1-x} (*l*) ($0.01 \leq x \leq 0.20$)

B: $SrAl_4$ (*s*) + Al (*s*)

C: $SrAl_4$ (*s*) + Sr_xAl_{1-x} (*l*) ($0.20 \leq x \leq 0.33$)

D: $SrAl_4$ (*s*) + $SrAl_2$ (*s*)

E: $SrAl_2$ (*s*) + Sr_xAl_{1-x} (*l*) ($0.33 \leq x \leq 0.72$)

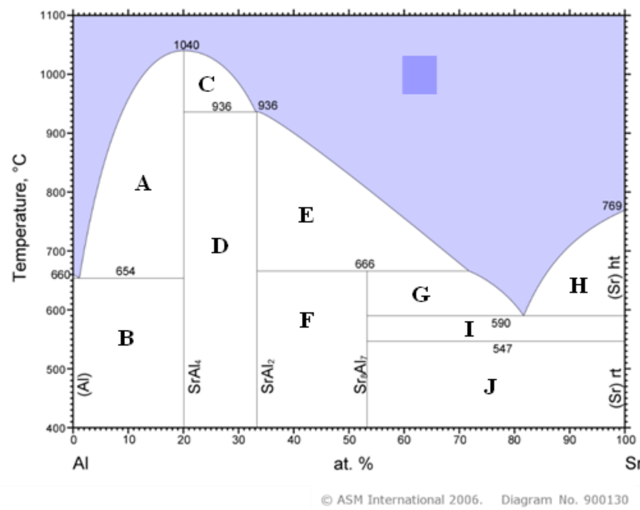
F: $SrAl_2$ (*s*) + Sr_8Al_7 (*s*)

G: Sr_8Al_7 (*s*) + Sr_xAl_{1-x} (*l*) ($0.72 \leq x \leq 0.82$)

H: Sr (*s*; ht) + Sr_xAl_{1-x} (*l*) ($0.82 \leq x \leq 1.00$)

I: Sr_8Al_7 (*s*) + Sr (*s*; ht)

J: Sr_8Al_7 (*s*) + Sr (*s*; rt)



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

This line indicates the polymorphic transition between rt-Sr(*s*) and ht-Sr(*s*).

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

666°C:	**Peritectic Temperature**	**Sr_8Al_7 (*s*) ⇌ 2.41 $SrAl_2$ (*s*) + 7.76 $Sr_{0.72}Al_{0.28}$ (*l*)**
654°C:	**Eutectic Temperature**	**$Sr_{0.01}Al_{0.99}$ (*l*) ⇌ 0.01 $SrAl_2$ (*s*) + 0.97 Al (*s*)**
590°C:	**Eutectic Temperature**	**$Sr_{0.82}Al_{0.18}$ (*l*) ⇌ 0.03 Sr_8Al_7 (*s*) + 0.61 Sr (*s*; ht)**

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

Since Sr_8Al_7 (*s*) melts incongruently, it will not be effective to use a stoichiometric mixture of Sr and Al. Select an initial mixture of Sr and Al such that the mole fraction of Sr is close to 0.75 (no smaller than 0.72) and heat this mixture above 769° C (the melting point of Sr) to obtain a liquid. On cooling, crystals of Sr_8Al_7 will precipitate from the melt when the temperature reaches the liquidus curve of region G at a temperature below 666° C and above 590° C. By holding the temperature in this range, then crystals of Sr_8Al_7 can grow.

(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?

FW(Sr_8Al_7) = 889.834 g/mol; 10.00 g Sr_8Al_7 = 11.24 mmol.

On heating from 25°C, Sr_8Al_7(*s*) melts peritectically at 666°C into $SrAl_2$(*s*) and $Sr_{0.72}Al_{0.28}$(*l*):

Sr_8Al_7 (*s*) → 2.41 $SrAl_2$ (*s*) + 7.76 $Sr_{0.72}Al_{0.28}$ (*l*)

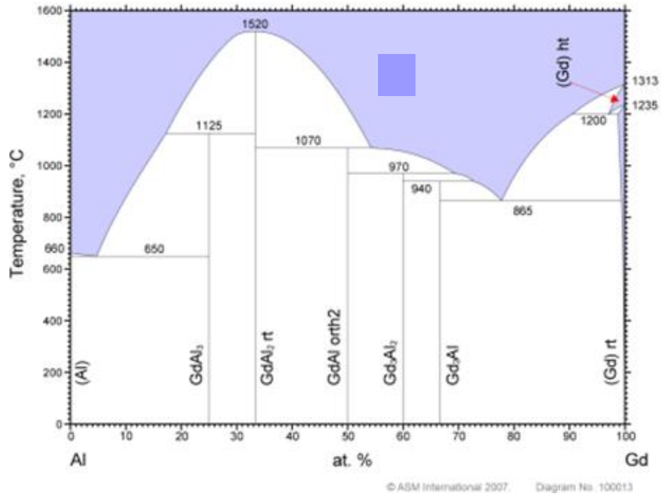
Therefore, the sample converts into 27.09 mmol or 3.84 g $SrAl_2$(*s*) and 87.22 mmol or 6.16 g liquid with mole fraction of Sr at 0.72.

(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?

As the sample cools, $SrAl_2$(*s*) will precipitate from the liquid mixture when the temperature reaches the liquidus curve at ~800ºC. At 666ºC, Sr_8Al_7(*s*) forms as the liquid phase gets richer in Sr. Ultimately, at 590ºC, Sr(*s*) will form. Due to rapid cooling, it is doubtful that true equilibrium can be established so that the sample will contain a mixture of Sr_8Al_7(*s*), $SrAl_2$(*s*), and Sr(*s*).

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

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



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

$GdAl_3$(*s*) and $Gd_{0.08}Al_{0.92}$(*l*);

$GdAl_3 = Gd_{0.25}Al_{0.75}$(*s*).

Fraction $GdAl_3 = \frac{0.15-0.08}{0.25-0.08} = 0.41$

Fraction $Gd_{0.08}Al_{0.92} = 0.59$

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

Gd_3Al_2(*s*) and Gd_2Al(*s*);

$Gd_2Al = Gd_{0.67}Al_{0.33}$(*s*).

Fraction $Gd_2Al = \frac{0.62-0.60}{0.67-0.60} = 0.29$

Fraction $Gd_3Al_2 = 0.71$

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

The peritectic melting point of GdAl(*s*):

$Gd_{0.5}Al_{0.5}(s) \rightleftharpoons 0.19\ Gd_{0.33}Al_{0.67}(s) + 0.81\ Gd_{0.54}Al_{0.46}(l)$

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

Only $Gd_{0.70}Al_{0.30}$(*l*)

(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.

650ºC: **$Gd_{0.05}Al_{0.95}(l) \rightleftharpoons 0.80\ Al(s) + 0.20\ Gd_{0.25}Al_{0.75}(s)$**

$Gd_{0.05}Al_{0.95}(l) \rightleftharpoons 0.80\ Al(s) + 0.05\ GdAl_3(s)$

865ºC: **$Gd_{0.78}Al_{0.22}(l) \rightleftharpoons 0.66\ Gd_{0.67}Al_{0.33}(\ s) + 0.34\ Gd_{0.99}Al_{0.01}(s)$**

$Gd_{0.78}Al_{0.22}(l) \rightleftharpoons 0.22\ Gd_2Al(s) + 0.34\ Gd_{0.99}Al_{0.01}(ss)$

940ºC: **$Gd_{0.67}Al_{0.33}(s) \rightleftharpoons 0.46\ Gd_{0.60}Al_{0.40}(s) + 0.54\ Gd_{0.73}Al_{0.27}(l)$**

$Gd_2Al(s) \rightleftharpoons 0.27\ Gd_3Al_2(s) + 1.62\ Gd_{0.73}Al_{0.27}(l)$

970ºC: **$Gd_{0.60}Al_{0.40}(s) \rightleftharpoons 0.48\ Gd_{0.50}Al_{0.50}(s) + 0.52\ Gd_{0.69}Al_{0.31}(l)$**

$Gd_3Al_2(s) \rightleftharpoons 1.20\ GdAl(s) + 2.60\ Gd_{0.69}Al_{0.31}(l)$

1070ºC: **$Gd_{0.50}Al_{0.50}(s) \rightleftharpoons 0.19\ Gd_{0.33}Al_{0.67}(s) + 0.81\ Gd_{0.54}Al_{0.46}(l)$**

$GdAl(s) \rightleftharpoons 0.12\ GdAl_2(s) + 1.62\ Gd_{0.54}Al_{0.46}(l)$

1125ºC: **$Gd_{0.25}Al_{0.75}(s) \rightleftharpoons 0.50\ Gd_{0.33}Al_{0.67}(s) + 0.50\ Gd_{0.17}Al_{0.83}(l)$**

$GdAl_3(s) \rightleftharpoons 0.68\ GdAl_2(s) + 2.00\ Gd_{0.17}Al_{0.83}(l)$

1200ºC: **$Gd_{0.97}Al_{0.03}(s) \rightleftharpoons 0.83\ Gd_{0.98}Al_{0.02}(s) + 0.17\ Gd_{0.92}Al_{0.08}(l)$**

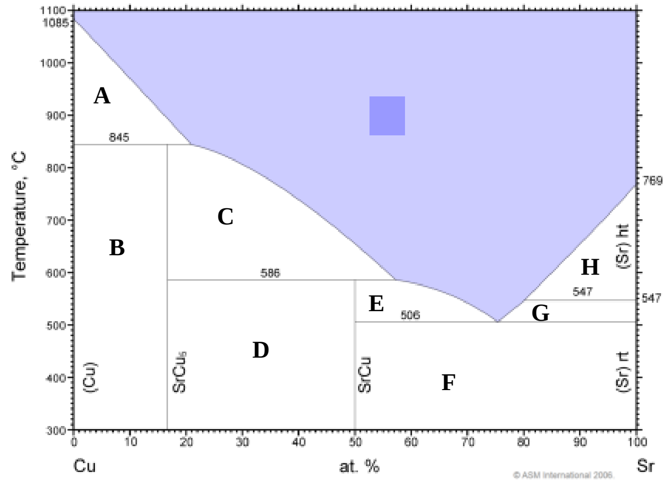
1520ºC: **$GdAl_2(s) \rightleftharpoons GdAl_2(l)$**

(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?

$GdAl_2$(*s*) melts congruently at 1520ºC. Using excess Al can lower the temperature at which crystals of $GdAl_2$ can be obtained. Heating a mixture that is ~80 mole percent Al, ~20 mole percent Gd up to 1200ºC will melt Al; Gd will dissolve in molten Al over time. Once the mixture is completely molten, then it should be cooled to 1150ºC. Crystals of $GdAl_2$ can grow. Finally, the sample should be quenched to room 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.



A: Cu(*s*) + Sr_xCu_{1-x}(*l*), ($0 \le x \le 0.21$)

B: Cu(*s*) + $SrCu_5$(*s*)

C: $SrCu_5$(*s*) + Sr_xCu_{1-x}(*l*), ($0.21 \le x \le 0.57$)

D: $SrCu_5$(*s*) + SrCu(*s*)

E: SrCu(*s*) + Sr_xCu_{1-x}(*l*), ($0.57 \le x \le 0.75$)

F: SrCu(*s*) + Sr(*s*, rt)

G: Sr(*s*, rt) + Sr_xCu_{1-x}(*l*), ($0.75 \le x \le 0.80$)

H: Sr(*s*, ht) + Sr_xCu_{1-x}(*l*), ($0.80 \le x \le 1$)

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

This line indicates the polymorphic transition between rt-Sr(*s*) and ht-Sr(*s*).

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

506ºC:	**Eutectic Temperature**	**$Sr_{0.75}Cu_{0.25}(l) \rightleftharpoons 0.25\ SrCu(s) + 0.50\ Sr(s, rt)$**
586ºC:	**Peritectic Temperature**	**$SrCu(s) \rightleftharpoons 0.76\ SrCu_5(s) + 0.41\ Sr_{0.57}Cu_{0.43}(l)$**
845ºC:	**Peritectic Temperature**	**$SrCu_5(s) \rightleftharpoons 1.24\ Cu(s) + 4.76\ Sr_{0.21}Cu_{0.79}(l)$**

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

Heat a mixture of ~60 mole percent Sr, ~40 mole percent Cu until it fully melts (the mixture can be heated to 1100ºC where both elements are molten). Then, slowly cool and hold when the temperature gets just below 580ºC and no lower than 510ºC. Centrifuge or separate the crystals of SrCu from the flux.

(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?

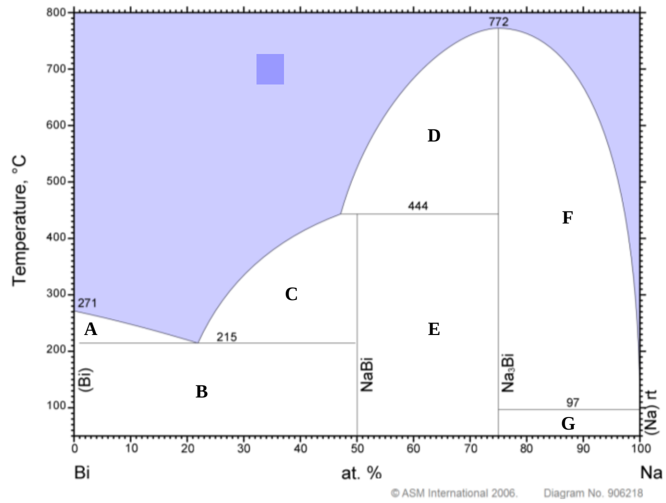
FW($SrCu_5$) = 405.35 g/mol; 5.00 g $SrCu_5$ = 12.34 mmol.

On heating from 25°C, $SrCu_5$(*s*) melts peritectically at 845°C into Cu(*s*) and $Sr_{0.21}Cu_{0.79}$(*l*):

$$SrCu_5(s) \rightarrow 1.24\ Cu(s) + 4.76\ Sr_{0.21}Cu_{0.79}(l)$$

Therefore, the sample converts into 15.30 mmol or 0.97 g Cu(*s*) and 58.74 mmol or 4.03 g liquid with mole fraction of Sr at 0.21.

(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.

A: Bi(*s*) + Na_xBi_{1-x}(*l*), ($0 \le x \le 0.22$)

B: Bi(*s*) + NaBi(*s*)

C: NaBi(*s*) + Na_xBi_{1-x}(*l*), ($0.22 \le x \le 0.48$)

D: Na_3Bi(*s*) + Na_xBi_{1-x}(*l*), ($0.48 \le x \le 0.75$)

E: NaBi(*s*) + Na_3Bi(*s*)

F: Na_3Bi(*s*) + Na_xBi_{1-x}(*l*), ($0.75 \le x < 1.00$)

G: Na_3Bi(*s*) + Na(*s*)

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

97ºC: Eutectic Temperature **$Na_{0.99}Bi_{0.01}$(*l*) ⇌ 0.01 Na_3Bi(*s*) + 0.96 Na(*s*)**

This is very difficult to read from the phase diagram; the liquid phase is a very dilute solution of Bi dissolved in Na(*s*).

215ºC: Eutectic Temperature **$Na_{0.22}Bi_{0.78}$(*l*) ⇌ 0.56 Bi(*s*) + 0.22 NaBi(*s*)**

444ºC: Peritectic Temperature **NaBi(*s*) ⇌ 0.04 Na_3Bi(*s*) + 1.85 $Na_{0.48}Bi_{0.52}$(*l*)**

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

Heat a mixture of ~40 mole percent Na, ~60 mole percent Bi to ~500ºC until it fully melts. Then, slowly cool and hold when the temperature gets to ~350ºC. Centrifuge or separate the crystals of NaBi from the flux.

(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?

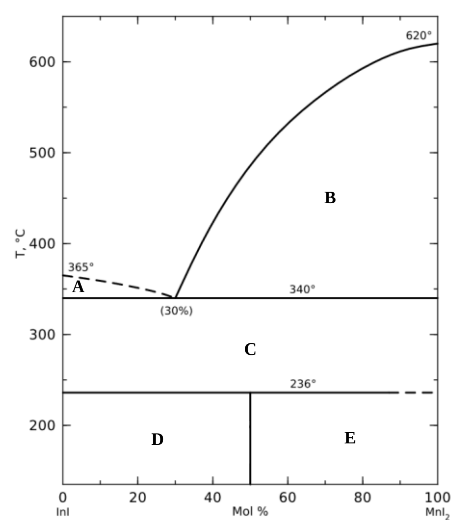
FW(NaBi) = 405.35 g/mol; 5.00 g NaBi = 12.34 mmol.

