Introduction to the Thermodynamics of Materials

4th. Edition

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Preliminaries

Settings

```
Off[General::spell]
```

Physical Constants Needed for Problems

Heat Capacities

The generic heat capcity

$$Cp = a + \frac{b\,T}{10^3} + \frac{c\,10^5}{T^2};$$

The heat capacities of various elements and compounds are

```
CpAgs = Cp /. {a → 21.30, b → 8.54, c → 1.51};
```

```
CpAgl = Cp /. {a → 30.50, b → 0, c → 0};
```

$$CpAl = Cp + \frac{20.75\,T^2}{10^6} /. \{a \to 31.38,\ b \to -16.4,\ c \to -3.6\};$$

```
CpAll = Cp /. {a → 31.76, b → 0, c → 0};
```

— General::spell1 : Possible spelling error:
new symbol name "CpAll" is similar to existing symbol "CpAl".

```
CpAl2O3 = Cp /. {a → 117.49, b → 10.38, c → -37.11};
```

```
CpCaO = Cp /. {a → 50.42, b → 4.18, c → -8.49};
```

```
CpCaTiO3 = Cp /. {a → 127.39, b → 5.69, c → -27.99};
```

```
CpCord = Cp /. {a → 626.34, b → 91.21, c → -200.83};
```

$$CpCr = Cp + \frac{2.26\,T^2}{10^6} /. \{a \to 21.76,\ b \to 8.98,\ c \to -0.96\};$$

```
CpCr2O3 = Cp /. {a → 119.37, b → 9.30, c → -15.65};
```

```
CpCO = Cp /. {a → 28.41, b → 4.10, c → -0.46};
```

— *General::spell1 : Possible spelling error:
new symbol name "CpCO" is similar to existing symbol "CpCaO".*

```
CpCO2 = Cp /. {a → 44.14, b → 9.04, c → -8.54};
```

$$CpCu = Cp + \frac{9.47\,T^2}{10^6} \text{ /. } \{a \to 30.29,\ b \to -10.71,\ c \to -3.22\};$$

```
CpDiamond = Cp /. {a → 9.12, b → 13.22, c → -6.19};
```

$$CpGraphite = Cp - \frac{17.38\,T^2}{10^6} \text{ /. } \{a \to 0.11,\ b \to 38.94,\ c \to -1.48\};$$

```
CpH2Og = Cp /. {a → 30.00, b → 10.71, c → -0.33};
```

N2 over range 298-2500K

```
CpN2 = Cp /. {a → 27.87, b → 4.27, c → 0};
```

O2 over range 298-3000K

```
CpO2 = Cp /. {a → 29.96, b → 4.18, c → -1.67};
```

— *General::spell : Possible spelling error: new
symbol name "CpO2" is similar to existing symbols {CpCO2, CpN2}.*

Si3N4 over range 298-900K

$$CpSi3N4 = Cp - \frac{27.07\,T^2}{10^6} \text{ /. } \{a \to 76.36,\ b \to 109.04,\ c \to -6.53\};$$

SiO2 (alpha quartz) for 298-847K

```
CpSiO2Q = Cp /. {a → 43.93, b → 38.83, c → -9.69};

CpTiO2 = Cp /. {a → 73.35, b → 3.05, c → -17.03};

CpZra = Cp /. {a → 22.84, b → 8.95, c → -0.67};

CpZrb = Cp /. {a → 21.51, b → 6.57, c → 36.69};
```

— *General::spell1 : Possible spelling error: new
symbol name "CpZrb" is similar to existing symbol "CpZra".*

```
CpZraO2 = Cp /. {a → 69.62, b → 7.53, c → -14.06};

CpZrbO2 = Cp /. {a → 74.48, b → 0, c → 0};
```

— *General::spell1 : Possible spelling error: new
symbol name "CpZrbO2" is similar to existing symbol "CpZraO2".*

- **Enthalpies at 298K and Enthalpies of Transitions**

Here are some enthalpies at 298. For compounds, these are enthalpies for formation from elements. The enthalpies of pure elements are taken, by convention to be zero.

```
HAl2O3 = -1675700;
```

```
HAlmelt = 10700;
HCaO = -634900;
HCaTiO3 = -1660600;
HCH4 = -74800;
HCr2O3 = -1134700;
HCO2 = -393500;
HDiamond = 1500;
HH2Og = -241800;
HO2 = 0;
HSi3N4 = -744800;
HSiO2Q = -910900;
HTiO = -543000;
HTiO2 = -944000;
HTi2O3 = -1521000;
HTi3O5 = -2459000;
```

Transformation Zr(a) to Zr(b)

```
DHZratob = 3900;
```

Transformation Zr(a)O(2) to Zr(b)O2

```
DHZrO2atob = 5900;
```

Formation of Zr(a)O(2)

```
HZraO2 = -1100800;
```

- **Entropies at 298K**

There are absolute entropies of some elements at compounds at 298K

```
SCaO = 38.1;
SCaTiO3 = 93.7;
SN2 = 191.5;
SO2 = 205.1;
SSi3N4 = 113.0;
SSiO2Q = 41.5;
```

```
STiO = 34.7;

STiO2 = 50.6;

STi2O3 = 77.2;

STi3O5 = 129.4;

SZra = 39.0;

SZraO2 = 50.6;
```

- **Molecular Weights**

```
massAl = 26.98;

massAu = 196.97;

massCr = 52.;

massCu = 63.55;

massFe = 55.85;

massH = 1.008;

massMg = 24.31;

massN = 14.007;

massO = 16;

massC = 12;

massCa =  40.08;

massSi = 28.04;

massTi = 47.88;

massMn  =  54.94;

massF = 19 ;

massZn  =  65.38 ;
```

- **Vapor Pressure**

```
vapor =  -A / T + B Log[T] + C
```

$$C - \frac{A}{T} + B\,Log[T]$$

Hg for the range 298-630K

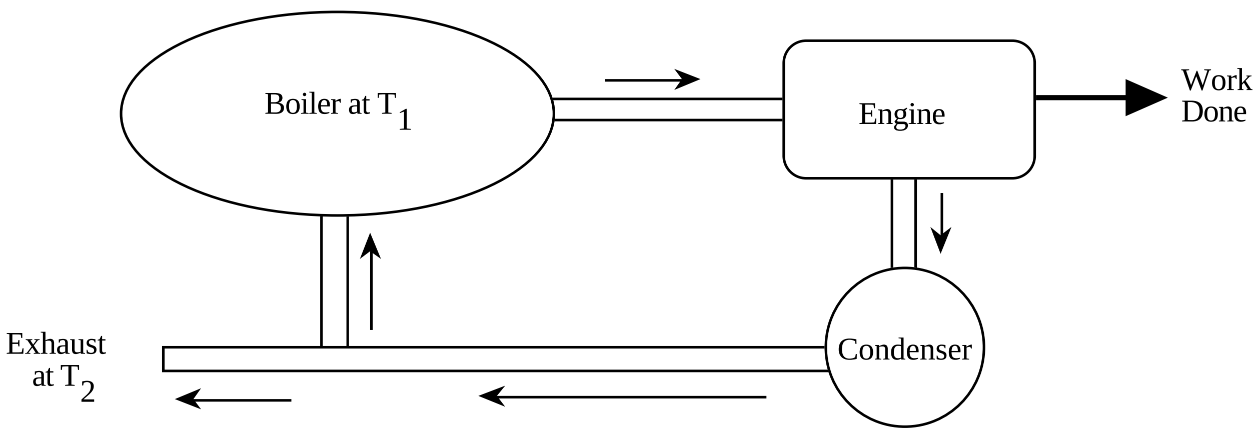
```
lnvapHgl = vapor /. {A -> 7611 , B -> -0.795, C -> 17.168} ;
```

```
lnvapSiCl4 = vapor /. {A -> 3620 , B -> 0, C -> 10.96} ;
lnvapCO2s = vapor /. {A -> 3116 , B -> 0, C -> 16.01} ;
lnvapMn = vapor /. {A -> 33440 , B -> -3.02, C -> 37.68} ;
lnvapFe = vapor /. {A -> 45390 , B -> -1.27, C -> 23.93} ;
lnvapZn = vapor /. {A -> 15250 , B -> -1.255, C -> 21.79} ;
```

Chapter 1: Introduction and Definition of Terms

History

Thermodynamics began with the study of heat and work effects and relations between heat and work. Some early thermodynamics problems were for very practical problems. For example, in a steam engine heat is supplied to water to create steam. The steam is then used to turn an engine which does work. Finally, the water is exhasted to the environment or in a cyclic engine it can be condensed and recyled to the heating chamber or boiler



Steam power plant or steam engine

An early goal for thermodynamics was to analyze the steam engine and to figure out the maximum amount of work that could be done for an engine operating between the input temperature T_1 and the output temperature T_2.

Some of the most important work on thermodynamics of heat engines was done by Nicholas Carnot around 1810. He was a French engineer and wrote one paper, *Reflections on the Motive Power of Heat*, that introduced the "Carnot" cycle and helped explain the maximum efficiency of heat engines. It is interesting to note that the first steam engines were invented in 1769. Thus the practical engineering was done without knowledge of thermodynamics and well before the theory of the heat engine was developed. It can be said that the invention of the steam engine spawned the development of thermodynamics or that the steam engine did much more for thermodynamics than thermodynamics ever did for the steam engine.

Although analysis of devices like steam engines, combustion engines, refrigerators, etc., are important, thermodynamics has much wider applicability. In material science, one is normally not that interested in heat and work, but interested more the state of matter and how things might change when mixed, heated, pressurized, etc. Some important effects are chemical reactions (such as oxidation), formation of solutions, phase transformations.

Other issues might include response of materials to stress, strain, electrical fields, or magnetic fields. In other words, the changes in the matter are more interesting than the heat and work effects.

■ System and Surroundings

The universe is divided into the *System* and the *Surroundings*. The system is any collection of objects that we choose to analyze. The surrodings is the rest of the universe, but in more practical terms is the environment of the system. Our interest is in understanding the system. The system and surroundings interact be exchanging heat and work. The surroundings can supply heat to the system or do work on the system. Alternatively, the system may give off heat (supply heat to the surroundings) or do work on the surroundings.

Some examples of material science type systems are a metalllic alloy in a crucible, a multi-component, multiphase ceramic, a blend of polymer molecules, a semiconductor alloy, or a mixutre of gases in a container. In material science, our main interest in such systems is the equilibrium state of the system, will the components react, will they mix or phase separate, will there by phase transitions, and how will they respond to externally applied stimuli such as pressure, temperature, stress, strain, electrical field, or magnetic filed.

Thermodynamics is concerned only with the equilibrium state of matter and not in the rate at which matter reaches the equlibrium state. Early thermodynamics was on heat (thermo) and work (dynamics) effects. In heat engines with gases and liquids, equilibrium is often reached very fast and the rate of reaching equilibrium is very fast. The “dynamics” part refers to work effects and not to rates of processes. The study of the rates of processes is known as “kinetics.”

In material science, particularly problems dealing with solids or condensed matter, it is possible to deviate from equilbrium for long times. For example, a polymer glass well below its glass transition is a non-equilibrium structure. A detailed thermodynamic analysis of glass polymers (a difficult problem) would predict that the polymer should exist in a different state than it actually does. At sufficient low temperatures, the polymer, however, will remain in the non-equilibrium glassy state; the equilibrium state will not be realized on any practical time scale.

■ Concept of State

Matter contains elementary particles such as atoms and molecules. The state of a system can be defined by specifying the masses, velocities, positions, and all modes of motion (*e.g.*, accelerations) of all of the particles in the system. Such a state is called the *microscopic state* of the system. Given the microscopic state, we could deduce all the properties of the system. Normally, however, we do not have such detailed knowledge because there will always be a large number of particles (*e.g.* 10^{23} molecules in 1 mole of molecules). Fortunately such detailed knowlege is not required. Instead, it is possible to define a *macroscopic state* of the system by specifying only a few macroscopic and measurable variables such as pressure, volume, and temperature. It is found that when only a few of these variables are fixed, the entire state of the system is also fixed. Thus, the thermodynamic state of a system is uniquely fixed when a small number of macroscopic, independent variables are fixed.

For example, consider a gas or a liquid of constant composition such as a pure gas or liquid. The three key variables are pressure, P, temperature, T, and volume, V. It has been observed that when P and T are fixed that V always has a unique value. In other words, P and T are the independent variables and V is a function of P and T:

```
Volume = V[P, T] ;
```

Such an equation is called an *equation of state*. Once P and T are known, V (and all other properties in this simple example) are determined. P, V, and T are all known as state variables; they only depend on the current state and not the path the system took to reach the current state.

The use of P and T as the independent variables is simply a matter of choice and is done usually because P and T are easy to control and measure. It would be equally acceptable to define V and T as the independent variables and define the system by an equation of state for pressure:

```
Pressure = P[V, T] ;
```

or to use P and V is independent variables and define the system by an equation of state for temperature:

```
Temperature = T[P, V] ;
V =. ; P =.; T =.;
```

More than Two Independent Variables

Pure gases and liquids are particularly simple because their state depends only on two independent variables. Other systems require more variables, but the number required is always relatively small. For example, the volume of a mixture of two gases will depend on the P and T and the compositions of the two gases or

$$\text{Volume} = V[P, T, n_1, n_2];$$

where n_1 and n_2 are the number of moles of the two gases. The volume of the system will depend not only on P and T, but also on which gases are present. As above, this new equation of state could be done instead as an equation for P in terms of V, T, and composition:

$$\text{Pressure} = P[V, T, n_1, n_2];$$

or similarly as an equation for T in terms of P, V, and composition.

Pressure or volume are all that are needed to define mechanical stimuli on a gas or a liquid. For solids, however, the matter might experience various states of stress and strain. For a pure solid, the natural variables are temperature, stress σ (instead of P), and strain ϵ (instead of V). Unlike P and V which are scalar quantities, stress and strain are tensors with 6 independent coordinates. In general, the strain components are a function of T and the stress components

$$\text{StrainComponent} = \varepsilon_i[T, \sigma_i];$$

where ε_i and σ_i are components of stress and strain. Alternatively, stress can be written as a function of temperature and strain

$$\text{StressComponent} = \sigma_i[T, \varepsilon_i];$$

These equations of state are the thermomechanical stress-strain relations for a material. If the material is not a pure material, such as a composite material, the stress-strain relations will also depend on the compositions of the material and typically on the geometry of the structure.

For interactions of matter with other stimuli suich as electric or magnetic fields, the equations of state will also depend on the intensity of those fields.

Thus, in summary, the thermodynamic state can also be expressed as an equation of state that is a function of a relatively small number of variables. For most problems encountered in thermodynamics, the variables are limited to P, T, V, ε_i, σ_i, composition, and applied fields. The simplest examples involve only two variables. More complicated systems require more variables.

Multivariable Mathematics

An equation of state is a function that defines one variable in terms of several other variables. Thus equations of state follow the rules of mutlivariable mathematics. In thermodynamics, we are often concered with how something changes as we change the independent variables. A general analysis of such a problem can be written down purely in mathematical terms. Let $f[x_1, x_2, \ldots x_n]$ be a function of **n** variables x_1 to x_n. The total differential in **f** (**df**) is given by

$$df = \sum_{i=1}^{n} \left(\frac{\partial f}{\partial x_i}\right) dx_i \,;$$

where the partial derivative is taken with all $x_j \neq x_i$ being held constant. In *Mathematica* notation, this total differential is written as

$$df = \sum_{i=1}^{n} \partial_{x_i} f\, dx_i \,;$$

where $\partial_{x_i} f$ means the partial derivative of **f** with respect to x_i while all other variables (here $x_j \neq x_i$) are held constant. This *Mathematica* notation will be used throughout these notes which were prepared in a *Mathematica* notebook.

Example: V[P,T]

For example, the equation of state V[P,T] for a pure gas depends on only two variables and has the total differential

$$dV = \partial_P V[P, T]\, dP + \partial_T V[P, T]\, dT$$

$$dT\, V^{(0,1)}[P, T] + dP\, V^{(1,0)}[P, T]$$

Note: blue text is these notes is *Mathematica* output after evaluating an input expression in red. Many input expressions are followed be semicolons which simple supresses uninteresting *Mathematica* output.

Any change in volume due to a change in T and P can be calculated by integrating **dV**:

$$DeltaV = \int_i^f dV \,;$$

where **i** and **f** are the initial and final values of **T** and **P**.

This expression for **dV** is simply treating **V[P,T]** as an mathematical function of P and T. In thermodynamics we are usually dealing with physical quantities. In general, the partial derviatives for the total differentials themselves often have physical significance. In other words, they often correspond to measurable quanties. In the dV expression, $\partial_T V[P, T]$ is the change in volume per degree at constant pressure which is thermal expansion of the matter. Thermal expansion coefficient is normalized to give

$$\alpha = \frac{\partial_T V[P, T]}{V[P, T]}$$

$$\frac{V^{(0,1)}[P, T]}{V[P, T]}$$

Likewise, ∂_P **V[P, T]** is the change in volume due to pressure at constant temperature which is the compressibility of the matter. After normalizing and adding a minus sign to make it positive, compressibility is

$$\beta = -\frac{\partial_P\, V[P, T]}{V[P, T]}$$

$$-\frac{V^{(1,0)}[P, T]}{V[P, T]}$$

In terms of thermal expansion and compressibility, the total differential for volume becomes:

$$\alpha = .\,;\ \beta = .\,;\ dV = -\beta\, V[P, T]\, dP + \alpha\, V[P, T]\, dT$$

$$dT\,\alpha\,V[P, T] - dP\,\beta\,V[P, T]$$

Many thermodynamic relations involve writing total differentials functions and then evaluating the physical significance of the terms. Sometimes the physical significance is not clear. In such problems, the partial derivative is defined as having having physical significance or it becomes a new thermodynamic quantity. One good example to be encountered later in this course is chemical potential.

State Variables

A state variable is a variable that depends only on the state of a system and not on how the system got to that that state. For example **V** is a state variable. It depends only on the independent variables (**P**, **T**, and perhaps others) and not on the path taken to get to the variables. There are many thermodynamic state variables and they are very important in thermodynamics.

There are some thermodynamic quantities that are not state variables. The two most important are heat and work. The heat supplied to a system or the work done by a system depend on the path taken between states and thus by definition, heat and work are not state variables.

Equilibrium

As stated before, thermodynamics always deals with the equilibrium state of matter. The previous sections define equations of state for matter. Equilibrium is the state of the system when the variable reaches the value it should have as defined by the equation of state. For example, a pure gas has an equation of state **V[P,T]**. Equilibrium is reached when after changing **P** and **T** to some new values, the volume becomes equal to the **V[P,T]** defined by the equation of state.

All systems naturally proceed towards equilibrium. They are driven there by natural tendencies to minimize energy and to maximize entropy. These concepts will be discussed later. Although all systems tend towards equilibrium, thermodynamics says nothing about the rate at which they will reach equilibrium. Some systems, particularly condensed solids as encountered in material science, may not approach equilibrium on a pratical time scale.

Equation of State of an Ideal Gas

Charles's law is that volume is proportional to temperature (which is true no matter what temperature scale is used) at constant pressure. In other words **dV/dT** is constant at constant pressure. If we take **Tc** as the temperature on the centigrate scale and let **V0 a0 = dV/dT**, where **V0** and **a0** are the volume and thermal expansion coefficient at 0˚C, then volume at any other temperature on the centigrate scale is found by integration

```
V = Collect[V0 + ∫_0^Tc V0 a0 ⅆT , V0]
```

$(1 + a0\ Tc)\ V0$

But, this result implies that the volume will become zero when

```
Solve[V == 0 , Tc]
```

$\{\{Tc \to -\frac{1}{a0}\}\}$

and become negative if **Tc** drops lower. It is physcially impossible to have negative volume, thusw **Tc = -1/a0** must define the lowest possible temperature or absolute zero. In 1802, Guy-Lussac measured **a0** to be $\frac{1}{267}$ or absolute zero to be at -267˚C. More accurate experiments later (and today) show that **a0** = $\frac{1}{273.15}$ or absoloute zero to be at -273.15. These observations lead to the absolute or Kelvin temperature T defined by

```
T = Tc + 1/a0 /. a0 -> 1/273.15
```

$273.15 + Tc$

On the absolute scale

```
T =. ; V = Simplify[V /. Tc -> T - 1/a0]
```

$a0\ T\ V0$

Thus the volume is zero at **T=0** and increases linearly with T (as observed experimentally).

Boyle found that at constant **T** that **V** is inversely proportional to **P**. Combining the laws of Boyle and Charles, an ideal gas can be defined by

```
V =.; constant = P V/T
```

$\frac{P\ V}{T}$

The constant for one mole of gas is defined as the gas constant **R**. Thus, the equation of state for **V** for **n** moles of gas is

```
V = n R T/P
```

$\frac{n\ R\ T}{P}$

The thermal expansion coefficient of an ideal gas is

$$\alpha = \frac{\partial_T \mathbf{V}}{\mathbf{V}}$$

$$\frac{1}{T}$$

The compressibility of an ideal gas is

$$\beta = -\frac{\partial_P \mathbf{V}}{\mathbf{V}}$$

$$\frac{1}{P}$$

Thus for the special case of an ideal gas, we can write

```
V = . ; dV = α V dT - β V dP
```

$$-\frac{dP\,V}{P} + \frac{dT\,V}{T}$$

Equations of state for P and T can be solved by simple rearrangement

```
V = . ; Solve[V == n R T/P , P]
```

$$\left\{\left\{P \to \frac{n\,R\,T}{V}\right\}\right\}$$

```
Solve[V == n R T/P , T]
```

$$\left\{\left\{T \to \frac{P\,V}{n\,R}\right\}\right\}$$

```
P = . ; V = . ; T = . ;
```

Units of Work and Energy

P V has units of Force/Area X Volume = Force X length. These are the units of work or energy. Thus, **R** must have units of energy/degree/mole. When **R** was first measured, **P** was measured in atm and **V** in liters; thus **P V** or work or energy has units liter-atm. In these units, **R** is

```
Rla = 0.082057 ;
```

with units liter-atm/(degree mole).

SI units for energy is Joules. Also, in SI units, 1 atm is

```
oneatm = 101325. ;
```

N/m^2. Because 1 liter is 1000 cm^3 or 10^{-3} m^3, 1 liter-atm is

```
onela = oneatm 10^-3
```

101.325

Joules. Then, in SI units of J/(degree mole), the gas constant is

```
RSI = Rla onela
```

101.325 Rla

In cgs units with energy units of egs = 10^{-7} J, the gas constant is

```
Rerg = RSI 10^7
```

1.01325×10^{9} *Rla*

Finally, there are .239 cal/J. The gas constant using calories as the energy unit is

```
Rcal = RSI .239
```

24.2167 Rla

Note that in early studies of work and heat, calories were used for heat energy and Joules (or an equivalent F X length) for work or mechanical energy. The first law of thermodynamics connects the two energy units and allows one to relate heat and work energy or to relate calories and Joules.

■ Extensive and Intensive Properties

Properties (or state variables) are *extensive* or *intensive*. Extensive variables depend on the size of the system such as volume or mass. Intensive variables do not depend on the size such as pressure and temperature. Extensive variables can be changed into intensive variables by dividing them by the mass or number of moles. Such intensive variables are often called specific or molar quantities. For example, the volume per mole or molar volume is an intensive variable of a system. Similarly, mass is an extensive property, by mass per unit volume or density is an intensive property.

■ Phase Diagrams and Thermodynamics Components

A Phase diagram is a 2D representation that plots the state of a system as a function of two independent variables.

Systems are characterized by the number of components and the type of phase diagrams depend on the number of components. Examples are one-component (unary), two-component (binary), three-component (ternary), four-component (quarternary), etc..

In each zone, one state is the most stable state. On lines, two phases can coexist. At triple points, three phases can coexist. Example of unary is water phase diagram. Unary diagrams usually use two variables like P and T.

Binary diagrams add composition as a third variable. Binary diagrams are usually for one variable (T, P, or V) together with the composition variable. The complete phase space is 3D. Thus, 2D binary plots are sections of the 3D curves. Zones can be single phase solutions or two-phase regions. The relative proportions of phases in two-phase regions are given by the lever rule.Choice of components is arbitrary.

■ Overview

Zeroth law of thermodynamics defines temperature. First law connected heat and work and clarified conservation of energy in all systems. The key new energy term that developed from the first law is internal energy. Internal energy often has a nice physical significance; sometimes, it significance is less apparent. The first law says energy is conserved, but it makes no statement about the possible values of heat and work. The second law defines limits on heat and work in processes. It was used to define the efficiency of heat engines. The second law also lead to the definition of entropy. Entropy was slow to be accepted, because it has less apparent physical significance than internal energy. Rougly speaking, entropy is the degree of mixed-upedness. Some thermodynamic problems require an absolute value of entropy, the third law of thermodynamics defines the entropy of a pure substance at absolute zero to be zero.

The principles of thermodynamics is are nearly fully defined after defining the laws of thermodynamics, internal energy, and entropy. The rest of the study of thermodynamics is application of those principles to various problems. All systems try to minimize energy and maximize entropy. Most problems we ever encounter can be solved from these basic principles. It turns out, however, that direct use of internal energy and entropy can be difficult. Instead, we define new functions called free energy - Gibbs free energy or Helmholz free energy. These new energies perform the same function as other thermodynamics functions, but that are physcially much more relevant to typical problems of chemistry and material science. In particular, Gibbs free energy is the most common term needed for chemical and material science problems that are typically encountered in various states of applied temperature and pressure.

Chapter 2: The First Law of Thermodynamics

■ Ideal Gas Change of State

■ Change in Internal Energy

Because $\left(\frac{\partial U}{\partial V}\right)_T = 0$ for an ideal gas an $\left(\frac{\partial U}{\partial T}\right)_V = n\, c_v$ for an ideal gas, the total differential for internal energy for any change of state of an ideal gas is $dU = n\, c_v\, dT$. The total change in internal energy is thuys always given by:

$$\Delta U = \int_{T_1}^{T_2} n\, c_v\, dT$$

$$-n\, c_v\, T_1 + n\, c_v\, T_2$$

which can be rewritten as

$$\Delta U = \frac{c_v}{R}\, n\, R\, \Delta T;$$

where $\Delta T = T_2 - T_1$. For an ideal gas, $n\, R(T_2 - T_1) = P_2\, V_2 - P_1\, V_1 = \Delta(PV)$. Thus internal energy can also be written as

$$\Delta U = \frac{c_v}{R}\, \Delta\, (PV);$$

- **Change in Enthalpy**

Once the change in internal energy is known, the change in enthalpy is easily found from

$$\Delta H = \Delta U + \Delta(PV) = \left(\frac{C_v}{R} + 1\right)\Delta(PV)$$

But, for an ideal gas $c_p - c_v = R$ which leads to $(\frac{c_v}{R} + 1) = \frac{c_p}{R}$. The total change in enthalpy can be written two ways as:

$$\Delta H = \frac{C_p}{R}\Delta(PV) \; ; \; \Delta H = \frac{C_p}{R} n R \Delta T;$$

- **Heat and Work in Various Processes**

The previous sections gave results for **ΔU** and **ΔH** for any change of state in a ideal gas. The values for heat and work during a change of state, however, will depend on path. This section gives some results for heat and work during some common processes:

1. Adiabatic Process

The definition of an adiabatic process is that **q=0**; thus all the change in **U** is caused by work or:

$$q = 0; \; w = -\Delta U;$$

2. Isometric Process

In an isometric process volume is constant which means **w=0**. Heat and work are thus:

$$q = \Delta U; \; w = 0;$$

3. Isobaric Process

The definition of enthalpy is the it is equal to the heat during a constant pressure or isobaric process; thus **q = ΔH**. Work is found thethe first law as **w = q - ΔU**; thus

$$q = \Delta H; \; w = \Delta(PV);$$

4. Isothermal Process

Because **U** is a function only of **T** for an ideal gas, **ΔU = ΔH = 0** for an isothermal process. These results also follow from the general results by using **ΔT = Δ(PV) = 0** for an isothermal process. In general, all that can be said about **q** and **w** for an isothermal process is

$$q = w; \; w = q;$$

The actually value of **q** and **w** will depend on whether the process is conducted reversibly or irreversibly. For a reversible process **q** and **w** can be calculated from **P dV** work as

$$q = w = \int_{V_1}^{V_2} P\, dV;$$

which using the ideal gas equation of state becomes

$$q = w = \int_{V_1}^{V_2} \frac{n R T}{V}\, dV$$

$$-n R T \, Log[V_1] + n R T \, Log[V_2]$$

or because **PV = constant**, we can write

$$q = w = n R T \text{Log}\left[\frac{V_2}{V_1}\right]; \quad q = w = n R T \text{Log}\left[\frac{P_1}{P_2}\right];$$

5. Any Processes

For any other process, **w** can be calculated for the **P dV** integral and **q** from the first law of thermodynamics. Thus, we can write

$$q = \Delta U + \int_{V_1}^{V_2} P \, dV; \quad w = \int_{V_1}^{V_2} P \, dV;$$

To do these calculations, we need to know **P** as a function of **V** throughout the process. This result applies for both reversible and irreversible processes; **P**, however, will be given by an equation of state only for reversible processes.

Numerical Examples

V_1 liters or and ideal gas at T_1 and P_1 are expanded (or compressed) to a new pressure P_2. Here are some constants defined in a table used to get numerical results:

$$\text{nums} = \{V_1 \to 10, \; T_1 \to 298, \; P_1 \to 10, \; P_2 \to 1, \; R \to 8.3144, \; \text{Rla} \to 0.082057\};$$

The number of moles can be calculated from the starting state:

$$\text{nmols} = \frac{P_1 V_1}{\text{Rla}\, T_1} \;/.\; \text{nums};$$

$$\text{subs} = \text{Append}[\text{nums}, n \to \text{nmols}]$$

$$\{V_1 \to 10, \; T_1 \to 298, \; P_1 \to 10, \; P_2 \to 1, \; R \to 8.3144, \; \text{Rla} \to 0.082057, \; n \to 4.08948\}$$

Finally, this constant will convert liter-atm energy units to Joule energy units. All results are given in Joules:

$$\text{laToJ} = 101.325;$$

1. Reversible, Isothermal Process

In an isothermal process for an ideal gas,

$$\Delta U = 0; \quad \Delta H = 0;$$

thus heat and work are equal and given by:

$$q = w = n R T_1 \text{Log}\left[\frac{P_2}{P_1}\right] J \;/.\; \text{subs}$$

$$-23330.9\, J$$

2. Reversible Adiabatic Expansion

In an adiabatic expansion

$$q = 0;$$

and $P\,V^\gamma$ is a constant. Thus the final state has

$$V_2 = \left(\frac{P_1 V_1^\gamma}{P_2}\right)^{1/\gamma};\ T_2 = \frac{P_2 V_2}{n\,Rla}\ /.\ \gamma \to 5/3$$

$$\frac{P_2 \left(\frac{P_1 V_1^{5/3}}{P_2}\right)^{3/5}}{n\,Rla}$$

For an ideal gas $c_v = 3R/2$; thus

$$\Delta U = \frac{3}{2} n\,R\,(T_2 - T_1)\ /.\ subs$$

$$-9147.99$$

or we can use

$$\Delta U = \frac{3}{2}(P_2 V_2 - P_1 V_1)\ laToJ\ /.\ Append[subs,\ \gamma \to 5/3]$$

$$-9148.02$$

For some numeric results, the final temperature and volumes were

$$ad2 = N[\{V_2,\ T_2\}\ /.\ Append[subs,\ \gamma \to 5/3]]$$

$$\{39.8107,\ 118.636\}$$

The work done is

$$dw = -\Delta U$$

$$9148.02$$

For an ideal gas $c_p = 5R/2$; thus the enthalpy change is

$$\Delta H = \frac{5}{2}(P_2 V_2 - P_1 V_1)\ laToJ\ /.\ Append[subs,\ \gamma \to 5/3]$$

$$-15246.7$$

or

$$\Delta H = \frac{5}{2} n R (T_2 - T_1) \ /. \ subs$$

-15246.7

For numerical results in the subsequent examples, the initial and final states for the adiabatic process are

```
V2 =. ; T2 =. ;
sub2 = Join[subs, {V2 -> ad2[[1]] , T2 -> ad2[[2]], γ -> N[5 / 3]}]
```

$\{V_1 \to 10,\ T_1 \to 298,\ P_1 \to 10,\ P_2 \to 1,\ R \to 8.3144,\ Rla \to 0.082057,\ n \to 4.08948,\ V_2 \to 39.8107,\ T_2 \to 118.636,\ \gamma \to 1.66667\}$

■ Altenate Paths to End of Adiabatic Expansion

(i) Get to $P_2\ V_2\ T_2$ by isothermal process followed by constant volume process. **ΔU** for isothermal step is zero (because of the ideal gas). The constant volume step has the total **ΔU** which is

$$\Delta U = \frac{3}{2} n R (T_2 - T_1) \ /. \ sub2$$

-9147.99

(ii) Get to $P_2\ V_2\ T_2$ by isometric process followed by isothermal process. **ΔU** for isothermal step is zero (because of the ideal gas). The constant volume step is same as above and thus obviously gives the same result.

(iii) Get to $P_2\ V_2\ T_2$ by isothermal process followed by constant pressure process. **ΔU** for isothermal step is zero (because of the ideal gas). The enthalpy change for the constant pressure step is simply the same as before

$$\Delta U = \frac{3}{2} n R (T_2 - T_1) \ /. \ sub2$$

-9147.99

(iv) Get to $P_2\ V_2\ T_2$ by isometric process followed by constant pressure process. For isometric process, we only need to know the intermediate temperature given by

$$T_i = \frac{P_2 V_1}{n\, Rla};$$

Thus, the first step has

$$\Delta Ui = \frac{3}{2} n R (T_i - T_1) \ /. \ sub2$$

-13678.8

The internal energy change in the second step is

$$\Delta Uii = \frac{3}{2} n R (T_2 - T_i) \text{ /. sub2}$$

4530.84

Thus total energy change is

$$\Delta U = \Delta Ui + \Delta Uii$$

−9147.99

(v) Get to P_2 V_2 T_2 by constant pressure process followed by constant volume process. The final temperature of the constant pressure process is

$$T_i = \frac{P_1 V_2}{n \, Rla};$$

The internal energy change is thus

$$\Delta Ui = \frac{3}{2} n R (T_i - T_1) \text{ /. sub2}$$

45308.4

The constant volume step has:

$$\Delta Uii = \frac{3}{2} n R (T_2 - T_i) \text{ /. sub2}$$

−54456.4

The total energy change is

$$\Delta U = \Delta Ui + \Delta Uii$$

−9147.99

(comment) These same examples are given in the text. For several of the steps the text calculates **ΔH** first and then subtracts **Δ(PV)** to get **ΔU**. This extra work is not needed because in all cases, **ΔU** can be calculated directly from the same information used to first get **ΔH**.

