Examples of the Use of Spreadsheet Software for Making Thermodynamic Calculations

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Thermodynamics is one of the engineering sciences used in the design and analysis of processes. Your text covers the basics of thermodynamics, and gives many examples for applying it to materials processing. The examples and exercises in your text have sometimes been simplified in order to make the calculations manageable. The availability of spreadsheet software means that more complex thermodynamic problems can be handled, and simple problems can be treated in depth. This document contains descriptions of 22 examples of the use of thermodynamic data and typical spreadsheet tools. Most of the examples use a spreadsheet as a calculational tool, while others illustrate the use of a specialized software package called THERBAL.

The example descriptions below are keyed in with the calculations on the Microsoft®Excel workbook ThermoXmples.xls, and relevant material from the text. The example name is the same as the worksheet name in the workbook. All of the data came from the Excel workbook ThermoTables.xls.

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Volume and Temperature Changes During Adiabatic Compression of Steam (**Example STM**)

The behavior of an ideal gas during reversible adiabatic compression. Application of the First Law. Use of Excel's formula bar and charting tools. *See text, Sections* 2.7-2.8.

Example Description

100 liters of steam, initially at 1 atm and 400 K, is compressed adiabatically until the temperature reaches 650 K. Calculate the volume and temperature as a function of pressure.

Calculations and Results

The equation of state of an ideal gas is given by Equation [1]:

PV = nRT

where R = 0.08206 liter•atm/degree•mol, and n = number of moles. Most gases come close to ideal behavior, especially at elevated temperatures. In this example, steam is assumed to behave ideally above 400 K. When an ideal gas is compressed adiabatically, the work results in an increase in temperature. The relationships between the state variables are shown graphically in text Figure 2.2 and 2.3.

The text Example 2.10 was worked out for a gas having a fixed value of Cv. However, Cp (and necessarily Cv) for steam varies with temperature over the specified range, as shown in the Excel workbook ThermoTables.xls. Over a moderate temperature range, Cp and Cv vary in a linear manner with temperature. This is shown in Figure 1 of worksheet STM of the ThermoXmples.xls workbook. Here, Excel's *trendline* tool was used to obtain a linear approximation to the molar Cp equation for steam. The statistical validity of using a linear approximation for the variation in Cp with temperature is shown by a value of the statistical regression parameter $R^2 > 0.995$. Cv is obtained by subtracting the gas constant R (here, R = 8.314 Joules/degree•mol) from the Cp equation, to obtain:

Cv = 21.34 + 0.0111(T)

The text equations in Section 2.7 assume a constant value of Cv with temperature. Using the Cv expression from Equation [2] gives:

$$21.34\ln(T_2/T_1) + 0.0111(T_2 - 400) = -R\ln(V_2/100)$$

Terms were collected, and the equation was written as a formula in cell J7 of the STM worksheet. The fill command was used to calculate $-\ln V_2$ vs. T at 50° intervals, between 400 and 650 K. V_2 was calculated in column K and P in column L by use of Equation [1].

The results were plotted in Figure 2, using the left-hand scale for temperature, and the right-hand scale for volume. The pressure must be increased to about 7.9 atm to attain the specified 650 K temperature, which causes a decrease in volume to about one-fifth of the initial volume.

Assignment

Calculate and plot the work done on the system during the adiabatic compression. Calculate the temperature if the steam undergoes free expansion to 1 atm.

[2]

[3]

[1]

Changes in Heat and Entropy of Solidification of Supercooled Tin as a Function of Temperature **(Example SNF)**

Application of the second law to the solidification of a supercooled liquid metal. See text Example 2, Section 3.17.

Example Description

Clean metals and alloys can be supercooled tens of degrees below their melting points, and in some cases, even more for short time periods. A thermodynamic analysis of supercooling involves calculating the thermodynamic properties of supercooled metals. This example shows how these properties may be estimated by extrapolating the data for the stable liquid phase to the reference temperature of 298.15 K, and errors associated with such extrapolation. Tin is used as the metal for this example. The objective is to calculate a thermodynamic data table for Sn(l) valid to 298 K*, and to calculate values for Δ H and Δ S of solidification of 1 mol of the supercooled metal.