On heating from 25°C, NaBi(*s*) melts peritectically at 444°C into Na_3Bi(*s*) and $Na_{0.48}Bi_{0.52}$(*l*):

NaBi(*s*) → 0.04 Na_3Bi(*s*) + 1.85 $Na_{0.48}Bi_{0.52}$(*l*)

Therefore, the sample converts into 15.30 mmol or 0.97 g Na_3Bi(*s*) and 58.74 mmol or 4.03 g liquid with mole fraction of Na at 0.48.

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



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

A: InI(*s*) + $(InI)_{1-x}(MnI_2)_x$(*l*), ($0 \le x \le 0.30$)

B: MnI_2(*s*) + $(InI)_{1-x}(MnI_2)_x$(*l*), ($0.30 \le x \le 1$)

C: InI(*s*) + MnI_2(*s*)

D: InI(*s*) + $InMnI_3$(*s*)

E: MnI_2(*s*) + $InMnI_3$(*s*)

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

236ºC: $InMnI_3$(*s*) ⇌ InI(*s*) + MnI_2(*s*)

340ºC: $(InI)_{0.70}(MnI_2)_{0.30}$(*l*) ⇌ 0.70 InI(*s*) + 0.30 MnI_2(*s*

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

(1) At 236ºC, $InMnI_3$(*s*) → InI(*s*) + MnI_2(*s*)

(2) At 365ºC, InI(*s*) → InI(*l*) while some MnI_2 dissolves in the melt

(3) At ~480ºC, $MnI_2(s) \rightarrow MnI_2(l)$ completely melts

NOTE: It is unlikely that the mixture of InI(*s*) and $MnI_2(s)$ will create a eutectic mixture at 340ºC due to kinetic reasons.

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

Slow cooling a equimolar mixture of InI and MnI_2 will most likely yield a mixture of InI(*s*) and $MnI_2(s)$. One suggested approach is to melt the equimolar mixture followed by rapid cooling to ~230ºC and annealing at this temperature.

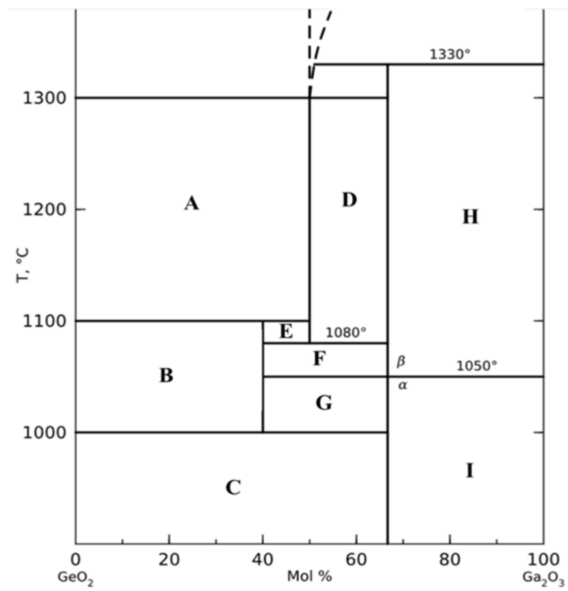
(e) If a mixture containing 80 mole percent MnI_2 is used to grow crystals of MnI_2, what fraction of the melt can be converted to large MnI_2 crystals?

Crystals of $MnI_2(s)$ will grow if some liquid remains in the reaction container. As $MnI_2(s)$ grows, the composition of the liquid follows the liquidus curve until the eutectic point is reached. Therefore, large crystals of MnI_2 form according to the reaction:

$$(InI)_{0.20}(MnI_2)_{0.80}(l) \rightarrow 0.28\ (InI)_{0.70}(MnI_2)_{0.30}(l) + 0.72\ MnI_2(s).$$

The fraction of the melt that can form large crystals of MnI_2 is 0.72 = (0.5/0.7) = (0.8–0.3) / (1.0–0.3).

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



(a) Identify all ternary compounds in the diagram.

$(Ga_2O_3)_{0.40}(GeO_2)_{0.60} = Ga_4Ge_3O_{12}$

$(Ga_2O_3)_{0.50}(GeO_2)_{0.50} = Ga_2GeO_5$

$(Ga_2O_3)_{0.67}(GeO_2)_{0.33} = Ga_4GeO_8$

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

A: $GeO_2(s) + Ga_2GeO_5(s)$

B: $GeO_2(s) + Ga_4Ge_3O_{12}(s)$

C: $GeO_2(s) + \alpha\text{-}Ga_4GeO_8(s)$

D: $Ga_2GeO_5(s) + \beta\text{-}Ga_4GeO_8(s)$

E: $Ga_4Ge_3O_{12}(s) + Ga_2GeO_5(s)$

F: $Ga_4Ge_3O_{12}(s) + \beta\text{-}Ga_4GeO_8(s)$

G: $Ga_4Ge_3O_{12}(s) + \alpha\text{-}Ga_4GeO_8(s)$

H: $\beta\text{-}Ga_4GeO_8(s) + Ga_2O_3(s)$

I: $\alpha\text{-}Ga_4GeO_8(s) + Ga_2O_3(s)$

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

1000ºC: $Ga_4Ge_3O_{12}(s) \rightleftharpoons 2\ GeO_2(s) + \alpha\text{-}Ga_4GeO_8(s)$

1080ºC: $4\ Ga_2GeO_5(s) \rightleftharpoons Ga_4Ge_3O_{12}(s) + \beta\text{-}Ga_4GeO_8(s)$

1100ºC: $Ga_4Ge_3O_{12}(s) \rightleftharpoons GeO_2(s) + 2\ Ga_2GeO_5(s)$

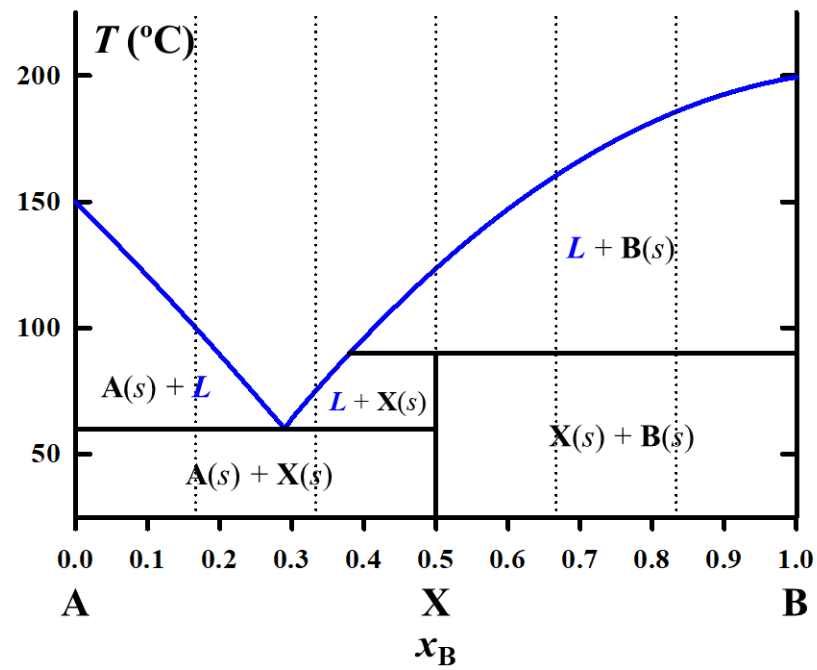
1300ºC: $2\ Ga_2GeO_5(s) \rightleftharpoons GeO_2(s) + \beta\text{-}Ga_4GeO_8(s)$

1330ºC: $\beta\text{-}Ga_4GeO_8(s) \rightleftharpoons Ga_2GeO_5(s) + Ga_2O_3(s)$ (In this case, the mol % of Ga_2O_3 in Ga_2GeO_5 is slightly higher than 50%.)

(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_B phase diagram for the **A-B** system consistent with these observations.

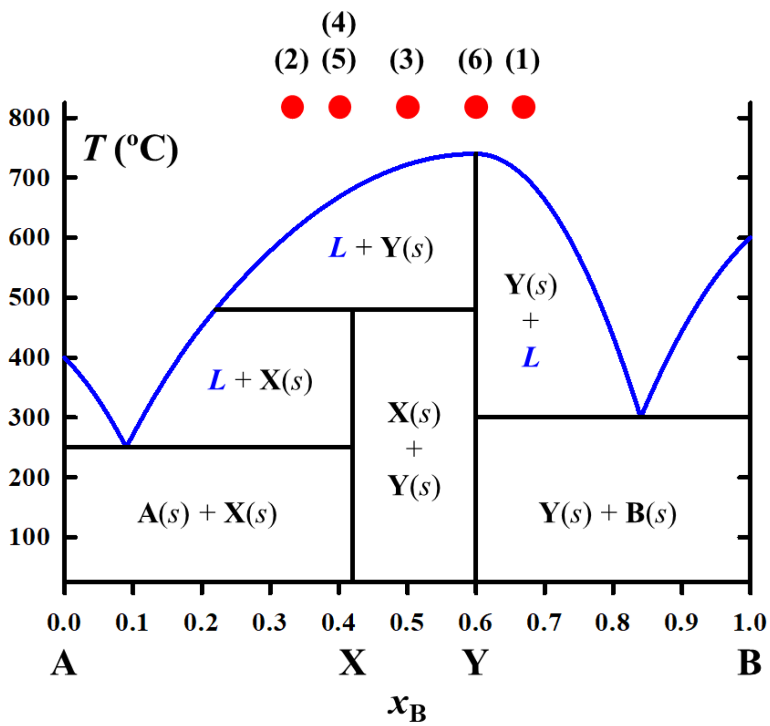


The vertical dotted lines indicate the 5 loaded compositions. Compound X, which is AB, melts peritectically at 90°C into B and an A-rich liquid. There is a eutectic point at 60°C and x_B just below 0.3.

(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_B phase diagram for the **A-B** system consistent with these observations.

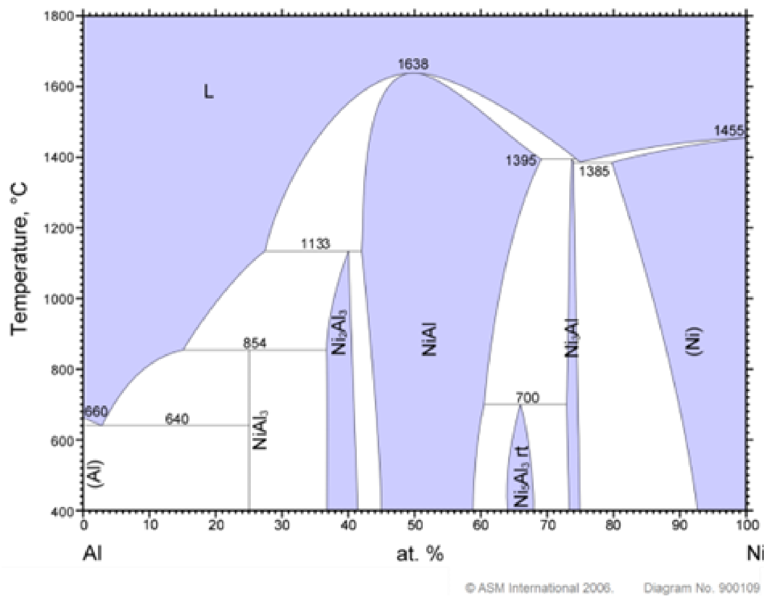


Reaction (6): **Y = A_2B_3 is a congruently melting phase.**

Reaction (1): **On cooling this A:2B liquid mixture, Y crystallizes (precipitates) and there is a remaining liquid that provides a medium for the growth of good crystals of Y. The mixture approaches a eutectic point, at which B (rapidly) crystallizes.**

Reactions (2-5): **X decomposes peritectically and has a composition close to A_3B_2. Since reaction (3) gives X and Y, the composition of X must be less than 50 atomic % B. From the conditions of (4) and (5), we can conclude that the peritectic temperature is slightly less than 500°C. There is a eutectic point for an A-rich composition, so that A precipitates for A-rich mixtures, as in (2).**

(60) In the Al-Ni phase diagram:



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

x_{Ni} = 0.82 at 1385ºC, which means 18 mole percent Al in fcc Ni(*s*).

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

15 mole percent Ni;

0.63 $NiAl_3$(*s*) and 0.37 $Ni_{0.09}Al_{0.91}$(*l*)

15 mole percent Al;

0.33 Ni_3Al(*s*) and 0.67 $Ni_{0.90}Al_{0.10}$(*s*)

66.7 mole percent Ni;

0.53 $Ni_{0.61}Al_{0.39}$(*s*) and 0.47 $Ni_{0.73}Al_{0.27}$(*s*)
These are NiAl and Ni_3Al solid solutions.

66.7 mole percent Al.

0.33 $NiAl_3$(*s*) and 0.67 $Ni_{0.37}Al_{0.63}$(*s*)

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

When the temperature reaches the liquidus curve at ~970ºC, then Al-rich Ni_2Al_3(*s*) precipitates ($Ni_{1.8}Al_3$). The solid continues to precipitate, getting slightly richer in Al, until 854ºC, which is the peritectic melting point of $NiAl_3$ and the composition of the melt is $Ni_{0.15}Al_{0.85}$(*l*). If equilibrium is achieved, then Al-rich Ni_2Al_3(*s*) and the liquid will convert into an even more Al-rich liquid and $NiAl_3$(*s*). At 640ºC, Al(*s*) will form. If equilibrium can be maintained, then there should be 20 mole percent Al(*s*) and 80 mole percent $NiAl_3$(*s*). However, if the cooling rate is too fast to establish proper equilibrium, there could be some Al-rich Ni_2Al_3(*s*) as well.

(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*).

<u>Minimum Ni content</u>: 1133°C, 42 atomic percent Ni, $Ni_{0.42}Al_{0.58}$(*s*). Each atomic site is surrounded, on average, by 3.4 Ni atoms and 4.6 Al atoms.

<u>Maximum Ni content</u>: 1395°C, 69 atomic percent Ni, $Ni_{0.69}Al_{0.31}$(*s*). Each atomic site is surrounded, on average, by 5.5 Ni atoms and 2.5 Al atoms.

(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?

1638°C is the melting point of NiAl(*s*). At this temperature, NiAl(*s*) is in equilibrium with NiAl(*l*), so that $G^{(s)}(\text{NiAl}) = G^{(l)}(\text{NiAl})$. Therefore, $G^{(l)}(\text{NiAl})$ is the free energy of mixing relative to the unmixed elemental liquids:

$$G^{(s)}(\text{NiAl}) = G^{(l)}(\text{NiAl}) = 2(8.314)(1911)[0.5\ln 0.5 + 0.5\ln 0.5] = -22,026\ \text{J/mol}.$$

(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.

The homogeneity range of NiAl(*s*) is wider on the Ni-rich side than on the Al-rich side. This solid solution is most likely a substitutional alloy, for which Ni atoms replace Al atoms or vice versa, depending on the overall composition. Since Ni has a higher cohesive energy than Al, Ni-rich NiAl solid solutions will have lower free energy (via the enthalpy term) than Al-rich NiAl solid solutions. As a result, the homogeneity width of NiAl extends further toward Ni-rich compositions than they do toward Al-rich compositions.