■ Problems

■ Problem 2.1

The initial conditions are

```
init =
{T₁ -> 300 , V₁ -> 15 , P₁ -> 15 , R -> 8.3144 , Rla -> 0.082057 } ;
```

a. Reversible isothermal expansion to 10 atm pressure

Final volume is

$$P_2 = 10\ ;\ V_2 = N\left[\frac{P_1\,V_1}{P_2}\ /.\ \text{init}\right]$$

$$22.5$$

For isothermal process, **ΔU=0** and **q=w**. They are given by (using **PV = nRT**):

$$q = w = 101.325\,P_1\,V_1\,\text{Log}\left[\frac{V_2}{V_1}\right]\ /.\ \text{init}$$

$$9243.84$$

For an ideal gas, **ΔU = 0** for an isothermal process (**U** only a function of **T**). Finally **ΔH=0** because **ΔU=0** and **PV = constant**.

b. Reversible adiabatic expansion to **P=10** atm.

The final volume is

$$V_2 = N\left[\left(\frac{P_1\,V_1{}^{\gamma}}{P_2}\right)^{1/\gamma}\ /.\ \text{Append}[\text{init},\ \gamma \to 5/3]\right]$$

$$19.1314$$

The final temperature is

$$T_2 = \frac{T_1\,P_2\,V_2}{P_1\,V_1}\ /.\ \text{init}$$

$$255.085$$

The number of moles is

$$n = \frac{P_1\,V_1}{T_1\,\text{Rla}}\ /.\ \text{init}$$

$$9.13999$$

Thus the total change in internal energy is

$$dU = \int_{T_1}^{T_2} n\,1.5\,R\,dT\ /.\ \text{init}$$

$$-5119.88$$

The heat work done for his adiabatic process is

$$q = 0;\ w = -dU$$

5119.88

The change in enthalpy is

$$dH = dU + 101.325\,(P_2 V_2 - P_1 V_1)\ /.\ init$$

-8533.15

■ **Problem 2.2**

The starting conditions and a calculation of the initial volume are:

$$T_1 = 273;\ P_1 = 1;\ n = 1;\ Rla = 0.082057;\ R = 8.3144;$$
$$c_v = \frac{3R}{2};\ c_p = \frac{5R}{2};\ onela = 101.325;\ V_1 = \frac{n\,Rla\,T_1}{P_1}$$

22.4016

a. Doubling of volume at constant pressure

$$q = dH = \frac{c_p}{R} P_1\,(2V_1 - V_1)\ onela$$

5674.6

$$w = P_1\,(2V_1 - V_1)\ onela$$

2269.84

b. Then double the pressure at constant volume

$$q = dU = \frac{c_v}{R} 2V_1\,(2P_1 - P_1)\ onela$$

6809.51

$$w = 0;$$

c. Finally return to initial state along specific curve

$$w = onela \int_{2V_1}^{V_1} (0.0006643\,V^2 + 0.6667)\,dV$$

-3278.9

The total change in U on returning to initial state is

$$dU = \frac{c_v}{R} (V_1 P_1 - 2 V_1 2 P_1) \text{ onela}$$

-10214.3

Thus, heat is

$$q = dU + w$$

-13493.2

■ **Problem 2.3**

Initial state is P=1 atm, V=1 liter, and T=373 K. The number of moles is

$$R = 0.082057;\ T1 = 373;\ P1 = 1;\ V1 = 1;\ n = \frac{P1\,V1}{R\,T1}$$

0.032672

First expand gas isothermally to twice the volume or to V=2 liters and P=0.5 atm. Now cool at constant P=0.5 atm to volume V. Finally, adiabatic compression to 1 atm returns to initial volume. Because PV^γ is constant and initial state has PV^γ=1, final volume must be

$$V2 = 2;\ P2 = 0.5;\ V = (1/P2)^{1/\gamma}\ /.\ \{\gamma \to 5/3\}$$

1.51572

Total work done in first step (an isothermal process) is

$$w1 = N[n\,R\,T1\,Log[2]]$$

0.693147

The second step (at constant pressure) is

$$w2 = P2\,(V - V2)$$

-0.242142

The last step (adiabatic) has **w = −ΔU** or

$$w3 = -\frac{cv}{R} (P1\,V1 - P2\,V)\ /.\ cv \to 1.5\,R$$

-0.363213

Work can also be calculated by integrating with $P = 1/\gamma^{5/3}$:

$$w3alt = \int_{V}^{V1} \frac{1}{x^{5/3}} \, dx$$

-0.363213

The total work in Joules is

$$w = 101.325\,(w1 + w2 + w3)$$

8.89561

- **Problem 2.4**

The total change in internal energy with supplied q and w are

$$\Delta U = 34166 - 1216$$

32950

For an ideal gas, $\Delta U = n\, cv\, \Delta T$, thus the total change in temperature is

$$\Delta T = \frac{\Delta U}{(2)\,(1.5)\,(8.3144)}$$

$1321.$

The final temperature is thus

$$Tfinal = 300 + \Delta T$$

$1621.$

- **Problem 2.5**

The initial conditions are

$$n = 1;\ T = 273;\ P = 1;\ R = 8.3144;$$

a. The initial volume is

$$V = n\, 0.082057 \,\frac{T}{P}$$

22.4016

The 832 J of work at constant pressure causes volume to change by

$$\Delta V = 832 / 101.325$$

8.2112

Thus final volume is

$$V2 = V + \Delta V$$

$$30.6128$$

Final temperature is

$$T2 = P \frac{V2}{n\,0.082057}$$

$$373.067$$

b. Internal energy and enthalpy are

$$\{\Delta U = 3000 - 832\,,\ \Delta H = 3000\}$$

$$\{2168,\ 3000\}$$

c. The value of cp (for this one mole) and cv are

$$\left\{cp = \frac{3000}{T2 - T}\,,\ cv = \frac{2168}{T2 - T}\right\}$$

$$\{29.9799,\ 21.6655\}$$

■ Problem 2.6

The initial volume is

$$P1 = 10;\ T1 = 300;\ n = 10;\ R = 0.082057;\ V1 = n\,R\,\frac{T1}{P1}$$

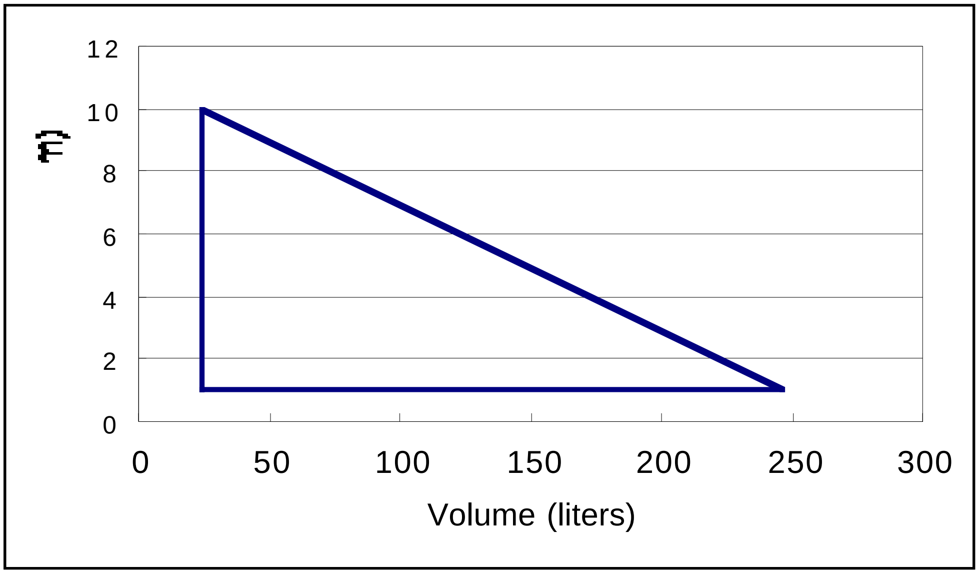
$$24.6171$$

After changing along a straight line to P2 = 1 atm, the volume increases by a factor of 10 to

$$P2 = 1;\ V2 = 10\,V1$$

$$246.171$$

The PV diagram for the cylic process is (P1,V1) to (P2,V2) isobaric to (P2,V1), constant volume to (P1,V1) is plotted as follows



The work done is the area of the triangle and it is positive work done by the gas. After conversion to Joules, the total work is

$$w = \frac{1}{2} (9) (V2 - V1) (101.325)$$

101020.

- **Problem 2.7**

The intial conditions are

$$n = 1;\ T1 = 25 + 273;\ P1 = 1;\ R = 0.082057;\ V1 = n R \frac{T1}{P1}$$

24.453

a. Isothermal expansion to P = 0.5 gives

$$P2 = 0.5;\ T2 = T1;\ V2 = n R \frac{T2}{P2}$$

48.906

b. Isobaric expansion to T3 = 100C

$$P3 = P2;\ T3 = 100 + 273;\ V3 = n R \frac{T3}{P3}$$

61.2145

c. Isothermal compression to P4 = 1

$$P4 = 1;\ T4 = T3;\ V4 = n\,R\,\frac{T4}{P4}$$

30.6073

d. Isobaric compression to 25C returns the gas to its initial state (state 1 above). The total work for these four steps are

$$w = n\,R\,T1\,\mathrm{Log}\left[\frac{V2}{V1}\right] + P2\,(V3 - V2) + n\,R\,T3\,\mathrm{Log}\left[\frac{V4}{V3}\right] + P4\,(V1 - V4)$$

-4.26582

The second process traces a squate on a PV diagram:
a. Isobaric expansion to 100C

$$P5 = P1;\ T5 = 100 + 272;\ V5 = n\,R\,\frac{T5}{P5}$$

30.5252

b. Change pressure at constant volume to P

$$P = .;\ P6 = P;\ V6 = V5;$$

c. Isobaric compression to initial state

$$P7 = P6;\ V7 = V1;$$

d. After returning to the intial state, the total work comes from the isobaric steps only; the constant volume steps do no work. Thus the total work is

$$walt = P1\,(V5 - V1) + P7\,(V7 - V6)$$

6.07222 - 6.07222 P

Finally, equate to (minus) initial work and solve for P

```
Solve[walt == -w, P]
```

{{P → 0.297486}}

- **Problem 2.8**

The PV diagram traces a circle or radius r=5. The work is the area of the circle (converted to Joules)

```
Pi (25) (101.325)
```

7958.05

The volume as a function of pressure has two possible values

```
P = . ; V1 = 10 + Sqrt[25 - (P - 10)^2]
```

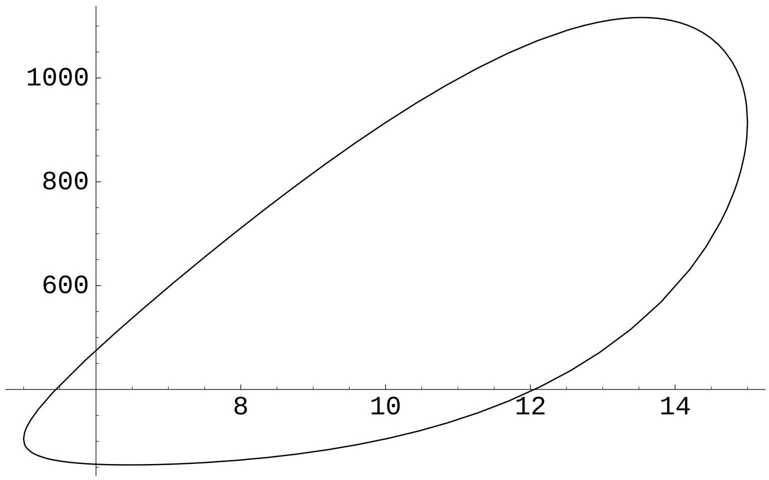
$$10+\sqrt{25-(-10+P)^2}$$

```
V2 = 10 - Sqrt[25 - (P - 10)^2]
```

$$10-\sqrt{25-(-10+P)^2}$$

The temperature during the cycle can be plotted

$$\texttt{n = 2 ; R = 0.082057 ; Plot}\left[\left\{P\,\frac{V1}{n\,R},\ P\,\frac{V2}{n\,R}\right\},\ \{P,\ 5,\ 15\}\right]$$



- Graphics -

The maximum occurs on the V1 curve at

$$\texttt{Solve}\left[D\left[P\,\frac{V1}{n\,R},\ P\right] == 0,\ P\right]$$

$$\{\{P\to 13.5355\}\}$$

which is gives a maximum temperature or

$$\texttt{Tmax} = P\,\frac{V1}{n\,R}\ \texttt{/. P -> 13.5355339059327373`}$$

$$1116.36$$

The minimum occurs on the V2 curve at

```
Solve[D[P V2/(n R), P] == 0, P]
```

{{P → 5. − 3.53553 I}, {P → 5. + 3.53553 I}, {P → 6.46447}}

Taking the real root, the minimum temperature is

```
Tmin = P V2/(n R) /. P -> 6.46447
```

254.636

Chapter 3: The Second Law of Thermodynamics

Problems

Problem 3.1

For any reversible change in state with variables **U** and **V**, the total differential for entropy can be written as

```
dSform = Solve[dU == T dS - P dV , dS]
```

$$\left\{\left\{dS \to -\frac{-dU - dV\,P}{T}\right\}\right\}$$

For one mole of an ideal gas we can rewrite this as

```
Simplify[dSform /. {dU -> Cv dT , P -> R T/V}]
```

$$\left\{\left\{dS \to \frac{dV\,R}{V} + \frac{dT\,C_v}{T}\right\}\right\}$$

which integrates upon a change in **V** and **T** to

$$\Delta S = C_v \,\mathrm{Log}\left[\frac{T_2}{T_1}\right] + R\,\mathrm{Log}\left[\frac{V_2}{V_1}\right];$$

Using $R = C_p - C_v$, $T_2 = P_2 V_2 / R$, $T_1 = P_1 V_1 / R$, $C_v = 3R/2$ $\gamma = C_p / C_v = 5/3$, this expression can be reworked into

$$\Delta S = \frac{3}{2} R\,\mathrm{Log}\left[\frac{P_2 V_2{}^{\gamma}}{P_1 V_1{}^{\gamma}}\right];$$

This result applies to any change in state of an ideal gas. Simpler expressions hold in some special cases.

a. For this isothermal change

$$\Delta S \;/.\; \{P_1 \to 10,\; V_1 \to V,\; P_2 \to 5,\; V_2 \to 2\,V,\; R \to 8.3144,\; \gamma \to 5/3\}$$

5.7631

b. For a reversible adiabatic change, q_{rev} **= 0** and thus **ΔS=0**. From the general equation above, **ΔS** is also obviously zero because $\mathbf{PV}^{\gamma}$ is constant during a reversible adiabatic processes.

c. For a constant volume change in pressure

$$\Delta S \;/.\; \{P_1 \to 10,\; V_1 \to V_2,\; P_2 \to 5,\; R \to 8.3144,\; \gamma \to 5/3\}$$

-8.64465

■ Problem 3.2

Some generic results for the change in a state function for one mole of an ideal monatomic gas are given below. There are two results for each term; either can be used, depending on which one is easier:

$$\Delta U_1 = \frac{3}{2}\,(P_2\,V_2 - P_1\,V_1);\; \Delta U_2 = \frac{3}{2}\,R\,(T_2 - T_1);$$

$$\Delta H_1 = \frac{5}{2}\,(P_2\,V_2 - P_1\,V_1);\; \Delta H_2 = \frac{5}{2}\,R\,(T_2 - T_1);$$

$$\Delta S_1 = \frac{3}{2}\,R\,\mathrm{Log}\left[\frac{P_2\,V_2{}^{\gamma}}{P_1\,V_1{}^{\gamma}}\right];\; \Delta S_2 = R\,\mathrm{Log}\left[\frac{T_2{}^{3/2}\,V_2}{T_1{}^{3/2}\,V_1}\right];$$

a. For free expansion of ideal gas, temperature remains constant. Here the volume triples. Thus

$$\text{stepa} = \{\Delta U_2,\; \Delta H_2,\; \Delta S_2\} \;/.\; \{T_2 \to T_1,\; V_2 \to 3\,V_1,\; R \to 8.3144\}$$

{0, 0, 9.1343}

For free expansion there is no work (**w=0**) and thus because **ΔU=0**, **q=0**.

b. Here we only need to know that the temperature changes from 300K to 400K at constant volume

$$\text{stepb} = \{\Delta U_2,\; \Delta H_2,\; \Delta S_2\} \;/.\; \{T_2 \to 400,\; T_1 \to 300,\; V_2 \to V_1,\; R \to 8.3144\}$$

{1247.16, 2078.6, 3.58786}

Because this process is at contant volume, **w=0,** which mean **q = ΔU = 1247 J**.

c. For any isothermal expansion to triple the volume, the state functions results are the same as part **a**. But here the process is reversible. Thus

$$q = w = R\,T\,\mathrm{Log}\left[\frac{V_2}{V_1}\right] \;/.\; \{R \to 8.3144,\; T \to 400,\; V_2 \to 3\,V_1\}$$

3653.72

d. For the state functions, we only need to known that at constant pressure **V** is proportional to **T** which implies $V_2 = 300\, V_1 / 400$:

```
stepd = {ΔU2, ΔH2 , ΔS2} /.
{T2 -> 300 , T1 -> 400 , V2 -> 300 V1 / 400, R -> 8.3144}
```

```
{-1247.16, -2078.6, -5.97976}
```

The book solution has a sign error in **ΔS**. At constant pressure **q** is equal to **ΔH** and work follows from that results:

```
q = -2078.6 ; w = q + 1247.16
```

```
-831.44
```

Notice that all calculations were done without ever calculating the actual volumes and pressures during the processes.

The total changes in **U**, **H**, and **S** during these steps are

```
stepa + stepb + stepa + stepd
```

```
{0., 0., 15.8767}
```

The total amount of heat and work are

```
{1247 + 3653.72 - 2078.6 , 3653.72 - 831.44}
```

```
{2822.12, 2822.28}
```

- **Problem 3.2**

a. For one mole of an ideal gas at contant pressure, $\mathbf{q} = C_p\, \Delta\mathbf{T}$, and $C_p = 5\, R / 2$, thus the temperature change is

$$\Delta T = \frac{q}{\frac{5}{2} R} \;/.\; \{q \to 6236 ,\; R \to 8.3144\}$$

```
300.01
```

From the entropy change we can calculate the absolute temperatures as well. Using the **ΔS** for one mole of an ideal gas at constant pressure we can solve

$$\text{Solve}\left[\Delta S == \frac{5 R}{2} \text{Log}\left[\frac{T_2}{T_1}\right] \;/.\; \{R \to 8.3144 ,\; T_2 \to T_1 + \Delta T,\; \Delta S \to 14.41\} ,\; T_1\right]$$

$$\{\{T_1 \to 299.945\}\}$$

Or $T_1 = 300\, K$ and $T_2 = 600\, K$.

b. For an isothermal expansion of an ideal gas **q=w**. Thus we only need to solve

$$\text{Solve}\left[\Delta S == \frac{q_{rev}}{T} \text{ /. } \{\Delta S \to 5.763,\ q_{rev} \to 1729\},\ T\right]$$

$$\{\{T \to 300.017\}\}$$

Problem 3.4

For this problem we need to integrate C_p for enthalpy or C_P / T for entropy where

$$C_p = 50.79 + 1.97\ 10^{-3}\ T - 4.92\ 10^{6}\ T^{-2} + 8.20\ 10^{8}\ T^{-3}$$

$$50.79 + \frac{8.2 \times 10^{8}}{T^{3}} - \frac{4.92 \times 10^{6}}{T^{2}} + 0.00197\ T$$

$$\Delta H = \int_{25+273}^{1000+273} C_p\, dT$$

$$42747.7$$

$$\Delta S = \int_{25+273}^{1000+273} \frac{C_p}{T}\, dT$$

$$59.6825$$

Problem 3.5

The two blocks of copper will exchange heat until they reach the same temperature. Heat flow is an integral of the constant-pressure heat capacity. If the heat capacity is independent of temperature, the final temperature will be the average of the two initial temperature. If the heat capacity is a function of temperature, however, we have to solve an integral equation by equating heats

$$C_p = a + b\, T;$$

The heat transferred into the cold block is

$$\text{qcold} = \int_{273}^{T_f} C_p\, dT$$

$$-273\, a - \frac{74529\, b}{2} + a\, T_f + \frac{b\, T_f^2}{2}$$

This heat must equal the heat leaving the hot body

$$\text{qhot} = -\int_{373}^{T_f} C_p\, dT$$

$$373\, a + \frac{139129\, b}{2} - a\, T_f - \frac{b\, T_f^2}{2}$$

Equate and solve for T_f :

```
Solve[qcold == qhot /. {a -> 22.64, b -> 0.00628} , Tf]
```

$\{\{T_f \to -7533.51\}, \{T_f \to 323.318\}\}$

The second root is the correct one or $T_f = 323.32\ K$. The quantity of heat transferred is

```
q = qcold /. {Tf -> 323.32, a -> 22.64, b -> 0.00628}
```

1233.47

The total change in entropy (considering both bodies) is

$$\Delta S = \int_{273}^{323.32} \frac{C_p}{T}\,dT - \int_{323.32}^{373} \frac{C_p}{T}\,dT \;/.\; \{a \to 22.64, b \to 0.00628\}$$

0.597977

In other words, the process was irreversible because entropy increased.

- **Problem 3.6**

The engine will stop producing work when it reaches its equilibrium temperature of T_f.To reach this temperature, the high-temperature bath will expel heat

$$q_2 = C_2\,(T_2 - T_f);$$

The engine will expel heat to the low temperature bath of

$$q_1 = C_1\,(T_f - T_1);$$

The total work then becomes

$$w = q_2 - q_1$$

$$C_2\,(T_2 - T_f) - C_1\,(-T_1 + T_f)$$

In this reversible engine, the total entropy change (reservoirs plus engine) must be zero. The engine operates in a cycle and thus must have no entropy change. Assuming constant heat capacities, the entropy changes from the reservoirs is

$$\Delta S = \int_{T_1}^{T_f} \frac{C_1}{T}\,dT + \int_{T_2}^{T_f} \frac{C_2}{T}\,dT$$

$$-\mathrm{Log}[T_1]\,C_1 + \mathrm{Log}[T_f]\,C_1 - \mathrm{Log}[T_2]\,C_2 + \mathrm{Log}[T_f]\,C_2$$

The final temperature to make T_f zero is found by solving

```
Solve[ΔS == 0 , Tf]
```

$$\left\{\left\{T_f \to E^{\frac{\mathrm{Log}[T_1]\,C_1 + \mathrm{Log}[T_2]\,C_2}{C_1 + C_2}}\right\}\right\}$$

This result is equivalent to the answer in the book.

Chapter 4: The Statistical Interpretation of Entropy

Problems

Problem 4.1

When an ideal gas expands (reversible or irreversibly) the temperature remains constant and therefore internal energy remains constant. The total differental in entropy (again assuming an ideal gas) is

$$dS = \frac{P\,dV}{T} \;/.\; P \to \frac{R\,T}{V}$$

$$\frac{dV\,R}{V}$$

Integrating over any volume change gives

$$\Delta S = \int_{V_1}^{V_2} \frac{R}{V}\,dV$$

$$-R\,Log[V_1] + R\,Log[V_2]$$

or

$$\Delta S = R\,Log\left[\frac{V_2}{V_1}\right];$$

Physically entropy increases when the volume increases.

a. Chamber 1 has 1 mole of A and chamber 2 has 1 mole of B. These ideal gases do not interact and thus the total energy change is the sum of entropy changes for each type of gas:

$$\Delta S = R\,Log[2] + R\,Log[2]$$

$$2\,R\,Log[2]$$

or **R Log[4]** as given in the text.

b. When there are 2 moles of A in chamber 1, the entropy change for that gas doubles giving:

$$\Delta S = 2\,R\,Log[2] + R\,Log[2]$$

$$3\,R\,Log[2]$$

or **R Log[8]** as given in the text.

c. When each chamber has gas A, we can not use the methods in parts a and b because they no longer act independently. When each chamber has 1 mole of A, removing the partition does not change anything. The system is still at equilibrium and thus **ΔS=0**.

d. When one chamber has 2 moles of A and the other has 1 mole of A, the two chambers will be at different pressures and removing the partition will causes changes and a non-zero change in entropy. This problem is best solved by first moving the partition to equalize pressures. Here it is moved from the middle (1/2, 1/2) to the position where the side with 2 moles of A is twice as large as the side with 1 mole of A (2/3, 1/3). This move will equalize pressure such that the subsequent removal of the partition can be done with **ΔS=0**. Thus the total change in entropy can be calculated from the initial change in volumes done to equalize pressures:

$$\Delta S = 2\,R\,\mathrm{Log}\left[\frac{2/3}{1/2}\right] + R\,\mathrm{Log}\left[\frac{1/3}{1/2}\right]$$

$$2\,R\,\mathrm{Log}\left[\frac{4}{3}\right] - R\,\mathrm{Log}\left[\frac{3}{2}\right]$$

which combines to **R Log[32/27]**.

Chapter 6: Cv, Cp, H, S, and 3rd Law of Thermosynamics

Problems

Problem 6.1

The heat of transformation for Zr(b) + O(2) to Zr(b)O(2) at 1600K is given by the following equation which starts with the heat of transformation at 298K and then integrates ΔCp from 298 to 1600K accounting for phase transitions or Zr (α->β) at 1136K and ZrO2 (α->β) at 1478 K. Notice that ΔH for the Zr (α->β) transition is entered with a minus sign because those components are on the left side of the reactions:

$$\begin{aligned} \mathrm{DH} = \mathrm{HZraO2} &+ \int_{298}^{1136} (\mathrm{CpZraO2} - \mathrm{CpZra} - \mathrm{CpO2})\, dT - \\ \mathrm{DHZratob} &+ \int_{1136}^{1478} (\mathrm{CpZraO2} - \mathrm{CpZrb} - \mathrm{CpO2})\, dT + \\ \mathrm{DHZrO2atob} &+ \int_{1478}^{1600} (\mathrm{CpZrbO2} - \mathrm{CpZrb} - \mathrm{CpO2})\, dT \end{aligned}$$

$$-1.08659 \times 10^{6}$$

For the entropy of reaction, we integrate Cp/T and include entropy of the required transitions. The entropy of reaction at 298K comes from absolute entropies of ZrO(2) - Zr - O(2). The entropy of transitions come from $\Delta H / T_{tr}$

$$\mathrm{DSrxn} = \mathrm{SZraO2} - \mathrm{SZra} - \mathrm{SO2};$$

$$\mathrm{DSZratob} = \frac{\mathrm{DHZratob}}{1136};\ \mathrm{DSZrO2atob} = \frac{\mathrm{DHZrO2atob}}{1478};$$

$$DS = N\left[DSrxn + \int_{298}^{1136} \frac{CpZraO2 - CpZra - CpO2}{T}\,dT - DSZratob + \int_{1136}^{1478} \frac{CpZraO2 - CpZrb - CpO2}{T}\,dT + DSZrO2atob + \int_{1478}^{1600} \frac{CpZrbO2 - CpZrb - CpO2}{T}\,dT\right]$$

-177.977

- **Problem 6.2**

The enthalpy of graphite at 1000K is

$$Hgr1000 = \int_{298}^{1000} CpGraphite\,dT$$

11829.5

The enthalpy of diamond at 1000K is

$$Hdia1000 = HDiamond + \int_{298}^{1000} CpDiamond\,dT$$

12467.1

The enthalpy of diamond is

$$Hdia1000 - Hgr1000$$

637.523

higher than that of graphite; thus the reaction to form CO from diamond is more exothermic (larger positive number on the left).

- **Problem 6.3**

These compounds have no transitions between 298K and 1000K. The initial heat of formation at 298K is

$$DHrxn = HCaTiO3 - HCaO - HTiO2$$

-81700

$$DHrxn1000 = DHrxn + \int_{298}^{1000} (CpCaTiO3 - CpTiO2 - CpCaO)\,dT$$

-80442.2

For entropy of the reaction we first need

```
DSrxn = SCaTiO3 - SCaO - STiO2
```

5.

$$\text{DSrxn1000} = \text{N}\left[\text{DSrxn} + \int_{298}^{1000} \frac{\text{CpCaTiO3} - \text{CpTiO2} - \text{CpCaO}}{\text{T}}\, dT\right]$$

7.03431

- **Problem 6.4**

The change in enthalpy of Cu by heating at constant pressure is integral of the constant pressure heat capacity. Heating to T=x give

$$\text{DHbyTemp} = \text{Chop}\left[\int_{298}^{x} \text{CpCu}\, dT\right]$$

$$-9631.41 + \frac{322000.}{x} + 30.29\, x - 0.005355\, x^2$$

Using **(dH/dP)T = V(1 - alpha T)**, the change in enthalpy at constant temperature from 1 to 1000 atm is

$$\text{DHbyPressure} = 101.325 \int_{1}^{1000} \left(\text{VCu}\,(1 - \text{alphaCu T})\ /.\ \left\{\text{VCu} \to \frac{7.09}{10^3},\ \text{alphaCu} \to \frac{0.493}{10^3},\ \text{T} \to 298\right\}\right) dP$$

612.239

The **101.325** converts liter-atm to J, the 10^-3 on **VCu** converts cm^3 to liters:

```
Solve[DHbyTemp == DHbyPressure , x]
```

{{x → 35.0427}, {x → 323.916}, {x → 5297.44}}

The correct root is the middle one or T = 323.916

The book calculated the pressure effect to cause the enthalpy to increase by 707 J. This answer can be obtained by using 0.493 10^-4 for thermal expansion (or by dividing the result given in the text by 10). The *Handbook of Chemistry and Physics* gives the thermal expansion of Copper as as 0.498 10^-4. Thus the text gave the wrong value in the problem, but used the correct value to derive the solution. Using the correct thermal expansion changes the above results to:

$$\text{DHbyPressure} = 101.325 \int_{1}^{1000} \left(\text{VCu}\,(1 - \text{alphaCu T})\ /.\ \left\{\text{VCu} \to \frac{7.09}{10^3},\ \text{alphaCu} \to \frac{0.493}{10^4},\ \text{T} \to 298\right\}\right) dP$$

707.132

```
Solve[DHbyTemp == DHbyPressure , x]
```

$\{\{x \to 34.6395\}, \{x \to 327.909\}, \{x \to 5293.85\}\}$

The middle root is the book solution.

Problem 6.5

DH and DS can be found form enthalpies and entropies of each compound in the reactions.

$$\left\{\text{HTi2O3} - \frac{\text{HO2}}{2} - 2\,\text{HTiO},\ \text{STi2O3} - \frac{\text{SO2}}{2} - 2\,\text{STiO}\right\}$$

$\{-435000, -94.75\}$

$$\left\{2\,\text{HTi3O5} - \frac{\text{HO2}}{2} - 3\,\text{HTi2O3},\ 2\,\text{STi3O5} - \frac{\text{SO2}}{2} - 3\,\text{STi2O3}\right\}$$

$\{-355000, -75.35\}$

$$\left\{3\,\text{HTiO2} - \frac{\text{HO2}}{2} - \text{HTi3O5},\ 3\,\text{STiO2} - \frac{\text{SO2}}{2} - \text{STi3O5}\right\}$$

$\{-373000, -80.15\}$

Problem 6.6*

The balanced reaction is Cr2O3 + 2Al -> Al2O3 + 2Cr. The initial number of moles of aluminum are

$$\text{moleAl} = N\left[\frac{1000}{\text{massAl}}\right]$$

37.0645

Assume need to add excess of Cr2O3 (add **moleCr** of Cr2O3) or that all the Al gets used up in the reaction. The products then contain **moleAl/2** moles of Al2O3, **moleAl** or Cr, and **moleCr - (moleAl/2)** moles of Cr2O3. The total enthalpy of these products (none of which have transitions between 298K and 1600K) is

$$\text{HProducts} = \frac{1}{2}\,\text{moleAl}\left(\text{HAl2O3} + \int_{298}^{1600} \text{CpAl2O3}\, dT\right) + \text{moleAl} \int_{298}^{1600} \text{CpCr}\, dT + \left(\text{moleCr} - \frac{\text{moleAl}}{2}\right)\left(\text{HCr2O3} + \int_{298}^{1600} \text{CpCr2O3}\, dT\right)$$

$-2.66044 \times 10^{7} - 972063.\ (-18.5322 + \text{moleCr})$

$-2.54783 \times 10^{7} - 935209.\ (-18.5322 + \text{moleCr})$

The enthalpy of the initial components at 700 C (=973 K), accounting for the melting transition of Al at 943K, was

$$\text{HInitial} = \text{moleAl}\left(\int_{298}^{943}\text{CpAl}\,dT + \text{HAlmelt} + \int_{943}^{973}\text{CpAll}\,dT\right) + \text{moleCr}\left(\text{HCr2O3} + \int_{298}^{973}\text{CpCr2O3}\,dT\right)$$

$$1.11638\times10^{6} - 1.05378\times10^{6}\ \text{moleCr}$$

The moles of Cr2O3 required to balance these enthalpies is

```
moleAns = Solve[HProducts == HInitial]
```

$$\{\{\text{moleCr}\to 118.78\}\}$$

In kilograms, the required mass is

$$\frac{\text{moleCr}\ (3\ \text{massO} + 2\ \text{massCr})}{1000}\ \text{/.}\ \text{moleAns}$$

$$\{18.0546\}$$

This result is higher than the book solution of 14.8 kg.