Calculations and Results

Data for Sn(b,l,g) was obtained from the workbook ThermoTables, and shown in Table I of worksheet SNF of workbook ThermoXmples.xls. The Cp for Sn(l) was calculated from the following equation (from row 27, highlighted in yellow):

 $Cp Sn(liquid) = 28.098 + 0.00017(T) + 183243/T^2$

[4]

A plot of Cp values for Sn(l) is shown in Figure 1 of worksheet SNF. Cp rises exponentially with decreased temperature, thus indicating a possible error in the extrapolation of an equation that was obtained by fitting experimental data obtained above 505.12 K. While keeping this in mind, the Cp for a Sn(l) data table was created in column M of Table III by using the above Cp equation (data in row 52 of Table III is the same as data in row 27 of Table I).

The high-temperature heat content H_T-H_{298} (also called enthalpy) of Sn(l) was calculated by integrating the Cp equation above, and determining the constant of integration F by setting $H_T-H_{298} = 0$ at 298 K. (See formula in cell R58). The parameters are shown in row 58 of Table III, and a set of data is shown in column N. The entropy of Sn(l) was calculated by integration of the Cp/T equation, and evaluating the constant of integration F by using S = 80.242 at 505.12 K (see formula in cell R64). A row of S data is shown in column O.

Values for the heat of formation of Sn(l) from Sn(b) (i.e., the Δ H of fusion of solid Sn) were calculated by the cyclic route described by text Figure 3.9. Solid Sn was cooled from T to 298, melted at 298, and liquid Sn heated to T. The formula for this calculation is shown in cell P7. The sum of these heat terms is equivalent to the Δ H of fusion of Sn at T. The results are shown in column P of Table III. The negative of these values is the Δ H of solidification of supercooled Sn, and is shown in column E of Table II. As expected, the values in cells F16 and P14 are the same.

The Δ H and Δ S of solidification of 1 mol of Sn, as shown in Table II, were plotted in Figure 2 as a function of the supercooling temperature below the normal melting point of 505.12 K. A noteworthy feature of both curves is that the slope changes direction at about 80° of supercooling, which indicates that the extrapolation of Cp of Sn(l) may be seriously in error below about 450 K. The discussion of text Example 2 indicates that Δ S of fusion should continually increase the lower the T, which does not happen for supercooling Sn more than about 80°. The results in Figure 2 should thus be considered increasingly in error for supercooling more than about 50°.

<u>Assignment</u>

A sample of tin is supercooled 30° at which time solid nucleates, and some tin freezes as the temperature increases to 505.12 K. Calculate the fraction of the sample that remains liquid.

^{*}As a shortcut, the value "298" is used in this text to designate the thermodynamic reference temperature of 298.15 K.

Calculation of the heat balance for adiabatic reduction of uranium fluoride with magnesium. *See text, Example 1, Section 6.9.*

Example Description

Metals such as titanium, vanadium, niobium, zirconium and uranium cannot be reduced by such common reducing agents as H_2 or CO. Either their oxide (or halide) is too stable, or they form carbides and hydrides instead of metal. A variety of techniques have been developed to produce these metals, such as electrowinning from a fused salt, or reduction by an even more reactive metal. The text describes the reduction of UF₄ by Mg to produce U and MgF₂ (both products as liquids).

The product must reach a temperature above the melting points of the products so that they can be easily separated. U melts at 1408 K, and MgF₂ at 1536 K, so a final process aim temperature should be \geq 1650 K to allow for heat losses to the container. The text example showed that for reactants entering at 298 K, the reaction did not develop sufficient heat for the products to reach 1773 K, hence the reactants had to be preheated to 859 K. In this example, some UF₆ will be added to increase the reaction heat. The aim is to calculate the amount of UF₆ to be added to eliminate the necessity to preheat the reactants.

Calculations and Results

This example will be solved using a graphical approach. The amount of UF_6 to be added will be calculated for several final process temperatures between 1650 and 1800 K. Data for all substances is shown at the top of worksheet URX. The necessary heat-content data is in a small table underneath the product species (MgF₂ and U). The stoichiometric reaction for production of 1 mol of U is:

A)UF₄ + (1-A)UF₆ + (3-A)Mg
$$\rightarrow$$
 U + (3-A)MgF₂ [5]

which goes to completion because of the large negative value of $\Delta G^{\circ}rx$ at all temperatures.