(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*)

When NaCl(*s*) is in equilibrium with pure Na(*s*), then the vapor pressure of Na is the equilibrium vapor pressure for Na(*s*). The following equilibria are relevant:

NaCl(*s*) ⇌ Na(*s*) + ½ Cl_2(*g*): $\Delta G°(298\text{ K}) = 411,150 - (90.55)(298) = 384,166.1$ **J/mol**

$K = p_{Cl_2}^{1/2} = e^{-155.1} = 4.56 \times 10^{-68}$

Na(*s*) ⇌ Na(*g*): $\Delta G°(298\text{ K}) = 107,320 - (102.4)(298) = 76,804.8$ **J/mol**

$K = p_{Na} = e^{-31.0} = 3.44 \times 10^{-14}$

½ Cl_2(*g*) ⇌ Cl(*g*): $\Delta G°(298\text{ K}) = 121,680 - (53.61)(298) = 105,704.2$ **J/mol**

$K = \frac{p_{Cl}}{p_{Cl_2}^{1/2}} = e^{-42.7} = 2.96 \times 10^{-19}$

Therefore, $p_{Cl_2} = 2.08 \times 10^{-135}$ **atm;** $p_{Cl} = 1.35 \times 10^{-86}$ **atm; and** $p_{Na} = 3.44 \times 10^{-14}$ **atm.**

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

When NaCl(*s*) is in equilibrium with Cl_2(*g*) at 1 atm pressure, then the activity of Na(*s*) is not unity and the vapor pressure of Na is lower than the equilibrium vapor pressure of pure Na(*s*). The following equilibria are relevant:

NaCl(*s*) ⇌ Na(*g*) + Cl(*g*): $\Delta G°(298\text{ K}) = 640,150 - (246.56)(298) = 566,675.1$ **J/mol**

$K = p_{Na}p_{Cl} = e^{-228.7} = 10^{-99.33} = 4.65 \times 10^{-100}$

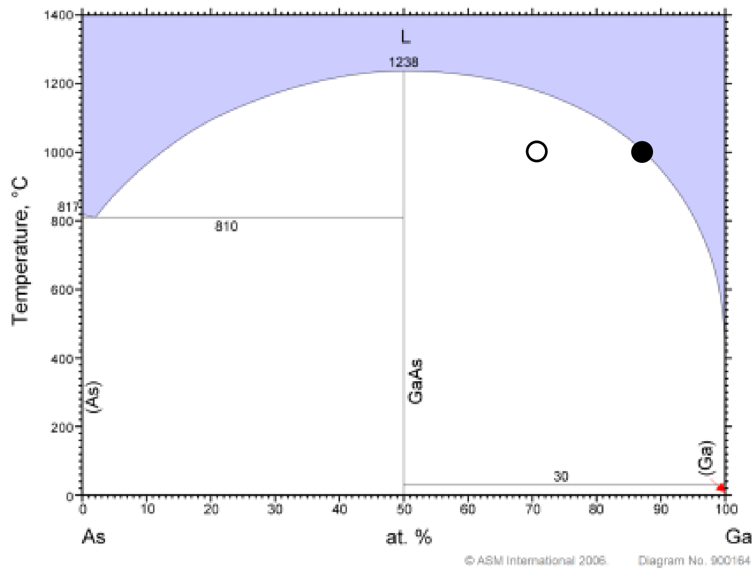
½ Cl_2(*g*) ⇌ Cl(*g*): $\Delta G°(298\text{ K}) = 121,680 - (53.61)(298) = 105,704.2$ **J/mol**

$K = \frac{p_{Cl}}{p_{Cl_2}^{1/2}} = e^{-42.7} = 2.96 \times 10^{-19}$

Therefore, $p_{Cl_2} = 1.00$ **atm;** $p_{Cl} = 2.96 \times 10^{-19}$ **atm; and** $p_{Na} = 1.57 \times 10^{-81}$ **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?



The black dot indicates the position on the liquidus curve that will give this result: $x_{Ga} = 0.87$.

Therefore, $Ga_{0.87}As_{0.13}(l)$, which can be expressed as $(GaAs)_{0.13}Ga_{0.74}(l)$. This formula can be re-expressed so that the subscripts add to 1 by multiplying each by 1/0.87. Then, from $(GaAs)_{0.149}Ga_{0.851}(l)$, the solubility is 14.9 mole percent.

FW(GaAs) = 144.645 g/mol.

1g GaAs = 6.913 mmol.

Need (6.913 mmol / 0.149)(0.851) or 39.48 mmol Ga = 2.753 g Ga.

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

The white dot indicates the position on the phase diagram, which identifies a mixture of GaAs(*s*) and $Ga_{0.87}As_{0.13}(l)$ as the two equilibrium phases. Using the lever rule, the fraction of the liquid is

(0.70 – 0.50) / (0.87 – 0.50) = 0.20 / 0.37 = 0.541

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

817°C identifies the melting point of As(*s*), which must occur at an elevated pressure above 1 atm. This pressure is ~28 atm.

(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*)

When GaAs(*s*) is in equilibrium with pure Ga(*s*), then the vapor pressure of Ga is the equilibrium vapor pressure for Ga(*s*). The following equilibria are relevant:

GaAs(*s*) ⇌ Ga(*g*) + ¼ $As_4(g)$: $\Delta G°(298\ \text{K}) = 375{,}800 - (184.8)(298) = 320{,}729.6$ **J/mol**

$K = p_{Ga}p_{As_4}^{1/4} = e^{-129.5} = 6.01 \times 10^{-57}$

Ga(*s*) ⇌ Ga(*g*): $\Delta G°(298\ \text{K}) = 272{,}000 - (128.2)(298) = 233{,}796.4$ **J/mol**

$K = p_{Ga} = e^{-94.4} = 1.04 \times 10^{-41}$

Therefore, $p_{Ga} = 1.04 \times 10^{-41}$ **atm;** $p_{As_4} = 1.12 \times 10^{-61}$ **atm.**

- Pure As(*s*)

When GaAs(*s*) is in equilibrium with pure As(*s*), then the vapor pressure of As is the equilibrium vapor pressure for As(*s*). The following equilibria are relevant:

GaAs(*s*) ⇌ Ga(*g*) + ¼ As$_4$(*g*): $\Delta G°(298\text{ K}) = 375,800 - (184.8)(298) = 320,729.6$ **J/mol**

$K = p_{\mathrm{Ga}} p_{\mathrm{As_4}}^{1/4} = e^{-129.5} = 6.01 \times 10^{-57}$

As(*s*) ⇌ ¼ As$_4$(*g*): $\Delta G°(298\text{ K}) = 36,000 - (55.5)(298) = 19,461.0$ **J/mol**

$K = p_{\mathrm{As_4}}^{1/4} = e^{-7.855} = 3.88 \times 10^{-4}$

Therefore, $p_{\mathrm{Ga}} = 1.55 \times 10^{-53}$ **atm;** $p_{\mathrm{As_4}} = 2.26 \times 10^{-14}$ **atm.**

(63) Elements **A** and **B** form two stoichiometric compounds **A$_2$B** and **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 **A$_2$B-AB$_2$** is $\log p_{\mathbf{B}} = -\frac{11{,}242}{T} + 6.53$ and the vapor pressure exerted by the equilibrated **A-A$_2$B** 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(*s*) ⇌ B(*g*): $\Delta G_{\mathrm{sub}}(T) = -RT\ln p_{\mathrm{B}}^0 = 187.225.4 - 108.79\,T = \Delta H_{\mathrm{sub}}(T) - T\Delta S_{\mathrm{sub}}(T)$.

$\Delta H_{\mathrm{sub}}(T) = 187.2\ \mathrm{kJ/mol}$

(b) Determine ΔG_f^0(**AB$_2$**) and ΔG_f^0(**A$_2$B**) at 1000°C.

2 AB$_2$(*s*) ⇌ A$_2$B(*s*) + 3 B(*s*): **For an equilibrated mixture of AB$_2$(*s*) and A$_2$B(*s*), their activities are 1. The relationship between Gibbs free energies at equilibrium is:**

$2G°(\mathrm{AB_2}) = G°(\mathrm{A_2B}) + 3(G°(\mathrm{B}) + RT\ln a_{\mathrm{B}})$, **so that**

$\Delta G° = \Delta G_f^0(\mathrm{A_2B}) - 2\Delta G_f^0(\mathrm{AB_2}) = -3RT\ln\frac{p_{\mathrm{B}}}{p_{\mathrm{B}}^0}$

$= -57.43\,T\left(\log p_{\mathrm{B}} - \log p_{\mathrm{B}}^0\right) = -57.43\,T\left(\frac{-1{,}462}{T} + 0.847\right)$

$= 83,962.7 - 48.64\,T$

At 1000°C, $\Delta G° = \Delta G_f^0(\mathrm{A_2B}) - 2\Delta G_f^0(\mathrm{AB_2}) = 22,044.0$ **J/mol**

A$_2$B(*s*) ⇌ 2 A(*s*) + B(*s*): **For an equilibrated mixture of A(*s*) and A$_2$B(*s*), their activities are 1. The relationship between Gibbs free energies at equilibrium is:**

$G°(\mathrm{AB_2}) = 2G°(\mathrm{A}) + (G°(\mathrm{B}) + RT\ln a_{\mathrm{B}})$, **so that**

$\Delta G° = -\Delta G_f^0(\mathrm{A_2B}) = -RT\ln\frac{p_{\mathrm{B}}}{p_{\mathrm{B}}^0} = -19.14\,T\left(\log p_{\mathrm{B}} - \log p_{\mathrm{B}}^0\right)$

$= -19.14\,T\left(\frac{-2{,}823}{T} + 1.217\right) = 54,032.2 - 23.29\,T$

At 1000°C, $\Delta G° = -\Delta G_f^0(\mathrm{A_2B}) = +24,384.0$ **J/mol**

Therefore, $\Delta G_f^0(\mathrm{A_2B}) = -24,384$ **J/mol** $\Delta G_f^0(\mathrm{AB_2}) = -23,214$ **J/mol**

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

The activities of A and B can over the entire range of "mixtures" can be evaluated from the free energy per mole of atoms over the range $0 \le x_{\mathrm{B}} \le 1$. The reference states are A(*s*) and B(*s*) at 1000°C, so their free energy values are 0 J/mol. The system contains two compounds and no solid solutions. Relative to A(*s*) and B(*s*), the free energy per mole of atoms of A$_2$B is $\Delta G_f^0(\mathrm{A_2B})/3$ = –8128 J/mol. Since 1 mole of A$_2$B contains 3 moles of atoms, the Gibbs free energy of formation must be divided by 3. Likewise, the free energy per mole of atoms of AB$_2$ is $\Delta G_f^0(\mathrm{AB_2})/3$ = –7738 J/mol. These values along with the free energy per mole of atoms of A and B, are plotted on the Gibbs free energy vs x_{B} for this system as 4 black dots. With no solid solution behavior, the Gibbs free energy for x_{B} values

between each pair of points is the straight line connecting these points because the physical mixture of the two solids has the lowest free energy. To obtain the activities of A and B, we construct the 3 straight lines intersecting each segment of the Gibbs free energy "curve" and see where these lines intersect the left-most ($x_B = 0$) and right-most ($x_B = 1$) intercepts. The values of the two intercepts for a given line are $RT \ln a_A$ at $x_B = 0$ and $RT \ln a_B$ at $x_B = 1$. Therefore,

$0 \le x_B \le 0.333$: $A_2B(s) \rightleftharpoons 2\,A(s) + B(s)$

Blue line: $\Delta G = -24,384\, x_B$

$\ln a_A = 0;\ a_A = 1$

$\ln a_B = -2.304;\ a_B = 0.100$

$0.333 \le x_B \le 0.667$: $2\,AB_2(s) \rightleftharpoons A_2B(s) + 3\,B(s)$

Green line: $\Delta G = 1,170\, x_B - 8,518$

$\ln a_A = -0.805;\ a_A = 0.447$

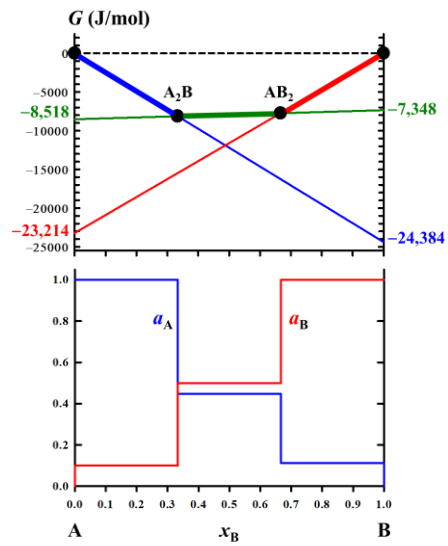
$\ln a_B = -0.694;\ a_B = 0.500$

$0.667 \le x_B \le 1$: $AB_2(s) \rightleftharpoons A(s) + 2\,B(s)$

Red line: $\Delta G = 23,214\, x_B - 23,214$

$\ln a_A = -2.193;\ a_A = 0.112$

$\ln a_B = 0;\ a_B = 1$



(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.

The relevant equilibria for melting and their Gibbs free energy relationships are:

FeO(*ss*) ⇌ FeO(*ls*): $G^0_{\text{FeO},s} + RT \ln x_{\text{FeO},s} = G^0_{\text{FeO},l} + RT \ln x_{\text{FeO},l}$

MnO(*ss*) ⇌ MnO(*ls*): $G^0_{\text{MnO},s} + RT \ln x_{\text{MnO},s} = G^0_{\text{MnO},l} + RT \ln x_{\text{MnO},l}$

Additional relationships include:

$G^0_{\text{FeO},l} - G^0_{\text{FeO},s} = \Delta G_{\text{fus}}(\text{FeO}) = 30,960 - 18.84\,T = RT\left[\ln x_{\text{FeO},s} - \ln x_{\text{FeO},l}\right];$

$G^0_{\text{MnO},l} - G^0_{\text{MnO},s} = \Delta G_{\text{fus}}(\text{MnO}) = 54,400 - 25.33\,T = RT\left[\ln x_{\text{MnO},s} - \ln x_{\text{MnO},l}\right];$

$x_{\text{MnO},s} = 1 - x_{\text{FeO},s}$; and $x_{\text{MnO},l} = 1 - x_{\text{FeO},l}$.

The system of equations that need to be solved are:

$$\ln x_{\text{FeO},s} - \ln x_{\text{FeO},l} = -0.6931 - \ln x_{\text{FeO},l} = \frac{3{,}723.8}{T} - 2.266 \quad \text{and}$$

$$\ln\left(1 - x_{\text{FeO},s}\right) - \ln\left(1 - x_{\text{FeO},l}\right) = -0.6931 - \ln\left(1 - x_{\text{FeO},l}\right) = \frac{6{,}543.2}{T} - 3.047.$$

To answer (a) and (b), $x_{\text{FeO},s} = 0.5$, which means

$$\ln x_{\text{FeO},l} = 1.5729 - \frac{3{,}723.8}{T} \quad \text{and} \quad \ln\left(1 - x_{\text{FeO},l}\right) = 2.3539 - \frac{6{,}543.2}{T}.$$

Solving these two equations gives:

(a) Temperature at which equilibrium melting begins is $T = 1888$ K.

(b) Composition of the first-formed liquid is $x_{\text{FeO},l} = 0.6708$; $x_{\text{MnO},l} = 0.3292$.

Therefore, the first-formed liquid is richer in FeO than MnO. As the 2-phase mixture of solid and liquid solutions continues to melt, the equilibrium compositions of both solutions become richer in MnO until $x_{\mathrm{FeO},l} = 0.5$, at which point, the sample becomes completely molten. We can obtain the temperature by the equations for $x_{\mathrm{FeO},s}$:

$$\ln x_{\mathrm{FeO},s} = \frac{3{,}723.8}{T} - 2.9591 \quad \text{and} \quad \ln(1 - x_{\mathrm{FeO},s}) = \frac{6{,}543.2}{T} - 3.047 .$$

Solving these two equations for T gives 1971 K.

(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 $\quad \Delta H_{\mathrm{fus}} = 77{,}400$ J

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

The relevant equilibria for melting and their Gibbs free energy relationships are:

MgO(*ss*) ⇌ MgO(*ls*): $G^0_{\mathrm{MgO},s} + RT \ln x_{\mathrm{MgO},s} = G^0_{\mathrm{MgO},l} + RT \ln x_{\mathrm{MgO},l}$

NiO(*ss*) ⇌ NiO(*ls*): $G^0_{\mathrm{NiO},s} + RT \ln x_{\mathrm{NiO},s} = G^0_{\mathrm{NiO},l} + RT \ln x_{\mathrm{NiO},l}$

Additional relationships include:

$$G^0_{\mathrm{MgO},l} - G^0_{\mathrm{MgO},s} = \Delta G_{\mathrm{fus}}(\mathrm{MgO}) = 77{,}400 - 27.64\,T = RT\left[\ln x_{\mathrm{MgO},s} - \ln x_{\mathrm{MgO},l}\right];$$

$$G^0_{\mathrm{NiO},l} - G^0_{\mathrm{NiO},s} = \Delta G_{\mathrm{fus}}(\mathrm{NiO}) = 50{,}600 - 25.30\,T = RT\left[\ln x_{\mathrm{NiO},s} - \ln x_{\mathrm{NiO},l}\right];$$

$x_{\mathrm{MgO},s} = 1 - x_{\mathrm{NiO},s}$**; and** $x_{\mathrm{MgO},l} = 1 - x_{\mathrm{NiO},l}$.