■ **Problem 6.7**

The adiabatic flame temperature can be found by finding out at what temperature the total enthalpy of the products is equal to the enthalpy of the initial material. This method works because total enthalpy is conserved for adiabatic, constant pressure conditions.

a. The reaction is CH4 + 2 O2 -> CO2 + 2 H2O. The starting components at 298K 2/3 O2 and 1/3 CH4 (ratio O2 to CH4 of 2.0). The final components are 1/3 CO2 and 2/3 H20. Enthalpy of starrint components is

$$\text{HInitial} = \frac{\text{HCH4}}{3}$$

$$-\frac{74800}{3}$$

The enthalpy of the products at the flame temperature is

$$\text{HProducts} = \frac{1}{3}\left(\text{HCO2} + \text{Chop}\left[\int_{298}^{\text{AFT}}\text{CpCO2}\,dT\right]\right) + \frac{2}{3}\left(\text{HH2Og} + \text{Chop}\left[\int_{298}^{\text{AFT}}\text{CpH2Og}\,dT\right]\right)$$

$$\frac{1}{3}\left(-409921. + \frac{854000.}{\text{AFT}} + 44.14\ \text{AFT} + 0.00452\ \text{AFT}^2\right) + \frac{2}{3}\left(-251326. + \frac{33000.}{\text{AFT}} + 30.\ \text{AFT} + 0.005355\ \text{AFT}^2\right)$$

```
Solve[HInitial == HProducts]
```

$\{\{AFT \to -11586.1\}, \{AFT \to 1.0983\}, \{AFT \to 4747.14\}\}$

The correct root is the last one or the flame temperature is 4747K.

b. For the reaction in air starting with one total mole of reactants, the fractions are

$$XN2 = \frac{.79\ 9.524}{10.524}$$

$$0.714933$$

$$XO2 = \frac{.21\ 9.524}{10.524}$$

$$0.190046$$

$$XCH4 = \frac{1}{10.524}$$

$$0.0950209$$

The enthalpy of the starting components is

$$HInitial = XCH4\ HCH4$$

$$-7107.56$$

After all the CH4 reacts with all the O2 to form **XO2** or H20 and **XCH4** of CO2, the enthalpy at the flame temperature is

$$HProducts = XCH4\left(HCO2 + Chop\left[\int_{298}^{AFT} CpCO2\, dT\right]\right) + XO2\left(HH2Og + Chop\left[\int_{298}^{AFT} CpH2Og\, dT\right]\right) + XN2\ Chop\left[\int_{298}^{AFT} CpN2\, dT\right]$$

$$0.714933\,(-8494.86 + 27.87\,AFT + 0.002135\,AFT^2) + 0.0950209\left(-409921. + \frac{854000.}{AFT} + 44.14\,AFT + 0.00452\,AFT^2\right) + 0.190046\left(-251326. + \frac{33000.}{AFT} + 30.\,AFT + 0.005355\,AFT^2\right)$$

```
Solve[HInitial == HProducts]
```

$\{\{AFT \to -12360.\}, \{AFT \to 1.02066\}, \{AFT \to 2330.39\}\}$

The correct root is the last one or the flame temperature is 2330K.

- **Problem 6.8***

The ΔG of the reaction at 298K is

```
DHrxn = 3 HSiO2Q - HSi3N4
```

-1987900

```
DSrxn = 3 SSiO2Q + 2 SN2 - SSi3N4 - 3 SO2
```

-220.8

```
DGrxn = DHrxn - 298 DSrxn
```

-1.9221×10^6

The ΔCp for the reaction is

```
DelCp = 2 CpN2 + 3 CpSiO2Q - CpSi3N4 - 3 CpO2;
```

The ΔG of the reaction at 800K found by integration (and there are no transitions in the compounds) or

$$\text{DG800} = \text{DHrxn} + \int_{298}^{800} \text{DelCp}\, dT - 800 \left(\text{DSrxn} + N\left[\int_{298}^{800} \frac{\text{DelCp}}{T}\, dT\right]\right)$$

-1.8163×10^6

If ΔCp was assumed to be zero, the DG would be calculated as

```
DGsimp = DHrxn - 800 DSrxn
```

-1.81126×10^6

The percent error cause by ignoring the ΔCp terms is

$$\text{err} = \frac{100\,(\text{DGsimp} - \text{DG800})}{\text{DG800}}$$

-0.277741

These results differ from the book answer which gets a much larger error between the two methods. The **`DGsimp`** agrees with the book, but the **`DG800`** in the book is different.

- **Problem 6.9**

```
Solve[{3 + a == b + 2 c, 1 + a == b + c, 3 + a == 2 b + c}]
```

{{a → 3, b → 2, c → 2}}

```
DH298 = c Hcc + b Hcb - a Hca - Hc1 /. {a → 3, b → 2, c → 2,
   Hc1 → -6646300, Hca → -3293200, Hcb → -4223700, Hcc → -3989400}
```

99700

```
DS298 = c Scc + b Scb - a Sca - Sc1 /. {a → 3, b → 2,
   c → 2, Sc1 → 241.4, Sca → 144.8, Scb → 202.5, Scc → 198.3}
```

125.8

```
DG298 = DH298 - 298 DS298
```

62211.6

Problem 6.10

The heat required to melt cordierite per mole is

$$\text{qmelt} = \int_{298}^{1738} \text{CpCord}\, dT$$

979799.

The MW or cordierite is

```
MWCord = 18 massO + 2 massMg + 4 massAl + 5 massSi
```

584.74

Thus, the heat required (in J) to heat 1 kg from 298K to 1738 K is

$$\text{totalHeat} = \frac{\text{qmelt } 1000}{\text{MWCord}}$$

1.67561×10^{6}

Chapter 7: Phase Equilibria in a One-Component System

Problems

All third editions of Gaskell have 9 problems. Some books have 9 problems that correctly correspond to the 9 solutions. Other books (probably early printings of the thrid edition) are missing the problem that goes with the first solution and have an extra problem that has no solution. These notes give the solutions to the 8 problems in common to all books. Some books have them as 7.1 to 7.8; others have them as 7.2 to 7.9.

- **Problem 7.1(2)**

The vapor pressure of Hg at 100C (373K) is

```
Exp[lnvapHgl /. T -> 373]
```

```
0.000354614
```

- **Problem 7.2(3)**

We assume that $SiCl_4$ vapor behaves as a ideal gas. At 350K, the total volume is

$$\text{Vfix} = \frac{R\,350}{1} \;/.\; R \to 0.082057$$

```
28.72
```

When cooled at this fixed volume, the pressure as a function of temperature is

$$\text{Pcool} = \frac{R\,T}{\text{Vfix}} \;/.\; R \to 0.082057$$

```
0.00285714 T
```

By this cooling path, the vapor will condence when **Pcool** becomes equal to the vapor pressure at that **T**. Equating to vapor pressure and solving gives a condensation temperature of

```
Tcondense = Solve[Log[Pcool] == lnvapSiCl4 , T]
```

$$\{\{T \to 328.382\},\ \{T \to 2.01306 \times 10^{7}\}\}$$

The first root is the physcially correct one. Once the vapor-liquid equilibrium is reached at constant volume, the **P** and **T** will remain on the transition curve but the vapor pressure will change with temperature. At the final temperature of 280K, **P** will be

```
Pfinal = Exp[lnvapSiCl4 /. T -> 280]
```

```
0.139656
```

The pure vapor pressure at 280K would be

$$\text{Ppure} = \frac{R\,T}{\text{Vfix}} \;/.\; \{R \to 0.082057,\ T \to 280\}$$

```
0.8
```

Thus, the percentage that has condensed must be

```
Fraction = 100 * (Ppure - Pfinal)/Ppure
```

```
82.543
```

- **Problem 7.3(4)**

Equating the two curves and solving, the cross at the triple point of

```
Solve[
-15780 / T - 0.755 Log[T] + 19.25 == -15250 / T - 1.255 Log[T] + 21.79]
```

```
{{T → 712.196}}
```

Above this temperature, the vapor pressure of the solid will be higher (for a given **T**, the liquid-vapor curve is below the solid-vapor curve). Taking 800K for example, the two curves give

```
{15780 / T - 0.755 Log[T] + 19.25,
-15250 / T - 1.255 Log[T] + 21.79} /. T -> 800
```

```
{33.9281, -5.66169}
```

Thus the first must be the vapor pressure of solid zinc. (Also, Table A-4 gives the second equation as the vapor pressure curve for liquid Zn).

- **Problem 7.4(5)**

From the Clausius-Clapeyron equation for a liquid-vapor transition where the vapor volume is assumed to be much larger than the liquid volume

```
ΔHvap = 101.325 (R T^2)/P dPdT /.
{R -> 0.082057, T -> 3330, P -> 1 , dPdT -> 3.72 10^-3}
```

```
342976.
```

(The leading constant of 101.325 converts the result fo Joules)

- **Problem 7.5(6)**

From the Clausius-Clapeyron equations, ΔHsub, or the heat of sublimation is

```
dlnPdT = D[lnvapCO2s, T] ; ΔHsub = R T^2 dlnPdT /. R -> 8.31443
```

```
25907.8
```

Thus, the ΔHvap, at the triple point is

```
ΔHvap = ΔHsub - ΔHmelt /. ΔHmelt -> 8330
```

17577.8

Assuming ΔHvap is constant, the vapor pressure curve for the liquid is

$$\text{lnPvap} = \frac{-\Delta\text{Hvap}}{\text{R T}} + \text{const} \;/.\; \text{R} \to 8.31443$$

$$\text{const} - \frac{2114.13}{T}$$

The constant is found from the triple point

```
Solve[lnPvap == lnvapCO2s /. T -> 273 - 56.2 , const]
```

$\{\{\text{const} \to 11.3888\}\}$

Thus, at 25C,

$$\text{lnvapCO2l} = \frac{-2114.13}{\text{T}} + 11.3888 \;/.\; \text{T} \to 273 + 25$$

4.2944

or the actual pressure is

```
Pvap = Exp[lnvapCO2l]
```

73.2885

Solid CO_2 is referred to as “dry ice” because the triple point is at

```
Exp[lnvapCO2s] /. T -> 273 - 56.2
```

5.1413

which is above 1 atm. Thus under atmospheric conditions, solid CO_2 vaporizes into gaseous CO_2.

- **Problem 7.6(7)***

From the Clapeyron equation (after converting volumes to liters, looking up melting transition properties of lead, and converting ΔH to liter-atm):

$$\text{dPdT} = \frac{\Delta\text{HPb}}{\text{Tm}\,(\text{Vl} - \text{Vs})} \;/.\; \{\text{Vs} \to 18.92 * 10^{-3},\; \text{Vl} \to 19.47 * 10^{-3},\; \text{Tm} \to 600,\; \Delta\text{HPb} \to 4810/101.325\}$$

143.852

If the temperture of the melting point changes by 20 (**dT = 20**), the pressure must change by:

```
dP = dPdT dT /. dT -> 20
```

2877.03

(Note: this result differs slightly from the book answer of 2822 atm).

Problem 7.7(8)

The information that the point P = 1 atm and T = 36K is on the α-β transition tells you that line is the one below the triple point. You are also given the slopes of the lines emanating from the triple point by using the Clapeyron equation:

$$\text{slope}\alpha\beta = \frac{\Delta S / 101.325}{\Delta V\, 10^{-3}} \;/.\; \{\Delta S \to 4.59,\ \Delta V \to 0.043\}$$

1053.48

The factors 101.325 and 10^{-3} convert slope to atm/K. For the other two lines

$$\text{slope}\alpha\gamma = \frac{\Delta S / 101.325}{\Delta V\, 10^{-3}} \;/.\; \{\Delta S \to 1.25,\ \Delta V \to 0.165\}$$

74.7669

$$\text{slope}\beta\gamma = \frac{\Delta S / 101.325}{\Delta V\, 10^{-3}} \;/.\; \{\Delta S \to 4.59 + 1.25,\ \Delta V \to 0.043 + 0.165\}$$

277.098

A sketch of lines emanating from a triple point with these slopes is given in the text.

Problem 7.8(9)

We assume ΔHvap is a constant, then

$$\text{lnPvap} = \frac{-A}{T} + B;$$

We can find the constants by solving

```
Solve[{Log[.3045] == lnPvap /. T -> 478 ,
Log[.9310] == lnPvap /. T -> 520} , {A, B}]
```

{{A → 6613.99, B → 12.6477}}

Then, we find the boiling point by solving for **T** when **P=1**:

$$\text{Solve}\left[0 == -\frac{6613.99}{T} + 12.6477,\ T\right]$$

{{T → 522.94}}

Chapter 8: The Behavior of Gases

Calculations with van der Waals Equation for a Non-Ideal Gas

Critical Conditions for a van der Waals Gas

Solving the van der Waals equation for **P** in terms of **T** and **V** gives

```
Solve[(P + a/V^2) (V - b) == R T, P]
```

$$\left\{\left\{P \to -\frac{a\,b - a\,V + R\,T\,V^2}{(b - V)\,V^2}\right\}\right\}$$

Thus the van der Waals equation for **P** is

```
Pform = P /. %[[1]]
```

$$-\frac{a\,b - a\,V + R\,T\,V^2}{(b - V)\,V^2}$$

At the critical point, this form gives

```
Pform = Pform /. {T -> Tcr, V -> Vcr}
```

$$-\frac{a\,b - a\,Vcr + R\,Tcr\,Vcr^2}{(b - Vcr)\,Vcr^2}$$

To find the critical condtions, we solve the following three equations for **Pcr**, **Vcr**, and **Tcr**:

```
crit = Solve[{Pcr == Pform, 0 == D[Pform, Vcr],
  0 == D[Pform, {Vcr, 2}]}, {Pcr, Vcr, Tcr}]
```

$$\left\{\left\{Pcr \to \frac{a}{27\,b^2},\ Tcr \to \frac{8\,a}{27\,b\,R},\ Vcr \to 3\,b\right\}\right\}$$

Plots of P vs T and V

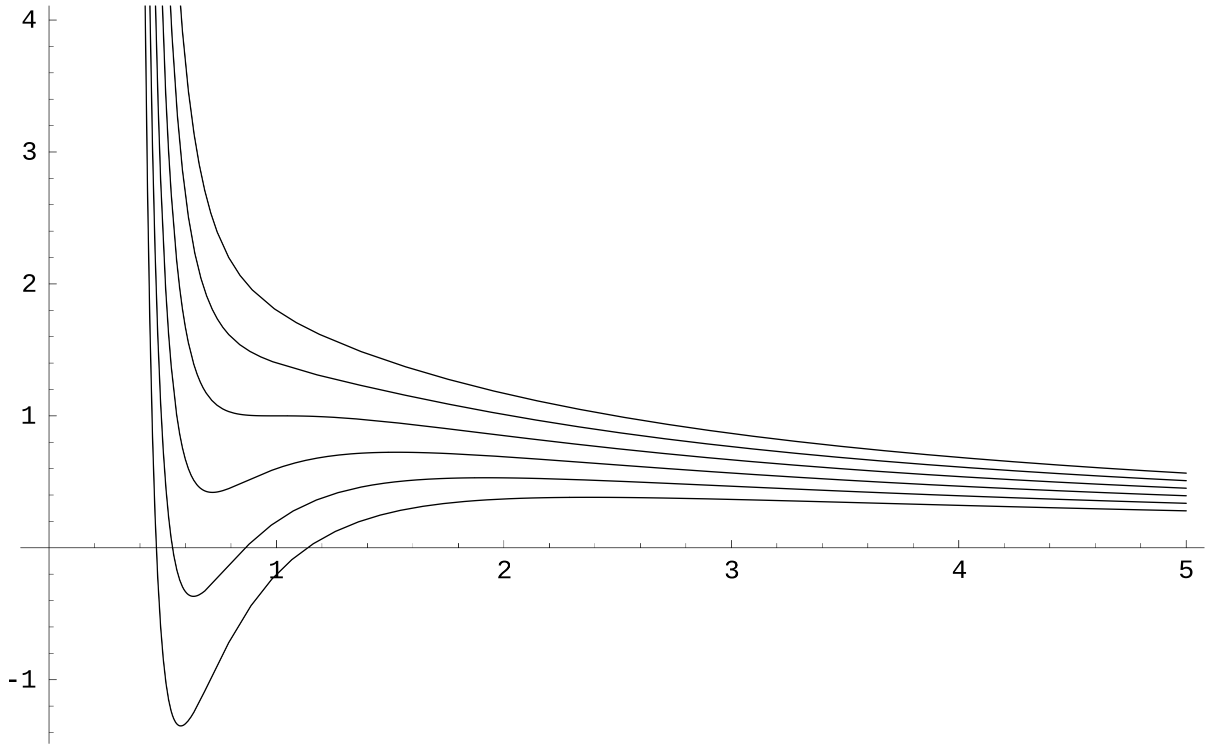
For convenience, we rewrite the van der Waals equations using reduced **P**, **V**, and **T** defined as **PR = P/Pcr**, **TR = T/Tcr**, and **VR = V/Vcr**. The result is

```
PR = Simplify[1/Pcr (R TR Tcr/(VR Vcr - b) - a/(VR^2 Vcr^2)) /. crit][[1]]
```

$$\frac{3 - 9\,VR + 8\,TR\,VR^2}{VR^2\,(-1 + 3\,VR)}$$

Here is a plot of several isothermal curves around the critical point (**TR** = .7,.8,.9,1.0,1.1, and 1.2):

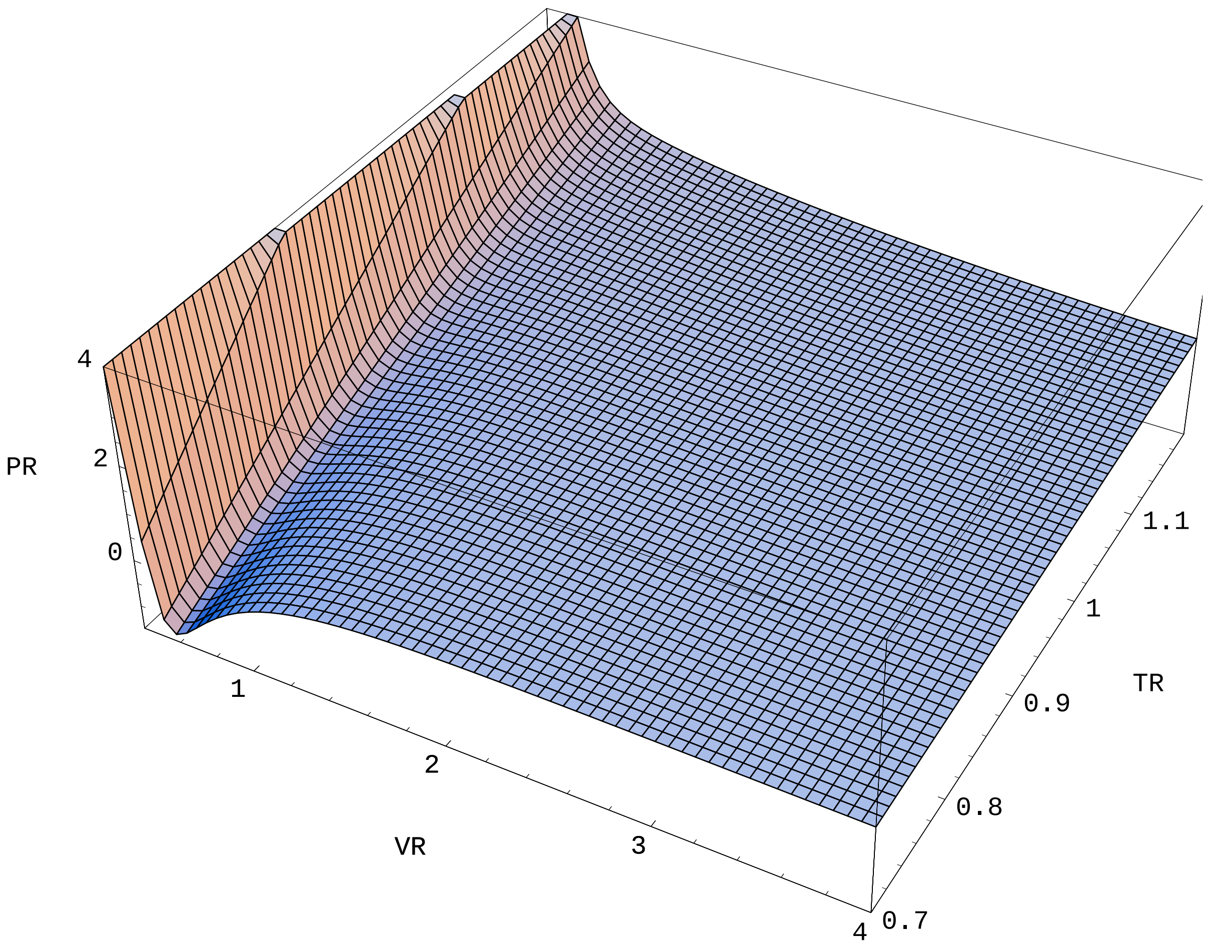
```
Plot[Release[Table[PR /. TR -> .6 + .1 i , {i, 1, 6}]] , {VR, .4, 5}]
```




```
- Graphics -
```

Here is a 3D plot:

```
Plot3D[PR, {VR, .4, 4}, {TR, .7, 1.2},
PlotPoints -> 60, AxesLabel -> {"VR", "TR", "PR"},
ClipFill -> None, PlotRange -> {-1.5, 4}]
```



- SurfaceGraphics -

■ Compressibility Factor Z as function PR and TR

Solving the van der Waals equation for **z = PV/RT** gives

$$z = 1 - \frac{a}{R\,T\,V} + \frac{P\,b}{R\,T} + \frac{a\,b}{R\,T\,V^2}$$

$$1 + \frac{b\,P}{R\,T} + \frac{a\,b}{R\,T\,V^2} - \frac{a}{R\,T\,V}$$

```
z2 = z /. {P -> PR Pcr, T -> TR Tcr, V -> VR Vcr}
```

$$1 + \frac{b\,Pcr\,PR}{R\,Tcr\,TR} + \frac{a\,b}{R\,Tcr\,TR\,Vcr^2\,VR^2} - \frac{a}{R\,Tcr\,TR\,Vcr\,VR}$$

```
z3 = z2 /. crit[[1]]
```

$$1+\frac{PR}{8\,TR}+\frac{3}{8\,TR\,VR^2}-\frac{9}{8\,TR\,VR}$$

To express in terms of **PR** and **TR**, we can solve the van der Waals equation for **VR** and take the first root (the real root):

$$\texttt{PReq} = \texttt{Simplify}\left[\frac{1}{\texttt{Pcr}}\left(\frac{\texttt{R TR Tcr}}{\texttt{VR Vcr - b}}-\frac{\texttt{a}}{\texttt{VR}^2\,\texttt{Vcr}^2}\right)\ \texttt{/. crit}\right]\texttt{[[1]]}$$

$$\frac{3-9\,VR+8\,TR\,VR^2}{VR^2\,(-1+3\,VR)}$$

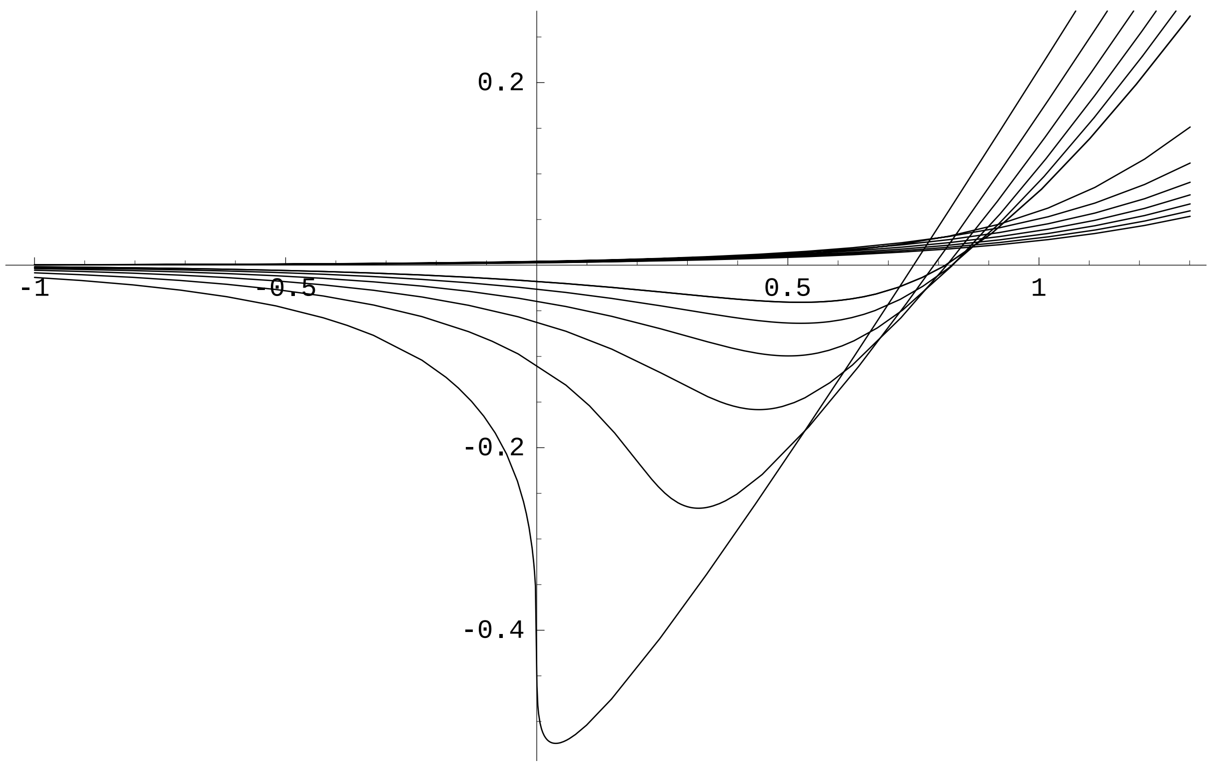
```
VRroots = Solve[PR == PReq, VR];
```

Now substitute back (the expressions are very long and therefore not shown):

```
z4 = z3 /. VRroots[[1, 1]];
```

Here is a plot of **z** vs **PR** for **TR** = 1, 1.2, 1.4, 1.6, 1.8, 2, 4, 6, 8, 10, 12, 14, and 16.

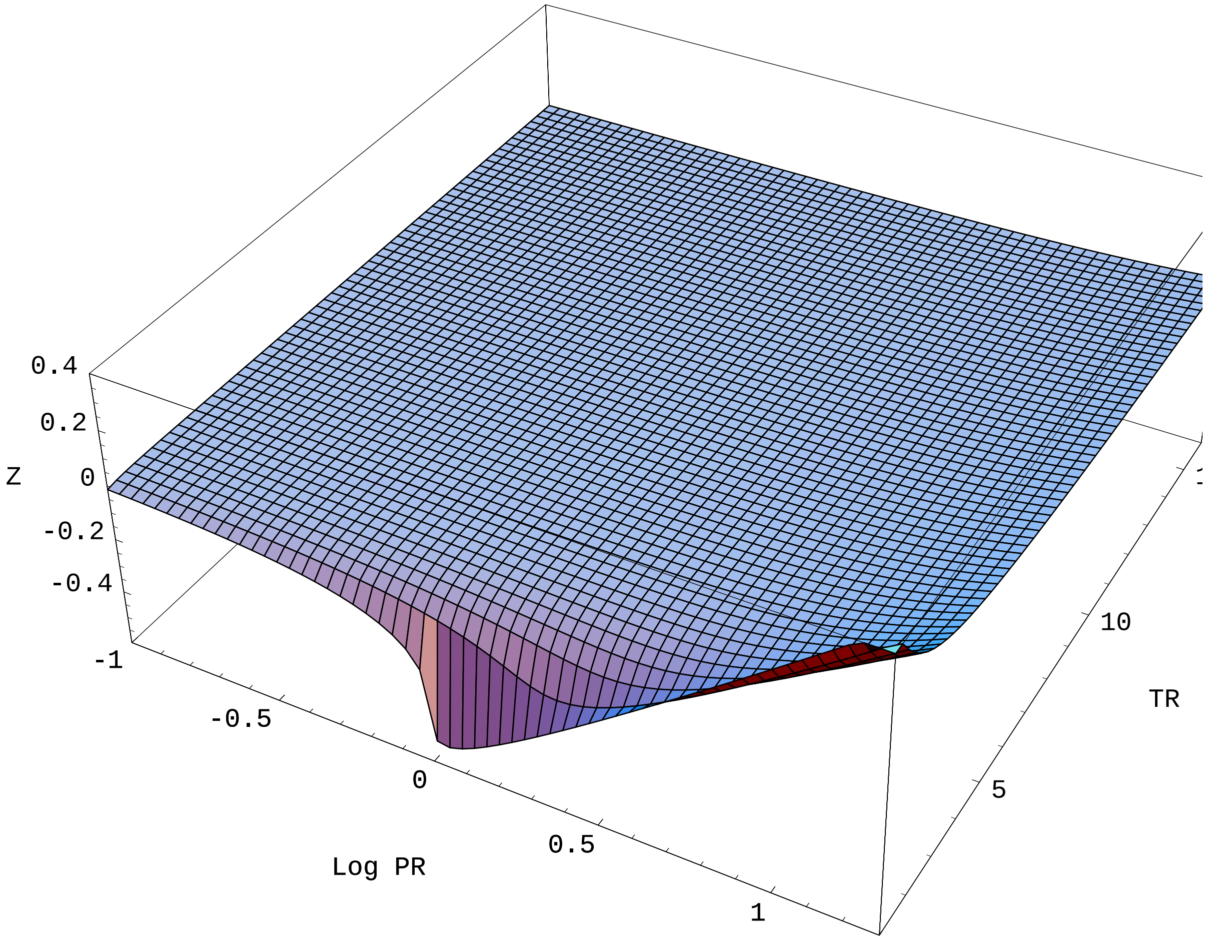
```
Plot[Release[
 {Table[Log[10, z4] /. {TR -> .8 + .2 i, PR -> 10^x}, {i, 1, 6}],
  Table[Log[10, z4] /. {TR -> 2 i, PR -> 10^x}, {i, 1, 8}]}],
   {x, -1, Log[10, 20]}]
```



- Graphics -

Here is a 3D plot of the "compressibility" surface:

```
Plot3D[Log[10, z4] /. PR -> 10^x, {x, -1, Log[10, 20]}, {TR, 1, 16},
   PlotPoints -> 60, AxesLabel -> {"Log PR", "TR", "Z"},
     PlotRange -> {-0.6, 0.4}, ClipFill -> None]
```




```
- SurfaceGraphics -
```

■ Problems

■ Problem 8.1

a. We rewrite the van der Waals equations using reduced **P**, **V**, and **T** defined as **PR = P/Pcr**, **TR = T/Tcr**, and **VR = V/Vcr**. The result is

$$PR=.;\ PR == \mathrm{Simplify}\left[\frac{1}{Pcr}\left(\frac{R\,TR\,Tcr}{VR\,Vcr-b}-\frac{a}{VR^2\,Vcr^2}\right)\ /.\ \left\{Pcr\to\frac{a}{27\,b^2},\ Tcr\to\frac{8\,a}{27\,b\,R},\ Vcr\to 3\,b\right\}\right]$$

$$PR == \frac{3-9\,VR+8\,TR\,VR^2}{VR^2\ (-1+3\,VR)}$$

A nicer form results by solving for **TR**:

$$\mathrm{Solve}[\%,\ TR]$$

$$\left\{\left\{TR\to\frac{(-1+3\,VR)\ (3+PR\,VR^2)}{8\,VR^2}\right\}\right\}$$

Note that this equation for **TR** does not depend on **a** or **b**; thus, in reduced variables, all van der Waal gases follow the same equation of state.

b. At the critical point

$$Z=\frac{Pcr\,Vcr}{R\,Tcr}\ /.\ \left\{Pcr\to\frac{a}{27\,b^2},\ Tcr\to\frac{8\,a}{27\,b\,R},\ Vcr\to 3\,b\right\}$$

$$\frac{3}{8}$$

This result is somewhat higher the results for real gases in Table 8.1

c. This problem is solved in the text (see page 197):

▪ Problem 8.2

a. Mixing of ideal gases is puring due to entropy effects. The maximum increase in entropy occurs when there are equal parts of each gas.

b. From partial molar results (eq. (8.15)), the free energy of the solution is

$$Gsoln = n_A\,GA0+n_B\,GB0+RT\,(n_A\,\mathrm{Log}[X_A]+n_B\,\mathrm{Log}[X_B]+(n_A+n_B)\,\mathrm{Log}[P])$$

$$GA0\,n_A+GB0\,n_B+RT\,(\mathrm{Log}[X_A]\,n_A+\mathrm{Log}[X_B]\,n_B+\mathrm{Log}[P]\,(n_A+n_B))$$

Because GA0 and GB0 are for constants that do not depend on subsequent increase in temperture, we need to solve for an increase in Gsoln using

$$\mathrm{Solve}[(1/2)\,RT\,(n_A\,\mathrm{Log}[X_A]+n_B\,\mathrm{Log}[X_B]) == RT\,(n_A\,\mathrm{Log}[X_A]+n_B\,\mathrm{Log}[X_B]+(n_A+n_B)\,\mathrm{Log}[P]),\ P]$$

$$\left\{\left\{P\to E^{\frac{-\mathrm{Log}[X_A]\,n_A-\mathrm{Log}[X_B]\,n_B}{2\,(n_A+n_B)}}\right\}\right\}$$

```
% /. {XA -> 0.5 , XB -> 0.5 , nA -> nB}
```

$$\{\{P \to 1.41421\}\}$$

- **Problem 8.3**

The volume of the tank is

```
Vtank = Pi r^2 l 10^3 /. {r -> .1, l -> 2}
```

$$62.8319$$

At constant volume, the number of moles in an ideal gas under the stated conditions is

```
nideal = Solve [
 P V == n R T /. {P -> 200 , T -> 300 , R -> 0.082057, V -> Vtank} , n]
```

$$\{\{n \to 510.473\}\}$$

For an van der Waals gas, the number of moles would be

```
nvander = Solve [ (P + n^2 a / V^2) (V - n b) == n R T /. {P -> 200 , T -> 300 ,
   R -> 0.082057, a -> 1.36 , b -> 0.0318, V -> Vtank} , n]
```

$$\{\{n \to 564.889\},\ \{n \to 705.478 - 1238.13\,I\},\ \{n \to 705.478 + 1238.13\,I\}\}$$

From the real root, the van der Waal gas has more moles. If you pay by the mole, you would prefer the ideal gas because it would be cheaper. If you pay by the container, you would prefer the van der Waals gas because you would get more moles per dollar.