A mass balance was calculated for values of A between 1 and 0.75, and shown in the table near cell Q15. Then the Δ H°rx at 298 K was calculated from the Δ H°f of products and reactants in row 18. The values range from -327,600 to -539,600 J/mol of U as A varies from 1 to 0.75. This indicates a substantial increase in the heat available for the products as UF₄ is replaced by UF₆. This will be partly counterbalanced by the increased amount of MgF₂ in the product mix.

The next step was the calculation of the high-temperature heat content (H_T - H_{298}) of the products between 1650 and 1800 K, as shown in the table near cell Q28. Finally, the net heat for the process was calculated by adding the $\Delta H^{\circ}rx$ and H_T - H_{298} values, and the results displayed in a table near cell Q34, with units of kJ/mol U. Clearly, the addition of UF₆ to replace some of the UF₄ provides sufficient energy to heat the products to above 1650 K without any need to preheat the reactants.* The net heat values were plotted in Figure 1 of worksheet URX. The adiabatic mix composition is located at the point where the temperature line crosses the net heat = 0 axis. Excel's trendline feature was used to obtain a linear approximation of each temperature line, and the resulting equation is displayed on Figure 1. The line intersection details are seen more clearly in Figure 2, which enlarges the region of interest.

The equation for each line was solved to obtain the % UF_6 in the fluoride mix, and the results shown in a table near cell W34. The final objective of the example is shown in Figure 3, where the specific % UF_6 is shown as a function of the aim product temperature (under adiabatic conditions). The trendline equation expresses these results:

 UF_6 in reaction mix = 0.0404(T) - 54.67

[6]

For a final reaction temperature of 1776 K (text example aim), the mix should contain about 17% UF₆ which would require about 220 g of Mg per kg of U produced.

Assignment

Calculate the amount of Ca to use (in place of Mg) to reach a product temperature of 1750 K using only UF4, with no reactants preheat. Neglect any heat of solution between CaF₂ and MgF₂.

^{*}The reactants can be ignited by an electrical discharge using a wire. Since the product temperature is above the b.p. of Mg, the charge should be contained in a pressure vessel to prevent evaporation of unreacted Mg.

Calculation of the adiabatic flame temperature for CH₄ combustion vs. amount of excess air used. *See text, Problem 6.7.*

Example Description

The combustion of hydrocarbon fuels is the most common way to provide heat for materials processing needs. One of the ways to rank fuels is by their adiabatic flame temperature (AFT), using either stoichiometric air or O_2 for the oxidant. The stoichiometric amount of oxidant is calculated by assuming complete combustion of the hydrocarbon to CO_2 and H_2O . (If the fuel contains S, combustion is to SO_2). This example will show how the AFT is calculated for various amounts of air in excess of stoichiometric amounts. Air is assumed to be 79% N_2 and 21% O_2 . The units used in this example are °C and kJ.

Calculations and Results

The standard reaction for the combustion of methane is written below for the formation of water vapor as the product. The stoichiometric amount of air is 9.524 mols. For reactants entering at 25°C, the heat content of the product gases plus Δ H°rx at 25°C must equal 0 for adiabatic conditions.

 $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O(g); \quad \Delta H^\circ rx \text{ at } 25^\circ C = -802.33 \text{ kJ}$ [7]

There are two different approaches to calculating the AFT for combustion. One approach would be to pick the AFT, and calculate the % excess oxidant amount. The other is to select the oxidant amount, and calculate the AFT. The latter approach is used in this example. Since we are solving for the AFT, we need an explicit equation for the heat content as a function of temperature, where the lowercase t indicates °C. An examination of the data indicates that Cp is very close to a linear function of t above about 1200°C, so the functional equation for H_t-H₂₅ has the form:

 $H_t-H_{25} = A(t) + B(t^2) + C$

[8]

Excel's regression tool was used to determine values of A, B, and C for each product species between 1227 and 2727°C. The results are shown just below each column of data on worksheet AFT (in row 67). The value of $R^2 \cong 1$, thus indicating that the quadratic equation is a very satisfactory fit to the data. The H_t-H₂₅ equation parameters were copied to row 7 past column AA for ease in use in making the heat balance calculations.