The system of equations that need to be solved are:

$$\ln x_{\mathrm{MgO},s} - \ln x_{\mathrm{MgO},l} = \frac{9{,}309.6}{T} - 3.3245 \quad \text{and}$$

$$\ln(1 - x_{\mathrm{MgO},s}) - \ln(1 - x_{\mathrm{MgO},l}) = \frac{6{,}086.1}{T} - 3.0431.$$

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;

$x_{\mathrm{MgO},l} = 0.5$**, which means**

$$\ln x_{\mathrm{MgO},s} = \frac{9{,}309.6}{T} - 4.0176 \quad \text{and} \quad \ln(1 - x_{\mathrm{MgO},s}) = \frac{6{,}086.1}{T} - 3.7362 .$$

Solving these two equations gives:

Temperature at which equilibrium solidification begins is $T = 2513$ K.

Composition of the first-formed solid is $x_{\mathrm{MgO},s} = 0.7312$; $x_{\mathrm{NiO},s} = 0.2688$.

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

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

$x_{\mathrm{MgO},l} = 0.75$**, which means**

$$\ln x_{\mathrm{MgO},s} = \frac{9{,}309.6}{T} - 3.6122 \quad \text{and} \quad \ln(1 - x_{\mathrm{MgO},s}) = \frac{6{,}086.1}{T} - 4.4294 .$$

Solving these two equations gives:

Temperature at which equilibrium solidification begins is $T = 2669$ K.

Composition of the first-formed solid is $x_{\mathrm{MgO},s} = 0.8617$; $x_{\mathrm{NiO},s} = 0.1383$.

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

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

$x_{\mathrm{MgO},l} = 0.3333$**, which means**

$$\ln x_{\mathrm{MgO},s} = \frac{9{,}309.6}{T} - 4.4231 \quad \text{and} \quad \ln(1 - x_{\mathrm{MgO},s}) = \frac{6{,}086.1}{T} - 3.4486 .$$

Solving these two equations gives:

Temperature at which equilibrium solidification begins is $T = 2387$ K.

Composition of the first-formed solid is $x_{MgO,s} = 0.5928$; $x_{NiO,s} = 0.4072$.

(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; $\Delta S_{fus} = 65.27$ J/mol·K

ZrF_4: $T_f = 1185$ K; $\Delta S_{fus} = 53.14$ J/mol·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 T and $x_s \equiv x_{ZrF_4,s}$ using $UF_4(s)$ and $ZrF_4(s)$ as the reference phases.

The free energy is just the free energy of mixing for an ideal solution:

$$\boldsymbol{G_s = RT[x_s \ln x_s + (1 - x_s)\ln(1 - x_s)].}$$

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

The free energy involves the free energy of the liquids plus the free energy of mixing:

$$\boldsymbol{G_l = [53.14(1185 - T)]x_l + [65.27(1308 - T)](1 - x_l) + \Omega x_l(1 - x_l)}$$
$$\boldsymbol{+ RT[x_l \ln x_l + (1 - x_l)\ln(1 - x_l)].}$$

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

At the eutectic point, the free energies of the solid and liquid solutions are equal. Furthermore, the slopes of the two free energy curves with respect to x are equal at this point because the activities of ZrF_4 (and of UF_4) are equal in the solid and liquid solutions.

Since $x_s = x_l$ at the eutectic point, the free energies of ideal mixing cancel each other, which leaves:

$$\boldsymbol{0 = [53.14(1185 - T)]x + [65.27(1308 - T)](1 - x) + \Omega x(1 - x),} \textbf{ or}$$
$$\boldsymbol{(85373.2 - 65.27\,T) + (12.13\,T - 22402.3)x + \Omega x(1 - x) = 0.}$$

The slope of this curve with respect to x, which is zero at the eutectic composition, is:

$$\boldsymbol{(12.13\,T - 22402.3) + \Omega(1 - 2x) = 0.}$$

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

The two equations to be solved are:

$$\boldsymbol{17622.94 - 9811.36\,x + \Omega x(1 - x) = 0.}$$
$$\boldsymbol{\Omega(1 - 2x) - 9811.36 = 0.}$$

The outcome is $\Omega = -49,060$ J/mol and $x = 0.600$ = the mole fraction of ZrF_4. The enthalpy of mixing in the liquid is strongly attractive and this model significantly underestimates the eutectic composition.

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

The two equations to be solved are:

$$\boldsymbol{68123.43 - 55.93\,T + 0.1771\,\Omega = 0.}$$
$$\boldsymbol{12.13\,T - 22402.3 - 0.54\,\Omega = 0.}$$

The outcome is $\Omega = -15,210$ J/mol and $T = 1170$ K. The enthalpy of mixing in the liquid is attractive and this model significantly overestimates the eutectic temperature.

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

The two equations to be solved are:

$$\boldsymbol{85373.2 - 65.27\,T + (12.13\,T - 22402.3)x - 25000x(1 - x) = 0.}$$
$$\boldsymbol{12.13\,T - 47402.3 + 50000\,x = 0.}$$

The outcome is $x = 0.673$ J/mol and $T = 1135$ K.

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

The model treating the liquid mixture as a regular solution and the solid mixture as an ideal solution consistently gives a negative enthalpy of mixing for the liquid solution to establish a eutectic point. However, the model does not replicate the experimental values of T and x that well. A more complex model of the enthalpy of the liquid solution is necessary.

(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; $\Delta H_{\text{fus}} = 10{,}900\ \text{J/mol}$

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

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.

The liquidus curve is the boundary of the two-phase region consisting of Bi(s) and the liquid:

Bi(s) ⇌ Bi(ls), $G_s^0(\text{Bi}) = G_l^0(\text{Bi}) + RT\ \ln(1 - x_{\text{Cd}})$, **where x_{Cd} = composition of the liquid.**

$$\ln(1 - x_{\text{Cd}}) = 2.410 - \frac{1{,}311.0}{T} \quad \text{or} \quad T = \frac{1{,}311.0}{2.410 - \ln(1 - x_{\text{Cd}})}.$$

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

The liquidus curve is the boundary of the two-phase region consisting of Cd(s) and the liquid:

Cd(s) ⇌ Cd(ls), $G_s^0(\text{Cd}) = G_l^0(\text{Cd}) + RT\ \ln x_{\text{Cd}}$, **where x_{Cd} = composition of the liquid.**

$$\ln x_{\text{Cd}} = 1.296 - \frac{769.8}{T} \quad \text{or} \quad T = \frac{769.8}{1.296 - \ln x_{\text{Cd}}}.$$

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

Setting the two equations in (a) and (b) equal to each other gives eutectic composition $x_{\text{Cd}} = 0.553$.
Then, substituting this value into either (a) or (b) gives eutectic temperature $T = 408$ K.

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

The agreement between the experimental values and the values derived from this simple model is quite good. The model temperature is slightly lower than from experiment. Taking into account the slight solubility of Bi in Cd(s) may improve the result.

(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; $\Delta H_{\text{fus}} = 12{,}700\ \text{J/mol}$

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

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

The liquidus curve is the boundary of the two-phase region consisting of Bi(s) and the liquid:

Au(s) ⇌ Au(ls), $G_s^0(\text{Au}) = G_l^0(\text{Au}) + RT\ \ln(1 - x_{\text{Si}})$, **where x_{Si} = composition of the liquid.**

$$\ln(1 - x_{\text{Si}}) = 1.143 - \frac{1{,}527.5}{T} \quad \text{or} \quad T = \frac{1{,}527.5}{1.143 - \ln(1 - x_{\text{Si}})}.$$

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

Si(s) ⇌ Si(ls), $G_s^0(\text{Si}) = G_l^0(\text{Si}) + RT\ \ln x_{\text{Si}}$, **where x_{Si} = composition of the liquid.**

$$\ln x_{\text{Si}} = 3.618 - \frac{6{,}089.7}{T} \quad \text{or} \quad T = \frac{6{,}089.7}{3.618 - \ln x_{\text{Si}}}.$$

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

Setting the two equations in (a) and (b) equal to each other gives eutectic composition $x_{Si} = 0.178$.

Then, substituting this value into either (a) or (b) gives eutectic temperature $T = 1140$ K.

The eutectic temperature from this simple model is much too high compared to experiment. Therefore, the enthalpy of mixing in the liquid solution is more exothermic than in the solid solution.

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

0.814 Au(s) + 0.186 Si(s) ⇌ $Au_{0.814}Si_{0.186}$(l). This is the equilibrium at the eutectic point

$$\Delta G = G(ls) - \left(0.814\, G_{Au}(s) + 0.186\, G_{Si}(s)\right) = 0 \text{ J/mol.}$$

0.814 Au(l) + 0.186 Si(l) ⇌ $Au_{0.814}Si_{0.186}$(l).

$$\Delta G = G(ls) - \left(0.814\, G_{Au}(l) + 0.186\, G_{Si}(l)\right)$$

$$\Delta G = G(ls) - \left(0.814\, G_{Au}(s) + 0.186\, G_{Si}(s)\right) - \left(0.814\, \Delta G_{fus}(\text{Au}) + 0.186\, \Delta G_{fus}(\text{Si})\right)$$

$$\Delta G = -\left(0.814\,(6,654.2) + 0.186\,(31,496.9)\right) = -11,275 \text{ J/mol}$$

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

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

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

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

The liquidus curves are (let $x = x_{PbF_2}$):

NaF(s) ⇌ NaF(ls), $G_s^0(\text{NaF}) = G_l^0(\text{NaF}) + RT\ \ln(1-x)$; $\ln(1-x) = 3.062 - \frac{4,011.3}{T}$.

PbF_2(s) ⇌ PbF_2(ls), $G_s^0(\text{PbF}_2) = G_l^0(\text{PbF}_2) + RT\ \ln x$; $\ln x = 1.576 - \frac{1,771.7}{T}$.

Solving these two equations for T and x gives the eutectic point:

$T = 928$ K = 655 ℃; $x = 0.716$ = mole fraction PbF_2

(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.

The Gibbs free energy expression for the liquid solution is:

$$G_l = x(14,730 - 13.105\,T) + (1-x)(33,350 - 25.458\,T) + \Omega x(1-x) + 8.314\,T\,[x\ln x + (1-x)\ln(1-x)]$$

At the eutectic point, $G_l = 2,713.11 + 4,158.57 + 0.2211\,\Omega - 4,297.14 = 0$.

Then, $\Omega = -11,640$ J/mol.

We can also evaluate Ω from the slope of G_l with respect to x:

$$\frac{\partial G_l}{\partial x} = (14,730 - 13.105\,T) - (33,350 - 25.458\,T) + \Omega(1-2x) + 8.314\,T\left[\ln\frac{x}{1-x}\right].$$

At the eutectic point, $\frac{\partial G_l}{\partial x} = 4,049.43 - 12,601.73 - 0.34\,\Omega + 4.798.60 = 0$.

Then, $\Omega = -11,040$ J/mol.

The two results reasonably agree with each other.

(70) **A** and **B** form two compounds **AB**(*s*) and AB_3(*s*) with

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

A(*s*) + 3 **B**(*s*) = 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_B for the temperature range 500 K to 1200 K.

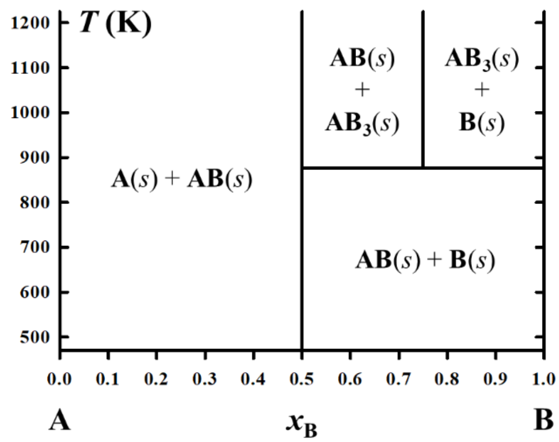
There are 4 distinct solid phases and there are 4 possible 3-phase equilibria:

AB(*s*) = A(*s*) + B(*s*): $\Delta G°(T) = 26{,}000 + 4.56T$,
AB(*s*) is stable relative to A(*s*) and B(*s*) for all *T*

3 AB(*s*) = 2 A(*s*) + AB_3(*s*): $\Delta G°(T) = 55{,}740 + 4.85T$,
AB(*s*) is stable relative to A(*s*) and AB_3(*s*) for all *T*

AB_3(*s*) = A(*s*) + 3 B(*s*): $\Delta G°(T) = 22{,}260 + 8.83T$,
AB_3(*s*) is stable relative to A(*s*) and B(*s*) for all *T*

AB_3(*s*) = AB(*s*) + 2 B(*s*): $\Delta G°(T) = –3{,}740 + 4.27T$,
AB_3(*s*) is stable relative to AB(*s*) and B(*s*) for *T* > 876 K



(71) Elements **A** and **B** form three compounds A_3B_2(*s*), **AB**(*s*), and 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_B for the temperature range 500 K to 3200 K.

There are 5 distinct solid phases and there are 10 possible 3-phase equilibria:

A_3B_2(*s*) = 3 A(*s*) + 2 B(*s*): $\Delta G°(T) = 135{,}900 – 51.20T$,
A_3B_2(*s*) is stable relative to A(*s*) and B(*s*) for *T* < 2654 K

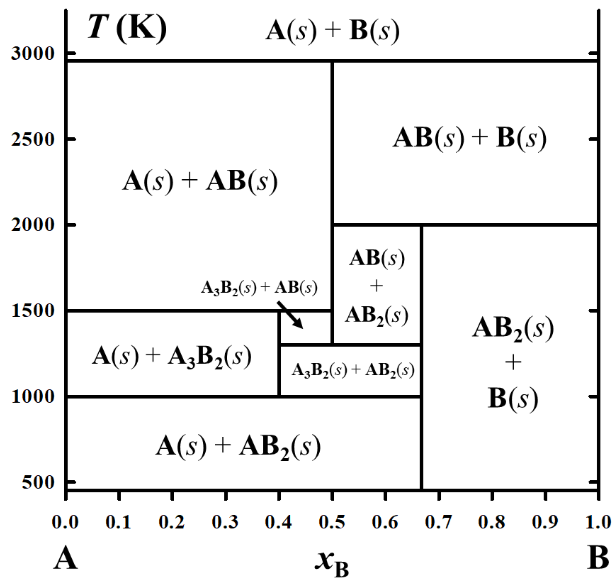
A_3B_2(*s*) = 2 A(*s*) + AB_2(*s*): $\Delta G°(T) = –14{,}100 + 14.11T$,
A_3B_2(*s*) is stable relative to A(*s*) and AB_2(*s*) for *T* > 999 K

A_3B_2(*s*) = A(*s*) + 2 AB(*s*): $\Delta G°(T) = 15{,}900 – 10.60T$,
A_3B_2(*s*) is stable relative to A(*s*) and AB(*s*) for *T* < 1500 K

AB(*s*) = A(*s*) + B(*s*): $\Delta G°(T) = 60{,}000 – 20.30T$,
AB(*s*) is stable relative to A(*s*) and B(*s*) for *T* < 2955 K

2 AB(*s*) = A(*s*) + AB_2(*s*): $\Delta G°(T) = –30{,}000 + 24.91T$,

	AB(*s*) is stable relative to A(*s*) and AB_2(*s*) for *T* > 1214 K
3 AB(*s*) = A_3B_2(*s*) + B(*s*):	**Δ*G*°(*T*) = 44,100 – 9.70*T*,** **A_3B_2(*s*) is stable relative to A(*s*) and AB(*s*) for *T* < 4546 K**
4 AB(*s*) = A_3B_2(*s*) + AB_2(*s*):	**Δ*G*°(*T*) = –45,900 + 35.31*T*,** **AB(*s*) is stable relative to A_3B_2(*s*) and AB_2(*s*) for *T* > 1300 K**
AB_2(*s*) = A(*s*) + 2 B(*s*):	**Δ*G*°(*T*) = 150,000 – 65.31*T*,** **AB_2(*s*) is stable relative to A(*s*) and B(*s*) for *T* < 2654 K**
3 AB_2(*s*) = A_3B_2(*s*) + 4 B(*s*):	**Δ*G*°(*T*) = 314,100 – 144.73*T*,** **AB_2(*s*) is stable relative to A_3B_2(*s*) and B(*s*) for *T* < 2170 K**
AB_2(*s*) = AB(*s*) + B(*s*):	**Δ*G*°(*T*) = 90,000 – 45.01*T*,** **AB_2(*s*) is stable relative to A(*s*) and AB(*s*) for *T* < 2000 K**