- **Problem 8.4**

We need to integrate pressure over the volume change. Pressure is given by the virial expansion, so all we need are the initial and final volumes. These come from solving

```
Solve[ P V / (R T) == 1 + A / V + B / V^2 /.
 {A -> -.265, B -> .03025, P -> 50 , R -> 0.082057, T -> 460}]
```

$$\{\{V \to 0.180158 - 0.159419\,I\},\ \{V \to 0.180158 + 0.159419\,I\},\ \{V \to 0.394608\}\}$$

```
Solve[ P V / (R T) == 1 + A / V + B / V^2 /.
 {A -> -.265, B -> .03025, P -> 100 , R -> 0.082057, T -> 460}]
```

$$\{\{V \to 0.100284 - 0.233434\,I\},\ \{V \to 0.100284 + 0.233434\,I\},\ \{V \to 0.176895\}\}$$

We take the real roots for the actual volume. Note that **A** and **B** were divided by **10^3** and **10^6**, respectively, to convert to units of liters. To find work done by the gas, we integrate **P** from **V1** to **V2** or to find the work done on the gas we reverse the integration and go from **V2** to **V1**. The result (after convertion to joules) is

$$\text{work} = 101.325 \int_{.176895}^{.3946087} R\,T\left(\frac{1}{V} + \frac{A}{V^2} + \frac{B}{V^3}\right) dV \;/.\; \{A \to -.265,\ B \to .03025,\ R \to 0.082057,\ T \to 460\}$$

1384.7

Problem 8.5

a. From the critical temperature and pressure, the van der Waals constants for the gas are

$$\text{Solve}\left[\left\{Pcr == \frac{a}{27\,b^2},\ Tcr == \frac{8\,a}{27\,b\,R}\right\},\ \{a, b\}\right] \;/.\; \{Tcr \to 430.7,\ Pcr \to 77.8,\ R \to 0.082057\}$$

{{a → 6.77306, b → 0.0567833}}

b. The critical volume comes from the critical compressibility ratio or

$$\text{Solve}\left[\frac{Pcr\,Vcr}{R\,Tcr} == \frac{3}{8},\ Vcr\right] \;/.\; \{Tcr \to 430.7,\ Pcr \to 77.8,\ R \to 0.082057\}$$

{{Vcr → 0.17035}}

c. Using the van der Waals equation with the above determined constants gives

$$\text{Pvander} = \frac{R\,T}{(V - b)} - \frac{a}{V^2} \;/.\; \{a \to 6.77306,\ b \to 0.0567833,\ R \to 0.082057,\ T \to 500,\ V \to .5\}$$

65.4776

The corresponding ideal gas has pressure

$$\text{Pideal} = \frac{R\,T}{V} \;/.\; \{T \to 500,\ V \to 0.5,\ R \to 0.082057\}$$

82.057

Problem 8.6

This problem asks for work calculated three different ways. First the calculations is done using the virial expansion

```
Solve[P V == n R T (1 + A P), P]
```

$$\left\{\left\{P \to -\frac{n R T}{A n R T - V}\right\}\right\}$$

$$\text{wVirial} = 101.325 \int_{10}^{30} \frac{n R T}{V - A n R T} \, dV \; /. \; \{R \to 0.082057, \; T \to 298, \; A \to 0.00064, \; n \to 100\}$$

$$301097.$$

(Note: the book has -301 kJ which must be to work done by the gas. Positive work must be done on a system to compress it).

If the gas is a van der Waal gas, the work is

$$\text{wvander} = 101.325 \int_{10}^{30} \left(\frac{n R T}{(V - n b)} - \frac{n^2 a}{V^2}\right) dV \; /. \; \{R \to 0.082057, \; T \to 298, \; a \to 0.2461, \; b \to .02668, \; n \to 100\}$$

$$309394.$$

Finally, the ideal gas result can come for either above result by setting extra constants to zero, or by directly integrating the ideal gas result:

$$\text{wIdeal} = 101.325 \int_{10}^{30} \frac{n R T}{V} \, dV \; /. \; \{R \to 0.082057, \; T \to 298, \; n \to 100\}$$

$$272203.$$

- **Problem 8.7**

a. To find fugacity from a virial expansion, it is easiest to integrate **(Z-1)/P** which here is simple the constant **A=0.00064**:

$$\text{lnfoverP} = \int_{0}^{P} A \, dP \; /. \; \{Z \to 1 + A P\}$$

$$A P$$

The fugacity at **500 atm** is:

```
fug = P Exp[A P] /. {P -> 500, A -> 0.00064}
```

$$688.564$$

b. Solve the equation and take the non-zero root:

```
Solve[2 P == P Exp[A P] , P] /. {A -> 0.00064}
```

$\{\{P \to 0\}, \{P \to 1083.04\}\}$

c. The fugacity at 1 atm is

```
fug1 = P Exp[A P] /. {P -> 1, A -> 0.00064}
```

1.00064

For the non-ideal gas

$$\Delta G = R\,T\,\mathrm{Log}\left[\frac{\mathrm{fug}}{\mathrm{fug1}}\right] \;/.\; \{R \to 8.3144,\; T \to 298\}$$

16189.2

The ideal gas result is

$$\Delta \mathrm{Gideal} = R\,T\,\mathrm{Log}\left[\frac{500}{1}\right] \;/.\; \{R \to 8.3144,\; T \to 298\}$$

15397.9

The extra free energy change due to a nonideal gas is

```
extraΔG = ΔG - ΔGideal
```

791.275

Chapter 9: The Behavior of Solutions

Regular Solutions

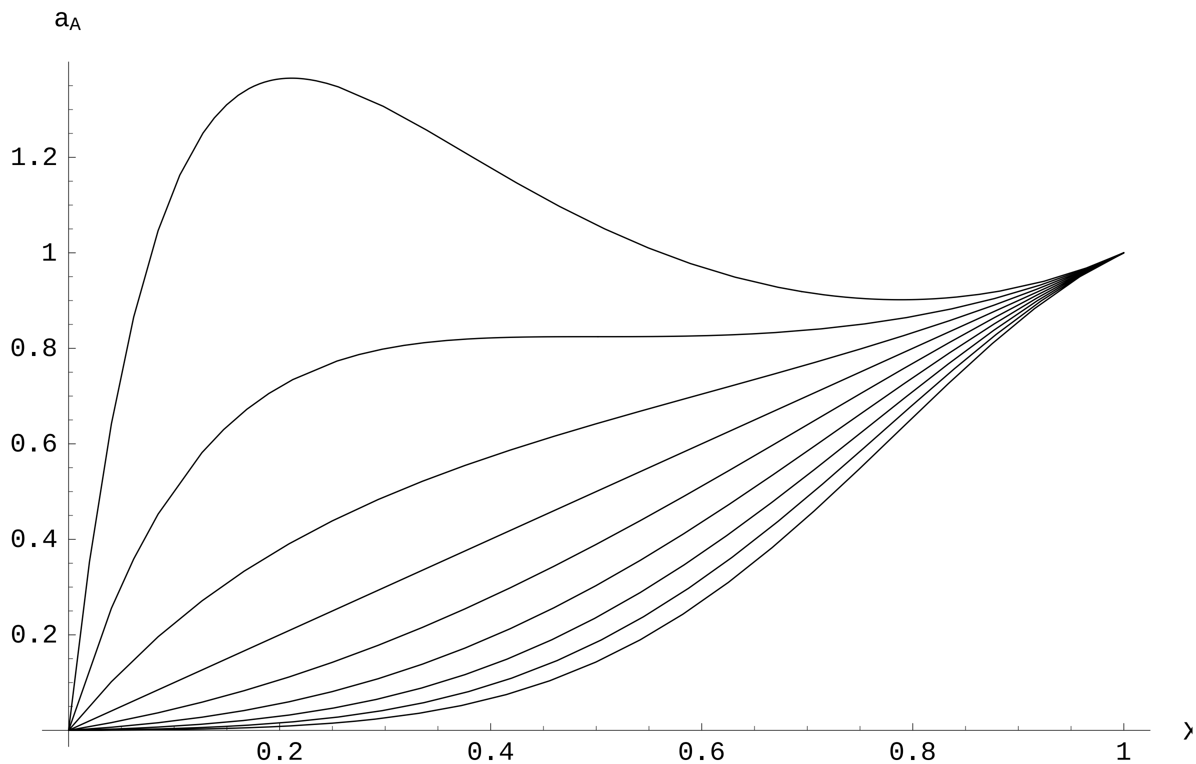
Activities

In a regular solution, we assume that

$$\gamma_A = \mathrm{Exp}\left[\frac{\Omega\,(1-XA)^2}{R\,T}\right];\; \gamma_B = \mathrm{Exp}\left[\frac{\Omega\,XA^2}{R\,T}\right];\; a_A = \gamma_A\,XA;$$
$$a_B = \gamma_B\,(1-XA);\; \ln\gamma_A = \frac{\Omega\,(1-XA)^2}{R\,T};\; \ln\gamma_B = \frac{\Omega\,XA^2}{R\,T};$$
$$\ln a_A = \ln\gamma_A + \mathrm{Log}[XA];\; \ln a_B = \ln\gamma_B + \mathrm{Log}[1-XA];$$

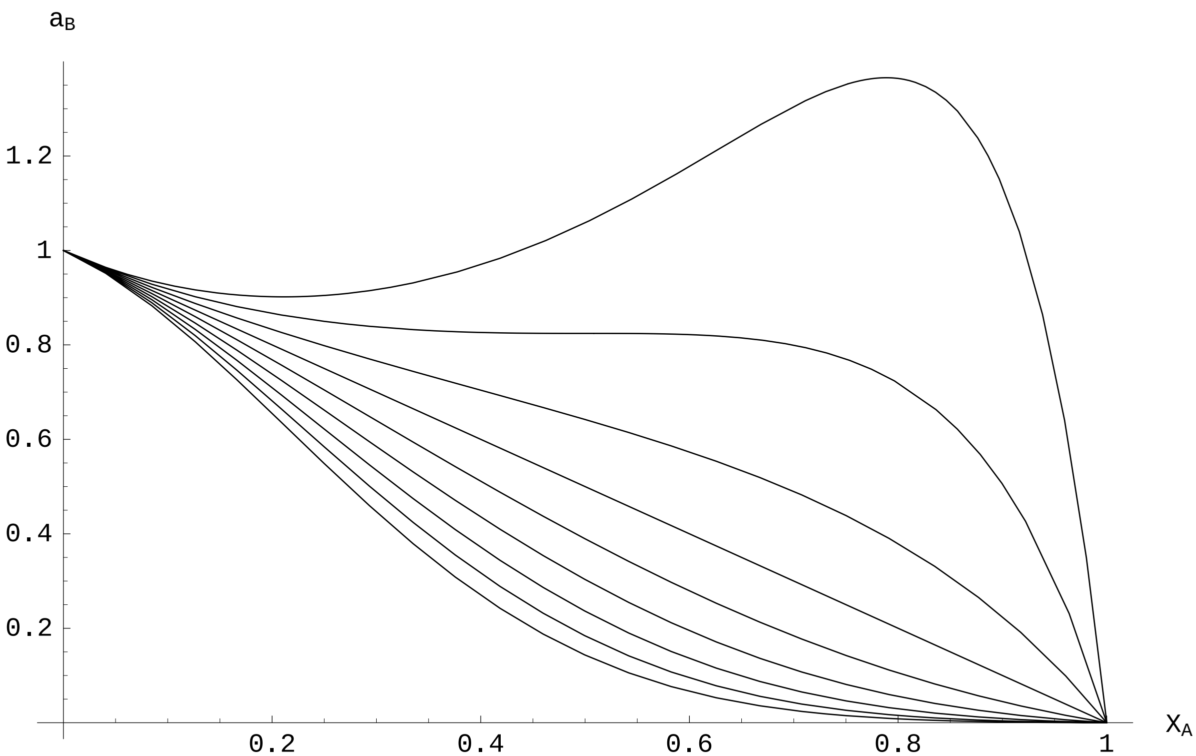
where Ω is a constant. It will be seen later to be assumed to be independent of temperature, but it may depend on pressure. We can plot the activity coefficients of **A** and **B** for various values of Ω:

```
Plot[ Release[Table[a_A , {Ω, -5, 3, 1}] /. {R -> 1 , T -> 1}],
      {XA, 0, 1}, AxesLabel -> {"X_A", "a_A"}]
```



- *Graphics* -

```
Plot[ Release[Table[aB , {Ω, -5, 3, 1}] /. {R -> 1 , T -> 1}],
     {XA, 0, 1}, AxesLabel -> {"XA", "aB"}]
```



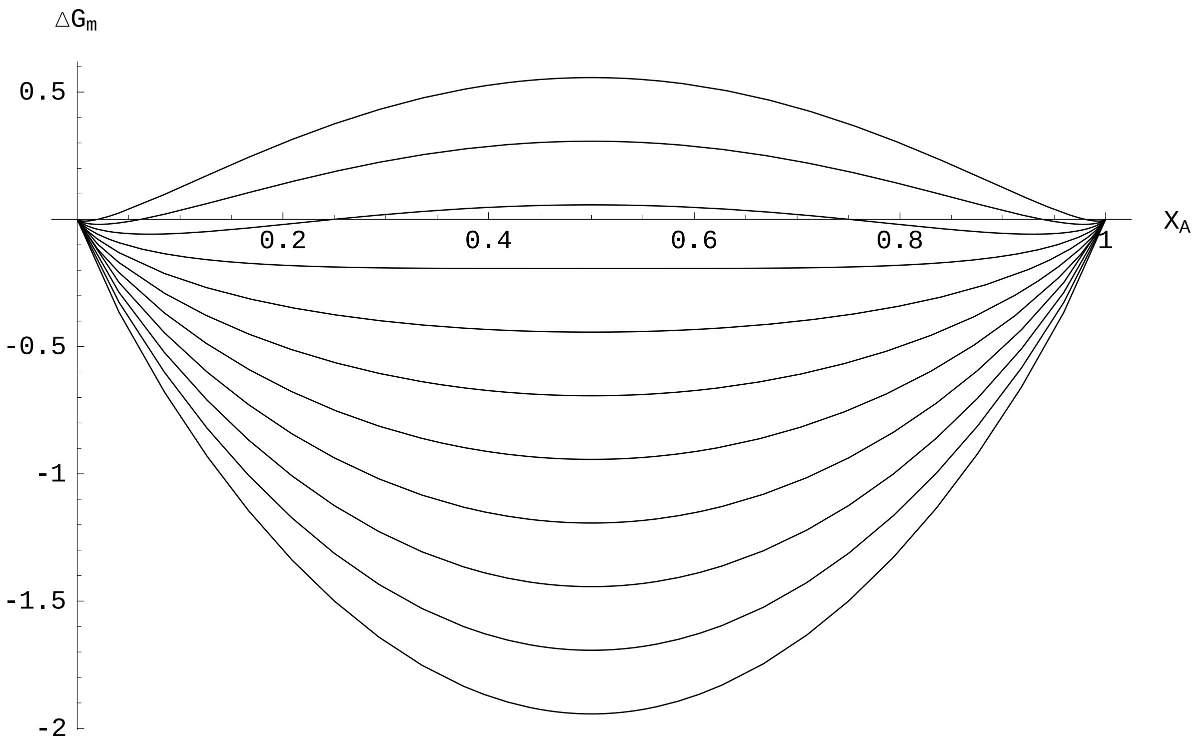
- Graphics -

■ **Free Energy of Mixing**

The free energy of mixing is

```
ΔGm = R T ( XA Log[aA] + (1 - XA) Log[aB]) ;
```

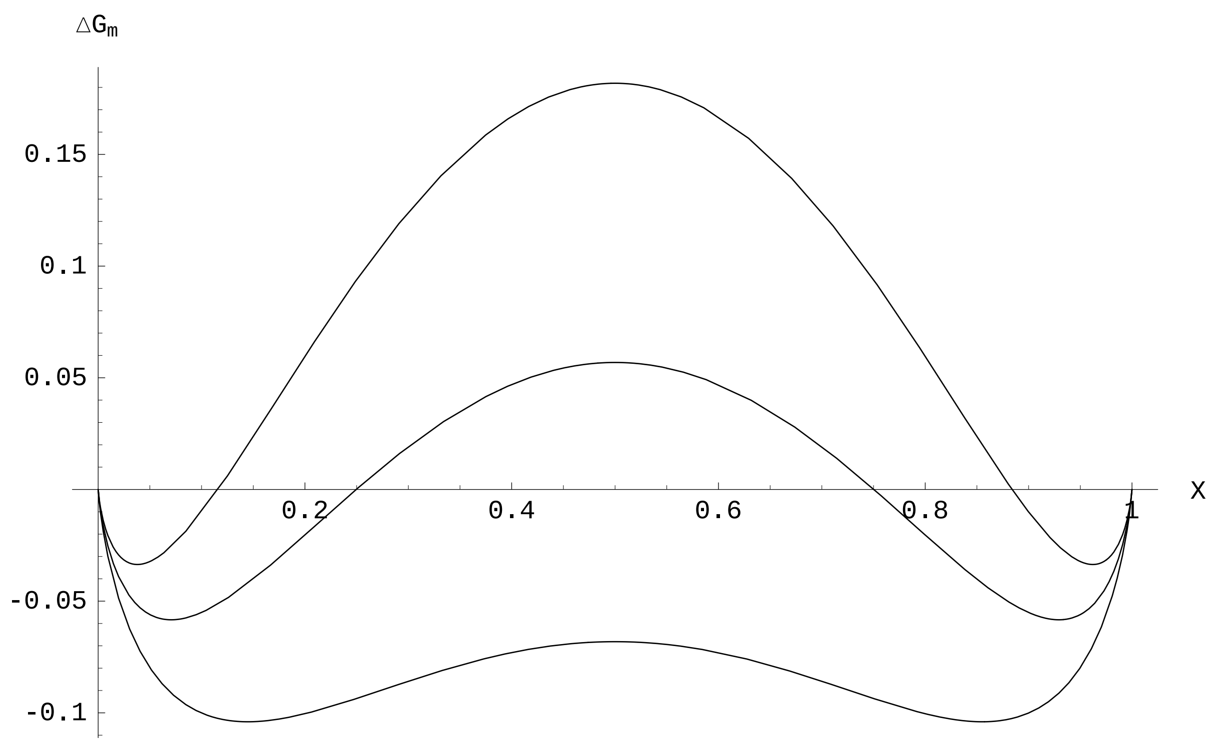
```
Plot[ Release[Table[ΔGm , {Ω, -5, 5, 1}] /. {R -> 1 , T -> 1}],
      {XA, 0, 1}, AxesLabel -> {"XA", "ΔGm"}]
```



- *Graphics* -

Note that **ΔGm** is always symmetric about $X_A = 0.5$; many real solution are not symmetric. When **Ω<0**, **ΔGm** is always negative and the two components disolve. When **Ω>0**, **ΔGm** may be positive or negative; positive values are solutions that will not mix. Here is blow up for some positive **Ω**:

```
Plot[ Release[Table[ΔGm , {Ω, 2.5, 3.5, .5}] /. {R -> 1 , T -> 1}],
      {XA, 0, 1}, AxesLabel -> {"XA", "ΔGm"}]
```




```
- Graphics -
```

A critical value of **Ω** is when **ΔGm**=0 at **XA=0.5** :

```
Solve[ΔGm == 0 /. {XA -> 0.5, R -> 1, T -> 1} , Ω]
```

```
– Solve::ifun :
   Inverse functions are being used by Solve, so some solutions may not be found.
```

```
{{Ω → 2.77259}}
```

■ Excess Free Energy of Mixing

The excess free energy of mixing is given by

```
ΔGmXS = Simplify[R T ( XA lnγA + (1 - XA) lnγB)]
```

```
- (-1 + XA) XA Ω
```

We can also calculate **ΔGm** directly from the activity coefficient. If will split Log[a_A] into Log[XA] + Log[γ_A] we can separately calculate the ideal free energy of mixing and the excess free energy of mixing. The results are:

```
ΔGmid = Simplify[R T (1 - XA)
  Integrate[Log[-XA]/(1 + XA)^2, {XA, -XA, 0}, Assumptions -> XA > 0]]
```

$$R\,T\,(-(-1+XA)\,Log[1-XA]+XA\,Log[XA])$$

```
ΔGmXS = Simplify[R T (1 - XA) Integrate[
  lnγA/(1 - XA)^2, {XA, 0, XA}, Assumptions -> {XA < 1, XA > 0}]]
```

$$-(-1+XA)\,XA\,\Omega$$

Finally, the partially molar free energy of mixing (for **A** or **B**, here for just **A**) is

```
ΔGmA = Simplify[R T lnaA]
```

$$(-1+XA)^2\,\Omega+R\,T\,Log[XA]$$

Excess Entropy of Mixing

If **Ω** is assumed to be independent of temperature, the excess entropy of mixing is obviously zero from

```
ΔSmXS = -∂T ΔGmXS
```

$$0$$

We can also calculate excess entropy for the excess entropy of mixing formula derived in class

```
ΔSmXS = Simplify[
 -R (XA lnγA + (1 - XA) lnγB) - R T (XA ∂T lnγA + (1 - XA) ∂T lnγB)]
```

$$0$$

The total entropy of mixing can be calculated from activity of just **A** using the partial molar entropy of mixing which is

```
ΔSmA = -R (lnaA + T ∂T lnγA)
```

$$-R\,Log[XA]$$

```
ΔSm = FullSimplify[(1 - XA) Integrate[
  ΔSmA/(1 - XA)^2, {XA, 0, XA}, Assumptions -> {XA < 1, XA > 0}]]
```

$$R\,(-1+XA)\,(-I\,\pi+Log[-1+XA])-R\,XA\,Log[XA]$$

which, if we ignore the complex term (?), is just the ideal entropy of mixing.

- **Excess Enthalpy of Mixing**

The excess enthalpy of mixing can easily be calculated from **ΔGmXS** and **ΔSmXS**:

```
ΔHmXS = ΔGmXS + T ΔSmXS
```

$-(-1 + XA)\, XA\, \Omega$

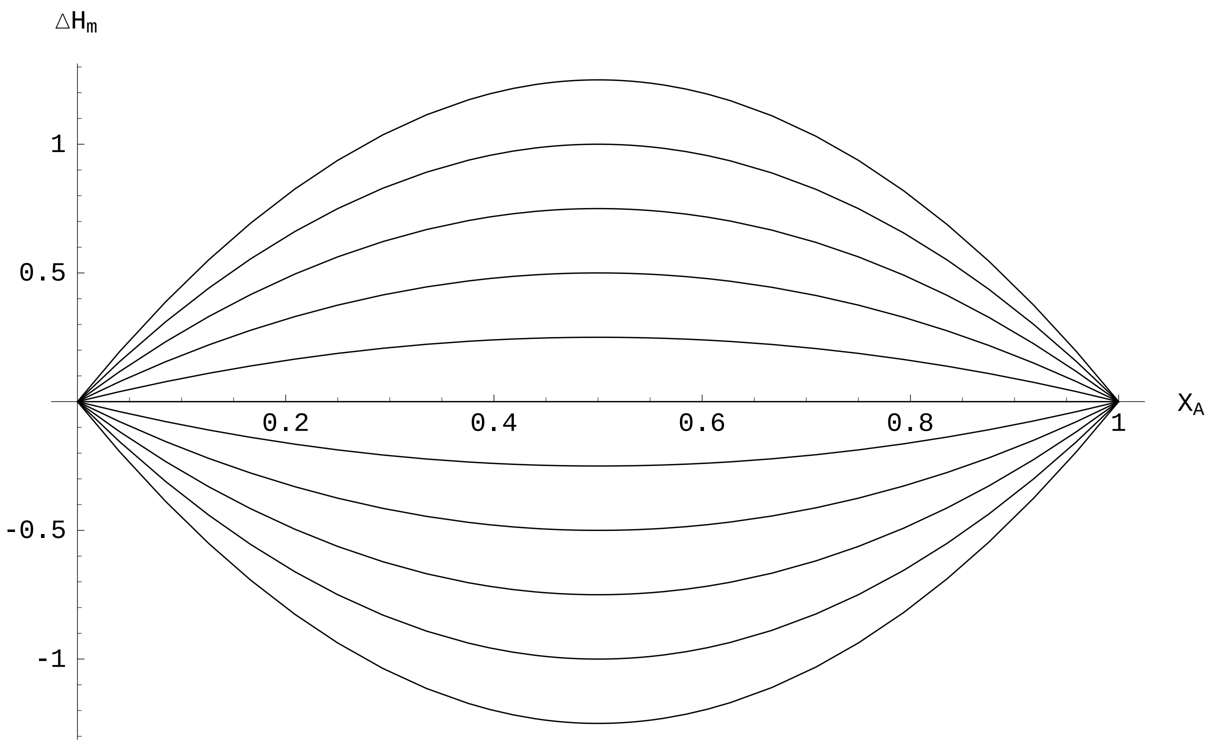
which is simply equal to the excess free energy of mixing. We can also use the formula derived in class

```
ΔHmXS = Simplify[-R T^2 (XA ∂_T lnγ_A + (1 - XA) ∂_T lnγ_B)]
```

$-(-1 + XA)\, XA\, \Omega$

Thus, the sign of **Ω** is also the sign of the enthaply effect. Some plots of excess enthalpy (which are actually total enthalpy of mixing) are:

```
Plot[ Release[Table[ΔHmXS, {Ω, -5, 5, 1}] /. {R -> 1 , T -> 1}],
     {XA, 0, 1}, AxesLabel -> {"X_A", "ΔH_m"}]
```



- *Graphics* -

If **Ω** gets sufficiently positive, the resulting positive enthalpy will eventually overwhelm the ideal entropy of mizing causing the free energy of mixing to be positive or causing the components to be insoluable.

The total enthalpy of mixing can be calculated from activity of just **A** using the partial molar enthalpy of mixing which is

$$\Delta HmA = -R\,T^2\,\partial_T\,\ln\gamma_A$$

$$(1 - XA)^2\,\Omega$$

$$\Delta Hm = \text{FullSimplify}\left[(1 - XA)\,\text{Integrate}\left[\frac{\Delta HmA}{(1 - XA)^2},\ \{XA, 0, XA\},\ \text{Assumptions} \to \{XA < 1,\ XA > 0\}\right]\right]$$

$$-(-1 + XA)\,XA\,\Omega$$

Regular Solutions with Temperature Dependence

Some experimental results in the text (see Fig. 9.23) suggest that α **T** (which is proportional to **Ω**) is not constant but rather decreases with temperature. If we take the results in Fig 9.23 to suggest **Ω** is linear in **T**, we can derive new non-ideal solution results using

$$\Omega = k_0 + k_1\,T\ ;\ \ln\gamma_A = \frac{\Omega\,(1 - XA)^2}{R\,T}\ ;\ \ln\gamma_B = \frac{\Omega\,XA^2}{R\,T}\ ;$$

The problem is solved by finding just the excess terms.

$$\Delta GmXS = \text{Simplify}[R\,T\,(XA\,\ln\gamma_A + (1 - XA)\,\ln\gamma_B)]$$

$$-(-1 + XA)\,XA\,(k_0 + T\,k_1)$$

$$\Delta SmXS = \text{Simplify}[-R\,(XA\,\ln\gamma_A + (1 - XA)\,\ln\gamma_B) - R\,T\,(XA\,\partial_T\,\ln\gamma_A + (1 - XA)\,\partial_T\,\ln\gamma_B)]$$

$$(-1 + XA)\,XA\,k_1$$

$$\Delta HmXS = \text{Simplify}[-R\,T^2\,(XA\,\partial_T\,\ln\gamma_A + (1 - XA)\,\partial_T\,\ln\gamma_B)]$$

$$-(-1 + XA)\,XA\,k_0$$

Notice that at constant temperature both **ΔGmA** and **ΔHmA** are proportional to $X_B{}^2$. The proportionality constants, however, are different which means they are not equal and furthermore the entropy change must differ from ideal results.

Partial Molar Quantities

Partial molar results can be derived from Gibbs-Duhem analysis

$$\Delta GmAXS = \text{Simplify}[\Delta GmXS + (1 - XA)\,\partial_{XA}\,\Delta GmXS]$$

$$(-1 + XA)^2\,(k_0 + T\,k_1)$$

```
ΔGmBXS = Simplify[ΔGmXS - XA ∂XA ΔGmXS]
```

$$XA^2\ (k_0 + T\ k_1)$$

```
ΔSmAXS = Simplify[ΔSmXS + (1 - XA) ∂XA ΔSmXS]
```

$$-(-1 + XA)^2\ k_1$$

```
ΔSmBXS = Simplify[ΔSmXS - XA ∂XA ΔSmXS]
```

$$-XA^2\ k_1$$

```
ΔHmAXS = Simplify[ΔHmXS + (1 - XA) ∂XA ΔHmXS]
```

$$(-1 + XA)^2\ k_0$$

```
ΔHmBXS = Simplify[ΔHmXS - XA ∂XA ΔHmXS]
```

$$XA^2\ k_0$$

■ Subegular Solutions

Subregular solution models are derived by letting **Ω** vary with composition. This change will make the curves no loner symmetrical about **XA=0.5**. The simplest model is to let **Ω** be linear in **XB** but we introduce this linear dependence in the excess free energy (for simplicity) instead of in the activity coefficient of **A** (this other method could be used if desired).

```
Ω = a + b (1 - XA) ; ΔGmXS = Ω XA (1 - XA)
```

$$(a + b\ (1 - XA))\ (1 - XA)\ XA$$

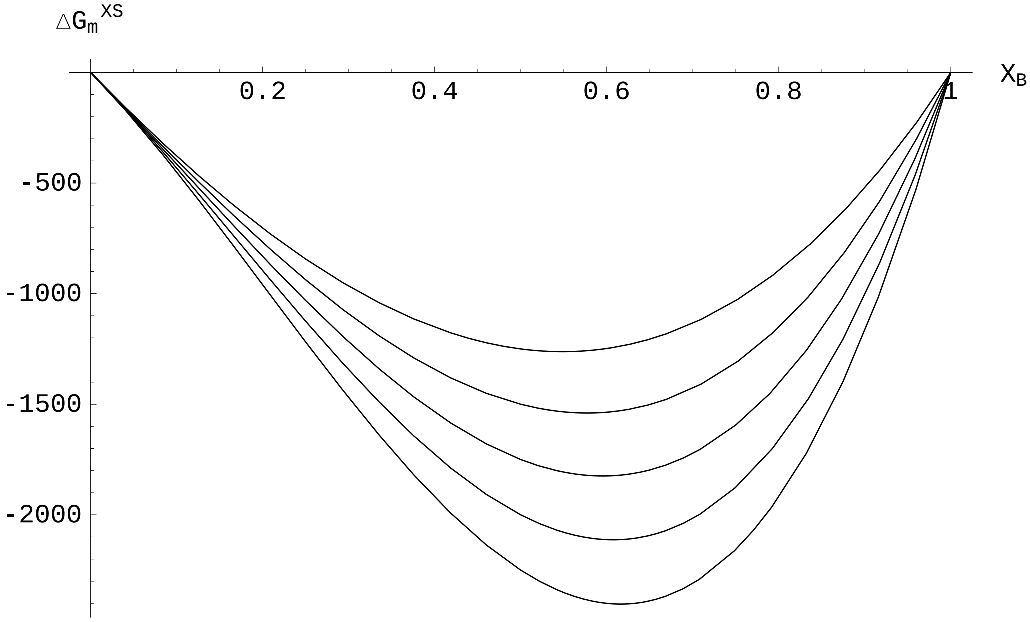
This excess free energy will have minima and/or maxima depending on the values of a and b. These occur where the derivative is zero or at

```
ΔGmXS2 = ΔGmXS /. XA -> 1 - XB ; Solve[∂XB ΔGmXS2 == 0, XB]
```

$$\left\{\left\{XB \to \frac{-a + b - \sqrt{a^2 + a\ b + b^2}}{3\ b}\right\},\ \left\{XB \to \frac{-a + b + \sqrt{a^2 + a\ b + b^2}}{3\ b}\right\}\right\}$$

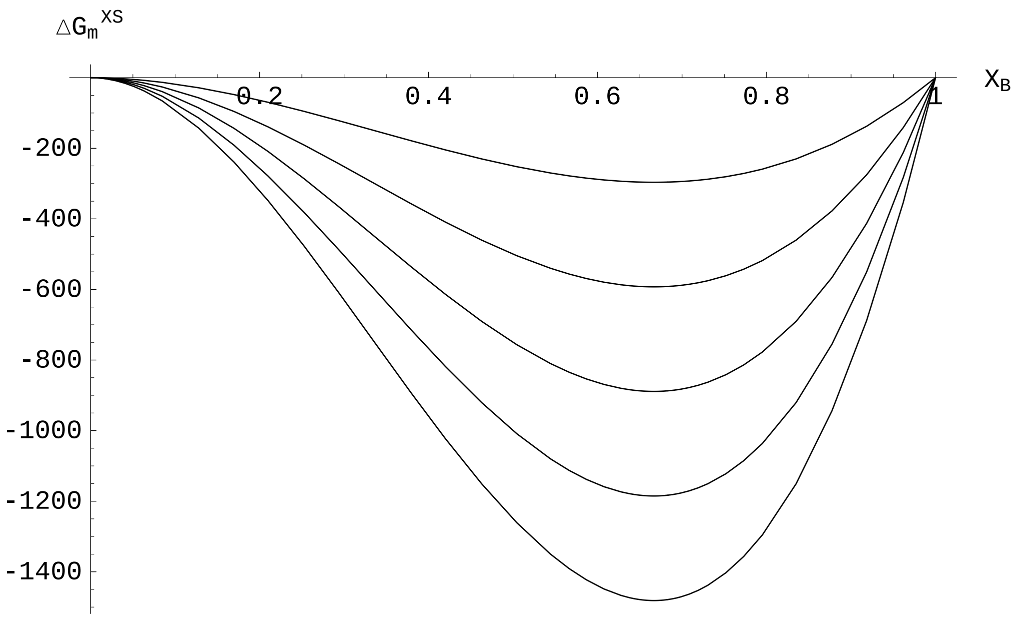
Some plots are on page 262 of the text. Here is a sample:

```
Plot[
Release[Table[ΔGmXS2 , {b, -10000, -2000, 2000}] /. a -> -4000],
{XB, 0, 1}, AxesLabel -> {"XB", "ΔGmXS"}]
```



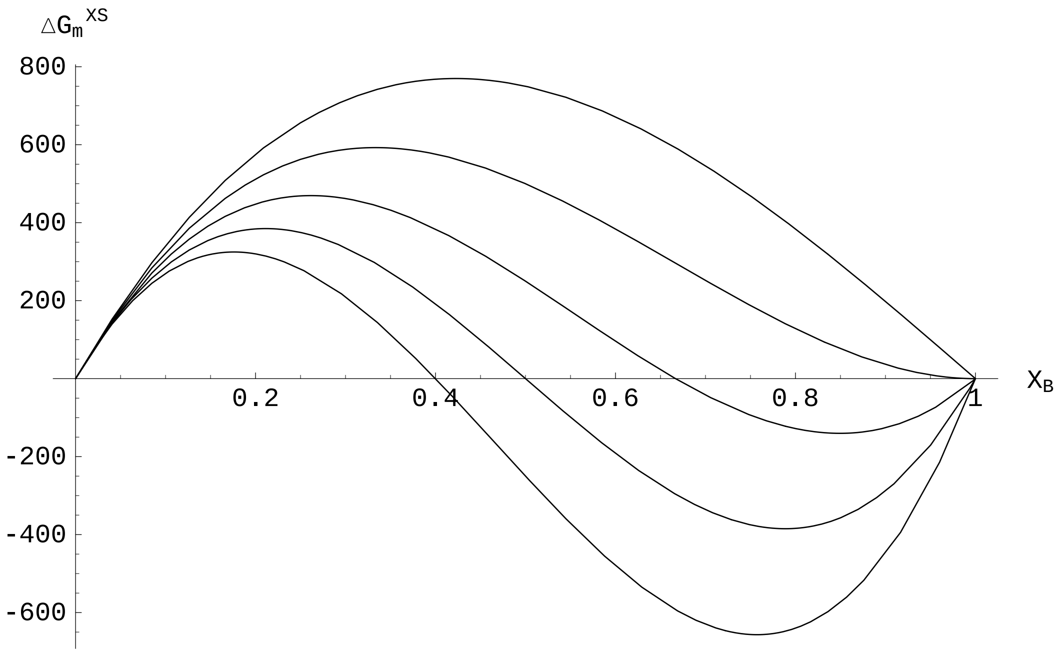
- Graphics -

```
Plot[ Release[Table[ΔGmXS2 , {b, -10000, -2000, 2000}] /. a -> 0],
      {XB, 0, 1}, AxesLabel -> {"X_B", "ΔG_m^XS"}]
```



- Graphics -

```
Plot[
Release[Table[ΔGmXS2 , {b, -10000, -2000, 2000}] /. a -> 4000],
    {XB, 0, 1}, AxesLabel -> {"X_B", "ΔG_m^XS"}]
```



- Graphics -

The excess entropy is

```
ΔSmXS = -∂_T ΔGmXS
```

0

It is still zero because there is no temperature dependence in **a** and **b** and therefore **ΔGmXS** is independent of temperature.