The mass balance relationships for various amounts of % excess air are shown in Table I. A heat balance for combustion was written by taking the sum of all heat effect terms in cells W21:W23; the term for C includes the Δ H°comb at 25°C for methane. The values of A, B, and C were inserted into a formula bar equation (cells X25:AC25) based on Equation [8], but revised to the format of the quadratic formula. The value of t was solved for each value of % excess air, and plotted in Figure 1. The AFT varies from about 2050°C at stoichiometric air, to 1210°C at double the stoichiometric air. Excel's trendline tool was used to fit a quadratic formula to the data line in Figure 1. The equation is shown in a text box on the Figure. The value of R² is >0.99, which indicates an excellent fit.

Care should be taken in making AFT calculations above 2000°C using the stoichiometry written in Equation [7]. This is because even with excess air, some CO and H_2 will be present in the gas, and even small amounts of O, H, and N. If the air is enriched with O₂, the calculated AFT may be well above 2500°C, but the actual AFT will be significantly less.

Assignment

Calculate the AFT for the burning of H₂, CO, and C with 150% of stoichiometric air.

Heat Balance for Calcination Furnace with Heat Exchanger (Example CHX)

Calculation of the heat balance on a process for calcination of MgCO₃, including a heat exchanger to preheat the combustion air. *See text, Chapter 6.*

Example Description

Calcination is a process whereby a complex compound (usually a carbonate, hydroxide or sulfate) is heated to a temperature such that the complex compound decomposes to the oxide. In this case, MgCO₃ is heated in a fluidized-bed furnace heated by combustion of CH₄ to produce MgO. The MgCO₃ and CH₄ enter at 25°C, and the MgO and furnace gases leave at 650°C. The furnace gases are passed through a heat exchanger to preheat the combustion air, thus increasing the efficiency of the process (in terms of fuel consumption per amount of MgCO₃ calcined). A sketch of the process is shown below. The objective of this example is to calculate the effect of air preheat temperature on amount of MgCO₃ calcined, and the temperature of the furnace gases leaving the heat exchanger. The basis is 1 mol of CH₄ burned with 11 mols of air (15.5% excess air), and heat losses of 60,000 J in the calcination furnace and 40,000 J in the heat exchanger.



Calculations and Results

Worksheet CHX contains the relevant data, with the heat content at 650° C (H_{650} - H_{25}) for each product species calculated in row 27 by interpolation between the 900 and 950 K values of H_T - H_{298} . Since the temperature of the warm furnace gas is an unknown, an expression is needed to relate H_t - H_{25} and t of the product gas species. Considering the variability and imprecision of the heat losses, a linear equation was used instead of the quadratic equation of Example AFT. In this application, the relevant H_t - H_{25} values were plotted and the trendline tool used to obtain the equation parameters. Since the furnace gas temperature does not go below about 200°C, the lower temperature points were omitted in the fitting. Figure 1 of the worksheet shows the results. Table II lists the H_t - H_{25} parameters obtained from the trendline fit.

The stoichiometric reaction for calcination is:

$$CH_4 + (11)N_{1.58}O_{.42} + (X)MgCO_3 \rightarrow (1+X)CO_2 + 2H_2O + (7.524)N_2 + (1.476)N_{1.58}O_{.42} + (X)MgO$$
[9]

The value of X is calculated by writing the heat balance equation in terms of X, and solving. In addition to CO_2 and H_2O , the product gas is chosen to be a mixture of N_2 and the excess combustion air. The heat input to the calcining part of the system is the ΔH° combustion of CH_4 at 25°C plus the H_t - H_{25} of the preheated air. The heat output is the calcining reaction, H_{650} - H_{25} of the hot furnace gases, H_{650} - H_{25} of the MgO, and the heat loss (60,000 J). Table I gives the mols of MgO produced as a function of the air preheat t, °C. The heat balance equation is written in column S. With no air preheat, about 2.8 mols of MgO are produced per mol CH_4 burned. At the upper limit on air preheat temperature,^{*} about 4 mols of MgO could be produced.