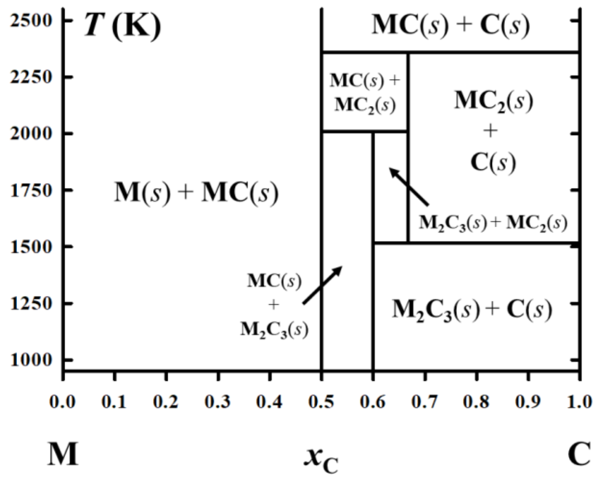
(72) MC_2(*s*) can be equilibrated with MC(*s*) and C(*s*) at high temperature and can be equilibrated with M_2C_3(*s*) and C(*s*) at lower temperature. Using the following information, construct the T-x_C phase diagram for the M-C carbide system in the 1000-2500 K range:

M(*s*) + C(*s*) = MC(*s*);	Δ*G*°(*T*) = –105,000 + 6.28*T* J/mol
2 M(*s*) + 3 C(*s*) = M_2C_3(*s*);	Δ*G*°(*T*) = –236,800 + 25.1*T* J/mol
M(*s*) + 2 C(*s*) = MC_2(*s*);	Δ*G*°(*T*) = –115,900 + 10.9*T* J/mol

There are 5 distinct solid phases and there are 10 possible 3-phase equilibria:

MC(*s*) = M(*s*) + C(*s*):	**Δ*G*°(*T*) = 105,000 – 6.28*T*,** **MC(*s*) is stable relative to M(*s*) and C(*s*) for *T* < 16720 K**
2 MC(*s*) = M(*s*) + MC_2(*s*):	**Δ*G*°(*T*) = 94,100 – 1.66*T*,** **MC(*s*) is stable relative to M(*s*) and MC_2(*s*) for *T* < 56690 K**
3 MC(*s*) = M(*s*) + M_2C_3(*s*):	**Δ*G*°(*T*) = 78,200 + 6.26*T*,** **MC(*s*) is stable relative to M(*s*) and M_2C_3(*s*) for all *T***
M_2C_3(*s*) = 2 M(*s*) + 3 C(*s*):	**Δ*G*°(*T*) = 236,800 – 25.10*T*,** **M_2C_3(*s*) is stable relative to M(*s*) and C(*s*) for *T* < 9430 K**
M_2C_3(*s*) = 2 MC(*s*) + C(*s*):	**Δ*G*°(*T*) = 26,800 – 12.54*T*,** **M_2C_3(*s*) is stable relative to MC(*s*) and C(*s*) for *T* < 2140 K**
2 M_2C_3(*s*) = M(*s*) + 3 MC_2(*s*):	**Δ*G*°(*T*) = 125,900 – 17.50*T*,**

	$M_2C_3(s)$ is stable relative to $M(s)$ and $MC_2(s)$ for $T < 7190$ K
$M_2C_3(s) = MC(s) + MC_2(s)$:	**$\Delta G°(T) = 15{,}900 - 7.92T$, $M_2C_3(s)$ is stable relative to $MC(s)$ and $MC_2(s)$ for $T < 2010$ K**
$MC_2(s) = M(s) + 2\ C(s)$:	**$\Delta G°(T) = 115{,}900 - 10.90T$, $MC_2(s)$ is stable relative to $M(s)$ and $C(s)$ for $T < 10650$ K**
$2\ MC_2(s) = M_2C_3(s) + C(s)$:	**$\Delta G°(T) = -5{,}000 + 3.30T$, $MC_2(s)$ is stable relative to $M_2C_3(s)$ and $C(s)$ for $T > 1520$ K**
$MC_2(s) = MC(s) + C(s)$:	**$\Delta G°(T) = 10{,}900 - 4.62T$, $MC_2(s)$ is stable relative to $MC(s)$ and $C(s)$ for $T < 2360$ K**



(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 $\mu_{\mathbf{B}} = RT\ln x_{\mathbf{B}} + \Omega x_{\mathbf{A}}^2$.

The molar Gibbs free energy of a regular solution, relative to the unmixed components A and B, is:

$$g = x_A\mu_A + x_B\mu_B = RT[x_A\ln x_A + x_B\ln x_B] + \Omega x_A x_B$$

In terms of the chemical potentials, the molar Gibbs free energy is

$$\mu_A = (x_A + x_B)\mu_A = x_A\mu_A + x_B\mu_A = (g - x_B\mu_B) + x_B\mu_A = g - x_B(\mu_B - \mu_A) = g - x_B\left(\frac{\partial g}{\partial x_B}\right) = g + x_B\left(\frac{\partial g}{\partial x_A}\right).$$

$$= (RT[x_A\ln x_A + x_B\ln x_B] + \Omega x_A x_B) + x_B[RT(\ln x_A + 1 - \ln x_B - 1) + \Omega x_B - \Omega x_A]$$

$$= (x_A + x_B)RT\ln x_A + \Omega x_B^2 = RT\ln x_A + \Omega x_B^2.$$

$$\mu_B = (x_A + x_B)\mu_B = x_A\mu_B + x_B\mu_B = (g - x_A\mu_A) + x_A\mu_B = g + x_A(\mu_B - \mu_A) = g + x_A\left(\frac{\partial g}{\partial x_B}\right).$$

$$= (RT[x_A\ln x_A + x_B\ln x_B] + \Omega x_A x_B) + x_A[RT(-\ln x_A - 1 + \ln x_B + 1) + \Omega x_A - \Omega x_B]$$

$$= (x_A + x_B)RT\ln x_B + \Omega x_A^2 = RT\ln x_B + \Omega x_A^2.$$

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

The molar Gibbs free energy of the liquid solution $Mg_{1-x_{Si}}Si_{x_{Si}}(l)$ is:

$$G(l) = (1 - x_{Si})G^0_{Mg}(l) + x_{Si}G^0_{Si}(l) + RT[(1 - x_{Si})\ln(1 - x_{Si}) + x_{Si}\ln x_{Si}] + \Omega(1 - x_{Si})x_{Si}.$$

At 1358 K, the standard states of Mg and Si are Mg(*l*) and Si(*s*). Since this temperature is the melting point of Mg_2Si, then $G^0_{Mg_2Si}(s) = G^0_{Mg_2Si}(l)$. Therefore,

$$G^0_{Mg_2Si}(s; T = 1358\text{ K}) = -100,400 + 39.3(1358) = -47,030.6\text{ J/mol}$$

$$G^0_{Mg}(l; T = 1358\text{ K}) = 0\text{ J/mol}; \quad G^0_{Si}(l; T = 1358\text{ K}) = 50,630 - 30.0(1358) = 9,890\text{ J/mol}$$

$$G^0_{Mg_2Si}(l; T = 1358\text{ K}) = 3G(l; x_{Si} = 1/3)$$

$$= 3\left[\frac{2}{3}(0) + \frac{1}{3}(9,890) + 11,290.4(-0.6365) + \frac{2}{9}\Omega\right] = \frac{2}{3}\Omega - 11,669$$

From $G^0_{Mg_2Si}(s; T = 1358\text{ K}) = G^0_{Mg_2Si}(l; T = 1358\text{ K})$, the parameter $\Omega = -53,042$ J/mol.

The liquidus curve is determined using the 3 equilibria:

Mg(*s*) ⇌ Mg(*ls*):

$$G^0_{Mg}(s; T) = G^0_{Mg}(l; T) + RT\ln(1 - x_{Si}) - 53,042x_{Si}^2$$

$$9.54\,T - 8,790 = 8.314\,T\ln(1 - x_{Si}) - 53,042x_{Si}^2$$

$$T = \frac{8,790 - 53,042x_{Si}^2}{9.54 - 8.314\ln(1 - x_{Si})}$$

Si(*s*) ⇌ Si(*ls*):

$$G^0_{Si}(s; T) = G^0_{Si}(l; T) + RT\ln x_{Si} - 53,042(1 - x_{Si})^2$$

$$30.0\,T - 50,630 = 8.314\,T\ln x_{Si} - 53,042(1 - x_{Si})^2$$

$$T = \frac{50,630 - 53,042(1 - x_{Si})^2}{30.0 - 8.314\ln x_{Si}}$$

Mg_2Si(*s*) ⇌ 2 Mg(*ls*) + Si(*ls*): **Mg_2Si(*s*) ⇌ 2 Mg(*l*) + Si(*s*),** $\Delta G° = 100,400 - 39.3\,T$

Si(*s*) ⇌ Si(*l*), $\Delta G° = 50,630 - 30.0\,T$

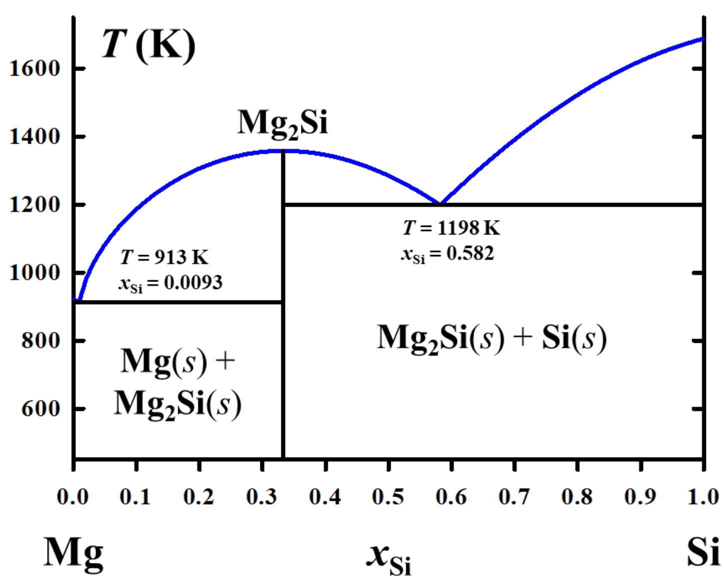
$$\Delta G° = 151,030 - 69.3\,T$$

$$G^0_{Mg_2Si}(s; T) = G^0_{Mg_2Si}(l; T) + 16.628\,T\ln(1 - x_{Si}) - 106,084x_{Si}^2 + 8.314\,T\ln x_{Si} - 53,042(1 - x_{Si})^2$$

$$69.3\,T - 151,030 = 16.628\,T\ln(1 - x_{Si}) - 106,084x_{Si}^2 + 8.314\,T\ln x_{Si} - 53,042(1 - x_{Si})^2$$

$$T = \frac{151,030 - 106,084x_{Si}^2 - 53,042(1 - x_{Si})^2}{69.3 - 16.628\ln(1 - x_{Si}) - 8.314\ln x_{Si}}$$

These 3 expressions for $T(x_{Si})$ are represented by the blue curve on the phase diagram below. The experimental eutectic points are (x_{Si} = 0.015, T = 911 K) and (x_{Si} = 0.541, T = 1219 K).



(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.

The molar Gibbs free energy of the liquid solution $A_{1-x_B}B_{x_B}(l)$ is:

$$G(l) = (1-x_B)G_A^0(l) + x_B G_B^0(l) + RT[(1-x_B)\ln(1-x_B) + x_B \ln x_B] + \Omega(1-x_B)x_B.$$

At 983 K (710°C), choose the standard states of A and B to be A(s) and B(s), so that $G_A^0(s) = 0$ and $G_B^0(s) = 0$. Since this temperature is the melting point of AB$_2$, then $G_{AB_2}^0(s) = G_{AB_2}^0(l)$. Therefore,

$$G_{AB_2}^0(s; T = 983\text{ K}) = -13{,}400 - 8.37(983) = -21{,}627.71 \text{ J/mol}$$

$$G_A^0(l; T = 983\text{ K}) = 8{,}540 - 7.673(983) = 997.44 \text{ J/mol;}$$

$$G_B^0(l; T = 983\text{ K}) = 8{,}480 - 9.187(983) = -550.82 \text{ J/mol}$$

$$G_{AB_2}^0(l; T = 983\text{ K}) = 3G(l; x_B = 2/3)$$

$$= 3\left[\frac{1}{3}(997.44) + \frac{2}{3}(-550.82) + 8{,}172.66(-0.6365) + \frac{2}{9}\Omega\right] = \frac{2}{3}\Omega - 15{,}709.89$$

From $G_{AB_2}^0(s; T = 983\text{ K}) = G_{AB_2}^0(l; T = 983\text{ K})$, the parameter $\Omega = -8{,}876.7$ J/mol.

The liquidus curve is determined using the 3 equilibria:

A(s) ⇌ A(ls):

$$G_A^0(s; T) = G_A^0(l; T) + RT\ln(1-x_B) - 8{,}876.7\,x_B^2$$

$$7.673\,T - 8{,}540 = 8.314\,T\ln(1-x_B) - 8{,}876.7\,x_B^2$$

$$T = \frac{8{,}540 - 8{,}876.7\,x_B^2}{7.673 - 8.314\ln(1-x_B)}$$

B(s) ⇌ B(ls):

$$G_B^0(s; T) = G_B^0(l; T) + RT\ln x_B - 8{,}876.7\,(1-x_B)^2$$

$$9.187\,T - 8{,}480 = 8.314\,T\ln x_B - 8{,}876.7\,(1-x_B)^2$$

$$T = \frac{8.480 - 8{,}876.7\,(1-x_B)^2}{9.187 - 8.314\ln x_B}$$

AB$_2$(s) ⇌ A(ls) + 2 B(ls):

AB$_2$(s) ⇌ A(s) + 2 B(s), $\Delta G° = 13{,}400 + 8.37\,T$

A(s) ⇌ A(l), $\Delta G° = 8{,}540 - 7.673\,T$

2 B(s) ⇌ 2 B(l), $\Delta G° = 16{,}960 - 18.374\,T$

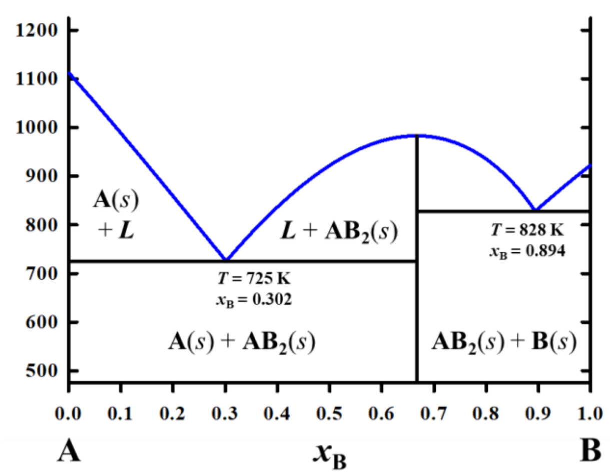
$$\Delta G° = 38{,}900 - 17.677\,T$$

$$G_{AB_2}^0(s; T) = G_{AB_2}^0(l; T) + 8.314\,T\ln(1-x_B) - 8{,}876.7\,x_B^2 + 16.628\,T\ln x_B - 17{,}753.4\,(1-x_B)^2$$

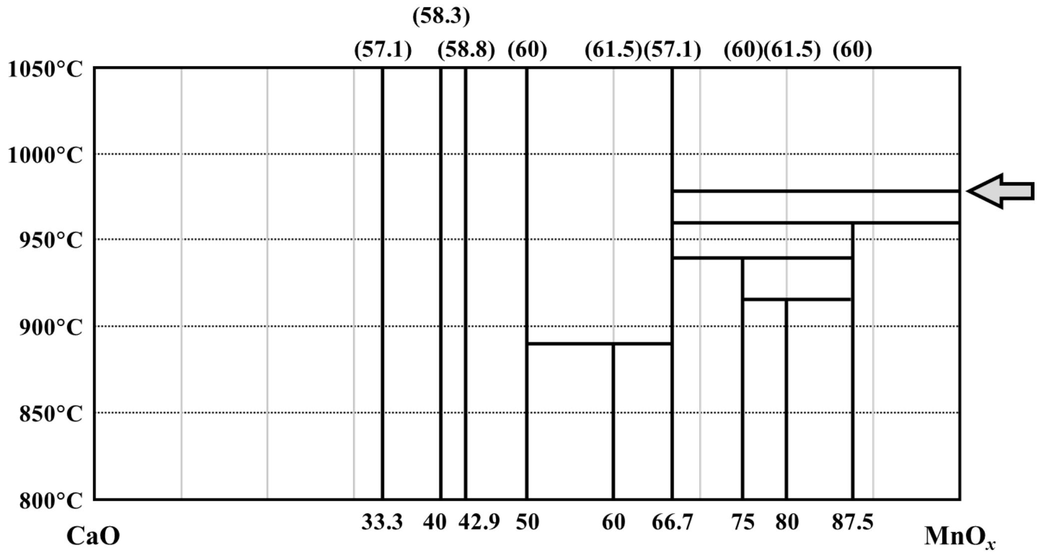
$$17.677\,T - 38{,}900 = 8.314\,T\ln(1-x_B) - 12{,}179.2\,x_B^2 + 16.628\,T\ln x_B - 24{,}358.4\,(1-x_B)^2$$

$$T = \frac{38{,}900 - 8{,}876.7x_B^2 - 17{,}753.4(1-x_B)^2}{17.677 - 8.314\ln(1-x_B) - 16.628\ln x_B}$$

Using the 3 expressions for $T(x_B)$, the phase diagram is:



(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?