Finally, the excess enthalpy is simply equal to the excess free energy, or by a calculation:

```
ΔHmXS = ΔGmXS + T ΔSmXS
```

$(a + b\,(1 - XA))\,(1 - XA)\,XA$

■ Partial Molar Quantities

Partial molar results can be derived from Gibbs-Duhem analysis

```
ΔGmAXS = Simplify[ΔGmXS + (1 - XA) ∂_XA ΔGmXS]
```

$(-1 + XA)^2\,(a + b - 2\,b\,XA)$

```
ΔGmBXS = Simplify[ΔGmXS - XA ∂_XA ΔGmXS]
```

$$(a - 2\,b\,(-1 + XA))\,XA^2$$

```
ΔSmAXS = Simplify[ΔSmXS + (1 - XA) ∂_XA ΔSmXS]
```

$$0$$

```
ΔSmBXS = Simplify[ΔSmXS - XA ∂_XA ΔSmXS]
```

$$0$$

```
ΔHmAXS = Simplify[ΔHmXS + (1 - XA) ∂_XA ΔHmXS]
```

$$(-1 + XA)^2\,(a + b - 2\,b\,XA)$$

```
ΔHmBXS = Simplify[ΔHmXS - XA ∂_XA ΔHmXS]
```

$$(a - 2\,b\,(-1 + XA))\,XA^2$$

- **Activity Coefficients**

The activity coefficients can be derived from the partial molar free energies

$$\text{ln}\gamma_A = \frac{\Delta\text{GmAXS}}{R\,T}$$

$$\frac{(-1 + XA)^2\,(a + b - 2\,b\,XA)}{R\,T}$$

$$\text{ln}\gamma_B = \frac{\Delta\text{GmBXS}}{R\,T}$$

$$\frac{(a - 2\,b\,(-1 + XA))\,XA^2}{R\,T}$$

Alternatively we can calculate $\mathbf{ln}\gamma_A$ from Gibbs-Duhem results:

$$\text{ln}\gamma\text{Acalc} = \text{Simplify}\left[-(1 - XA)\,XA\,\frac{\text{ln}\gamma_B}{XA^2} - \int_1^{XA} \frac{\text{ln}\gamma_B}{XA^2}\,dXA\right]$$

$$\frac{(-1 + XA)^2\,(a + b - 2\,b\,XA)}{R\,T}$$

or, vice-versa, we can calulate $\mathbf{ln}\gamma_B$ from Gibbs-Duhem results:

$$\texttt{ln}\gamma\texttt{Bcalc} = \texttt{Simplify}\left[-(1-XA)\,XA\,\frac{\ln\gamma_A}{(1-XA)^2} + \int_0^{XA} \frac{\ln\gamma_A}{(1-XA)^2}\,dXA\right]$$

$$\frac{(a-2\,b\,(-1+XA))\,XA^2}{R\,T}$$

Subegular Solutions with Temperature Dependence

We can add temperautre dependence to subregular solutions by adding a third parameter to give

$$\Omega = (a+b\,(1-XA))\left(1-\frac{T}{\tau}\right) \quad ;\ \Delta\texttt{GmXS} = \Omega\,XA\,(1-XA)$$

$$(a+b\,(1-XA))\,(1-XA)\,XA\left(1-\frac{T}{\tau}\right)$$

For fixed temperature, **Ω** is linear in **XB** (as above for subregular solutions). For constant composition **Ω** is now linear in **T**. This temperature dependence will lead to non-zero excess entropy of mixing.

$$\Delta\texttt{SmXS} = -\partial_T\,\Delta\texttt{GmXS}$$

$$\frac{(a+b\,(1-XA))\,(1-XA)\,XA}{\tau}$$

$$\Delta\texttt{HmXS} = \texttt{Simplify}[\Delta\texttt{GmXS} + T\,\Delta\texttt{SmXS}]$$

$$-(-1+XA)\,XA\,(a+b-b\,XA)$$

(Note: the book calculated excess entropy and enthalpy incorrectly).

Partial Molar Quantities

Partial molar results can be derived from Gibbs-Duhem analysis

$$\Delta\texttt{GmAXS} = \texttt{Simplify}[\Delta\texttt{GmXS} + (1-XA)\,\partial_{XA}\,\Delta\texttt{GmXS}]$$

$$-\frac{(-1+XA)^2\,(a+b-2\,b\,XA)\,(T-\tau)}{\tau}$$

$$\Delta\texttt{GmBXS} = \texttt{Simplify}[\Delta\texttt{GmXS} - XA\,\partial_{XA}\,\Delta\texttt{GmXS}]$$

$$-\frac{(a-2\,b\,(-1+XA))\,XA^2\,(T-\tau)}{\tau}$$

$$\Delta\texttt{SmAXS} = \texttt{Simplify}[\Delta\texttt{SmXS} + (1-XA)\,\partial_{XA}\,\Delta\texttt{SmXS}]$$

$$\frac{(-1+XA)^2\,(a+b-2\,b\,XA)}{\tau}$$

$$\Delta SmBXS = \text{Simplify}[\Delta SmXS - XA\,\partial_{XA}\,\Delta SmXS]$$

$$\frac{(a - 2\,b\,(-1 + XA))\,XA^2}{\tau}$$

$$\Delta HmAXS = \text{Simplify}[\Delta HmXS + (1 - XA)\,\partial_{XA}\,\Delta HmXS]$$

$$(-1 + XA)^2\,(a + b - 2\,b\,XA)$$

$$\Delta HmBXS = \text{Simplify}[\Delta HmXS - XA\,\partial_{XA}\,\Delta HmXS]$$

$$(a - 2\,b\,(-1 + XA))\,XA^2$$

- **Activity Coefficients**

The activity coefficients can be derived from the partial molar free energies

$$\ln\gamma_A = \frac{\Delta GmAXS}{R\,T}$$

$$-\frac{(-1 + XA)^2\,(a + b - 2\,b\,XA)\,(T - \tau)}{R\,T\,\tau}$$

$$\ln\gamma_B = \frac{\Delta GmBXS}{R\,T}$$

$$-\frac{(a - 2\,b\,(-1 + XA))\,XA^2\,(T - \tau)}{R\,T\,\tau}$$

Alternatively we can calculate $\mathbf{ln}\boldsymbol{\gamma}_A$ from Gibbs-Duhem results:

$$\ln\gamma Acalc = \text{Simplify}\left[-(1 - XA)\,XA\,\frac{\ln\gamma_B}{XA^2} - \int_1^{XA}\frac{\ln\gamma_B}{XA^2}\,dXA\right]$$

$$-\frac{(-1 + XA)^2\,(a + b - 2\,b\,XA)\,(T - \tau)}{R\,T\,\tau}$$

or, vice-versa, we can calulate $\mathbf{ln}\boldsymbol{\gamma}_B$ from Gibbs-Duhem results:

$$\ln\gamma Bcalc = \text{Simplify}\left[-(1 - XA)\,XA\,\frac{\ln\gamma_A}{(1 - XA)^2} + \int_0^{XA}\frac{\ln\gamma_A}{(1 - XA)^2}\,dXA\right]$$

$$-\frac{(a - 2\,b\,(-1 + XA))\,XA^2\,(T - \tau)}{R\,T\,\tau}$$

■ Create Your Own Non-Ideal, Binary Solution

■ Ideal Solution Starting Point

The subsequeent calculations will only be for excess functions. To plot total function, these excess functions should be added to the following ideal solutions results:

$$\Delta\text{Gmid} = \text{R T} (\text{XA Log}[\text{XA}] + (1 - \text{XA}) \text{Log}[1 - \text{XA}])$$

$$R\,T\,((1 - XA)\,Log[1 - XA] + XA\,Log[XA])$$

$$\Delta\text{Smid} = \text{Simplify}[-\partial_T \Delta\text{Gmid}]$$

$$-R\,(-(-1 + XA)\,Log[1 - XA] + XA\,Log[XA])$$

$$\Delta\text{Hmid} = \text{Simplify}[\Delta\text{Gmid} + \text{T}\,\Delta\text{Smid}]$$

$$0$$

■ Start From Activity Coefficient or Excess Free Energy

You can design a non-ideal solution by writing down any function for activity coefficient of component **A** that tells how it depends on temperature, pressure, and mole fraction. To create a solution, enter a function for $\ln\gamma_A$ using **T** for temperature, **P** for pressure, and **XA** for mole fraction of component **A**. Express everything using **XA**; for **XB**, use **(1-XA)** instead. **Note**: whatever function you select, it should approach **0** (or activity coefficient of **1**) as **XA->1** and should approach a Henry's law coefficient as **XA->0**.

$$\text{ln}\gamma_A = \frac{\left(a + \frac{b}{T} + c\,P\right)\left((1 - XA)^2 + d\,(1 - XA)^3\right)}{R\,T}$$

$$\frac{\left(a + c\,P + \frac{b}{T}\right)\left((1 - XA)^2 + d\,(1 - XA)^3\right)}{R\,T}$$

Alternatively, you can design a non-ideal solution by writing down an expression for excess free energy of mixing. As above, this function should be a function of **T** , **P**, and **XA**. For example, we could try

$$\Delta\text{GmXS} = \text{R T}\left(a + \frac{b}{T}\right)\text{Sin}[\pi\,\text{XA}]$$

$$R\left(a + \frac{b}{T}\right)T\,Sin[\pi\,XA]$$

From the excess free energy, we can calculate the partial molar excess free energy of **A**; dividing this result by **R T** gives $\ln\gamma_A$.

$$\texttt{ln}\gamma_A = \texttt{Simplify}\left[\frac{\Delta\texttt{GmXS} + (1 - \texttt{XA})\,\partial_{\texttt{XA}}\,\Delta\texttt{GmXS}}{\texttt{R T}}\right]$$

$$-\frac{(b + a\,T)\,(\pi\,(-1 + XA)\,Cos[\pi\,XA] - Sin[\pi\,XA])}{T}$$

Now both approaches have been expressed in terms of $\mathbf{ln}\boldsymbol{\gamma}_A$. The remainder of this section thus derives all terms for the solution from that result. Here the sample results are based on the first $\mathbf{ln}\boldsymbol{\gamma}_A$ given above. Result based on **ΔGmXS** could easily be created by reevaluating all equations.

Activity Coefficients: Using the Gibbs-Duhem equation and its application for calculating activity coefficients, we can calculate $\mathbf{ln}\boldsymbol{\gamma}_B$ from $\mathbf{ln}\boldsymbol{\gamma}_A$ using the following form of the “alpha” equation (which has been transformed from the equation in the text to be an integral of **XA** instead of over **XB**):

$$\texttt{ln}\gamma_B = \texttt{Simplify}\left[-(1 - \texttt{XA})\,\texttt{XA}\,\frac{\texttt{ln}\gamma_A}{(1 - \texttt{XA})^2} + \int_0^{\texttt{XA}} \frac{\texttt{ln}\gamma_A}{(1 - \texttt{XA})^2}\,d\texttt{XA}\right]$$

$$-\frac{(b + (a + c\,P)\,T)\,XA^2\,(-2 + d\,(-3 + 2\,XA))}{2\,R\,T^2}$$

Excess Functions: Using the above activity coefficients we can easily calculate all excess functions. The simplest method is to calculate ΔGmXS first and then differentiate it to find the other functions. Alternatively, the other excess functions could be determined directly from activity coefficients.

$$\Delta\texttt{GmXS} = \texttt{Simplify}[\texttt{R T}\,(\texttt{XA ln}\gamma_A + (1 - \texttt{XA})\,\texttt{ln}\gamma_B)]$$

$$\frac{(b + (a + c\,P)\,T)\,(-2 + d\,(-2 + XA))\,(-1 + XA)\,XA}{2\,T}$$

$$\Delta\texttt{SmXS} = \texttt{Simplify}[-\partial_T\,\Delta\texttt{GmXS}]$$

$$\frac{b\,(-2 + d\,(-2 + XA))\,(-1 + XA)\,XA}{2\,T^2}$$

$$\Delta\texttt{HmXS} = \texttt{Simplify}[\Delta\texttt{GmXS} + \texttt{T}\,\Delta\texttt{SmXS}]$$

$$\frac{(2\,b + (a + c\,P)\,T)\,(-2 + d\,(-2 + XA))\,(-1 + XA)\,XA}{2\,T}$$

$$\Delta\texttt{VmXS} = \texttt{Simplify}[\partial_P\,\Delta\texttt{GmXS}]$$

$$\frac{1}{2}\,c\,(-2 + d\,(-2 + XA))\,(-1 + XA)\,XA$$

Partial Molar Excess Functions: Using the “method of tangents” which was calculated from the Gibbs-Duhem equation, we can calculate partial molar excess functions from each of the above excess functions:

$$\Delta\texttt{GmAXS} = \texttt{Simplify}[\Delta\texttt{GmXS} + (1 - \texttt{XA})\,\partial_{\texttt{XA}}\,\Delta\texttt{GmXS}]$$

$$-\frac{(b + (a + c\,P)\,T)\,(-1 + d\,(-1 + XA))\,(-1 + XA)^2}{T}$$

```
ΔGmBXS = Simplify[ΔGmXS - XA ∂XA ΔGmXS]
```

$$-\frac{(b+(a+c\,P)\,T)\,XA^2\,(-2+d\,(-3+2\,XA))}{2\,T}$$

```
ΔSmAXS = Simplify[ΔSmXS + (1 - XA) ∂XA ΔSmXS]
```

$$-\frac{b\,(-1+d\,(-1+XA))\,(-1+XA)^2}{T^2}$$

```
ΔSmBXS = Simplify[ΔSmXS - XA ∂XA ΔSmXS]
```

$$\frac{b\,(2+d\,(3-2\,XA))\,XA^2}{2\,T^2}$$

```
ΔHmAXS = Simplify[ΔHmXS + (1 - XA) ∂XA ΔHmXS]
```

$$-\frac{(2\,b+(a+c\,P)\,T)\,(-1+d\,(-1+XA))\,(-1+XA)^2}{T}$$

```
ΔHmBXS = Simplify[ΔHmXS - XA ∂XA ΔHmXS]
```

$$-\frac{(2\,b+(a+c\,P)\,T)\,XA^2\,(-2+d\,(-3+2\,XA))}{2\,T}$$

```
ΔVmAXS = Simplify[ΔVmXS + (1 - XA) ∂XA ΔVmXS]
```

$$-c\,(-1+d\,(-1+XA))\,(-1+XA)^2$$

```
ΔHmBXS = Simplify[ΔVmXS - XA ∂XA ΔVmXS]
```

$$\frac{1}{2}\,c\,(2+d\,(3-2\,XA))\,XA^2$$

Alternate Methods: By using the various equations derived from the Gibbs-Duhem analysis, many of the ablve resutls could be calculated by alternate methods. For example, ΔGmXS can be calculated directly from $\ln\gamma_A$ using

```
ΔGmXS = Simplify[R T (1 - XA) Integrate[
   lnγA/(1 - XA)^2, {XA, 0, XA}, Assumptions -> {XA < 1, XA > 0}]]
```

$$\frac{(b+(a+c\,P)\,T)\,(-2+d\,(-2+XA))\,(-1+XA)\,XA}{2\,T}$$

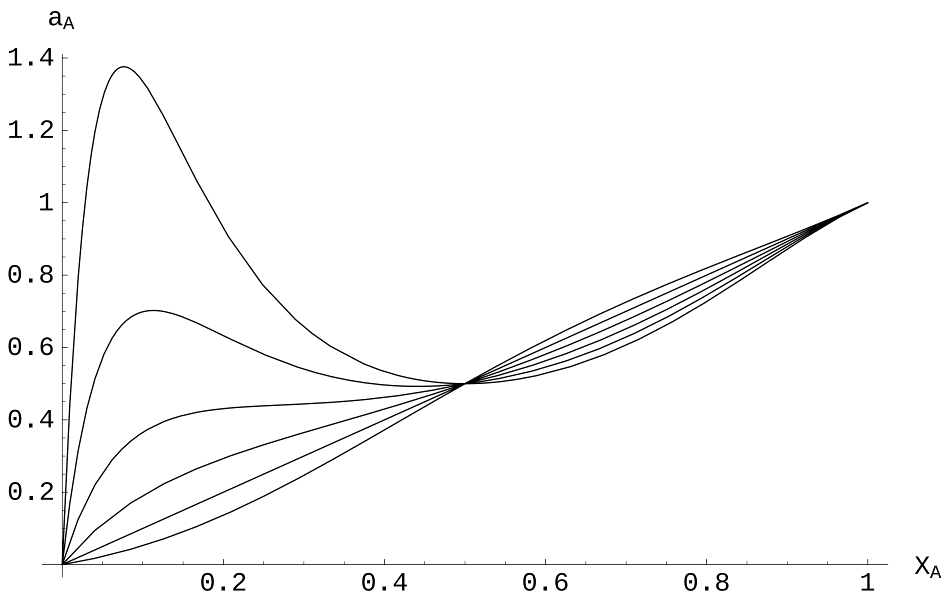
Plotting Parameters: The rest of this section is to plot the results for the above solution. To do those plots, you need to define some set of parameters. Using the following table command, create a table of tables where each element is a set of parameters for subsequent plots. To create different plots, redefine the parameters and execute the plot functions again.

```
parameters =
Table[{R -> 1, T -> 1, P -> 1 , a -> 1, b -> value, c -> -2 , d -> -2} ,
    {value, -3, 2, 1}]
```

```
{{R → 1, T → 1, P → 1, a → 1, b → -3, c → -2, d → -2},
 {R → 1, T → 1, P → 1, a → 1, b → -2, c → -2, d → -2},
 {R → 1, T → 1, P → 1, a → 1, b → -1, c → -2, d → -2},
 {R → 1, T → 1, P → 1, a → 1, b → 0, c → -2, d → -2},
 {R → 1, T → 1, P → 1, a → 1, b → 1, c → -2, d → -2},
 {R → 1, T → 1, P → 1, a → 1, b → 2, c → -2, d → -2}}
```

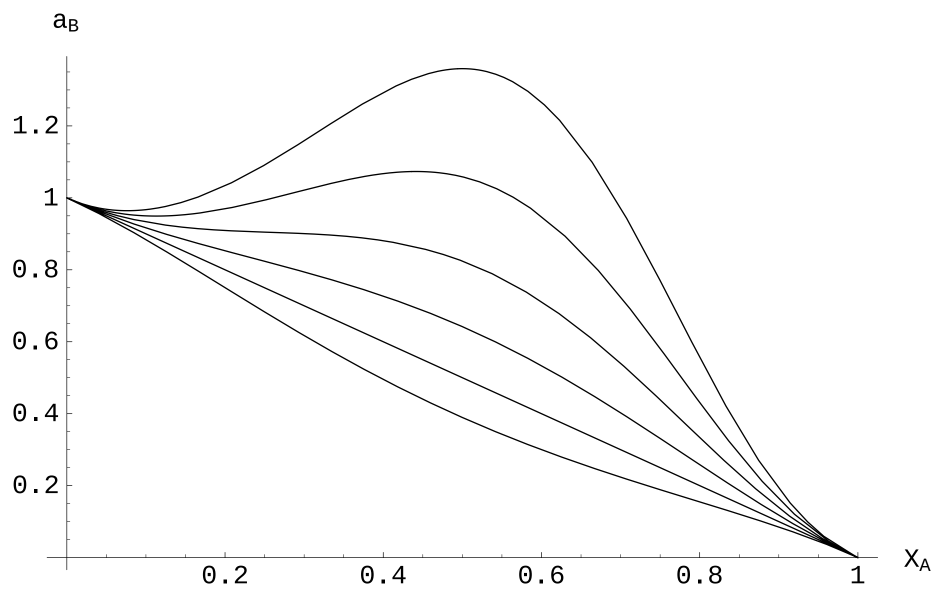
Activity Coefficients of Components A and B:

```
Plot[ Release[XA Exp[lnγA] /. parameters ],
  {XA, 0, 1}, AxesLabel -> {"XA", "aA"}]
```



- Graphics -

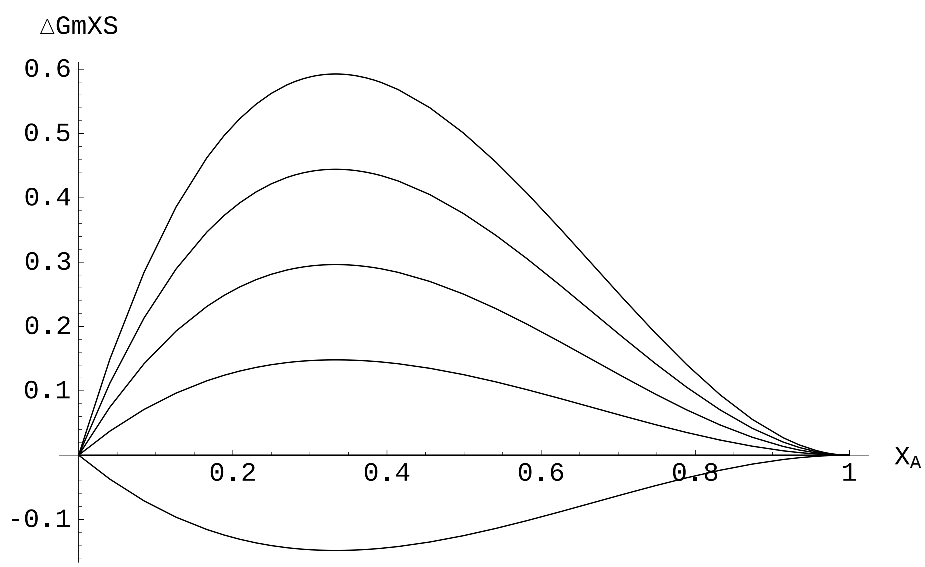
```
Plot[ Release[(1 - XA) Exp[lnγB] /. parameters ],
    {XA, 0, 1}, AxesLabel -> {"XA", "aB"}]
```



- Graphics -

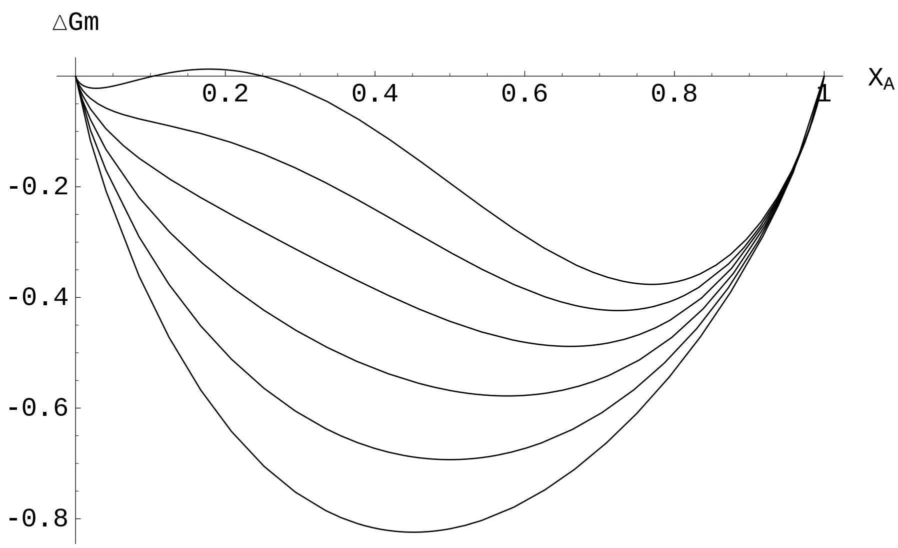
Excess and Total Free Energy of Mixing

```
Plot[ Release[ΔGmXS /. parameters ],
  {XA, 0, 1}, AxesLabel -> {"XA", "ΔGmXS"}]
```



- Graphics -

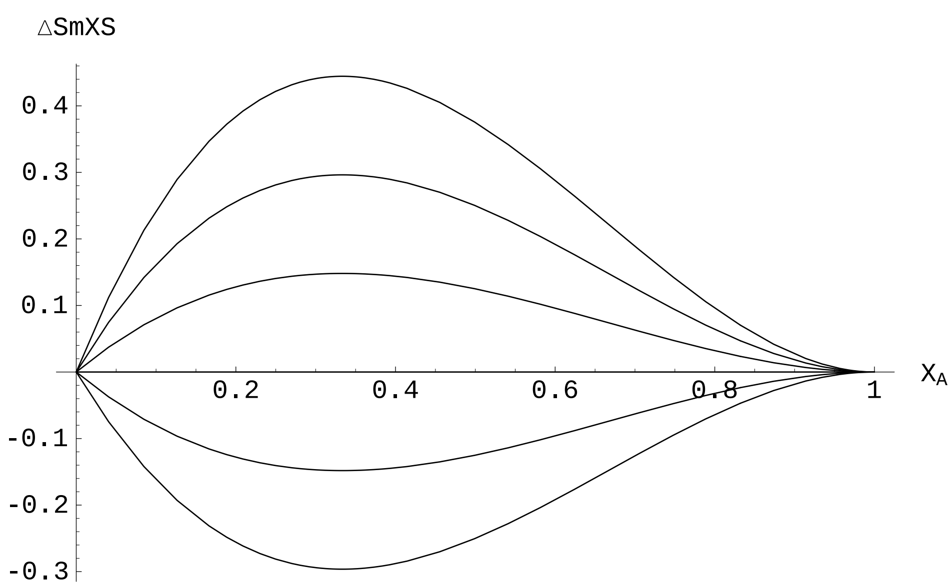
```
Plot[ Release[ΔGmid + ΔGmXS /. parameters ],
  {XA, 0, 1}, AxesLabel -> {"XA", "ΔGm"}]
```



- Graphics -

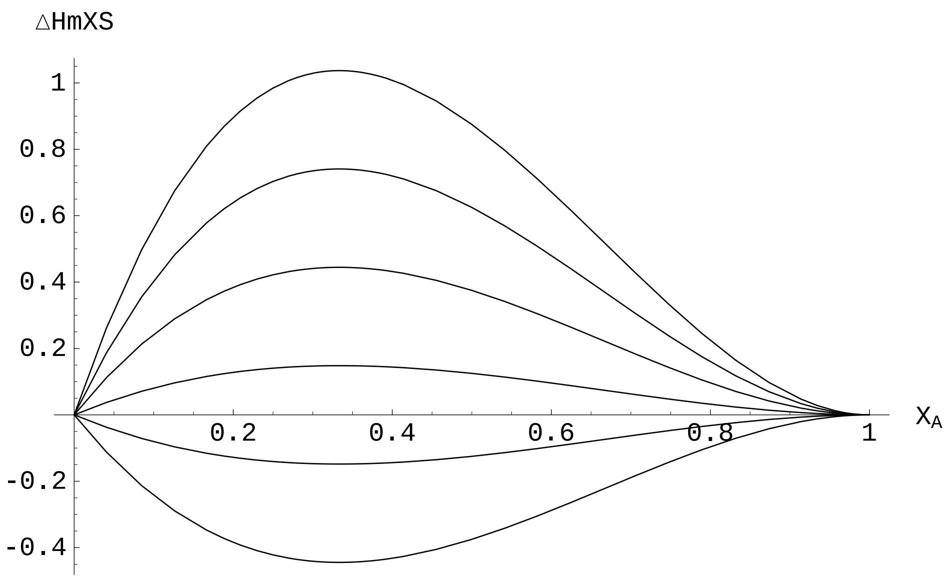
Excess Entropy, Enthalpy, and Volume

```
Plot[ Release[ΔSmXS /. parameters ],
{XA, 0, 1}, AxesLabel -> {"XA", "ΔSmXS"}]
```



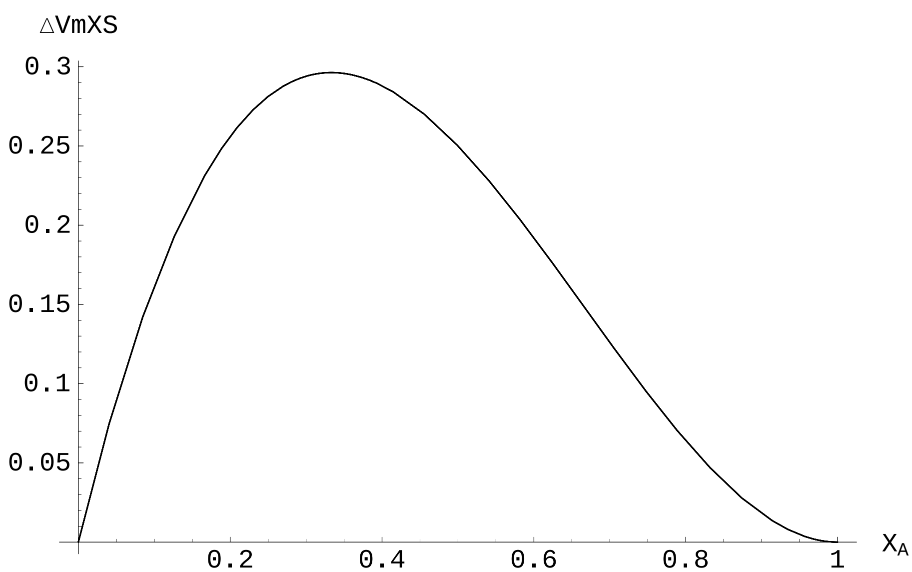
- Graphics -

```
Plot[ Release[ΔHmXS /. parameters ],
{XA, 0, 1}, AxesLabel -> {"XA", "ΔHmXS"}]
```



- *Graphics* -

```
Plot[ Release[ΔVmXS /. parameters ],
{XA, 0, 1}, AxesLabel -> {"XA", "ΔVmXS"}]
```



- *Graphics* -

Problems

Problem 9.1

a. Enthal;py: From table A-5, **ΔHm** for $\mathbf{Al_2\ O_3}$ is **107500 J** and its melting point is **Tm=2324K**. This data suffices to calculate ΔSm as

```
ΔSm = N[107500/2324]
```

46.2565

As stated in the problem, this is also the entropy of melting for $\mathbf{Cr_2\ O_3}$ (I do not know why the text simply did not include ΔHm for the $\mathbf{Cr_2\ O_3}$ in Table A-5 instead of using this arbitrary relation given in this problem). Given the entropy of melring, the enthlapy of melting of $\mathbf{Cr_2\ O_3}$ for its melting point or

```
ΔHm = ΔSm Tm /. {Tm -> 2538}
```

117399.