^{*} The theoretical upper temperature limit on air preheat is 650°C, but no practical heat exchanger would have such perfect heat transfer capabilities.

As the hot furnace gas passes through the heat exchanger, it transfers heat to the combustion air and loses heat (40,000 J) to the surroundings. Table III contains the heat balance calculations for the heat exchanger. Column X is the value of H_{650} - H_{25} for the entering furnace gas, which increases with air preheat temperature because it contains more CO₂ from calcination. Column Y lists the H_t - H_{25} of the warm furnace gas exiting the heat exchanger. The warm furnace gas temperature is calculated by the heat balance formula written in column Z, using the H_t - H_{25} parameters from Table II.

In practical terms, the calciner would aim for a specific MgO production rate, and vary the fuel and air input in response to the extent of air preheat temperature. This example picked a basis of 1 mol of CH₄ burned to simplify the arithmetic, but the results can easily be converted to a more practical basis. Table IV shows the kg of MgO produced per m³ (STP) of CH₄ burned (column U) and the m³ (STP) of CH₄ required to calcine 1 tonne of MgO (column V). Preheating the air to 627°C gives about a 30% decrease in fuel consumption.

The process results are summarized in Figure 2 of the worksheet. The warm furnace gas temperature shows a linear decrease in temperature with the air preheat temperature. Even with a highly efficient heat exchanger, the warm furnace gas exits above 200°C. A quadratic expression was required to express the specific fuel consumption as a function of air preheat temperature.

<u>Assignment</u>

Calculate the effect of cutting the combustion air to 10 mols/mol of CH₄. What is the effect of cutting the heat losses in half on fuel consumption?

Condensation of Zinc from Vapor Stream (Example ZNV)

Calculation of the heat balance for the condensation of zinc from a vapor stream containing Zn and CO. See text, Chapter 7, Section 7.9 (Example #1) and Problem 7.3.

Example Description

Metal vapors are encountered in many processing situations. Condensation (to a liquid or a solid) can occur deliberately or inadvertently when the gas cools. In this example, 100 mols of a gas from a metal refining process contains 50% Zn and 50% CO at 1150 K, and the zinc is recovered as liquid in three condensation stages. The gas is cooled by spraying liquid zinc at 700 K into it. The objective is to calculate the amount of zinc coolant required for each stage, and the overall recovery of zinc from the process. Ignore heat losses. The first stage operates at 1050 K, the second at 900 K, and the third at 750 K. The cooling takes place so fast that the CO doesn't have time to react. A sketch of the process is shown below. Gas flow is shown as a dashed line, and liquid as a solid line.

Calculations and Results

The data for the relevant species is listed in worksheet ZNV. As an adjunct to the solution of this example, the vapor pressures of solid and liquid Zn are calculated past their normal stability temperatures. The p(Zn,solid) is calculated from the data in Table I up to the mp of Zn (692.73 K), and extrapolated to 850 K using an equation developed from the 300-692.73 K data. Excel's regression tool was used to obtain a 3-term equation similar to that used in the text, with the result shown at the bottom of Table I. A similar equation for p(Zn,liquid) was obtained from the data in Table II.

Log(pZn,solid) = 8.423 - 6914/T - 0.749(logT)

[10a] [10b]

Log(pZn,liquid) = 9.552 - 6675/T - 1.268(logT) [10b] Calculating the T that satisfies both equations indicates the excellent fit of the data by these 3-term equations. A trialand-error solution gives $\cong 692$ K as the triple-point temperature for Zn.*



Equations [10a,b] were used to calculate the pZn for solid and liquid near the melting point, as shown in Table III. The results are displayed in Figure 1 of the worksheet, where the slight differences in pZn for the 2 phases is readily apparent. The temperature where the lines cross is difficult to see, but is about 693 K. The red line drawn to represent the solid/liquid phase boundary is vertical because the small pressure range of Figure 1 has no effect on the melting point. Compare this to text Figure 7.16.

^{*} This example uses Zn(liq) as the stable form of zinc at 298.15. Choice of a standard state is arbitrary, so long as the calculations are carried out correctly.