For the Mn-O line, *C* = 2 and ρ = 1 because there is restriction on pressure. The number of degrees of freedom *F* = 2 – *P* + 2 – 1 = 3 – *P*. Therefore, 3 phases can coexist. Since one phase is $O_2(g)$, then at most 2 solid manganese oxide phases can coexist.

(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.

For the system containing $O_2(g)$, $MnO_2(s)$, $Mn_2O_3(s)$, and $Mn_3O_4(s)$, the following 3-phase equilibria involving $O_2(g)$ with their corresponding free energies are:

$3\ Mn_2O_3(s) \rightleftharpoons 2\ Mn_3O_4(s) + \frac{1}{2}\ O_2(g)$:	$\Delta G° = 109,170 - 87.2\ T$	$\Delta G° < 0$ for $T > 950$°C
$3\ MnO_2(s) \rightleftharpoons Mn_3O_4(s) + O_2(g)$:	$\Delta G° = 177,810 - 211.9\ T$	$\Delta G° < 0$ for $T > 566$°C
$2\ MnO_2(s) \rightleftharpoons Mn_2O_3(s) + \frac{1}{2}\ O_2(g)$:	$\Delta G° = 82,150 - 112.2\ T$	$\Delta G° < 0$ for $T > 459$°C

Low temperatures prefer the more oxidized manganese oxide; high temperatures prefer more reduced manganese oxide. The arrow represents the temperature at which the identity of "MnO_x" changes on the phase diagram: below the arrow is $Mn_2O_3(s)$; above the arrow is $Mn_3O_4(s)$

(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.

The formula of each compound is $(CaO)_{1-u}(MnO_x)_uO_v$, in which *u* = mole fraction MnO_x. The mole percent O is:

$$100\left(\frac{1-u+xu+y}{2-u+xu+y}\right).$$

***u* = 0.333:** **$Ca_2MnO_4 = (Ca^{2+})_2(Mn^{4+})O_4$**

***u* = 0.400:** **$Ca_3Mn_2O_7 = (Ca^{2+})_3(Mn^{4+})_2O_7$**

***u* = 0.429:** $Ca_4Mn_3O_{10} = (Ca^{2+})_4(Mn^{4+})_3O_{10}$

***u* = 0.500:** $CaMnO_3 = (Ca^{2+})(Mn^{4+})O_3$

***u* = 0.600:** $Ca_2Mn_3O_8 = (Ca^{2+})_2(Mn^{4+})_3O_8$

***u* = 0.667:** $CaMn_2O_4 = (Ca^{2+})(Mn^{3+})_2O_4$

***u* = 0.750:** $CaMn_3O_6 = (Ca^{2+})(Mn^{4+})(Mn^{3+})_2O_6$; **Mixed-valent compound**

***u* = 0.800:** $CaMn_4O_8 = (Ca^{2+})(Mn^{4+})_2(Mn^{3+})_2O_8$; **Mixed-valent compound**

***u* = 0.875:** $CaMn_7O_{12} = (Ca^{2+})(Mn^{4+})(Mn^{3+})_6O_{12}$; **Mixed-valent compound**

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

Just below 900°C: $Ca_2Mn_3O_8(s) \rightleftharpoons CaMnO_3(s) + CaMn_2O_4(s) + \frac{1}{2} O_2(g)$

Since the solid compounds involve different oxidation states of Mn, $O_2(g)$ is necessary. The additional component (Ca) now allows 4 phases to coexist at equilibrium.

Just above 900°C: $4\ CaMn_4O_8(s) \rightleftharpoons 3\ CaMn_3O_6(s) + CaMn_7O_{12}(s) + O_2(g)$

A compound with an equal concentration of Mn^{4+} and Mn^{3+} coexists with compounds that have higher concentrations of Mn^{3+}. Therefore, $O_2(g)$ is necessary.

Just below 950°C: $5\ CaMn_3O_6(s) \rightleftharpoons 4\ CaMn_2O_4(s) + CaMn_7O_{12}(s) + O_2(g)$

Just above 950°C: $2\ CaMn_7O_{12}(s) \rightleftharpoons 2\ CaMn_2O_4(s) + 5\ Mn_2O_3(s) + \frac{1}{2} O_2(g)$

The temperature of this 3-solid phase equilibrium is below the arrow, so the ternary oxides are in equilibrium with Mn_2O_3.

Chemical Vapor Transport

(77) For the transport of ZnS(*s*) using iodine 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 $\Delta p(I_2) = 5.0 \times 10^{-3}$ atm between the opposite ends of the tube.

The transport equilibrium is $ZnS(s) + I_2(g) \rightleftharpoons ZnI_2(g) + \frac{1}{2} S_2(g)$. There is a 1:1 molar ratio between ZnS(*s*) and the transport agent iodine. Iodine will be in the hot end, so we can use the higher temperature for the following calculations. The initial pressure of iodine is

$$p_{TOT} = \frac{n_{I_2}RT}{V} = \frac{(m_{I_2}/V)RT}{MW_{I_2}} = \frac{(0.002\ g/cm^3)(82.05\ cm^3{\cdot}atm/mol{\cdot}K)(1173\ K)}{(253.8\ g/mol)} = 0.758\ atm$$

If x atm I_2 reacts with ZnS, then x atm of $ZnI_2(g)$ and $x/2$ atm $S_2(g)$ are created, so that the total pressure becomes 0.758 atm – x + x + x/2 = 0.758 atm + x/2 ≈ 0.758 atm, since very little gas is created compared with the background of iodine vapor.

The transport rate (moles ZnS/hour) is

$$\frac{n_{ZnS}}{t}\ (mol/hr) = \left(\frac{1}{1}\cdot\frac{\Delta p_{I_2}}{p_{TOT}}\right)\frac{T^{0.8}A}{s}(1.8\times10^{-4}) = \frac{0.005\ atm}{0.758\ atm}\cdot\frac{(1173\ K)^{0.8}[\pi(0.5\ cm)^2]}{20\ cm}\cdot 1.8\times10^{-4}$$
$$= 1.33\times10^{-5}\ mol/hr$$

Therefore, (1.33×10^{-5} mole/hr)(97.5 g/mole)(1000 mg/1 g) = 1.30 mg/hr is the approximate transport rate of ZnS(*s*) in this reaction.

(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.

(I) $Nb_3SI_7(s) + 4\ I_2(g) \rightleftharpoons 3\ NbI_5(g) + \frac{1}{2} S_2(g)$; $\Delta S° < 0$.

(II) $Nb_3SI_7(s) + 5/2\ I_2(g) \rightleftharpoons 3\ NbI_4(g) + \frac{1}{2} S_2(g)$; $\Delta S° > 0$.

To be an effective transport reaction, the signs of $\Delta S°$ and $\Delta H°$ should be the same. Since transport occurs from low T to high T, the transport reaction must be exothermic, $\Delta H° < 0$. Therefore, reaction (I) is the expected transport equilibrium.

(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.

With $I_2(g)$ as the transport agent, there are four possible equilibria for each silicide:

$FeSi(s) + 2\ I_2(g) \rightleftharpoons FeI_2(g) + SiI_2(g)$; $\Delta S° \sim 0$
$FeSi(s) + 5/2\ I_2(g) \rightleftharpoons FeI_3(g) + SiI_2(g)$; $\Delta S° < 0$
$FeSi(s) + 3\ I_2(g) \rightleftharpoons FeI_2(g) + SiI_4(g)$; $\Delta S° < 0$
$FeSi(s) + 7/2\ I_2(g) \rightleftharpoons FeI_3(g) + SiI_4(g)$; $\Delta S° < 0$

$FeSi_2(s) + 3\ I_2(g) \rightleftharpoons FeI_2(g) + 2\ SiI_2(g)$; $\Delta S° \sim 0$
$FeSi_2(s) + 7/2\ I_2(g) \rightleftharpoons FeI_3(g) + 2\ SiI_2(g)$; $\Delta S° < 0$
$FeSi_2(s) + 5\ I_2(g) \rightleftharpoons FeI_2(g) + 2\ SiI_4(g)$; $\Delta S° < 0$
$FeSi_2(s) + 11/2\ I_2(g) \rightleftharpoons FeI_3(g) + 2\ SiI_4(g)$; $\Delta S° < 0$

(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.

With $SiI_4(g)$ as the transport agent, there are no possible transport equilibria for FeSi(*s*) and there are two possible equilibria for $FeSi_2(s)$:

$FeSi_2(s) + 3\ SiI_4(g) \rightleftharpoons FeI_2(g) + 5\ SiI_2(g)$; $\Delta S° > 0$

$FeSi_2(s) + 7/2\ SiI_4(g) \rightleftharpoons FeI_3(g) + 11/2\ SiI_2(g)$; $\Delta S° > 0$

(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?

FeSi(*s*): **Transport equilibria can only be written using $I_2(g)$ as the transport agent. Three of these have negative reaction entropies, which is consistent with cold-to-hot transport because it requires an exothermic transport process. FeSi(*s*) is transported by $I_2(g)$.**

$FeSi_2(s)$: **Transport equilibria can be written using either $I_2(g)$ or $SiI_4(g)$ as the transport agent. Only the equilibria with $SiI_4(g)$ have positive reaction entropies, which is consistent with hot-to-cold transport because it requires an endothermic transport process. $FeSi_2(s)$ is transported by $SiI_4(g)$.**

(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.

The transport equilibrium is $MCl_3(s) + MCl_5(g) \rightleftharpoons 2\ MCl_4(g)$.

$\Delta H° = +105.4$ **kJ/mol** $\quad \Delta S° = +176.5$ **J/mol·K**

The optimum median temperature for transport = $\Delta H°/\Delta S°$ = 597 K = 324°C.

(b) What is the direction of transport?

The transport equilibrium is endothermic, and the enthalpy and entropy have the same sign, so transport of $MCl_3(s)$ should be hot-to-cold.

(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.

The equilibrium constant for the transport equilibrium is $K_p(T) = \frac{(p(\mathrm{NbCl_4}))^2}{p(\mathrm{NbCl_5})} = \frac{(2x)^2}{(1.0-x)}$. The second expression arises by treating the problem of having an initial pressure of $NbCl_5(g)$ of 1.0 atm. As the equilibrium is achieved, then some $NbCl_5(g)$ is consumed while $NbCl_4(g)$ is formed. The total pressure in each end of the transport tube will be (1.0 – *x*) + 2*x* = (1.0 + *x*) atm.

From the thermodynamic information, $\log K_p(T) = 9.22 - \frac{5505.7}{T}$.

Combining the two expressions for $K_p(T)$ gives $x(T) = \left(\sqrt{K^2 + 16K} - K\right)/8$.

Using a program like Excel allows evaluation of $K_p(T)$ and $x(T)$ for temperature values above and below 597 K (the median temperature). The pressure differential is 0.2 atm ~ $x(T_{high}) - x(T_{low})$. At 597 K, *x*(597 K) = 0.390 atm, so we look for $x(T_{low})$ ~ 0.29 atm and $x(T_{high})$ ~ 0.49 atm. This analysis gives T_{high} ~ 616 K = 343°C and T_{low} ~ 577 K = 304°C, so there should be ~40°C temperature differential between the hot and cold end of the transport tube.

(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 $MCl_3(s)$?

The transport rate (moles MCl_3/hour) is

$$\frac{n_{\mathrm{MCl_3}}}{t}\ (\mathrm{mol/hr}) = \left(\frac{1}{1}\cdot\frac{\Delta p_{\mathrm{MCl_3}}}{p_{\mathrm{TOT}}}\right)\frac{T^{0.8}A}{s}(1.8\times10^{-4}) = \frac{0.2\ \mathrm{atm}}{1.0\ \mathrm{atm}}\cdot\frac{(597\ \mathrm{K})^{0.8}[\pi(0.5\ \mathrm{cm})^2]}{20.0\ \mathrm{cm}}\cdot 1.8\times10^{-4}$$

$$= \mathbf{2.35 \times 10^{-4}}\ \textbf{mol/hr}$$

Therefore, (2.35 ×10^{-4} mol/hr)(150.0 g/mole) = 0.0352 g/hr is the approximate transport rate of MCl_3(*s*) in this reaction. To transport 1.0 g MCl_3(*s*) would take approximately 1/0.0352 = 28.4 hours, or slightly more than 1 day.

(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.

Si(*s*) + $SiCl_4$ (*g*) ⇌ 2 $SiCl_2$ (*g*)

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

$\Delta \boldsymbol{G}° = \mathbf{316,050 - 196.3}\ \boldsymbol{T}$**:** $\Delta \boldsymbol{H}° = \mathbf{+316,050}$ **J/mol** $\Delta \boldsymbol{S}° = \mathbf{+196.3}$ **J/mol·K**

Since the equilibrium reaction is endothermic, transport occurs from 1000ºC to 800ºC (hot-to-cold).

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

$$\ln \boldsymbol{K}(\mathbf{800}℃) = \frac{-105{,}420.1}{8.314 \cdot 1073} = \mathbf{-11.817}; \quad \boldsymbol{K}(\mathbf{800}℃) = \mathbf{7.377 \times 10^{-6}}$$

$$\ln \boldsymbol{K}(\mathbf{1000}℃) = \frac{-66{,}160.1}{8.314 \cdot 1273} = \mathbf{-6.251}; \quad \boldsymbol{K}(\mathbf{1000}℃) = \mathbf{1.928 \times 10^{-3}}$$

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

$\boldsymbol{p} = \mathbf{0.100}$ **atm;** $\boldsymbol{T} = \mathbf{1273}$ **K;** $\boldsymbol{V} = (\mathbf{18.0})[\boldsymbol{\pi}(\mathbf{0.45})^2] = \mathbf{11.45}$ **cm^3 = 0.01145 L**

Therefore, $\boldsymbol{n} = \frac{(0.100)(0.01145)}{(0.08206)(1273)} = \mathbf{1.096 \times 10^{-5}}$ **mole $SiCl_4$**

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

If the initial pressure of $SiCl_4$ (*g*) drops by *x*, then the equilibrium pressure of $SiCl_2$ (*g*) is 2*x*.