Assuming this enthalpy of melting is independent of temperature and that the solution is ideal (as stated) and therefore contributes no extra enthalpy effects, this result is the total enthalpy change on disolving solid $\mathbf{Cr_2\ O_3}$ into the liquid solution.

b. To get the total enropy change we add the entropy of melting to the entropy change on disolving the $\mathbf{Cr_2\ O_3}$. It is stated that the solution is very large, thus the entropy change is just the entropy of the added component which, for 1 mole added, is just the partial molar entropy of that component. Thus

```
ΔStotal = ΔSm - R Log[XA] /. {R -> 8.3144 , XA -> 0.2}
```

59.638

Problem 9.2

Assuming the gas is made up of 1 mole of argon gas and the evaporated Mn gas, the partial pressure due to Mn gas comes from its mole fraction in the total gas which is stated to be at 1 atm:

$$\text{pMn} = \frac{1.5}{\text{massMn}} \Big/ \left(1 + \frac{1.5}{\text{massMn}}\right)$$

$$\frac{1.5}{\left(1 + \frac{1.5}{\text{massMn}}\right)\text{massMn}}$$

To get activity, we need to find the vapor pressure of pure Mn. Using the results in Table A-4, the pure pressure is

```
pMnPure = Exp[lnvapMn /. T -> 1863]
```

E^{lnvapMn}

Thus the activity is

```
aMn = pMn / pMnPure
```

$$\frac{1.5\, E^{-\text{lnvapMn}}}{\left(1+\frac{1.5}{\text{massMn}}\right)\text{massMn}}$$

Finally, dividing by the mole fraction gives the activity coefficient:

```
gammaMn = aMn / XMn /. XMn -> 0.5
```

$$\frac{3.\, E^{-\text{lnvapMn}}}{\left(1+\frac{1.5}{\text{massMn}}\right)\text{massMn}}$$

- **Problem 9.3***

a. If the solution is regular than **ΔGmXS** should be **Ω XA XB**. In other words, **ΔGmXS/(XA XB)** should be constant and equal to the regular solution interaction term. Evaluating that ratio for the result in the book gives

```
GmXS = {395, 703, 925, 1054, 1100, 1054, 925, 703, 395};
```

$$\Omega\text{test} = \text{Table}\left[\frac{\text{GmXS}[[i]]}{0.1\, i\, (1-0.1\, i)}, \{i, 1, 9\}\right]$$

```
{4388.89, 4393.75, 4404.76, 4391.67,
4400., 4391.67, 4404.76, 4393.75, 4388.89}
```

Thus **Ω** is constant and equal to **4400 J**. This constant **Ω** does not prove the solution is regular. To prove that there would have to ba additional experiments showing that the entropy of mixing is zero and therefore the excess enthalpy is equal to the excess free energy (note: I think the book got **Ω** wrong and is off by a factor of **4**).

b. The partial molar quantities for a regular solution are given by

$$\text{GFeXS} = \text{XB}^2\, \Omega \text{ /. } \{\text{XB} \to 0.6,\ \Omega \to 4400\}$$

$$4400\, \text{XB}^2$$

$$\text{GFeMn} = \text{XA}^2\, \Omega \text{ /. } \{\text{XA} \to 0.4,\ \Omega \to 4400\}$$

$$4400\, \text{XA}^2$$

c. The total free emergy of mixing is

```
ΔGm = R T (XA Log[XA] + XB Log[XB]) + Ω XA XB /.
{R -> 8.3144, T -> 1863 , XA -> 0.4 , XB -> 0.6, Ω -> 4400}
```

$$-10424.8 + 4400\, \text{XA}\, \text{XB}$$

d. First we need to get the activities from the partial molar free energies

```
aFe = Exp[XB^2 Ω/(R T) + Log[XA]] /.
  {R -> 8.3144, XB -> 0.2 , XA -> 0.8, T -> 1863, Ω -> 4400}
```

$$E^{-0.223144+\frac{4400\,XB^2}{R\,T}}$$

```
aMn = Exp[XA^2 Ω/(R T) + Log[XB]] /.
  {R -> 8.3144, XB -> 0.2 , XA -> 0.8, T -> 1863, Ω -> 4400}
```

$$E^{-1.60944+\frac{4400\,XA^2}{R\,T}}$$

The pure vapor pressures are

```
pFePure = Exp[lnvapFe /. T -> 1863]
```

$$E^{lnvapFe}$$

```
pMnPure = Exp[lnvapMn /. T -> 1863]
```

$$E^{lnvapMn}$$

Finally, the partial vapor pressures over the solutions are

```
pFe = aFe pFePure
```

$$E^{-0.223144+lnvapFe+\frac{4400\,XB^2}{R\,T}}$$

```
pMn = aMn pMnPure
```

$$E^{-1.60944+lnvapMn+\frac{4400\,XA^2}{R\,T}}$$

(Note: all results above agree with the book solution if Ω=1052 instead of 4400 as found here).

- **Problem 9.4**

The heat required is the total changein enthalpy. First, we have to use the methods of Chapter 6 to find the enthalpy required to heat 1 mole of Cu and 1 mole of Ag from 298K to 1356 K. Accounting for

$$\Delta HCu = \int_{298}^{1356} CpCu\, dT + \Delta HmCu \;/.\; \{\Delta HmCu \to 12970\}$$

$$12970 + 1058\,CpCu$$

$$\Delta\text{HAg} = \int_{298}^{1234} \text{CpAgs}\, dT + \Delta\text{HmAg} + \int_{1234}^{1356} \text{CpAgl}\, dT \; /. \; \{\Delta\text{HmAg} \to 11090\}$$

$$11090 + 122\,\text{CpAgl} + 936\,\text{CpAgs}$$

Next, these two liquids are mixed with the resulting excess enthalpy of

$$\Delta\text{HXS} = 2\,(\Omega\,\text{XA}\,(1 - \text{XA}))\; /. \;\{\text{XA} \to 0.5,\ \Omega \to -20590\}$$

$$-41180\,(1 - \text{XA})\,\text{XA}$$

The total heat required is the sum of these three enthalpies

$$\Delta\text{HCu} + \Delta\text{HAg} + \Delta\text{HXS}$$

$$24060 + 122\,\text{CpAgl} + 936\,\text{CpAgs} + 1058\,\text{CpCu} - 41180\,(1 - \text{XA})\,\text{XA}$$

■ Problem 9.5

a. For a regular solution, natural log of activity is given by

$$\text{lnaPb} = \frac{(1 - \text{XPb})^2\,\Omega}{R\,T} + \text{Log}[\text{XPb}];$$

We can thus find Ω by solving

$$\text{Solve}[\text{lnaPb} == \text{Log}[0.055],\ \Omega]\; /. \;\{R \to 8.3144,\ T \to 473 + 273,\ \text{XPb} \to 0.1\}$$

– *General::ivar :* $(a + b\,(1 - XA))\left(1 - \frac{T}{\tau}\right)$ *is not a valid variable.*

– *General::ivar :* $(a + b\,(1 - XA))\left(1 - \frac{746}{\tau}\right)$ *is not a valid variable.*

$$\text{Solve}\left[-2.30259 + 0.000130592\,(a + b\,(1 - XA))\left(1 - \frac{746}{\tau}\right) == -2.90042,\ (a + b\,(1 - XA))\left(1 - \frac{746}{\tau}\right)\right]$$

b. To find any other activity, use the appropriate formula for a regular solution. Here

$$\text{aSn} = \text{Exp}\left[\frac{(1 - \text{XSn})^2\,\Omega}{R\,T} + \text{Log}[\text{XSn}]\right]\; /. \;\{R \to 8.3144,\ T \to 473 + 273,\ \text{XSn} \to 0.5,\ \Omega \to -4577.91\}$$

$$E^{-0.693147 - \frac{4577.91\,(1 - XSn)^2}{R\,T}}$$

■ Problem 9.6

This problem has to be solved by graphical or numerical integration which is hard to in *Mathematica*. The method used here is to fit the data to a function and then use *Mathematica* methods to numercially integrate the results.

a. Use Eq. (9.55): Here is the data from the problem as x-y pairs of moles fraction and activity of Cu **(XB, aB)** (here **B** is for Cu and **A** is for Fe)

```
aCuData = {{1, 1}, {0.9, .935}, {0.8, .895},
  {0.7, .865}, {0.6, .850}, {0.5, .830}, {0.4, .810},
  {0.3, 0.780}, {0.2, .720}, {0.1, .575}, {0.05, .40}};
```

This table divides the activity by mole fraction to get x-y pairs of **(XB,γB)**:

```
γCuData = Table[{aCuData[[i, 1]], aCuData[[i, 2]] / aCuData[[i, 1]]}, {i, 1, 11}]
```

```
{{1, 1}, {0.9, 1.03889}, {0.8, 1.11875},
 {0.7, 1.23571}, {0.6, 1.41667}, {0.5, 1.66}, {0.4, 2.025},
 {0.3, 2.6}, {0.2, 3.6}, {0.1, 5.75}, {0.05, 8.}}
```

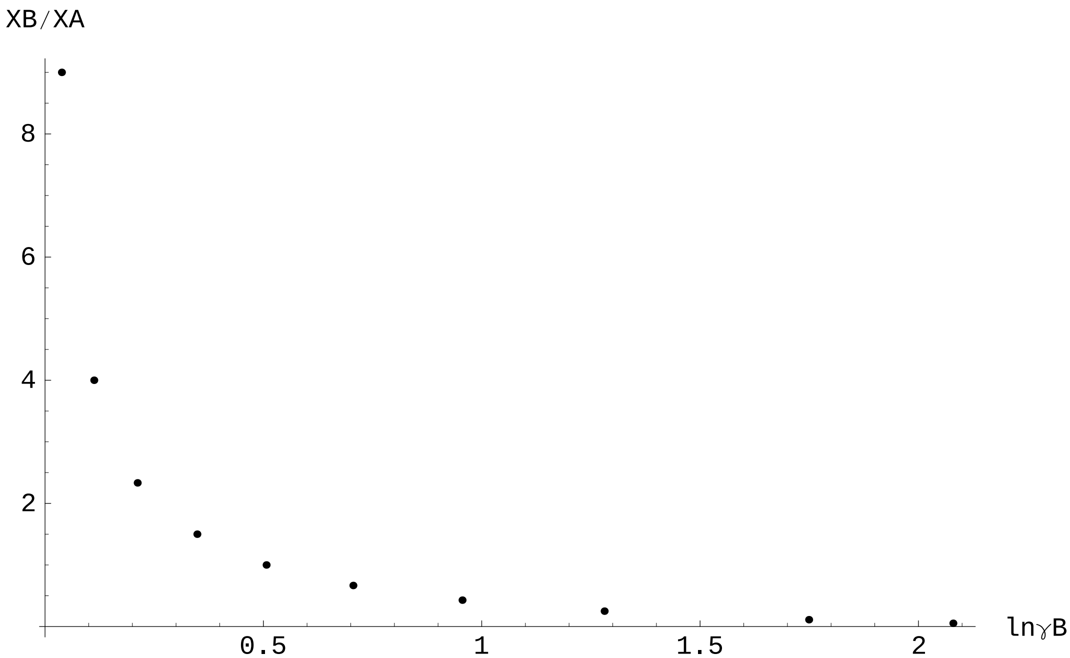
For equation (9.55) we need to integrate **XB/XA** as a function of **lnγB**. This tables has the x-y pairs for **(XB/XA, lnγB).** The frist point is left off because **XB/XA** is infinite when **XA=0**:

```
eq955Data =
 Table[{Log[γCuData[[i, 2]]], aCuData[[i, 1]] / (1 - aCuData[[i, 1]])}, {i, 2, 11}]
```

```
{{0.0381518, 9.}, {0.112212, 4.},
 {0.211649, 2.33333}, {0.348307, 1.5}, {0.506818, 1.},
 {0.70557, 0.666667}, {0.955511, 0.428571},
 {1.28093, 0.25}, {1.7492, 0.111111}, {2.07944, 0.0526316}}
```

Here is a plot of the points which is the same as Fig 9.15 in the text (except that here I am using natural log instead of base 10 log, this change scales the x axis by 2.303):

```
dp = ListPlot[eq955Data, AxesLabel -> {"lnγB", "XB/XA"}]
```



- *Graphics* -

To do calculations in *Mathematica*, one method is to fit the data and then numerically integrate the fit function. Here the fit should include **1/x** terms because the function looks like a **1/x** plot.

```
eq955Fit = Fit[eq955Data, {1/x, 1, x, x^2, x^3}, x]
```

$$1.71542 + \frac{0.283895}{x} - 3.57707\,x + 2.49897\,x^2 - 0.577878\,x^3$$

We next need the integration limits. The lower limit is the intercept of the **XB/XA** plot with the **x** axis. Solving for where the fit is zero gives:

```
lowlim = Solve[eq955Fit == 0 , x]
```

$$\{\{x \to -0.128116\},\ \{x \to 1.17158 - 0.667313\,I\},\ \{x \to 1.17158 + 0.667313\,I\},\ \{x \to 2.10935\}\}$$

This the lower limit of the integration is **2.10935** which is **lnγB** when **XA=1**. For now the upper limit is just **lnγB**:

$$\text{ln}\gamma\text{A} = -\int_{2.10935}^{\text{ln}\gamma\text{B}} \text{eq955Fit}\, dx$$

$$0.830274 + 0.144469\,(-2.91747 + \text{ln}\gamma\text{B})\,(-1.03553\times10^{-15} + \text{ln}\gamma\text{B})\,(4.06993 - 2.84839\,\text{ln}\gamma\text{B} + \text{ln}\gamma\text{B}^2) - 0.283895\,\text{Log}[0. + \text{ln}\gamma\text{B}]$$

To convert to Fe activity coefficients, we insert the data for **lnγB** at each value of **XB**. This table thus gives **γA** as a function of **XB** in x-y pairs **(XB, γA)**:

```
γFeData = Table[{γCuData[[i + 1, 1]],
  Exp[lnγA] /. lnγB -> eq955Data[[i, 1]]} , {i, 1, 10}]
```

```
{{0.9, 5.44468}, {0.8, 3.59712}, {0.7, 2.66594},
 {0.6, 2.04645}, {0.5, 1.67248}, {0.4, 1.42267}, {0.3, 1.25957},
 {0.2, 1.14507}, {0.1, 1.03832}, {0.05, 1.00035}}
```

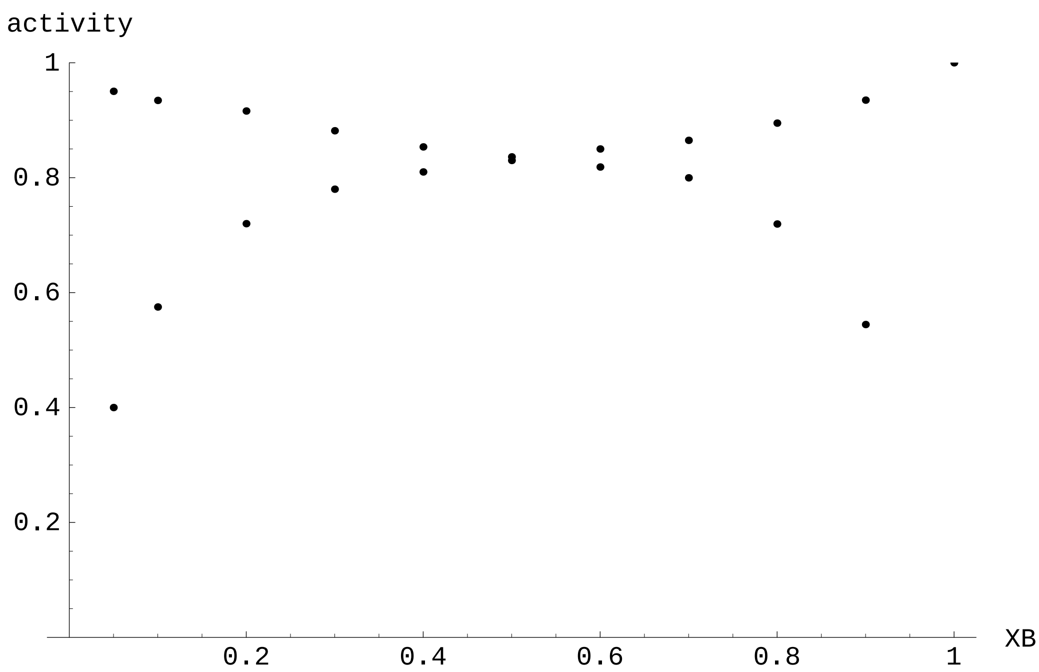
Finally, we get activity by multiplying by **XA = 1-XB**:

```
aFeData = Table[{γFeData[[i, 1]],
  γFeData[[i, 2]] (1 - γFeData[[i, 1]])}, {i, 1, 10}]
```

```
{{0.9, 0.544468}, {0.8, 0.719424}, {0.7, 0.799783}, {0.6, 0.818581},
 {0.5, 0.836241}, {0.4, 0.853601}, {0.3, 0.881697},
 {0.2, 0.916058}, {0.1, 0.93449}, {0.05, 0.950336}}
```

Here is a plot of the activity of Fe as calculated and compared to activity of Cu. This plot is identical to Fig 9.9 in the text:

```
ListPlot[Join[aCuData, aFeData],
  AxesLabel -> {"XB", "activity"}, PlotRange -> {0, 1}]
```



- Graphics -

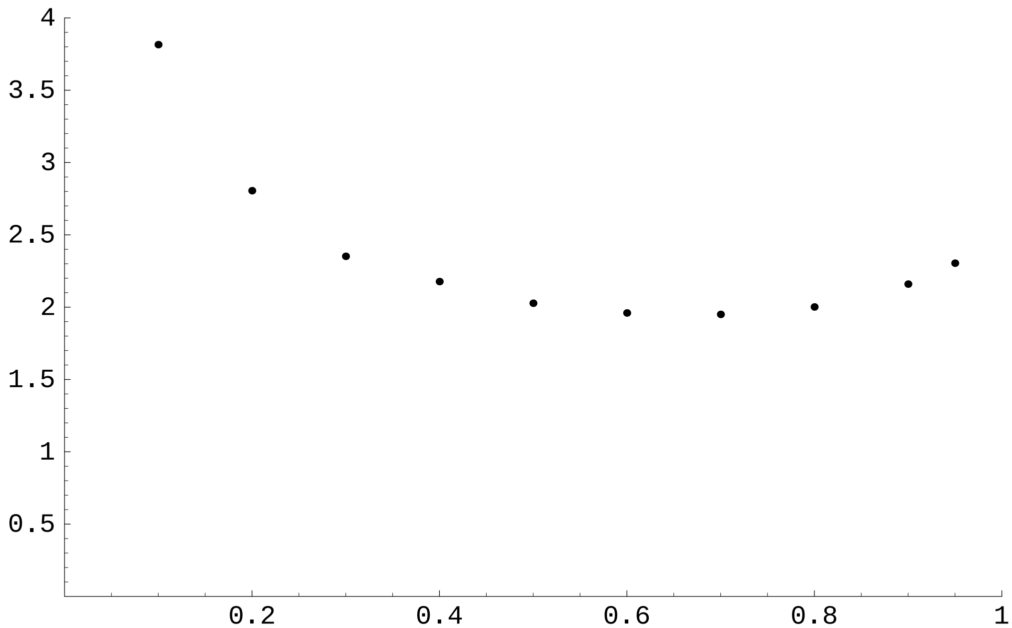
b. Use Eq. (9.61): Eq. (9.61) is the last equation on page 242 and it is not labeled. First we convert the activity coefficient data to x-y pairs of **(XA,αB)** which is the function that needs to be integrated:

```
eq961Data =
  Table[{1 - γCuData[[i, 1]], Log[γCuData[[i, 2]]] / (1 - γCuData[[i, 1]])^2}, {i, 2, 11}]
```

```
{{0.1, 3.81518}, {0.2, 2.8053}, {0.3, 2.35166},
 {0.4, 2.17692}, {0.5, 2.02727}, {0.6, 1.95992}, {0.7, 1.95002},
 {0.8, 2.00146}, {0.9, 2.15951}, {0.95, 2.30409}}
```

Here is a plot of αB. This should be the same as plot 9.17 in the text. It has the same form, but here I am using natural log instead of base 10 log. Thus the y axis here is scaled by a factor of 2.303.

```
ap = ListPlot[eq961Data, PlotRange -> {{0, 1}, {0, 4}}]
```




```
- Graphics -
```

Here is a good fit fuction. The **1/x** is required to get a nice fit:

```
eq961Fit = Fit[eq961Data, {1, 1/x, x, x^2, x^3}, x]
```

$$1.86931 + \frac{0.197163}{x} - 0.0315193\,x - 2.18802\,x^2 + 2.58653\,x^3$$

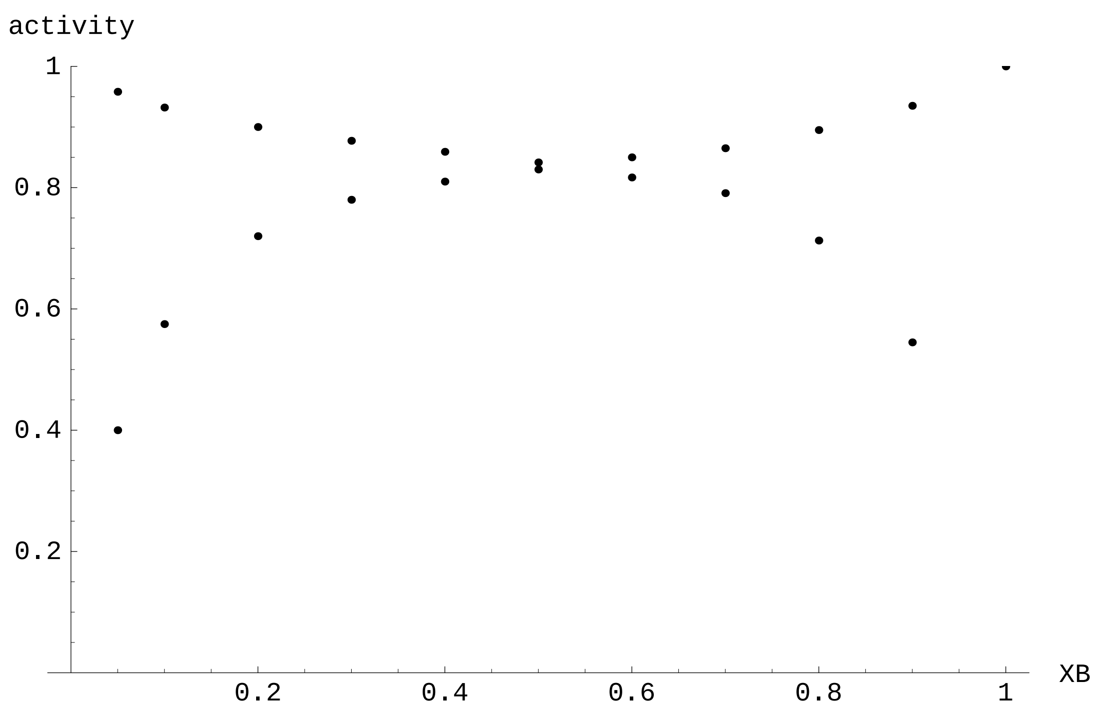
Finally, we do all the calculations in one step. These x-y pairs are **(XB,aA)** where **aA** is calculation equation (9.61). But, Eq. (9.61) gives **lnγA**; thus we have to use exponential to get activity coefficient and multiply by **XA** to get activity or **aA = XA Exp[lnγA]**:

```
aFe961 = Table[{1 - eq961Data[[i, 1]] , eq961Data[[i, 1]] Exp[
  - (1 - XA) XA alpha - ∫_1^XA eq961Fit ⅆx /. {XA -> eq961Data[[i, 1]],
      alpha -> eq961Data[[i, 2]]}] }, {i, 1, 10}]
```

```
{{0.9, 0.544856}, {0.8, 0.712799}, {0.7, 0.790949}, {0.6, 0.816825},
  {0.5, 0.841623}, {0.4, 0.859137}, {0.3, 0.877303},
  {0.2, 0.900018}, {0.1, 0.932132}, {0.05, 0.95813}}
```

Here is a plot of data which again is identical to Fig 9.9 in the text:

```
ListPlot[Join[aCuData, aFe961],
  AxesLabel -> {"XB", "activity"}, PlotRange -> {0, 1}]
```



- *Graphics* -

■ Problem 9.7

This problem is identical to Problem 9.6 except the data is different and we need to veroiify that the function forms used to fit the results for numerical integration are god fitting functions

a. Use Eq. (9.55): Here is the data from the problem as x-y pairs of moles fraction and activity of Ni **(XB, aB)** (here **B** is for Ni and **A** is for Fe)

```
aNiData = {{1, 1}, {0.9, .89},
  {0.8, .766}, {0.7, .62}, {0.6, .485}, {0.5, .374},
  {0.4, .283}, {0.3, 0.207}, {0.2, .136}, {0.1, .067}} ;
```

This table divides the activity by mole fraction to get x-y pairs of **(XB,γB)**:

```
γNiData = Table[{aNiData[[i, 1]], aNiData[[i, 2]]/aNiData[[i, 1]]}, {i, 1, 10}]

{{1, 1}, {0.9, 0.988889}, {0.8, 0.9575},
 {0.7, 0.885714}, {0.6, 0.808333}, {0.5, 0.748},
 {0.4, 0.7075}, {0.3, 0.69}, {0.2, 0.68}, {0.1, 0.67}}
```

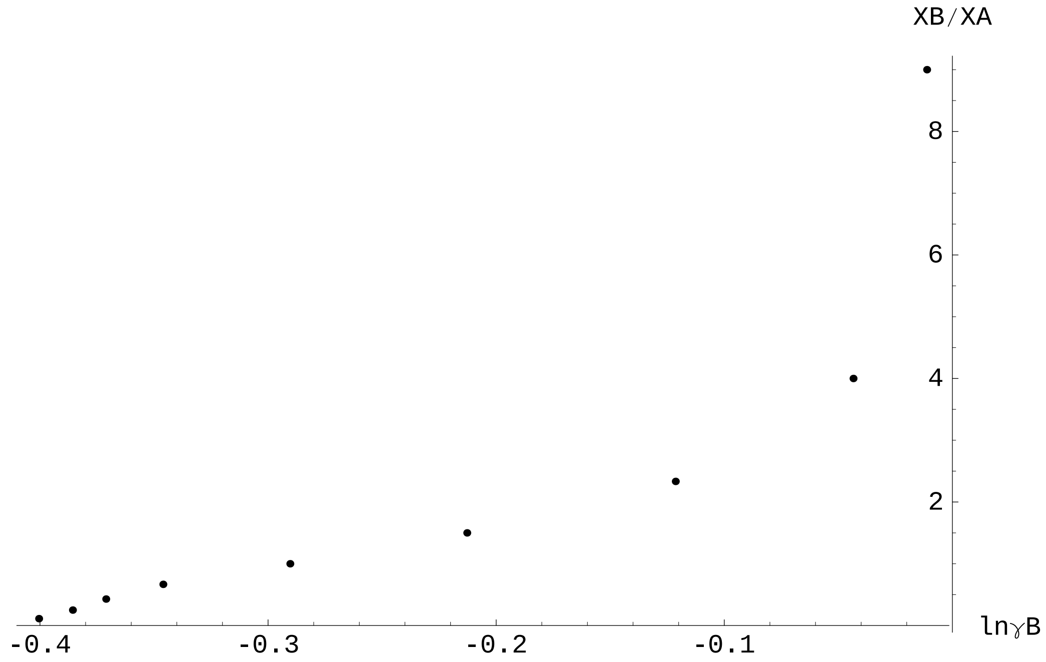
For equation (9.55) we need to integrate **XB/XA** as a function of **lnγB**. This tables has the x-y pairs for **(XB/XA, lnγB).** The frist point is left off because **XB/XA** is infinite when **XA=0**:

```
eq955Data =
Table[{Log[γNiData[[i, 2]]], aNiData[[i, 1]]/(1 - aNiData[[i, 1]])}, {i, 2, 10}]

{{-0.0111733, 9.}, {-0.0434296, 4.}, {-0.121361, 2.33333},
 {-0.212781, 1.5}, {-0.290352, 1.}, {-0.346018, 0.666667},
 {-0.371064, 0.428571}, {-0.385662, 0.25}, {-0.400478, 0.111111}}
```

Here is a plot of the points which is the same as Fig 9.14 in the text (except for a scaling of 2.303 in the x axis because of use of natural log instead of base 10 log)

```
dp = ListPlot[eq955Data, AxesLabel -> {"lnγB", "XB/XA"}]
```




```
- Graphics -
```

To do calculations in *Mathematica*, one method is to fit the data and then numerically integrate the fit function. Here the fit should include **1/x** terms because the function looks like a **1/x** plot.

```
eq955Fit = Fit[eq955Data, {1/x, 1, x, x^2, x^3}, x]
```

$$2.95126 - \frac{0.0692434}{x} + 13.845\,x + 38.2076\,x^2 + 55.8155\,x^3$$

We next need the integration limits. The lower limit is the intercept of the **XB/XA** plot with the **x** axis. Solving for where the fit is zero gives:

```
lowlim = Solve[eq955Fit == 0 , x]
```

```
{{x → -0.411755}, {x → -0.147001 - 0.346932 I},
 {x → -0.147001 + 0.346932 I}, {x → 0.0212219}}
```

This the lower limit of the integration is **-0.411755** which is **lnγB** when **XA=1**. For now the upper limit is just **lnγB**:

$$\ln\gamma A = -\int_{-0.411755}^{\ln\gamma B} \text{eq955Fit}\, dx$$

```
(-0.468087 - 0.217534 I) -
 13.9539 (7.52373×10^-17 + lnγB) (0.650056 + lnγB)
 (0.325358 + 0.262657 lnγB + lnγB^2) + 0.0692434 Log[0. + lnγB]
```

To convert to Fe activity coefficients, we insert the data for **lnγB** at each value of **XB**. This table thus gives **γA** as a function of **XB** in x-y pairs **(XB, γA)**:

```
γFeData = Table[{γNiData[[i + 1, 1]],
 Re[Exp[lnγA] /. lnγB -> eq955Data[[i, 1]]]} , {i, 1, 9}]
```

```
{{0.9, 0.473713}, {0.8, 0.565996}, {0.7, 0.713072},
 {0.6, 0.846538}, {0.5, 0.934413}, {0.4, 0.978622},
 {0.3, 0.991411}, {0.2, 0.996371}, {0.1, 0.999303}}
```

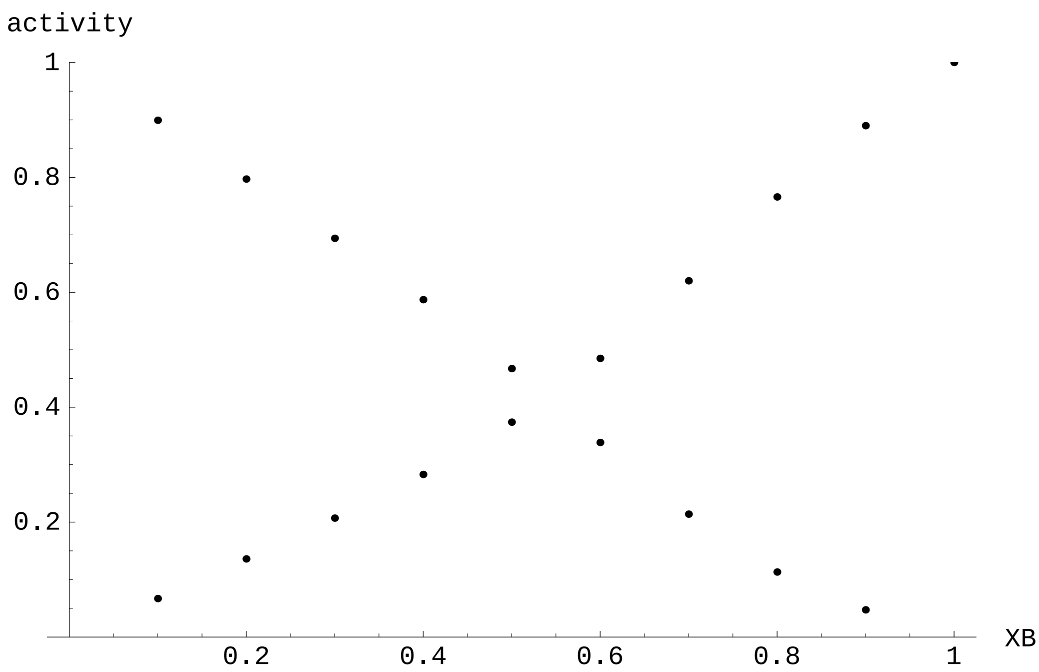
Finally, we get activity by multiplying by **XA = 1-XB**:

```
aFeData = Table[{γFeData[[i, 1]],
 γFeData[[i, 2]] (1 - γFeData[[i, 1]])}, {i, 1, 9}]
```

```
{{0.9, 0.0473713}, {0.8, 0.113199}, {0.7, 0.213922},
 {0.6, 0.338615}, {0.5, 0.467206}, {0.4, 0.587173},
 {0.3, 0.693988}, {0.2, 0.797097}, {0.1, 0.899373}}
```

Here is a plot of the activity of Fe as calculated and compared to activity of Ni. This plot is identical to Fig 9.8 in the text:

```
ListPlot[Join[aNiData, aFeData],
  AxesLabel -> {"XB", "activity"}, PlotRange -> {0, 1}]
```




```
- Graphics -
```

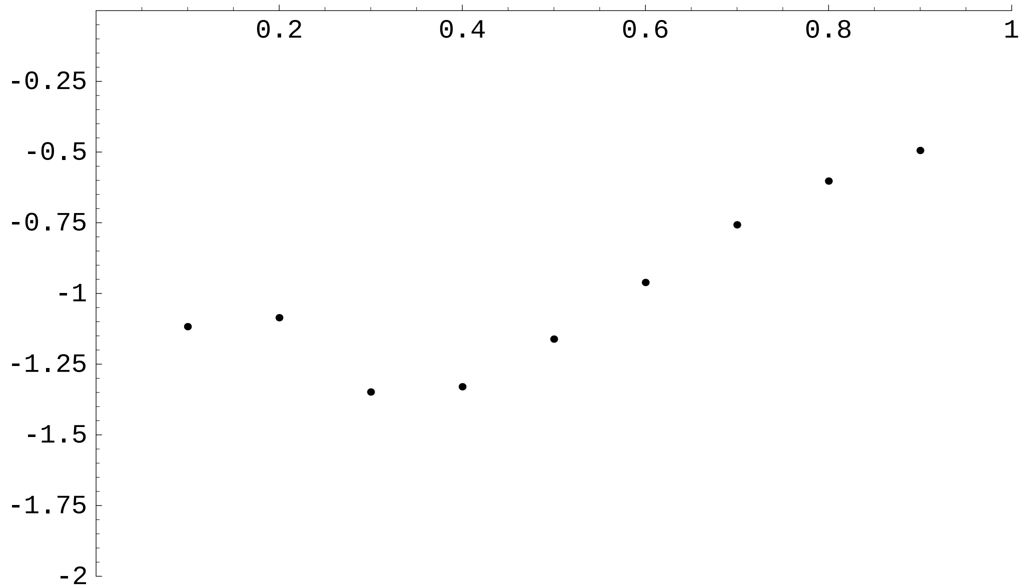
b. Use Eq. (9.61): Eq. (9.61) is the last equation on page 242 and it is not labeled. First we convert the activity coefficient data to x-y pairs of **(XA,αB)** which is the function that needs to be integrated:

```
eq961Data =
  Table[{1 - γNiData[[i, 1]], Log[γNiData[[i, 2]]] / (1 - γNiData[[i, 1]])^2}, {i, 2, 10}]
```

```
{{0.1, -1.11733}, {0.2, -1.08574}, {0.3, -1.34845},
 {0.4, -1.32988}, {0.5, -1.16141}, {0.6, -0.96116},
 {0.7, -0.757273}, {0.8, -0.602598}, {0.9, -0.494417}}
```

Here is a plot of αB. This should be the same as plot 9.16 in the text. It has the same form, but scaled here by 2.303 because of the use of natural logs instead of base 10 logs. Also the plot reversed the direction of the y axis and this this plot is also a mirror image of the book plot.

```
ap = ListPlot[eq961Data, PlotRange -> {{0, 1}, {-2, 0}}]
```



- *Graphics* -

Here is a good fit fuction. The **1/x** is required to get a nice fit:

```
eq961Fit = Fit[eq961Data, {1, x, x^2, x^3}, x]
```

$$-0.689222 - 4.48737\,x + 9.54183\,x^2 - 4.76855\,x^3$$

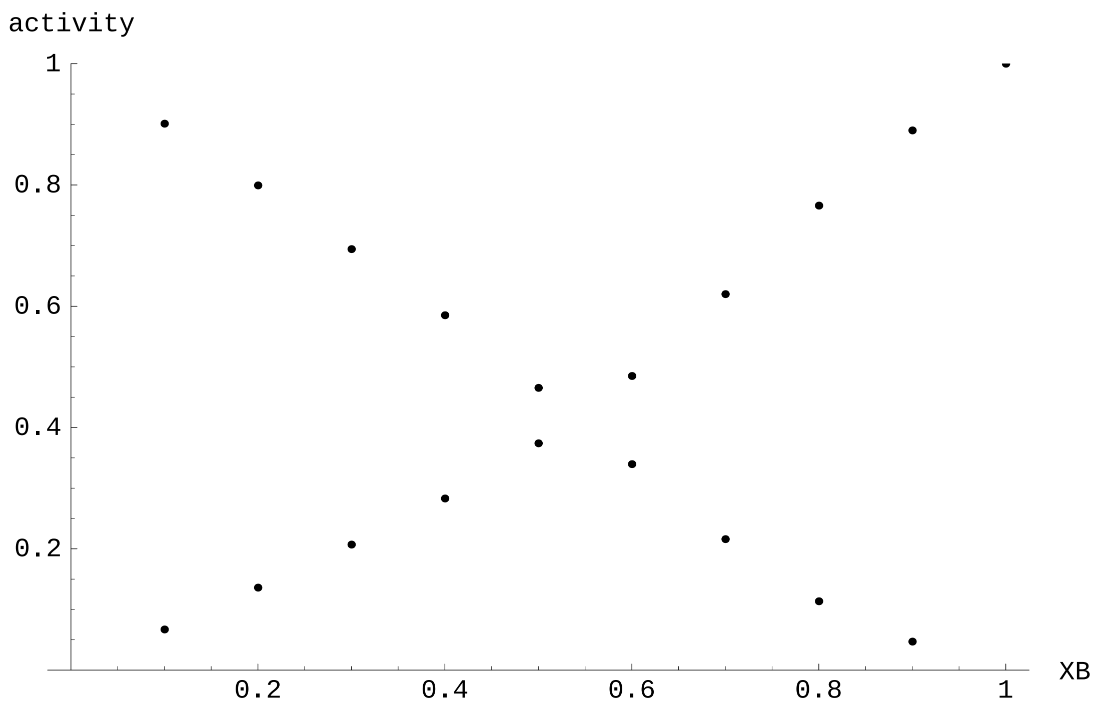
Finally, we do all the calculations in one step. These x-y pairs are **(XB,aA)** where **aA** is calculation equation (9.61). But, Eq. (9.61) gives **lnγA**; thus we have to use exponential to get activity coefficient and multiply by **XA** to get activity or **aA = XA Exp[lnγA]**:

$$\text{aFe961} = \text{Table}\left[\left\{1 - \text{eq961Data}[[i,1]],\ \text{eq961Data}[[i,1]]\ \text{Exp}\left[-(1-\text{XA})\,\text{XA alpha} - \int_1^{\text{XA}} \text{eq961Fit}\,dx\ /.\ \{\text{XA} \to \text{eq961Data}[[i,1]],\ \text{alpha} \to \text{eq961Data}[[i,2]]\}\right]\right\},\ \{i, 1, 9\}\right]$$

```
{{0.9, 0.046974}, {0.8, 0.113483}, {0.7, 0.21594},
 {0.6, 0.339624}, {0.5, 0.465444}, {0.4, 0.585182},
 {0.3, 0.69424}, {0.2, 0.799316}, {0.1, 0.901121}}
```

Here is a plot of data which again is identical to Fig 9.8 in the text:

```
ListPlot[Join[aNiData, aFe961],
  AxesLabel -> {"XB", "activity"}, PlotRange -> {0, 1}]
```



- Graphics -

■ Problem 9.8*

When one mole of a substance is added to a large amount of a substance, the dilute substance is in the Henrian limit while the other substance is in the ideal or Raoult's limit. The total enthalpy change is the partial molar enthalpy of the dilute substanct times the number of moles of the diluite substance. Using the formula for partial molar enthalpy we find

$$\Delta HmA = -nA\, R\, T^2\, \partial_T \left(\frac{-840}{T} + 1.58\right) \;/.\; nA \to 1$$

$$-840\, R$$

This result is negative and thus heat is released. In adiabatic conditions, this heat increased the temperature of the allow according to its heat capacity:

```
Solve[n Cp ΔT == - ΔHmA /. {n -> 100, Cp -> 29.5, R -> 8.3144} , ΔT]
```

$\{\{\Delta T \to 2.36749\}\}$

This result is a factor of 10 lower than the book solution.