At 800ºC: $\boldsymbol{K} = \mathbf{7.377 \times 10^{-6}} = \frac{(2x)^2}{0.100-x} = \frac{4x^2}{0.100-x}$**, and *x* = 4.285 × 10^{-4}.**

$\boldsymbol{p}_{\mathbf{SiCl_4}} = \mathbf{0.0996}$ **atm** $\boldsymbol{p}_{\mathbf{SiCl_2}} = \mathbf{0.000857}$ **atm**

At 1000ºC: $\boldsymbol{K} = \mathbf{1.928 \times 10^{-3}} = \frac{(2x)^2}{0.100-x} = \frac{4x^2}{0.100-x}$**, and *x* = 6.706 × 10^{-3}.**

$\boldsymbol{p}_{\mathbf{SiCl_4}} = \mathbf{0.0933}$ **atm** $\boldsymbol{p}_{\mathbf{SiCl_2}} = \mathbf{0.0134}$ **atm**

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

$$\boldsymbol{n}_{\mathbf{Si}} \approx (\mathbf{0.00018})\left[\left(\frac{0.033}{0.100}\right)\right]\left[\frac{1273^{0.8}(0.636)}{18.0}\right](\mathbf{24}) = \mathbf{0.0153}\ \textbf{moles} \rightarrow \textbf{431 mg Si}$$

(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.

Fe_2O_3(*s*) + 6 HCl(*g*) ⇌ 2 $FeCl_3$(*g*) + 3 H_2O(*g*).

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

$\Delta \boldsymbol{G}° = \mathbf{129,340 - 4.2}\ \boldsymbol{T}$**. Since $\Delta G° = \Delta H° - T\Delta S°$, the transport equilibrium is endothermic, and the entropy is nearly zero. Therefore, transport of Fe_2O_3(*s*) should be hot-to-cold.**

(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.

Volume of the tube = (18 cm)[π(0.45 cm)²] = 11.45 cm³ = 11.45 × 10⁻³ L

Hot end (T = 1273 K): $\mathbf{p_0(HCl) = \frac{(4.6\times10^{-6})(0.08206)(1273)}{(5.725\times10^{-3})} = 0.0839\ atm}$

Cold end (T = 1073 K): $\mathbf{p_0(HCl) = \frac{(4.6\times10^{-6})(0.08206)(1073)}{(5.725\times10^{-3})} = 0.0707\ atm}$

- Estimate the difference in partial pressures of HCl(*g*) from one end of the tube to the other.

$\Delta G°(1273\ K) = 123{,}990$ J/mol; $K(1273\ K) = 8.17\times10^{-6} = \frac{(2x)^2(3x)^3}{(0.0839-6x)^6}$

x = 0.00165, so that p(HCl) = 0.0740 atm

$\Delta G°(1073\ K) = 124{,}830$ J/mol; $K(1073\ K) = 8.37\times10^{-7} = \frac{(2x)^2(3x)^3}{(0.0707-6x)^6}$

x = 0.000903, so that p(HCl) = 0.0653 atm

The pressure differential for HCl(*g*) is 0.0087 atm.

- Estimate how many grams of iron(III) oxide will be transported during 10 hours.

The transport rate of Fe_2O_3(*s*) is

$$\frac{n_{Fe_2O_3}}{t}\ (mol/hr) = \left(\frac{1}{6}\cdot\frac{\Delta p_{HCl}}{p_{TOT}}\right)\frac{T^{0.8}A}{s}(1.8\times10^{-4}) = \left(\frac{1}{6}\cdot\frac{\Delta p_{HCl}}{p_{TOT}}\right)\frac{(1173\ K)^{0.8}[\pi(0.45\ cm)^2]}{18\ cm}(1.8\times10^{-4})$$

The ratio $\frac{\Delta p_{HCl}}{p_{TOT}}$ can be approximated in two equivalent ways: (1) taking the HCl(*g*) pressure difference (0.0087 atm) and divide by the average total pressure (0.076 atm); or (2) taking the temperature difference (200 K) and divide by the average temperature (1173 K). Therefore,

$\frac{\Delta p_{HCl}}{p_{TOT}} = \frac{0.0087}{0.076} = 0.11$ **(using pressures);** $\frac{\Delta p_{HCl}}{p_{TOT}} = \frac{200}{1173} = 0.17$ **(using temperatures).**

So, choose the ratio to be 0.15. Then,

$$\frac{n_{Fe_2O_3}}{t}\ (mol/hr) = \left(\frac{1}{6}\cdot 0.15\right)\frac{(1173\ K)^{0.8}[\pi(0.45\ cm)^2]}{18\ cm}(1.8\times10^{-4}) = 4.54\times10^{-5}\ mol/hr$$

Therefore, (4.54 ×10⁻⁵ mole/hr)(159.687 g/mole)(10.0 hr) = 0.0725 g Fe_2O_3 will be transported.

(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)

TiN(*s*) + 3 HCl(*g*) ⇌ $TiCl_3$(*g*) + NH_3(*g*)

Δ*G*° = 22,890 + 95.0 *T*, Δ*H*° = +22.9 kJ/mol, Δ*S*° = –95.0 J/mol·K

There is no optimum temperature (Δ*H*° / Δ*S*° < 0 K).

This equilibrium does not support transport.

TiN(*s*) + 3 HCl(*g*) ⇌ $TiCl_3$(*g*) + 1/2 N_2(*g*) + 3/2 H_2(*g*)

Δ*G*° = 76,130 – 21.2 *T*, Δ*H*° = +76.1 kJ/mol, Δ*S*° = +21.2 J/mol·K

Optimum transport temperature = Δ*H*° / Δ*S*° = 3590 K = 3320°C

Endothermic reaction: Transport will be from hot-to-cold.

TiN(*s*) + 4 HCl(*g*) ⇌ $TiCl_4$(*g*) + NH_3(*g*) + 1/2 H_2(*g*)

Δ*G*° = –104,380 + 170.0 *T*, Δ*H*° = –104.4 kJ/mol, Δ*S*° = –170.0 J/mol·K

Optimum transport temperature = $\Delta H^o / \Delta S^o$ = 614 K = 341ºC
Exothermic reaction: Transport will be from cold-to-hot.

$TiN(s) + 4\ HCl(g) \rightleftharpoons TiCl_4(g) + 1/2\ N_2(g) + 2\ H_2(g)$

$\Delta G^o = -51{,}140 + 53.8\ T$, $\Delta H^o = -51.1$ kJ/mol, $\Delta S^o = -53.8$ J/mol·K

Optimum transport temperature = $\Delta H^o / \Delta S^o$ = 951 K = 678ºC
Exothermic reaction: Transport will be from cold-to-hot.

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

Among the four possible transport equilibria, the one with an optimum transport temperature close to 1200 K involves the oxidation of TiN(*s*) with gas-phase species including $TiCl_4(g)$, $N_2(g)$, and $H_2(g)$. At this temperature, the equilibrium $2\ NH_3(g) \rightleftharpoons N_2(g) + 3\ H_2(g)$ favors $N_2(g)$ and $H_2(g)$ over $NH_3(g)$.

(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.

See: *Journal of Solid-State Chemistry* **1988**, *75*, 99-104.
Journal of Solid-State Chemistry **1988**, *77*, 342-347.
Chemistry of Materials **2002**, *14*, 4517-4521.

(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.

$ZrH_2(s) + NH_4Cl(g) \longrightarrow ZrNCl(s) + 3\ H_2(g)$

or

$ZrH_2(s) + NH_3(g) + HC\ (g) \longrightarrow ZrNCl(s) + 3\ H_2(g)$

$ZrH_2 \equiv Zr^{2+}(H^-)_2$ $ZrNCl \equiv Zr^{4+}(N^{-3})(Cl^-)$
$NH_4Cl \equiv (N^{-3})(H^+)_3(Cl^-)$ $H_2 \equiv (H^0)_2$

This reaction is a *reduction-oxidation* reaction. Hydrogen atoms in the metal hydride and ammonium chloride *synproportionate* to form hydrogen gas. The reaction generates more moles of gas in the products than in the reactants because 3 moles of H_2 (*g*) are produced from 1-2 moles of gas in the reactants: at 610 K, NH_4Cl (*s*) will start decomposing into NH_3 (*g*) and HCl (*g*) and at 623 K, it will sublimate. Thus, $\Delta S > 0$, which can give $\Delta G < 0$ at elevated 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.

β-$ZrNCl(s) + 5\ NH_4Cl(s) \longrightarrow (NH_4)_2ZrCl_6(s) + 4\ NH_3(g)$

(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.

$(NH_4)_2ZrCl_6(s) \longrightarrow ZrCl_4(g) + 2\ NH_3(g) + 2\ HCl(g)$

Checking this reaction against the data: 5 moles of gas are produced, which agrees well with vapor pressure measurements (ca. 4.9 moles of gas per mole of solid). In the mass spectrum, NH_3^+ (17 amu)

and HCl^+ (36 amu) are directly observed. The remaining five peaks come from $ZrCl_4^+$ (233 amu) and its fragments: $ZrCl_3^+$ (197 amu), $ZrCl_2^+$ (162 amu), $ZrCl^+$ (126 amu) and Zr^+ (91 amu).

(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.

β-ZrNCl(*s*) + 5 NH_4Cl(*s*) ⟶ $ZrCl_4$(*g*) + 6 NH_3(*g*) + 2 HCl(*g*)

Since NH_4Cl(*s*) ⟶ NH_3(*g*) + HCl(*g*), the net reaction becomes

β-ZrNCl(*s*) + 3 HCl(*g*) ⟶ $ZrCl_4$(*g*) + NH_3(*g*).

In this reaction, 3 moles of gas produce 2 moles of gas, so $\Delta S < 0$. To serve as a proper chemical transport reaction, this reaction must be *exothermic*, i.e., $\Delta H < 0$. For an exothermic reaction, transport takes place from the cold end to the hot end – the solid β-ZrNCl(*s*) forms in the hot end of the transport tube.

In this reaction, the transport agent is HCl(*g*).

To estimate the time needed to transport β-ZrNCl(*s*), we evaluate the transport rate:

$$\frac{n_{\mathrm{ZrNCl}}}{t}\ (\mathrm{mol/hr}) = \left(\frac{1}{3}\cdot\frac{\Delta p_{\mathrm{HCl}}}{p_{\mathrm{TOT}}}\right)\frac{T^{0.8}A}{s}(1.8\times10^{-4}) \sim \left(\frac{1}{3}\cdot\frac{0.1\ \mathrm{atm}}{1.0\ \mathrm{atm}}\right)\cdot\frac{(1023\ \mathrm{K})^{0.8}[\pi(0.4\ \mathrm{cm})^2]}{15\ \mathrm{cm}}\cdot 1.8\times10^{-4}$$
$$= 5.14\times10^{-5}\ \mathrm{mol/hr}$$

The pressure differential is estimated from the relative temperature differential, which is 100 K / ~1000 K = ~0.1. For a total pressure of 1.0 atm, the estimated pressure differential is ~0.1 atm. Using this approximation, the time needed to transport 0.5 g β-ZrNCl(*s*) is

$$t \sim (0.5\ \mathrm{g})/(140\ \mathrm{g/mol})/\left(5.14\times10^{-5}\ \mathrm{mol/hr}\right) = 69.5\ \mathrm{hr}.$$

So, the reaction will take just under 3 days to run its full course.

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

$(NH_4)_2ZrCl_6$(*s*) ⟶ β-ZrNCl(*s*) + NH_3(*g*) + 5 HCl(*g*)

$(NH_4)_2ZrCl_6$(*s*) ⟶ ZrN(*s*) + NH_3(*g*) + 5 HCl(*g*) + ½ Cl_2(*g*)

Another option to consider is the decomposition:

8 β-ZrNCl(*s*) ⟶ 6 ZrN(*s*) + 2 $ZrCl_4$(*g*) + N_2(*g*)

Then,

$(NH_4)_2ZrCl_6$(*s*) ⟶ 3/4 ZrN(*s*) + 1/4 $ZrCl_4$(*g*) + 1/8 N_2(*g*) + NH_3(*g*) + 5 HCl(*g*)

(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°;
- Determine the direction of transport of Si(*s*); and
- Determine the optimal median transport temperature.

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

$Si(s) + SiCl_4(g) \rightleftharpoons 2\ SiCl_2(g)$; **$\Delta G^o = 316{,}050 - 196.3\ T$**

$\Delta H^o = +316.05$ kJ/mol **Hot → Cold**

$\Delta S^o = +196.3$ J/mol·K **$T_{opt} = 1618$ K = 1345°C**

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

$2\ Si(s) + 4\ HCl(g) \rightleftharpoons SiH_4(g) + SiCl_4(g)$; **$\Delta G^o = -258{,}910 + 252.8\ T$**

$\Delta H^o = -258.91$ kJ/mol **Cold → Hot**

$\Delta S^o = -252.8$ J/mol·K **$T_{opt} = 1024$ K = 751°C**

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

$Si(s) + 2\ I_2(g) \rightleftharpoons SiI_4(g)$; **$\Delta G^o = -231{,}340 + 116.1\ T$**

$\Delta H^o = -231.34$ kJ/mol **Cold → Hot**

$\Delta S^o = -116.1$ J/mol·K **$T_{opt} = 1993$ K = 1720°C**

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

$Si(s) + 2\ HI(g) \rightleftharpoons SiH_2I_2(g)$; **$\Delta G^o = -91{,}060 + 107.1\ T$**

$\Delta H^o = -91.06$ kJ/mol **Cold → Hot**

$\Delta S^o = -107.1$ J/mol·K **$T_{opt} = 850$ K = 577°C**

(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 $I_2(g)$:

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

$\Delta G_f^0(SiI_2, g) = 26{,}840 - 36.0\ T$ (J/mol)

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

$Si(s) + I_2(g) \rightleftharpoons SiI_2(g)$

$\Delta H^o = +26.84$ kJ/mol **Hot → Cold**

$\Delta S^o = +36.0$ J/mol·K **$T_{opt} = 745$ K = 472°C**

$Si(s) + 2\ I_2(g) \rightleftharpoons SiI_4(g)$

$\Delta H^o = -231.34$ kJ/mol **Cold → Hot**

$\Delta S^o = -116.1$ J/mol·K **$T_{opt} = 1993$ K = 1720°C (above melting point of Si)**

$Si(s) + SiI_4(g) \rightleftharpoons 2\ SiI_2(g)$

$\Delta G^o = 285{,}020 - 188.1\ T$ (J/mol)

$\Delta H^o = +285.02$ kJ/mol **Hot → Cold**

$\Delta S^o = +188.1$ J/mol·K **$T_{opt} = 1515$ K = 1242°C**

The first and third equilibria are possible and effective transport equilibria for transporting Si(*s*) below its melting point with 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?

Start by evaluating the equilibrium constants at 1073 K for the following equilibria:

$I_2(g) \rightleftharpoons 2\ I(g)$: **$\Delta G^o(1073\ K) = +20{,}078.3$ J/mol** $K = \frac{p_I^2}{p_{I_2}} = 0.105$

$Si(s) + I_2(g) \rightleftharpoons SiI_2(g)$: **$\Delta G^o(1073\ K) = -11{,}788.0$ J/mol** $K = \frac{p_{SiI_2}}{p_{I_2}} = 3.749$

$Si(s) + 2\ I_2(g) \rightleftharpoons SiI_4(g)$: **$\Delta G^o(1073\ K) = -106{,}764.7$ J/mol** $K = \frac{p_{SiI_4}}{p_{I_2}^2} = 1.576 \times 10^5$

Now $p_{TOT} = p_{I_2} + p_I + p_{SiI_2} + p_{SiI_4} = 1.00$ atm. Using the expressions for each equilibrium constant allows this equation to be solved "graphically" (using Excel). The partial pressures must take values between 0 and 1, which leads to a single solution:

$p_{I_2} = 0.00248$ **atm,** $p_I = 0.0161$ **atm,**

$p_{SiI_2} = 0.00930$ **atm,** $p_{SiI_4} = 0.969$ **atm.**

All of these gases originated from the initial $I_2(s)$ placed into the transport container. Therefore, the initial number of moles/cm³ of I_2 placed into the container is:

$$\left(0.00248 + \frac{0.0161}{2} + 0.00930 + 2(0.969)\right)\left(\frac{1}{0.08206 \cdot 1073}\right)\left(\frac{1}{1000}\right) = 2.22 \times 10^{-5} \text{ mol } I_2/\text{cm}^3$$

(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 temperatures increase, the tendency for gaseous halogen molecules to form halogen atoms increases. Explain this phenomenon.