Problem 9.10

This problem is most easily calculated using Eq. (9.61)

$$\text{ln}\gamma\text{Zn} = \text{a1 XCd}^2 + \text{a2 XCd}^3$$

$$a1\ XCd^2 + a2\ XCd^3$$

which is substituted into Eq. (9.61)

$$\text{ln}\gamma\text{Cd} = \text{Simplify}\left[-(1-\text{XCd})\ \text{XCd}\ \frac{\text{ln}\gamma\text{Zn}}{\text{XCd}^2} - \int_1^{\text{XCd}} \frac{\text{ln}\gamma\text{Zn}}{\text{XCd}^2}\, d\text{XCd}\right]$$

$$\frac{1}{2}\ (-1 + XCd)^2\ (2\ a1 + a2 + 2\ a2\ XCd)$$

$$\text{Expand[Simplify[ln}\gamma\text{Cd /. \{XCd -> 1 - XZn , a1 -> 0.875, a2 -> -.3\}]]}$$

$$0.425\ XZn^2 + 0.3\ XZn^3$$

Thus activity of **Cd** is when **XCd=0.5** is

$$\text{aCd = XCd Exp[ln}\gamma\text{Cd] /. \{XCd -> 0.5, a1 -> 0.875, a2 -> -0.3\}}$$

$$0.577298$$

Problem 9.11*

The activity coefficients can be calculated from the method of tangents applied to the excess free energy of mixing which is given as

$$\Delta\text{GmXS} = \text{XNi}\ (1-\text{XNi})\ (24140\ (1-\text{XNi}) + 38280\ \text{XNi} - 14230\ \text{XNi}\ (1-\text{XNi}))\left(1 - \frac{\text{T}}{2660}\right)$$

$$\left(1 - \frac{T}{2660}\right)\ (1 - XNi)\ XNi\ (24140\ (1 - XNi) + 38280\ XNi - 14230\ (1 - XNi)\ XNi)$$

The full activity coefficients are

$$\text{ln}\gamma\text{Ni} = \text{Simplify}\left[\frac{\Delta\text{GmXS} + (1-\text{XNi})\ \partial_{\text{XNi}}\ \Delta\text{GmXS}}{\text{R T}}\right]$$

$$-\frac{(-2660 + T)\ (-1 + XNi)^2\ (2414 - 18\ XNi + 4269\ XNi^2)}{266\ R\ T}$$

$$\text{ln}\gamma\text{Au} = \text{Simplify}\left[\frac{\Delta\text{GmXS} - \text{XNi}\,\partial_{\text{XNi}}\,\Delta\text{GmXS}}{\text{R T}}\right]$$

$$-\frac{(-2660 + T)\,XNi^2\,(2423 - 2864\,XNi + 4269\,XNi^2)}{266\,R\,T}$$

Thus, the activities are

```
aNi = XNi Exp[lnγNi] /. {XNi -> 0.5 , T -> 1100, R -> 8.3144}
```

0.872396

```
aAu = (1 - XNi) Exp[lnγAu] /. {XNi -> 0.5 , T -> 1100, R -> 8.3144}
```

0.695454

The book must have interchanged the activities in the final provided answer.

Chapter 10: The Phase Diagrams of Binary Systems

■ Problems

■ Problem 10.1*

From Table A-5, for CaF_2

$$\Delta H_m = 31200\,;\; T_m = 1691\,;\; \Delta S_m = N\left[\frac{\Delta H_m}{T_m}\right]$$

18.4506

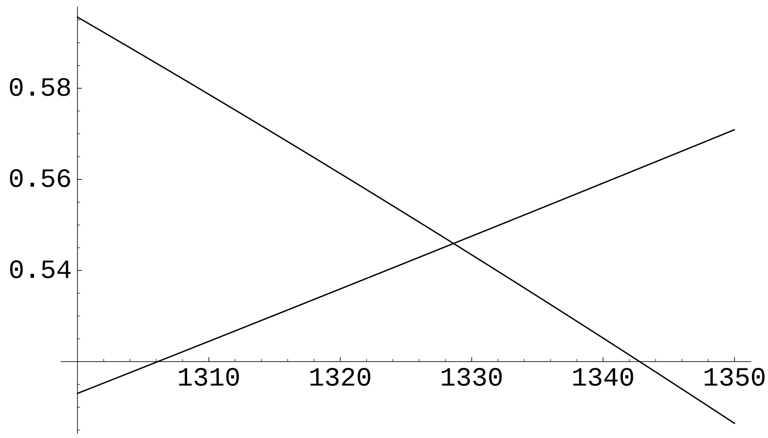
From Table A-5, for MgF_2

$$\Delta HB_m = 58160\,;\; TB_m = 1563\,;\; \Delta SB_m = N\left[\frac{\Delta HB_m}{TB_m}\right]$$

37.2105

Plotting the liquidus lines (using Eq. (10.23)) and assuming **ΔH** and **ΔS** are independent of temperature, because we do not know otherwise and the c_p for these compounds are not given in Table A-2) gives

$$\mathtt{Plot}\left[\mathtt{Release}\left[\left\{\mathtt{Exp}\left[\frac{-\Delta H_m + T\,\Delta S_m}{R\,T}\right],\ 1 - \mathtt{Exp}\left[\frac{-\Delta HB_m + T\,\Delta SB_m}{R\,T}\right]\right\} \mathtt{/.}\ R \mathtt{->} 8.3144\right],\ \{T,\ 1300,\ 1350\}\right]$$

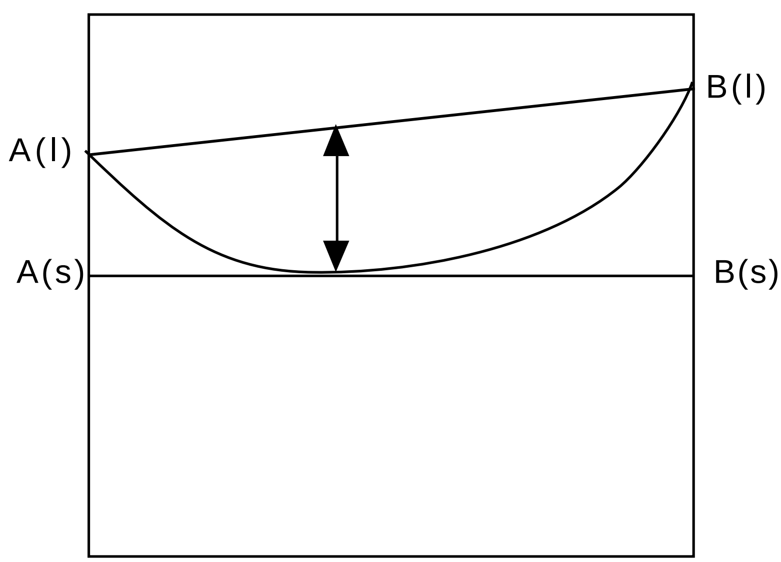


- *Graphics* -

These plots intersect at the predicted eutectic temperature about **1328K** and mole fraction **CaF_2 = 0.54**.These results differ from the actual eutectic composition and from the answers in the text.

■ Problem 10.2

1. Relative to the unmixed liquids we compare the line connecting the pure solid states, which goes through the free energy of the eutectic composition, to the line connecting the pure solid states, at the eutectic composition, as illustrated by the arrow in the following diagram:



Thus using

$$\Delta GSi = \Delta HSi \left(\frac{TSi - T}{TSi}\right) \text{ /. } \{\Delta HSi \to 50200,\ TSi \to 1685\}$$

$$\frac{10040\ (1685 - T)}{337}$$

$$\Delta GAu = \Delta HAu \left(\frac{TAu - T}{TAu}\right) \text{ /. } \{\Delta HAu \to 12600,\ TAu \to 1338\}$$

$$\frac{2100\ (1338 - T)}{223}$$

$$\Delta G1 = XSi\, \Delta GSi + (1 - XSi)\, \Delta GAu \text{ /. } \{XSi \to .186,\ T \to 636\}$$

$$11194.1$$

Note: some copies of the text has a mi-printed solution of 1119, which is a factor of 10 too low.

2. The energy difference relative to the solids is zero because the liquid solution curve just touches the line between the solid states at the eutectic composition (see above figure).

■ Problem 10.3

For ideal solid and liquid solutions, the liquidus and solidus lines are given be Eqs. (10.19) and (10.21). Associating **A** with $Al_2\,O_3$ and **B** with $Cr_2\,O_3$, with equal entropies of melting (as stated in the problem), we have

$$\Delta SA = N\left[\frac{\Delta Hm}{Tm} \text{ /. } \{\Delta Hm \to 107500,\ Tm \to 2324\}\right]$$

$$46.2565$$

$$\Delta GA = \Delta Hm - T\,\Delta Sm \text{ /. } \{\Delta Hm \to 107500,\ \Delta Sm \to \Delta SA\}$$

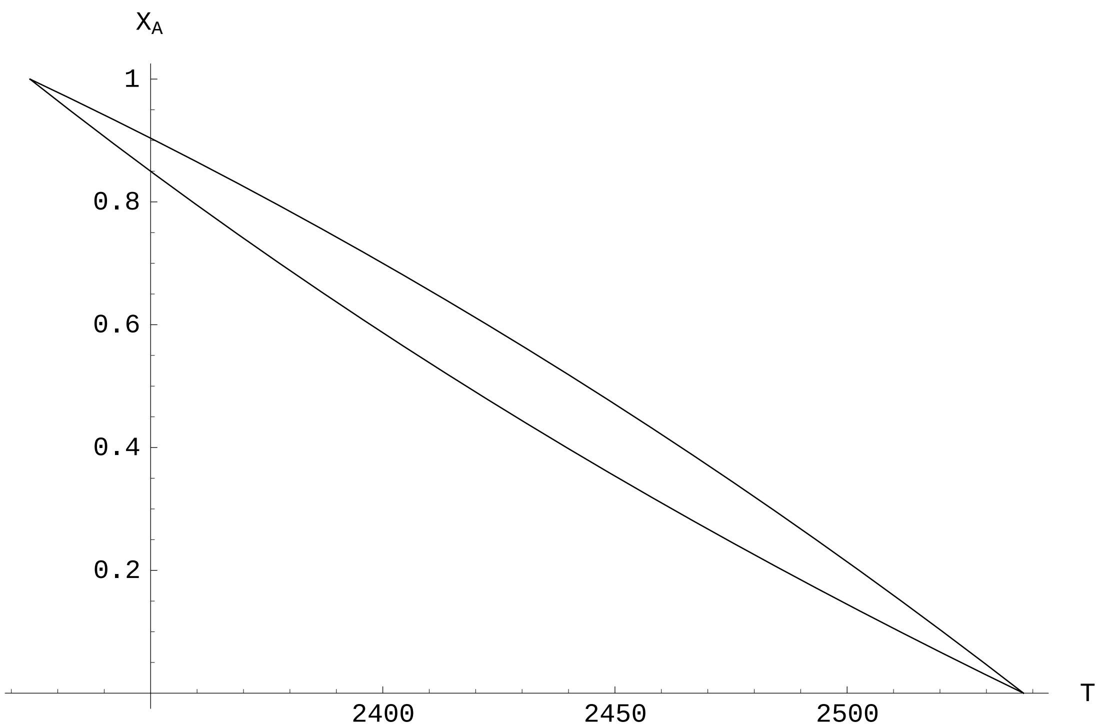
$$107500 - 46.2565\,T$$

$$\Delta GB = \Delta Hm - T\,\Delta Sm \text{ /. } \{\Delta Hm \to 2538\,\Delta SA,\ \Delta Sm \to \Delta SA\}$$

$$117399. - 46.2565\,T$$

The phase diagram can be plotted (as a reversed plot of X_A vs **T** instead of the more usual **T** vs X_A):

```
Plot[Release[{(1 - Exp[-ΔGB/(R T)])/(Exp[-ΔGA/(R T)] - Exp[-ΔGB/(R T)]), ((1 - Exp[-ΔGB/(R T)]) Exp[-ΔGA/(R T)])/(Exp[-ΔGA/(R T)] - Exp[-ΔGB/(R T)])} /.
  R -> 8.3144], {T, 2324, 2538}, AxesLabel -> {T, X_A}]
```



- Graphics -

Prodeeding graphically from this phase diagram (by expanding and plotting key sections), the answers are:

a. A compositiong of $\boldsymbol{X_A = 0.5}$begins to melt at **2418K**.

b. The initial composition of the melt is $\boldsymbol{X_A = 0.62}$

c. Melting is completed at **2443K**.

d. The last formed solid has $\boldsymbol{X_A = 0.38}$

- **Problem 10.4**

The liquid-liquid and solid-solid solutions resemble the curves in Fig. 10.20d except they are symmetric about the middle. To find the total $\mathbf{\Delta G}$, we add the $\mathbf{\Delta G}_m$ of each component to the ideal $\mathbf{\Delta G}_{\mathbf{mixing}}$. For $Na_2\,O\,B_2\,O_3$ using data in the appendix, we have:

```
ΔGA = N[ΔHm ((Tm - T)/Tm) /. {ΔHm -> 67000, Tm -> 1240}]
```

54.0323 (1240. - 1. T)

For $K_2\,O\,B_2\,O_3$ using data in the appendix, we have :

$$\Delta GB = N\left[\Delta Hm\left(\frac{Tm - T}{Tm}\right) /.\ \{\Delta Hm \to 62800,\ Tm \to 1220\}\right]$$

$$51.4754\ (1220. - 1.\ T)$$

The total **ΔG** is then the following sum (which remembers to use **1/2** a mole for each component):

$$\Delta G = R\,T\,\mathrm{Log}[0.5] + 0.5\,\Delta GA + 0.5\,\Delta GB\ /.\ \{T \to 1123,\ R \to 8.3144\}$$

$$-814.52$$

- **Problem 10.5**

The only information we need to know is that the solution is regular with minima at **XA=0.24** when **T=1794C**. Because the minima occur when the derivative of ΔG_{mixing} is zero (see page 277), we can solve for **Ω** using:

$$\mathrm{Solve}\left[\mathrm{Log}\left[\frac{XB}{XA}\right] + \frac{\Omega}{R\,T}\,(XA - XB) == 0\ /.\right.$$
$$\left.\{XA \to 0.24,\ XB \to 0.76,\ R \to 8.3144,\ T \to 1794 + 273\}\right]$$

$$\{\{\Omega \to 38095.8\}\}$$

Using the standard formula, the critical temperature is

$$T_{cr} = \frac{\Omega}{2\,R}\ /.\ \{\Omega \to 38095.8,\ R \to 8.3144\}$$

$$2290.95$$

- **Problem 10.6**

a. The intention of this problem is to use Eq. (10.20) for ideal solution liquidus mole fraction and solve for **ΔHmGe** as the only unknown. The free energies of melting of each component in terms of the enthalpies of melting are:

$$\Delta GmSi = \Delta Hm\left(\frac{Tm - T}{Tm}\right) /.\ \{\Delta Hm \to 50200,\ Tm \to 1685\}$$

$$\frac{10040\ (1685 - T)}{337}$$

$$\Delta GmGe = \Delta Hm\left(\frac{Tm - T}{Tm}\right) /.\ \{\Delta Hm \to \Delta HmGe,\ Tm \to 1210\}$$

$$\frac{(1210 - T)\ \Delta HmGe}{1210}$$

The following two terms are the exponential terms in Eqs. (10.19) and (10.20):

$$exSi = \mathrm{Exp}\left[\frac{-\Delta GmSi}{R\,T}\right];\ exGe = \mathrm{Exp}\left[\frac{-\Delta GmGe}{R\,T}\right];$$

Solving Eq. (10.21) for **ΔHmGe** gives:

```
Solve[XSil == (1 - exGe) exSi / (exSi - exGe) /.
  {T -> 1200 + 273 , XSil -> 0.32 , R -> 8.3144} , ΔHmGe]
```

```
{{ΔHmGe → 21529.2}}
```

b. Similarly, Eq. (10.19) can be solved to give:

```
Solve[XSis == (1 - exGe) / (exSi - exGe) /.
  {T -> 1200 + 273 , XSis -> 0.665 , R -> 8.3144} , ΔHmGe]
```

```
{{ΔHmGe → 33114.2}}
```

Comments: Part b gives the better result, but actually neither result is appropriate. Equations (10.19) and (10.20) are based on the assumption that *both* the liquid and the solid solutions are ideal. The problem says to assume that only one of them is ideal.Unfortunately, there is not enough information provided to find **ΔHmGe** when only one solution is ideal and the other is non-ideal.This problem is poorly written, but can the answers in the book can be obtained by using Eqs. (10.19) and (10.20) has shown above.

■ Problem 10.7

Let **XA1** be the mole fraction of MgO at the point of maximum soluability of MgO in CaO and let **XA2** be the mole fraction of MgO at the point of maximum soluability of CaO in MgO. At **XA1**, the activity of MgO (which obeys Henry's law) is **γA0 XA1** and in the Henry's limit we assume the activity of CaO is its mole fraction or **(1-XA1)**. Similar, at **XA2**, the activity of CaO is **γB0(1-XA2)** and the activity of MgO is **XA2.** Because these two compositions exist in equilibrium, we can equate the activities of the two components and solve for **XA1** and **XA2**:

```
Solve[{γA0 XA1 == XA2 , γB0 (1 - XA2) == (1 - XA1)} /.
   {γA0 -> 6.23 , γB0 -> 12.88}]
```

```
{{XA1 → 0.14992, XA2 → 0.934}}
```

The first answer is the maximum soluabiility of MgO in CaO. **1-0.934=0.066** is the maximum soluability of CaO in MgO.

Chapter 11: Reactions Involving Gases

■ Problems

■ Problem 11.1

For the reaction CO + (1/2) O_2-> CO_2, the free energy is given in the text as:

```
ΔGC = -282400 + 86.85 T
```

$-282400 + 86.85\, T$

For the reaction H_2 + (1/2) O_2-> H_2 O, the free energy is given in the text as:

```
ΔGH = -246400 + 54.8 T
```

$-246400 + 54.8\, T$

Subtracting the former from the latter gives the free energy for the reaction H_2 + CO_2 −> H_2 O + CO:

```
ΔG = ΔGH - ΔGC
```

$36000 - 32.05\, T$

The equilibrium constant for this reaction at 900C (1173K) is

$$Kp = Exp\left[\frac{-\Delta G}{R\,T}\right] \;/.\; \{R \to 8.3144,\; T \to 900 + 273\}$$

1.17763

After starting with .5 mole fraction CO and .25 mole fraction CO_2 nad H_2 and reacting x mole fraction towards the right, we have the following final mole fractions (note total number of moles is constant at 1)

```
mfs = {XCO -> .5 + x, XCO2 -> .25 - x, XH2 -> .25 - x, XH2O -> x};
```

Because P=1, the mole fractions are equal to the partial pressures and we just need to solve

$$extent = Solve\left[Kp == \frac{x\,(.5 + x)}{(.25 - x)^2}\right]$$

$\{\{x \to 0.0683606\}, \{x \to 6.0612\}\}$

which gives final mole fractions or

```
mfs /. extent
```

$\{\{XCO \to 0.568361, XCO2 \to 0.181639, XH2 \to 0.181639, XH2O \to 0.0683606\},$
$\{XCO \to 6.5612, XCO2 \to -5.8112, XH2 \to -5.8112, XH2O \to 6.0612\}\}$

Only the first solution is physcially possible and it agrees with the text.

- **Problem 11.2**

From section 11.6, the reaction SO_2 + (1/2) O_2-> SO_3 has

```
ΔG = -94600 + 89.37 T
```

$-94600 + 89.37\, T$

After mixing 1 mole of SO_2 and 1/2 mole of O_2, allowing x moles to reaction and equlibrating at 1 atm total pressure, the final mole fractions are

$$XSO2 = \frac{1 - x}{1.5 - .5\,x};\ XO2 = \frac{.5 - .5\,x}{1.5 - .5\,x};\ XSO3 = \frac{x}{1.5 - .5\,x};$$

Because total pressure is P=1 atm, these mole fractions are equal to partial pressures. The Kp for the reaction is

$$Kp = \mathrm{Exp}\left[\frac{-\Delta G}{R\,T}\right]\ /.\ \{R \to 8.3144,\ T \to 1000\}$$

$$1.87579$$

We find x by solving

$$extent = \mathrm{Solve}\left[Kp == \frac{XSO3}{XSO2\,\sqrt{XO2}},\ x\right]$$

$$\{\{x \to 0.463196\}\}$$

If x moles reaction, the heat evolved is

$$x\,(-\Delta H)\ /.\ \{x \to 0.4631956,\ \Delta H \to -94600\}$$

$$43818.3$$

■ Problem 11.3

For the reaction CO + (1/2) O_2 -> CO_2, the text gives:

$$\Delta GC = -282400 + 86.85\,T$$

$$-282400 + 86.85\,T$$

which leads to Kp at 1600C (1873K) of:

$$KpC = \mathrm{Exp}\left[\frac{-\Delta GC}{R\,T}\right]\ /.\ \{R \to 8.3144,\ T \to 1600 + 273\}$$

$$2182.81$$

For the reaction H_2 + (1/2) O_2 -> $H_2\,O$, the text gives:

$$\Delta GH = -246400 + 54.8\,T$$

$$-246400 + 54.8\,T$$

which leads to Kp at 1600C (1873K) of:

```
KpH = Exp[-ΔGH/(R T)] /. {R -> 8.3144 , T -> 1600 + 273}
```

$$10213.$$

We start with 1 mole of H_2 and R moles of CO_2 (thus the CO_2 to H_2 starting ratio is R). After allowing the CO_2 reaction to back react by x moles and the H_2 reaction to forward react by y moles, the number of moles of all components are:

```
nms = {nCO -> x, nCO2 -> R - x, nO2 -> (x - y)/2, nH2 -> 1 - y, nHOH -> y}
```

$$\left\{nCO \to x,\ nCO2 \to R - x,\ nO2 \to \frac{x - y}{2},\ nH2 \to 1 - y,\ nHOH \to y\right\}$$

The total number of moles is no longer constant; it is

```
nm = nCO + nCO2 + nO2 + nH2 + nHOH /. nms
```

$$1 + R + \frac{x - y}{2}$$

Thus, the mole fractions are as follows (note these are equal to the partial pressures because the total partial pressure is 1 atm):

```
pps = {XCO -> nCO/nm, XCO2 -> nCO2/nm,
XO2 -> nO2/nm, XH2 -> nH2/nm, XHOH -> nHOH/nm} /. nms
```

$$\left\{XCO \to \frac{x}{1 + R + \frac{x-y}{2}},\ XCO2 \to \frac{R - x}{1 + R + \frac{x-y}{2}},\right.$$
$$\left. XO2 \to \frac{x - y}{2\left(1 + R + \frac{x-y}{2}\right)},\ XH2 \to \frac{1 - y}{1 + R + \frac{x-y}{2}},\ XHOH \to \frac{y}{1 + R + \frac{x-y}{2}}\right\}$$

We are told the partial pressure of O_2 is 10^{-7} atm. This information can be used to eliminate x or y. Here we eliminate y by solving

```
elimy = Solve [XO2 == 10^-7 /. pps, y]
```

$$\left\{\left\{y \to \frac{-2 - 2R + 9999999\,x}{9999999}\right\}\right\}$$

In terms of x and R, the mole fractions (which are equal to the partial pressures) are:

```
xpps = Simplify[pps /. elimy]
```

$$\left\{\left\{XCO \to \frac{9999999\,x}{10000000\,(1 + R)},\ XCO2 \to \frac{9999999\,(R - x)}{10000000\,(1 + R)},\ XO2 \to \frac{1}{10000000},\right.\right.$$
$$\left.\left. XH2 \to \frac{10000001 + 2R - 9999999\,x}{10000000\,(1 + R)},\ XHOH \to \frac{-2 - 2R + 9999999\,x}{10000000\,(1 + R)}\right\}\right\}$$

Finally, solving the two equilibria for the above two reactions for the two unknowns gives the final answer:

```
Solve[
{XCO2 == √XO2 KpC XCO , XHOH == √XO2 KpH XH2} /. xpps , {x, R}]
```

```
{{x → 0.763573, R → 1.29064}}
```

The required initial ratio is this R value; the final reaction proceeds by extents x (given here) and

```
elimy /. %
```

```
{{{y → 0.763572}}}
```

■ Problem 11.4

From Table A-1, the free energy for the reaction LiBr -> Li + (1/2) Br_2 is:

```
ΔG = 333900 - 42.09 T
```

```
333900 - 42.09 T
```

If we start with 1 mole of LiBr of which x moles dissociate, we end with total numbers of moles of

$$nms = \left\{nLiBr \to 1 - x,\ nLi \to x,\ nBr \to \frac{x}{2}\right\}$$

$$\left\{nLiBr \to 1 - x,\ nLi \to x,\ nBr \to \frac{x}{2}\right\}$$

The total number of moles is

```
nm = nLiBr + nLi + nBr /. nms
```

$$1 + \frac{x}{2}$$

Thus the final mole fractions (which are equal to the final partial pressures because the total pressure is 1 atm) are

$$pp = \left\{pLiBr \to \frac{nLiBr}{nm},\ pLi \to \frac{nLi}{nm},\ pBr \to \frac{nBr}{nm}\right\} \text{ /. nms}$$

$$\left\{pLiBr \to \frac{1-x}{1+\frac{x}{2}},\ pLi \to \frac{x}{1+\frac{x}{2}},\ pBr \to \frac{x}{2\left(1+\frac{x}{2}\right)}\right\}$$

We are told that the final partial pressure of Li is 10^{-5} atm which can be used to solve for x:

$$elimx = Solve[pLi == 10^{-5} \text{ /. } pp,\ x]$$

$$\left\{\left\{x \to \frac{2}{199999}\right\}\right\}$$

The final partial pressures are thus

```
ppf = pp /. elimx
```

$$\left\{\left\{pLiBr \to \frac{199997}{200000},\ pLi \to \frac{1}{100000},\ pBr \to \frac{1}{200000}\right\}\right\}$$

which leads to an equilibrium constant of

$$Kp = N\left[\frac{pLi\sqrt{pBr}}{pLiBr} \text{ /. } ppf\right]$$

$$\{2.2361 \times 10^{-8}\}$$

The temperature at which this is the correct equilibrium constant is found by solving

$$Solve\left[2.2361\ 10^{-8} == Exp\left[\frac{-\Delta G}{R\ T}\right] \text{ /. } R \to 8.3144,\ T\right]$$

$$\{\{T \to 1770.83\}\}$$

- **Problem 11.5**

The decomposition reaction follows SO_3 -> SO_2 + (1/2) O_2 with free energy

```
ΔG = 94600 - 89.37 T
```

$$94600 - 89.37\ T$$

If x moles of an initial 1 mole of SO_3 decompose we end up with the following numbers of moles:

$$nms = \left\{nSO3 \to 1 - x,\ nSO2 \to x,\ nO2 \to \frac{x}{2}\right\}$$

$$\left\{nSO3 \to 1 - x,\ nSO2 \to x,\ nO2 \to \frac{x}{2}\right\}$$

The total number of moles is

```
nm = nSO3 + nSO2 + nO2 /. nms
```

$$1 + \frac{x}{2}$$

Thus the partial pressures (mole fractions time pressure P) are

$$pps = \left\{pSO3 \to \frac{nSO3\ P}{nm},\ pSO2 \to \frac{nSO2\ P}{nm},\ pO2 \to \frac{nO2\ P}{nm}\right\} \text{ /. } nms$$

$$\left\{pSO3 \to \frac{P\,(1-x)}{1+\frac{x}{2}},\ pSO2 \to \frac{P\,x}{1+\frac{x}{2}},\ pO2 \to \frac{P\,x}{2\,\left(1+\frac{x}{2}\right)}\right\}$$

We can eliminate x from the given information about pO2:

```
elimx = Solve[pO2 == .05 /. pps , x]
```

$$\left\{\left\{x \to \frac{2.}{-1. + 20.\,P}\right\}\right\}$$

Thus, the final partial pressures are:

```
ppsf = Simplify[ pps /. elimx]
```

{{pSO3 → -0.15 + 1. P, pSO2 → 0.1, pO2 → 0.05}}

Finally, we solve for the P required to make this pressures give the correct equilibrium constant:

$$Kp = Exp\left[\frac{-\Delta G}{R\,T}\right] \;/.\; \{R \to 8.3144,\; T \to 1000\}$$

0.533109

$$Solve\left[Kp == \frac{pSO2\,\sqrt{pO2}}{pSO3} \;/.\; ppsf,\; P\right]$$

{{P → 0.191944}}

If the total pressure is changed to P=1 atm, the new Kp is

$$Kp = \frac{pSO2\,\sqrt{pO2}}{pSO3} \;/.\; ppsf \;/.\; P \to 1$$

{0.0263067}

To find the temperature that gives this Kp, we solve

$$Solve\left[0.0263067 == Exp\left[\frac{-\Delta G}{R\,T}\right] \;/.\; R \to 8.3144,\; T\right]$$

{{T → 790.856}}

- **Problem 11.6**

For the reaction N_2-> 2N, the free energy is

```
ΔG = 945000 - 114.9 T
```

945000 - 114.9 T

At 3000K, the equiltibrium constant is

```
Kp = Exp[-ΔG/(R T)] /. {R -> 8.3144 , T -> 3000}
```

3.53162×10^{-11}

a. If x moles of an initial 1 mole of N_2 dissociates, the final partial pressures are

```
pp = {pN2 -> (1 - x) P/(1 + x) , pN -> 2 x P/(1 + x)}
```

$\left\{pN2 \to \frac{P\,(1-x)}{1+x},\ pN \to \frac{2\,P\,x}{1+x}\right\}$

The value of x to reach equilibrium is

```
Solve[Kp == pN^2/pN2 /. {pp /. P -> 1} , x]
```

$\{\{x \to -2.97137 \times 10^{-6}\},\ \{x \to 2.97137 \times 10^{-6}\}\}$

The positive root is the correct one. Thus

```
finalpN = 2 x P/(1 + x) /. {P -> 1 , x -> 2.97137 10^-6}
```

5.94272×10^{-6}

b. If pN2 is 90% of the total pressure, we can solve for x

```
elimx = Solve[pN2/(pN + pN2) == .9 /. pp , x]
```