Halogen molecules exist as diatomic molecules. Therefore, the relevant equilibrium is $X_2(g) \rightleftharpoons 2X(g)$. This reaction is endothermic, i.e., $\Delta H^o > 0$, and has a positive entropy, $\Delta S^o > 0$. As a result, the Gibbs free energy $\Delta G^o = \Delta H^o - T\Delta S^o$ decreases as temperature increases, which explains the increased tendency for halogen atoms to form as temperature increases.

(b) Given ΔG_f^0(I, g) = 76,840 – 52.9 T (in J/mol), what is the dominant iodine species for temperatures below 1000°C?

$I_2(g) \rightleftharpoons 2\,I(g)$: ΔG^o(1273 K) = +9,498.3 J/mol $\quad K = \frac{p_I^2}{p_{I_2}} = 0.408$

Therefore, at 1273 K, if $p_{I_2} + p_I = 1.00$ atm, then $p_I = 0.466$ atm and $p_{I_2} = 0.534$ atm. At lower temperatures, K decreases. As a result, $I_2(g)$ remains the dominant iodine species below 1000°C, but there is significant concentration of $I(g)$.

(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.

$\Delta G_f^0(FeI_2, g)$ = 18,500 – 50.8 T (in J/mol)

$\Delta G_f^0(Fe_2I_4, g)$ = –124,800 + 43.6 T (in J/mol)

Possible transport equilibria are:

$Fe(s) + I_2(g) \rightleftharpoons FeI_2(g)$
ΔH^o = +18,500 J/mol — **Hot → Cold**
ΔS^o = +50.8 J/mol·K — **T_{opt} = 364 K = 91°C**

$2\,Fe(s) + 2\,I_2(g) \rightleftharpoons Fe_2I_4(g)$
ΔH^o = –124,800 J/mol — **Cold → Hot**
ΔS^o = –43.6 J/mol·K — **T_{opt} = 2862 K = 2589°C**

$Fe(s) + 2\,I(g) \rightleftharpoons FeI_2(g)$
ΔG^o = –135,180 + 55.0 T
ΔH^o = –135,180 J/mol — **Cold → Hot**
ΔS^o = –55.0 J/mol·K — **T_{opt} = 2458 K = 2185°C**

$2\,Fe(s) + 4\,I(g) \rightleftharpoons Fe_2I_4(g)$
ΔG^o = –432,160 + 255.2 T
ΔH^o = –432,160 J/mol — **Cold → Hot**
ΔS^o = –255.2 J/mol·K — **T_{opt} = 1693 K = 1420°C**

Since Fe(s) is transported from cold-to-hot, the transport is driven by an exothermic process. Since the concentration of I(g) becomes significant at 800°C–1000°C, it can play an important role as a transport agent because the transport equilibria are exothermic.

(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.

$2\ FeI_2(g) \rightleftharpoons Fe_2I_4(g)$: **$\Delta G^o = -161{,}800 + 145.2\ T$**

This equilibrium favors $Fe_2I_4(g)$ for temperatures below 1114 K = 841°C and favors $FeI_2(g)$ above this same temperature.

At 800°C =1073 K, ΔG^o = –6,000.4 J/mol and K = 1.96, so that $Fe_2I_4(g)$ dominates over $FeI_2(g)$.

At 1000°C =1273 K, ΔG^o = +23,039.6 J/mol and K = 0.113, so that $FeI_2(g)$ dominates over $Fe_2I_4(g)$.

The molecular structure of FeI_2 could be either linear or bent I–Fe–I.

The molecular structure of Fe_2I_4, which is the dimer $(FeI_2)_2$, could involve either a direct Fe–Fe bond or I atoms bridging the Fe···Fe contact.

(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.

$5\ V(s) + SiO_2(s) \longrightarrow V_3Si(s) + 2\ VO(s)$

(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.

$V(s) + I_2(g) \longrightarrow VI_2(g)$

(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.

$11\ VI_2(g) + SiO_2(s) \longrightarrow V_3Si(s) + 2\ V_4O(s) + 11\ I_2(g)$

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

$7\ V_4O(s) + 2\ SiO_2(s) \longrightarrow 2\ V_3Si(s) + 11\ V_2O(s)$

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

$5\ V_2O(s) + SiO_2(s) \longrightarrow V_3Si(s) + 7\ VO(s)$

(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.

$V_3Si(s) + 8\ VCl_3(g) \rightleftharpoons 11\ VCl_2(g) + SiCl_2(g)$

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

$V_3Si(s) + 4\ SiCl_4(g) \rightleftharpoons 3\ VCl_2(g) + 5\ SiCl_2(g)$

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

$VO(s) + 3\ VCl_3(g) \rightleftharpoons VOCl_3(g) + 3\ VCl_2(g)$

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

$2\ VO(s) + 3\ SiCl_4(g) \rightleftharpoons 2\ VOCl_3(g) + 3\ SiCl_2(g)$

(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)

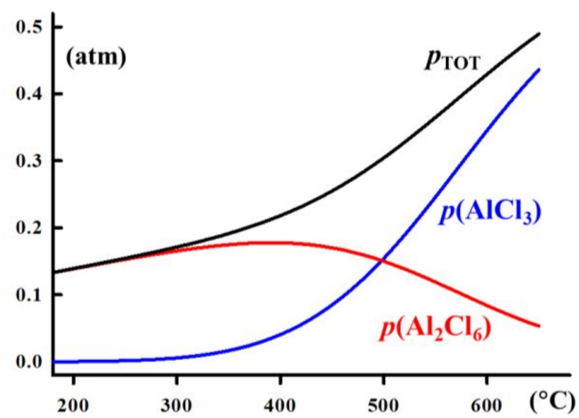
(a) 15.0 mg $AlCl_3(g)$ is loaded into a sealed tube of volume 15.7 cm^3. Plot the partial pressures of $AlCl_3(g)$ and $Al_2Cl_6(g)$ and the total pressure (in atm) as a function of temperature between 180°C and 650°C. Discuss the implications of these results for transport of Al(*s*).

2 $AlCl_3(g) \rightleftharpoons Al_2Cl_6(g)$: ΔG° = –123,010 + 143.8 *T*, $\ln K = \frac{14{,}796}{T} - 17.30$

 # moles $AlCl_3(g)$ = (0.015 g)/(133.33 g/mol) = 1.125 × 10^{-4} mol

Initial pressure of $AlCl_3(g)$ = (1.125 × 10^{-4})(0.08206) *T* / (15.7/1000) = (5.880 × 10^{-4})*T*

The equilibrium constant is $K(T) = \frac{p(Al_2Cl_6)}{p^2(AlCl_3)} = \frac{p}{(p_0 - 2p)^2}$. **The plot is:**



At low temperatures, the gas is almost entirely $Al_2Cl_6(g)$. Above ~400°C, the concentration of the monomer $AlCl_3(g)$ becomes significant compared to the concentration of the dimer. Therefore, during the transport of Al(*s*), it is possible that either $AlCl_3(g)$ or $Al_2Cl_6(g)$ could be transport agents.

(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?

2 Al(*s*) + $AlCl_3(g) \rightleftharpoons$ 3 AlCl(*g*): ΔG° = 425,470 – 299.6 *T*; Supports transport

ΔH° > 0: transport from hot-to-cold
Optimum median temperature is 1420 K = 1147°C.

Al(*s*) + 2 $AlCl_3(g) \rightleftharpoons$ 3 $AlCl_2(g)$: ΔG° = 324,620 – 200.8 *T*; Supports transport

ΔH° > 0: transport from hot-to-cold
Optimum median temperature is 1617 K = 1344°C.

4 Al(*s*) + $Al_2Cl_6(g) \rightleftharpoons$ 6 AlCl(*g*): ΔG° = 973,950 – 743.0 *T*; Supports transport

ΔH° > 0: transport from hot-to-cold
Optimum median temperature is 1311 K = 1038°C.

Al(*s*) + $Al_2Cl_6(g) \rightleftharpoons$ 3 $AlCl_2(g)$: ΔG° = 447,630 – 344.6 *T*; Supports transport

ΔH° > 0: transport from hot-to-cold
Optimum median temperature is 1299 K = 1026°C.

(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?

2 $AlCl_2(g) \rightleftharpoons$ AlCl(*g*) + $AlCl_3(g)$: ΔG° = –74,590 + 34.0 *T*

This reaction has negative Δ*G*º for temperatures above 2194 K. Therefore, at lower temperatures where the transport of Al will take place, the primary gas phase species are likely AlCl(*g*) and some mixture of $AlCl_3$(*g*) and Al_2Cl_6(*g*).

VAPOR PRESSURE OF THE METALLIC ELEMENTS

C. B. Alcock

This table gives coefficients in an equation for the vapor pressure of 65 metallic elements in both the solid and liquid state. Vapor pressures in the range 10^{-10} to 10^{2} Pa (10^{-15} to 10^{-3} atm) are covered. The equation is:

for p in pascals: $\log (p/\mathrm{Pa}) = 5.006 + A + BT^{-1} + C\log T + DT^{-3}$

for p in atmospheres: $\log(p/\mathrm{atm}) = A + BT^{-1} + C\log T + DT^{-3}$, where T is the temperature in K

This equation reproduces the observed vapor pressures to an accuracy of ±5% or better. Reprinted with permission of the publisher, Pergamon Press.

REFERENCE

Alcock, C. B., Itkin, V. P., and Horrigan, M. K., *Canadian Metallurgical Quarterly*, 23, 309, 1984.

Element, state	*A*	*B*	*C*	*D*	Temperature range
Li sol	5.667	-8310			298-m.p.
Li liq	5.055	-8023			m.p.-1000
Na sol	5.298	-5603			298-m.p.
Na liq	4.704	-5377			m.p.-700
K sol	4.961	-4646			298-m.p.
K liq	4.402	-4453			m.p.-600
Rb sol	4.857	-4215			298-m.p.
Rb liq	4.312	-4040			m.p.-550
Cs sol	4.711	-3999			298-m.p.
Cs liq	4.165	-3830			m.p.-550
Be sol	8.042	-17020	-0.4440		298-m.p.
Be liq	5.786	-15731			m.p.-1800
Mg sol	8.489	-7813	-0.8253		298-m.p.
Ca sol	10.127	-9517	-1.4030		298-m.p.
Sr sol	9.226	-8572	-1.1926		298-m.p.
Ba sol	12.405	-9690	-2.2890		298-m.p.
Ba liq	4.007	-8163			m.p.-1200
Al sol	9.459	-17342	-0.7927		298-m.p.
Al liq	5.911	-16211			m.p.-1800
Ga sol	6.657	-14208			298-m.p.
Ga liq	6.754	-13984	-0.3413		m.p.-1600
In sol	5.991	-12548			298-m.p.
In liq	5.374	-12276			m.p.-1500
Tl sol	5.971	-9447			298-m.p.
Tl liq	5.259	-9037			m.p.-1100
Sn sol	6.036	-15710			298-m.p.
Sn liq	5.262	-15332			m.p.-1850
Pb sol	5.643	-10143			298-m.p.
Pb liq	4.911	-9701			m.p.-1200
Sc sol	6.650	-19721	0.2885	-0.3663	298-m.p.
Sc liq	5.795	-17681			m.p.-2000
Y sol	9.735	-22306	-0.8705		298-m.p.
Y liq	5.795	-20341			m.p.-2300
La sol	7.463	-22551	-0.3142		298-m.p.
La liq	5.911	-21855			m.p.-2450
Ti sol	11.925	-24991	-1.3376		298-m.p.
Ti liq	6.358	-22747			m.p.-2400
Zr sol	10.008	-31512	-0.7890		298-m.p
Zr liq	6.806	-30295			m.p.-2500
Hf sol	9.445	-32482	-0.6735		298-m.p.
V sol	9.744	-27132	-0.5501		298-m.p.

VAPOR PRESSURE OF THE METALLIC ELEMENTS (continued)

Element, state	*A*	*B*	*C*	*D*	Temperature range
V liq	6.929	-25011			m.p.-2500
Nb sol	8.822	-37818	-0.2575		298-2500
Ta sol	16.807	-41346	-3.2152	0.7437	248-2500
Cr sol	6.800	-20733	0.4391	-0.4094	298-2000
Mo sol	11.529	-34626	-1.1331		298-2500
W sol	2.945	-44094	1.3677		298-2350
W sol	-54.527	-57687	-12.2231		2200-2500
Mn sol	12.805	-15097	-1.7896		298-m.p.
Re sol	11.543	-40726	-1.1629		298-2500
Fe sol	7.100	-21723	0.4536	-0.5846	298-m.p.
Fe liq	6.347	-19574			m.p.-2100
Ru sol	9.755	-34154	-0.4723		298-m.p.
Os sol	9.419	-41198	-0.3896		298-2500
Co sol	10.976	-22576	-1.0280		298-m.p.
Co liq	6.488	-20578			m.p.-2150
Rh sol	10.168	-29010	-0.7068		298-m.p.
Rh liq	6.802	-26792			m.p.-2500
Ir sol	10.506	-35099	-0.7500		298-2500
Ni sol	10.557	-22606	-0.8717		298-m.p.
Ni liq	6.666	-20765			m.p.-2150
Pd sol	9.502	-19813	-0.9258		298-m.p.
Pd liq	5.426	-17899			m.p.-2100
Pt sol	4.882	-29387	1.1039	-0.4527	298-m.p.
Pt liq	6.386	-26856			m.p.-2500
Cu sol	9.123	-17748	-0.7317		298-m.p.
Cu liq	5.849	-16415			m.p.-1850
Ag sol	9.127	-14999	-0.7845		298-m.p.
Ag liq	5.752	-13827			m.p.-1600
Au sol	9.152	-19343	-0.7479		298-m.p.
Au liq	5.832	-18024			m.p.-2050
Zn sol	6.102	-6776			298-m.p.
Zn liq	5.378	-6286			m.p.-750
Cd sol	5.939	-5799			298-m.p.
Cd liq	5.242	-5392			m.p.-650
Hg liq	5.116	-3190			298-400
Ce sol	6.139	-21752			298-m.p.
Ce liq	5.611	-21200			m.p.-2450
Pr sol	8.859	-18720	-0.9512		298-m.p.
Pr liq	4.772	-17315			m.p.-2200
Nd sol	8.996	-17264	-0.9519		298-m.p.
Nd liq	4.912	-15824			m.p.-2000
Sm sol	9.988	-11034	-1.3287		298-m.p.
Eu sol	9.240	-9459	-1.1661		298-m.p.
Gd sol	8.344	-20861	-0.5775		298-m.p.
Gd liq	5.557	-19389			m.p.-2250
Tb sol	9.510	-20457	-0.9247		298-m.p.
Tb liq	5.411	-18639			m.p.-2200
Dy sol	9.579	-15336	-1.1114		298-m.p.
Ho sol	9.785	-15899	-1.1753		298-m.p.
Er sol	9.916	-16642	-1.2154		298-m.p.
Er liq	4.668	-14380			m.p.-1900
Tm sol	8.882	-12270	-0.9564		298-1400
Yb sol	9.111	-8111	-1.0849		298-900
Lu sol	8.793	-22423	-0.6200		298-m.p.
Lu liq	5.648	-20302			m.p.-2350
Th sol	8.668	-31483	-0.5288		298-m.p.
Th liq	-18.453	-24569	6.6473		m.p.-2500
Pa sol	10.552	-34869	-1.0075		298-m.p.

VAPOR PRESSURE OF THE METALLIC ELEMENTS (continued)

Element, state	***A***	***B***	***C***	***D***	**Temperature range**
Pa liq	6.177	-32874			m.p.-2500
U sol	0.770	-27729	2.6982	-1.5471	298-m.p.
U liq	20.735	-28776	-4.0962		m.p.-2500
Np sol	19.643	-24886	-3.9991		298-m.p.
Np liq	10.076	-23378	-1.3250		m.p.-2500
Pu sol	26.160	-19162	-6.6675		298-600
Pu sol	18.858	-18460	-4.4720		500-m.p.
Pu liq	3.666	-16658			m.p.-2450
Am sol	11.311	-15059	-1.3449		298-m.p.
Cm sol	8.369	-20364	-0.5770		298-m.p.
Cm liq	5.223	-18292			m.p.-2200