$\{\{x \to 0.0526316\}\}$

Thus the partial pressure become:

```
ppf = pp /. elimx
```

$\{\{pN2 \to 0.9\,P,\ pN \to 0.1\,P\}\}$

The pressure is found from

```
Solve[Kp == pN^2/pN2 /. ppf , P]
```

$\{\{P \to 3.17846 \times 10^{-9}\}\}$

■ Problem 11.7

From Table A-1, for the reaction $(3/2)\,H_2 + (1/2)\,N_2$-> NH_3, the free energy is

$$\Delta G = \frac{1}{2} (-87030 + 25.8\, T\, \text{Log}[T] + 31.7\, T)$$

$$\frac{1}{2} (-87030 + 31.7\, T + 25.8\, T\, \text{Log}[T])$$

The equilibrium constant at 300C (575K) is

$$\text{Kp} = \text{Exp}\left[\frac{-\Delta G}{R\, T}\right] \;/.\; \{R \to 8.3144,\; T \to 300 + 273\}$$

$$0.0723638$$

If x mole of and initial 1 mole of NH_3 dissociates, the final partial pressures are

$$\text{pp} = \left\{\text{pNH3} \to \frac{(1 - x)\, P}{1 + x},\; \text{pH2} \to \frac{(3\, x / 2)\, P}{1 + x},\; \text{pN2} \to \frac{(x / 2)\, P}{1 + x}\right\}$$

$$\left\{\text{pNH3} \to \frac{P\, (1 - x)}{1 + x},\; \text{pH2} \to \frac{3\, P\, x}{2\, (1 + x)},\; \text{pN2} \to \frac{P\, x}{2\, (1 + x)}\right\}$$

If the mole fraction of N2 is 0.2, the x must be

$$\text{elimx} = \text{Solve}\left[\frac{x}{2\, (1 + x)} == 0.2,\; x\right]$$

$$\{\{x \to 0.666667\}\}$$

Thus, the partial pressures become

$$\text{ppx} = \text{pp} \;/.\; \text{elimx}$$

$$\{\{\text{pNH3} \to 0.2\, P,\; \text{pH2} \to 0.6\, P,\; \text{pN2} \to 0.2\, P\}\}$$

To equal the equilibrium constant, the pressure must be

$$\text{Solve}\left[\text{Kp} == \frac{\text{pNH3}}{\text{pH2}^{3/2}\, \text{pN2}^{1/2}} \;/.\; \text{ppx},\; P\right]$$

$$\{\{P \to 13.2974\}\}$$

b. At 300C, the entropy can be found from

$$\Delta S = -\partial_T\, \Delta G \;/.\; T \to 300 + 273$$

$$-110.676$$

which can be used to find the enthalpy

```
ΔH = ΔG + T ΔS /. T -> 300 + 273
```

```
-50906.7
```

- **Problem 11.8**

From Table A-1, the reaction $PCl_3 + Cl_2$-> PCl_5 has free energy

```
ΔG = -95600 - 7.94 T Log[T] + 235.2 T
```

```
-95600 + 235.2 T - 7.94 T Log[T]
```

At 500K, the equilibrium constant is

$$Kp = Exp\left[\frac{-\Delta G}{R\,T}\right] \;/.\; \{R \to 8.3144,\; T \to 500\}$$

```
1.90168
```

Let R be the startint ratio of PCl_5 to PCl_3. Starting with 1 mole of PCl_2 and reacting x moles, we end up with the following mole fractions (which are also partial pressures when P=1 atm):

$$pp = \left\{XPCl5 \to \frac{R - x}{1 + R + x},\; XPCl3 \to \frac{1 + x}{1 + R + x},\; XCl2 \to \frac{x}{1 + R + x}\right\}$$

$$\left\{XPCl5 \to \frac{R - x}{1 + R + x},\; XPCl3 \to \frac{1 + x}{1 + R + x},\; XCl2 \to \frac{x}{1 + R + x}\right\}$$

If the final partial pressure of Cl_2 is 0.1 atm, we can eliminate x by solving

$$elimx = Solve\left[\frac{x}{1 + R + x} == 0.1,\; x\right]$$

$$\{\{x \to 0.111111\,(1. + 1.\,R)\}\}$$

Thus, the partial pressures are

```
ppx = Simplify[pp /. elimx]
```

$$\left\{\left\{XPCl5 \to \frac{-0.1 + 0.8\,R}{1 + R},\; XPCl3 \to \frac{1. + 0.1\,R}{1 + R},\; XCl2 \to 0.1\right\}\right\}$$

Finally, we solve for R by equating to the equilibrium constant:

$$Solve\left[Kp == \frac{XPCl5}{XPCl3\,XCl2} \;/.\; ppx,\; R\right]$$

$$\{\{R \to 0.371542\}\}$$

▪ Problem 11.9*

From the text for the reaction $H_2 + (1/2)\,O_2 \rightarrow H_2\,O$, the free energy is:

```
ΔG = -246400 + 54.8 T
```

$$-246400 + 54.8\,T$$

At 1200K, the equilibrium constant is

$$Kp = \text{Exp}\left[\frac{-\Delta G}{R\,T}\right] \;/.\; \{R \to 8.3144,\; T \to 1200\}$$

$$7.29391 \times 10^{7}$$

If we mix 1 part H_2 to 4 parts air, the final partial pressures (after x moles of reaction) are:

$$nm = 5 - \frac{x}{2};\; pp = \left\{pH2 \to \frac{(1-x)\,P}{nm},\; pO2 \to \frac{\left(\frac{4*21}{100} - \frac{x}{2}\right)P}{nm},\; pN2 \to \frac{(4*79/100)\,P}{nm},\; pHOH \to \frac{x\,P}{nm}\right\}$$

$$\left\{pH2 \to \frac{P\,(1-x)}{5-\frac{x}{2}},\; pO2 \to \frac{P\left(\frac{21}{25}-\frac{x}{2}\right)}{5-\frac{x}{2}},\; pN2 \to \frac{79\,P}{25\left(5-\frac{x}{2}\right)},\; pHOH \to \frac{P\,x}{5-\frac{x}{2}}\right\}$$

a. At total pressure of 1 atm, the partial pressures are:

```
pp1 = pp /. P -> 1
```

$$\left\{pH2 \to \frac{1-x}{5-\frac{x}{2}},\; pO2 \to \frac{\frac{21}{25}-\frac{x}{2}}{5-\frac{x}{2}},\; pN2 \to \frac{79}{25\left(5-\frac{x}{2}\right)},\; pHOH \to \frac{x}{5-\frac{x}{2}}\right\}$$

The extent of reaction is nearly complete as found by solving

$$\text{Solve}\left[Kp == \frac{pHOH}{pH2\,\sqrt{pO2}} \;/.\; pp1\right]$$

$$\{\{x \to 1.\}\}$$

which converts to final partial pressures of

```
pp1 /. %
```

$$\{\{pH2 \to 1.10839 \times 10^{-8},\; pO2 \to 0.0755556,\; pN2 \to 0.702222,\; pHOH \to 0.222222\}\}$$

b. At a total pressure of 10 atm, the partial pressures are:

```
pp10 = pp /. P -> 10
```

$$\left\{pH2 \to \frac{10\,(1-x)}{5-\frac{x}{2}},\; pO2 \to \frac{10\left(\frac{21}{25}-\frac{x}{2}\right)}{5-\frac{x}{2}},\; pN2 \to \frac{158}{5\left(5-\frac{x}{2}\right)},\; pHOH \to \frac{10\,x}{5-\frac{x}{2}}\right\}$$

The extent of reaction is nearly complete as found by solving

$$\text{Solve}\left[Kp == \frac{pHOH}{pH2\sqrt{pO2}} \;/.\; pp10\right]$$

$$\{\{x \to 1.\}\}$$

which converts to final partial pressures of

```
pp10 /. %
```

$$\{\{pH2 \to 3.50505\times 10^{-8},\; pO2 \to 0.755556,\; pN2 \to 7.02222,\; pHOH \to 2.22222\}\}$$

The O_2 partial pressures agree with the solutions in the text, the the H_2 pressures are slightly different.

- **Problem 11.10***

From Table A-1, the reaction $H_2 + I_2$-> 2 HI has free energy

```
ΔG = -8370 - 17.65 T
```

$$-8370 - 17.65\,T$$

At 1500K, the equilibrium constant is

$$Kp = \text{Exp}\left[\frac{-\Delta G}{R\,T}\right] \;/.\; \{R \to 8.3144,\; T \to 1500\}$$

$$16.3454$$

After mixing and x moles of reaction, the final partial pressures (which are the mole fractions when P=1 atm) are

$$pp = \left\{pH2 \to \frac{1-x}{3},\; pI2 \to \frac{1-x}{3},\; pHI \to \frac{1+2x}{3}\right\}$$

$$\left\{pH2 \to \frac{1-x}{3},\; pI2 \to \frac{1-x}{3},\; pHI \to \frac{1}{3}(1+2x)\right\}$$

a. Solving for x at equilibrium gives

$$\text{Solve}\left[Kp == \frac{pHI^2}{pH2\,pI2} \;/.\; pp,\; x\right]$$

$$\{\{x \to 0.503553\},\; \{x \to 2.46847\}\}$$

The first root is the correct one. Thus the mole fractions (which at P=1 atm are the partial pressures) are

```
pp /. x -> 0.503553
```

$\{pH2 \to 0.165482,\ pI2 \to 0.165482,\ pHI \to 0.669035\}$

This answers differs from the solution in the text.

b. Now change the temperature such that pHI is five times pH2. Using this information we can eliminate

```
Solve[pHI == 5 pH2 /. pp , x]
```

$\left\{\left\{x \to \frac{4}{7}\right\}\right\}$

The final partial pressure become

```
ppf = pp /. %
```

$\left\{\left\{pH2 \to \frac{1}{7},\ pI2 \to \frac{1}{7},\ pHI \to \frac{5}{7}\right\}\right\}$

This give the correct equilibrium constant at the solution to the following equation

$$\text{Solve}\left[\text{Exp}\left[\frac{-\Delta G}{8.3144\,T}\right] == \frac{pHI^2}{pH2\ pI2} \ /.\ ppf\ ,\ T\right]$$

$\{\{T \to 918.466\}\}$

Chapter 12: Reactions Involving Pure Condensed Phases and Gases

Problems

Problem 12.1

From Table A-1, for $MgO + CO_2$-> $MgCO_3$, the free energy is

$$\Delta G0 = -117600 + 170\,T$$

$-117600 + 170\,T$

But this is for CO_2 at P=1 atm. If we add the above reaction to the change in pressure reaction CO_2(1 atm) -> CO_2(P) which has

$$\Delta GP = R\,T\,\text{Log}[P]$$

$R\,T\,\text{Log}[P]$

The total ΔG for the reaction with CO_2 at pressure is

```
ΔG = ΔG0 - ΔGP
```

$-117600 + 170\,T - R\,T\,\text{Log}[P]$

The T for equilibrium when P=0.01 is

```
Solve[ΔG == 0 /. {R -> 8.3144 , P -> 10^-2} , T]
```

$\{\{T \to 564.6\}\}$

At temperature below this result, ΔG<0 and the reaction proceeds to the right to form $MgCO_3$. At temperature above this result, $MgCO_3$ will decompose.

- **Problem 12.2**

Consider the two reactions. First Ni(s) + (1/2) O_2-> NiO(s) with free energy (in Table A-1):

$$\Delta Gs = \frac{1}{2}(-471200 + 172\,T)$$

$$\frac{1}{2}(-471200 + 172\,T)$$

Second Ni(l) + (1/2) O_2-> NiO(s) with free energy (in Table A-1):

$$\Delta Gl = \frac{1}{2}(-506180 + 192.2\,T)$$

$$\frac{1}{2}(-506180 + 192.2\,T)$$

a. The melting temperature is where these two free energies are equal:

```
Solve[ΔGs == ΔGl , T]
```

$\{\{T \to 1731.68\}\}$

b. Subtracting these two reactions gives the reaction **Ni(s)** -> **Ni(l)** with free energy

```
ΔGm = Simplify[ΔGs - ΔGl]
```

$17490. - 10.1\,T$

The ΔH_{melt} is easily found from

```
ΔHmelt = ΔGm /. T -> 0
```

$17490.$

The ΔS_{melt} is found from

$$\Delta\text{Smelt} = \text{Simplify}\left[\frac{\Delta\text{Hmelt} - \Delta\text{Gm}}{\text{T}}\right]$$

$$10.1$$

- **Problem 12.3**

For the reaction 2Ag + (1/2) O_2(1 atm) -> Ag_2O, the free energy is

$$\Delta\text{G0} = -30540 + 66.11\,\text{T}$$

$$-30540 + 66.11\,T$$

a. The decomposition temperature (or equilibrium temperature) is

$$\text{Solve}[\Delta\text{G0} == 0\,,\ \text{T}]$$

$$\{\{T \to 461.957\}\}$$

b. In air (which is 21 percent $\boldsymbol{O_2}$**,** the oxygen pressure is reduces. As in Problem 12.1, we need to subtract the change in free energy due to reducing the $\boldsymbol{O_2}$pressure. The new equilibrium temperature is

$$\text{Solve}\left[\Delta\text{G0} - \frac{1}{2}\,\text{R}\,\text{T}\,\text{Log}[\text{P}] == 0\ /.\ \{\text{R} \text{->} 8.3144,\ \text{P} \text{->} .21\}\,,\ \text{T}\right]$$

$$\{\{T \to 420.673\}\}$$

- **Problem 12.4**

The water reaction is 2 H_2 + O_2-> 2 H_2 O with

$$\Delta\text{GH} = 2\,(-247500 + 55.85\,\text{T})$$

$$2\,(-247500 + 55.85\,T)$$

The chromium reaction (on molar oxygen basis) is $\frac{4}{3}$Cr + O_2 -> $\frac{2}{3}$ Cr_2 O_3 with

$$\Delta\text{GCr} = \frac{2}{3}\,(-1110100 + 247.3\,\text{T})$$

$$\frac{2}{3}\,(-1110100 + 247.3\,T)$$

The difference of these reactions gives a reaction for oxidation of Cr by water as is $\frac{4}{3}$Cr + 2 H_2 O -> $\frac{2}{3}$ Cr_2 O_3+ 2 H_2 with

$$\Delta\text{G} = \text{Simplify}[\Delta\text{GCr} - \Delta\text{GH}]$$

$$-245067. + 53.1667\,T$$

The equilibrium constant is

$$K = \text{Exp}\left[\frac{-\Delta G}{R\,T}\right] \;/.\; \{R \to 8.3144,\; T \to 1500\}$$

$$571174.$$

The water pressure (when the H_2 pressure is 1 atm) at equilibrium is

$$\text{Solve}\left[K == \frac{1}{\text{Pmax}^2},\; \text{Pmax}\right]$$

$$\{\{\text{Pmax} \to -0.00132317\},\; \{\text{Pmax} \to 0.00132317\}\}$$

If the pressure is above this value, **ΔG** will become negative and the Cr oxidation will proceed. Thus, this pressure is the maximum water pressure to which Cr can be heater without oxidizing.

From the **ΔG** result above, the reaction is exothermic (**ΔH = -245067 < 0**).

- **Problem 12.5**

The two key reactions are H_2 + Cl_2->2HCl with

$$\Delta GH = -188200 - 12.80\,T$$

$$-188200 - 12.8\,T$$

and Sn + Cl_2-> $SnCl_2$ with

$$\Delta GSn = -333000 + 118.4\,T$$

$$-333000 + 118.4\,T$$

The difference of these reactions is H_2 + $SnCl_2$-> 2HCl + Sn with

$$\Delta G = \text{Simplify}[\Delta GH - \Delta GSn]$$

$$144800. - 131.2\,T$$

The final equilibrium constant from the given composition

$$Kq = \frac{\text{pHCl}^2}{\text{pH}} \;/.\; \{\text{pH} \to .5,\; \text{pHCl} \to .07\}$$

$$0.0098$$

From ΔG, the equilibrium constant should be

$$K = \text{Exp}\left[\frac{-\Delta G}{R\,T}\right] \;/.\; \{R \to 8.3144,\; T \to 900\}$$

$$0.0281339$$

Thus the mixture is not at equilibrium. The text book answer gives the actual equilibrium answer, but they might be in error. There does not seem to be enough information to find the final composition unless one knows the starting composition of Ar and H_2(it is not supplied). The question can be answered, however, without finding the final equilibrium.

- **Problem 12.6**

It is stated the Fe and FeO are in equilibrium with CO and CO_2 at some ratio and at 1273K. If the temperature is reduced, the lower slope of the 2Fe + O_2 −> 2 FeO line means the 2CO + O_2-> 2 CO_2 line would have to be rotated to the left to regain equilibium. This rotation to the left requires a lower pressure CO. Thus in the reaction FeO + CO -> Fe + CO_2, FeO and CO must react. The FeO will eventually disappear.

- **Problem 12.7**

The key reactions for Table A-1 are 2Mg(g) + O_2-> 2MgO(s) with

```
ΔGM = 2 (-729600 + 204 T)
```

$$2\,(-729600+204\,T)$$

2 MgO(s) + SiO_2-> $Mg_2\,SiO_4$ with

```
ΔG2 = -67200 + 4.31 T
```

$$-67200+4.31\,T$$

and Si + O_2-> SiO_2 with

```
ΔGS = -907100 + 175 T
```

$$-907100+175\,T$$

The reaction in the problem 4MgO + Si -> 2Mg(g) + $Mg_2\,SiO_4$ has

```
ΔG = ΔG2 - ΔGM + ΔGS
```

$$-974300+179.31\,T-2\,(-729600+204\,T)$$

The equilibirum contant at 1400 C is

$$K = \mathrm{Exp}\left[\frac{-\Delta G}{R\,T}\right] \;/.\; \{R \to 8.3144,\ T \to 1400+273\}$$

$$0.00063968$$

The only gas is Mg; thus its pressure is

$$\mathrm{Solve}[K == pMg^2]$$

$$\{\{pMg \to -0.0252919\},\ \{pMg \to 0.0252919\}\}$$

- **Problem 12.8**

$CaCO_3$ can decompose to a gas and a solid by $CaCO_3$-> CaO + CO_2 with

```
ΔG = 161300 - 137.2 T
```

$$161300 - 137.2\,T$$

The equilibrium constant is simply K=pCO2; thus

```
pCO2 = Exp[-ΔG/(R T)] /. R -> 8.3144
```

$$E^{-\frac{0.120273\,(161300-137.2\,T)}{T}}$$

The number of moles of CO_2 created as a function of T is

```
nmCO2 = (pCO2 V)/(R T) /. {V -> 1 , R -> 0.082057}
```

$$\frac{12.1867\,E^{-\frac{0.120273\,(161300-137.2\,T)}{T}}}{T}$$

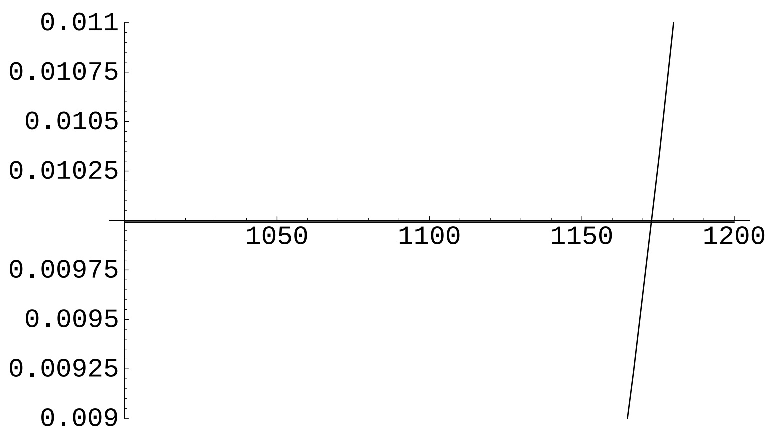
The initial number of moles of $CaCO_3$ were

```
nmCaCO3 = 1/(massCa + massC + 3 massO)
```

$$0.00999201$$

1. We need to equate the number of moles of CO_2 to $CaCO_3$ and solve for T. That equation can not be solved for T, but a plot over T shows the final temperature to be about 1173

```
Plot[Release[{nmCO2, nmCaCO3}],
{T, 1000, 1200}, PlotRange -> {0.009, .011}]
```



- Graphics -

This result can be checked by calculating the number of moles of CO_2:

```
nmCO2 /. T -> 1173
```

0.0100083

2. The pressure in the vessel at 1000K is

```
pCO2 /. T -> 1000
```

0.0551011

3. At 1500K, all $\mathbf{CaCO_3}$ hasconverted to $\mathbf{CO_2}$: thus

$$p = \frac{\text{nmCaCO3 R T}}{\text{V}} \text{ /. } \{R \to 0.082057, V \to 1, T \to 1500\}$$

1.22987

■ Problem 12.9

First consider the reaction CoO + SO_3-> $CoSO_4$ which is given in Table A-1 with

```
ΔG = -227860 + 165.3 T
```

$-227860 + 165.3\,T$

The only gas here is SO_3, thus its pressure is determined by the the equilibrium constant

$$K = \text{Exp}\left[\frac{-\Delta G}{R\,T}\right]$$

$$E^{-\frac{-227860+165.3\,T}{R\,T}}$$

thus, the presure is

$$pSO_3 = \frac{1}{K}\;/.\;\{R \to 8.3144\,,\; T \to 1223\}$$

$$0.0798805$$

Next, this SO_3 might decompose according to SO_3-> SO_2+ $\frac{1}{2}$ O_2 with

$$\Delta Gd = 94600 - 89.37\,T$$

$$94600 - 89.37\,T$$

From the decomposition, the pressure of O_2 must be exactly half the pressure of SO_2:

$$pO_2 = \frac{1}{2}\,pSO_2$$

$$\frac{pSO_2}{2}$$

The equilibrium constant for the decomposition reaction is

$$K = \text{Exp}\left[\frac{-\Delta Gd}{R\,T}\right]\;/.\;\{R \to 8.3144\,,\; T \to 1223\}$$

$$4.24436$$

The final pressures are found from

$$\text{Solve}\left[K == \frac{pSO_2\,\sqrt{pO_2}}{pSO_3}\,,\; pSO_2\right]$$

$$\{\{pSO_2 \to 0.612602\}\}$$

The total pressure is thus

$$pTotal = pSO_3 + pSO_2 + pO_2\;/.\;\%$$

$$\{0.998784\}$$

- **Problem 12.10**

Consider the three reactions from table A-1: C + $\frac{1}{2}$ O_2-> CO with

```
ΔG1 = -111700 - 87.65 T
```

$-111700 - 87.65\,T$

C + $\frac{1}{2}$ O_2 + $\frac{1}{2}$ S_2-> COS with

```
ΔG2 = -202800 - 9.96 T
```

$-202800 - 9.96\,T$

and Fe + $\frac{1}{2}$ S_2-> FeS with

```
ΔG3 = -150200 + 52.55 T
```

$-150200 + 52.55\,T$

Then the reaction in the problem of COS + Fe -> CO + FeS has

```
ΔG4 = ΔG1 - ΔG2 + ΔG3
```

$-59100 - 25.14\,T$

1. The problem means to remove sulfer from the COS. If **x** moles get removed the final partial pressures are:

```
pp = {pCOS -> .004 - x , pCO -> .9 + x}
```

$\{pCOS \to 0.004 - x,\ pCO \to 0.9 + x\}$

The equilibrium constant is

$$K4 = \text{Exp}\left[\frac{-\Delta G4}{R\,T}\right] \;/.\; \{R \to 8.3144,\ T \to 1000\}$$

25130.

Thus, the number of moles removed is

$$\text{Solve}\left[K4 == \frac{pCO}{pCOS} \;/.\; pp,\ x\right]$$

$\{\{x \to 0.00396403\}\}$

The percentage removed is

$$\frac{100\,x}{.004} \;/.\; \%$$

$\{99.1007\}$

2. The pressure of S_2 is calculated from reaction 3 and only one gas:

$$\text{K3} = \text{Exp}\left[\frac{-\Delta\text{G3}}{\text{R T}}\right] \text{ /. } \{\text{R} \to 8.3144, \ \text{T} \to 1000\}$$

$$126082.$$

which leads to

$$\text{Solve}\left[\text{K3} == \frac{1}{\sqrt{\text{pS}_2}}, \text{pS}_2\right]$$

$$\{\{pS_2 \to 6.29067 \times 10^{-11}\}\}$$

- **Problem 12.11**

In 1 liter (or 1 minute of time), .9/(R T) moles of enter the reaction and we take x as the number of these moles that react to reach equilibrium. Thus the total number of moles of water is

$$\text{nHOH} = \frac{.9\,\text{V}}{\text{R T}} - \text{x} \text{ /. } \{\text{R} \to 0.082057, \ \text{V} \to 1, \ \text{T} \to 298\}$$

$$0.0368053 - x$$

The Ar does not react, thus it has the following constant number of moles

$$\text{nAr} = \frac{.1\,\text{V}}{\text{R T}} \text{ /. } \{\text{R} \to 0.082057, \ \text{V} \to 1, \ \text{T} \to 298\}$$

$$0.00408948$$

The moles of HF formed are

$$\text{nHF} = 2\,\text{x}$$

$$2\,x$$

The total number of moles in the equilibrium mixture is

$$\text{nms} = \text{nHOH} + \text{nAr} + \text{nHF}$$

$$0.0408948 + x$$

In terms of x, the mass rate loss per hour

$$\text{rate} = 60\,\text{x}\,(\text{massCa} + 2\,\text{massF} - \text{massCa} - \text{massO})$$

$$1320.\,x$$

The x values at the two temperature determined from the two supplied mass loss rates

```
x1 = Solve[rate == expt /. expt -> 2.69 * 10^-4]
```

$\{\{x \to 2.03788 \times 10^{-7}\}\}$

```
x2 = Solve[rate == expt /. expt -> 8.30 * 10^-3]
```

$\{\{x \to 6.28788 \times 10^{-6}\}\}$

The equilibrium constants at the two temperatures are

$$K1 = \frac{nHF^2}{nms\ nHOH} \ /.\ x1[[1]]$$

1.10367×10^{-10}

$$K2 = \frac{nHF^2}{nms\ nHOH} \ /.\ x2[[1]]$$

1.05074×10^{-7}

The G's at the two temperature are

```
G1 = -R T Log[K1] /. {R -> 8.3144, T -> 900}
```

171563.

```
G2 = -R T Log[K2] /. {R -> 8.3144, T -> 1100}
```

146961.

Drawing a line through these two slopes, the entropy is

$$\Delta S = \frac{-(G2 - G1)}{200}$$

123.013

and the enthalpy is

$$\Delta H = G1 + \Delta S\ T \ /.\ T \to 900$$

282275.

The final variation of free energy with temperature is

$$\Delta G = \Delta H - T\,\Delta S$$

$282275. - 123.013\ T$

■ Problem 12.12*

It was not clear what the problem is asking or even if enough information is available. If you have a solution, let me know.

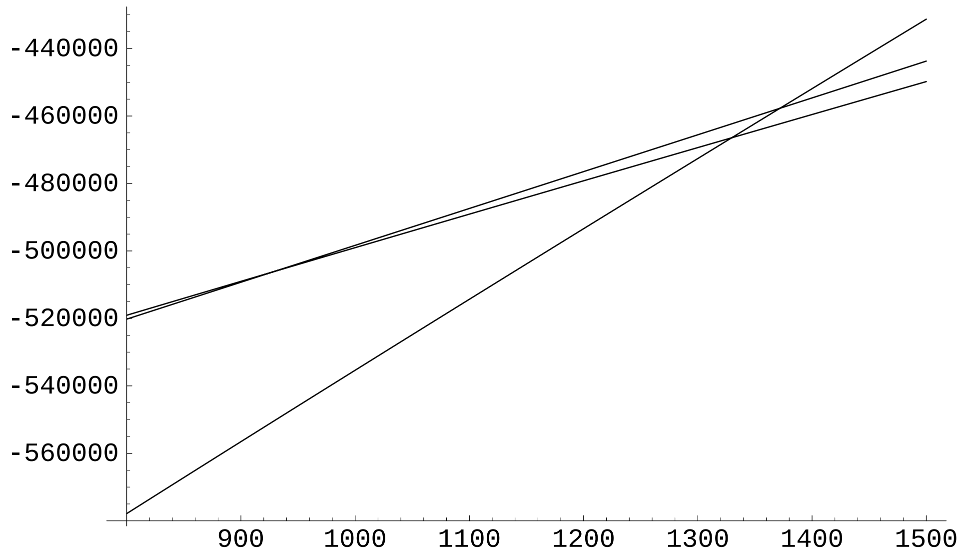
■ Problem 12.13

The three reactions are

```
ΔGi = -604000 - 5.36 T Log[T] + 142.0 T;
ΔGii = -759800 - 13.4 T Log[T] + 317 T;
ΔGiii = -608100 - 0.44 T Log[T] + 112.8 T;
```

We can plot then all

```
Plot[Release[{ΔGi, ΔGii, ΔGiii}], {T, 800, 1500}]
```




```
- Graphics -
```

The one with the steepest slope is obvious the gas oxidation (the largest -ΔS is caused by conversion of gas to solid). Similarly, the next steepest slope is the liquid oxidation. Thus, reaction (ii) is for the gas, but it is not clear whcih of (i) and (iii) has the steeper slope. Another approach is to find the intersections of each. From the plot abve (and identifying the gas, liquid, and solid oxidation from the slopes) the melting point is the highest intersection and the boiling point is the lowest intersection. From the following solutions

```
Solve[ΔGii == ΔGi, T]
```

$\{\{T \to 1329.68\}, \{T \to 2.83742 \times 10^9\}\}$

```
Solve[ΔGii == ΔGiii , T]
```

$\{\{T \to 1371.89\}, \{T \to 6.95165 \times 10^6\}\}$

```
Solve[ΔGi == ΔGiii , T]
```

$\{\{T \to 927.959\}\}$

we deduce the (ii) is the gas, (iii) is the liquid, and (i) is the solid. The melting point and boiling point are

$T_m = 928;\ T_b = 1372;$

Problem 12.14

First, we find the non-negligible vapor pressure of Zn:

```
pZn = Exp[lnvapZn /. T -> 1030]
```

0.178681

The reacion Zn + $\frac{1}{2}$ O_2-> ZnO has

```
ΔG = -460200 + 198 T
```

$-460200 + 198\,T$

in two moles of air (which as given elsewhere is 21% oxygen) has the following number of moles of O_2:

```
nO2 = .42 - x
```

$0.42 - x$

and moles of N_2

```
nN2 = 2 * .79
```

1.58

The partial pressure of O_2 and N_2 come from mole fraction (between O_2 and N_2) using total pressure due to just those compounds (the given .8 atm minus the vapor pressure of Zn):

$$pO2 = \frac{nO2\,P}{nO2 + nN2} \;/.\; P \to .8 - pZn$$

$$\frac{0.621319\,(0.42 - x)}{2. - x}$$

$$pN2 = \frac{nN2\, P}{nO2 + nN2} \;/.\; P \to .8 - pZn$$

$$\frac{0.981684}{2. - x}$$

The equilibirum constant is

$$K = Exp\left[\frac{-\Delta G}{R\, T}\right] \;/.\; \{R \to 8.3144,\; T \to 1030\}$$

$$9.89965 \times 10^{12}$$

which can be solved to get extent of reaction x. Note the due to the high K, the reaction is essentailly complete and all oxygen is used up:

$$Solve\left[K^2 == \frac{1}{pO2}\right]$$

$$\{\{x \to 0.42\}\}$$

Each mole of oxygen consummes 2 moles of Zn. The mass oxidized is thus

$$massOx = 2 * .42 * massZn$$

$$54.9192$$

Comparing Zn vapor pressure to the two moles of air, the mass of Zn in the vapor is

$$massVap = 2\, \frac{pZn}{.8}\, massZn$$

$$29.2054$$

- **Problem 12.15***

No solution.

- **Problem 12.16***

The reaction Hg(l) + (1/2) O_2-> HgO(s) has

$$\Delta G = -152200 + 207.2\, T$$

$$-152200 + 207.2\, T$$

with equilibrium constant at 600 K of

```
K = Exp[-ΔG/(R T)] /. {R -> 8.3144 , T -> 600}
```

```
267.387
```

Because O_2 is the only gas, it must develop partial pressure

```
Solve[K == 1/Sqrt[pO2] , pO2]
```

```
{{pO2 → 0.0000139868}}
```

```
pO2 = 0.0000139868;
```

The vapor pressure of the liquid Hg is

```
pHg = Exp[lnvapHgl /. T -> 600]
```

```
0.547409
```

Finally, the partial pressure of N_2 becomes

```
pN2 = P - pO2 - pHg /. P -> 2
```

```
1.45258
```

The mole fractions are half these values (because there total pressure is 2 atm):

```
{pO2/2 , pHg/2 , pN2/2}
```

```
{6.9934 × 10^-6, 0.273704, 0.726289}
```

These results differe from those in the text.

- **Problem 12.17***

This problem is related to section 12.7 of the text which was not covered in class and will not be on the final exam.

Final Exam

- **Problem 1**

The water reaction is $2\,H_2 + O_2 \text{->} 2\,H_2\,O$ with

```
ΔGH = 2 (-247500 + 55.85 T)
```

```
2 (-247500 + 55.85 T)
```

The silicon reaction (on molar oxygen basis) is Si + O_2 -> SiO_2 with

```
ΔGSi = -907100 + 175 T
```

$-907100 + 175\,T$

The difference of these reactions gives a reaction for oxidation of Si by water as Si + 2 $H_2\,O$ -> SiO_2 + 2 H_2 with

```
ΔG = Simplify[ΔGSi - ΔGH]
```

$-412100. + 63.3\,T$

The equilibrium constant is

$$K = \mathrm{Exp}\left[\frac{-\Delta G}{R\,T}\right] \;/.\; \{R \to 8.3144,\; T \to 1600\}$$

1.40317×10^{10}

The water pressure (when the H_2 pressure is 1 atm) at equilibrium is

$$\mathrm{Solve}\left[K == \frac{1}{\mathrm{Pmax}^2},\ \mathrm{Pmax}\right]$$

$\{\{Pmax \to -8.44199 \times 10^{-6}\}, \{Pmax \to 8.44199 \times 10^{-6}\}\}$

If the pressure is above this value, **ΔG** will become negative and the Si oxidation will proceed. Thus, this pressure is the maximum water pressure to which Si can be heated without oxidizing.

From the **ΔG** result above, the reaction is exothermic (**ΔH = -412100 < 0**).