Table IV gives the mass and heat balance for each condensation stage, in mols and J. 34.98 mols of Zn condense in stage #1, 12.04 in stage #2, and 2.93 in stage #3. There are different ways to carry out a heat balance; in this example, each stage was balanced as follows. A negative value in the table means that the process gives up heat.

- Cool gas phase from entering to stage temperature.
- Condense the requisite amount of zinc at the stage temperature.
- Sum the above and divide by the change in heat content for the entering Zn(l) from 700 K to the stage temperature.

This gives the mols of Zn(l) required to absorb the heat from cooling the gas and condensing the Zn(g).

The mols of Zn(l) required for each stage is given in column Z of Table IV, and the H_T - H_{298} for the Zn(l) leaving each stage is given in column AC. The process requires about 32 kg of coolant Zn(l) per m³ (STP) of entering gas. The overall loss of Zn to the final exit gas is about 0.1%. The temperature of the entire mass of Zn(l) leaving the system is given in cell AB55, and is about 614°C.

<u>Assignment</u>

The temperature of stage #3 could (in theory) be dropped as low as \approx 700 K to scavenge a bit more Zn(g). Calculate the amount of Zn(l) required as a function of stage #3 temperature in 5° intervals, down to 705 K.

Calculation of the heat recovered in steam from a waste heat boiler. See text, Chapter 8.

Example Description

Many pyrometallurgical processes produce a hot gas that contains potentially useful heat. A common way to recover that heat (for use elsewhere in the plant, or conversion into electricity) is in a waste heat boiler, where the heat is used to make superheated steam. Later the steam is converted back to warm water, which is recycled back to the WHB. The objective is to calculate the amount of heat that can be absorbed by 1 kg of water entering the WHB at 60°C, to superheated steam (SHS) at temperatures above 200°C. Also, compare the volume of 1 kg of steam as listed from experimental data to that calculated assuming steam behaves ideally and like a van der Waals gas.

Calculations and Results

In the simplest case, a WHB consists of an insulated chamber containing steel tubes. The warm water enters under pressure, absorbs heat from the process gas, and is converted to high-pressure steam. The water can be considered to absorb heat in 3 stages.

- First, the warm water (60°C) is heated to the boiling point (190 to 220°C, depending on P).
- Second, the water boils.
- Third, the steam is heated 40° above the b.p.

The heat effect for the first step can be calculated from the data in the worksheet (Table I) because the properties of H2O(liq) are relatively unaffected by pressure. However an additional source of data is needed for the other 2 steps because steam is far from ideal at typical boiler pressures. The necessary thermodynamic data for H₂O is found in so-called steam tables.* These tables use 0° C as the basis temperature, and units of kJ/kg and bars (convert atm to bar by multiplying atm by 1.0133).

Table I of worksheet WHB summarizes pertinent steam and water data from ThermoTables (FREED data). This data is for reference purposes, and is not used in the example because it is based on different units than the steam table data. Table II lists data from the steam tables between 60° and 300°C. The values in column AF represent the enthalpy of water above 0°C. Since the WHB water enters at 60°C, it has 251 fewer kJ of heat than listed in the table. The data in column AG represent the heat of vaporization of 1 kg of water, which is the heat of the second stage described earlier. The values listed in column AI represent the sum of stages 1 and 2 (i.e., heat absorbed by 1 kg of water going from 60°C to saturated steam). These values are plotted in Figure 1 of the worksheet. It is interesting to note that the enthalpy of saturated steam (green line) reaches a maximum at about 240°C.

Steam is typically superheated to prevent condensation in the boiler tubes outside the WHB. Stage 3 is the 40° superheating of saturated steam. The steam tables do not explicitly list the heat required for this step (it requires interpolation from tables), so a different approach was used here. The Cp of saturated and superheated steam from the steam tables was used to generate parameters for an equation linear in p and t. The steam table data is shown in Table III, and the regression tool results are shown in Table IV. The results were:

Cp SHS = 0.0544p - 0.006129t

[11]

[12]

This equation was used to calculate Cp vs. t for the saturation pressures at 190_i, 200_i, 210_i, and 220_iC. Cp at saturation temperature and for the 4 superheat cases was plotted in Figure 2. The discrepancy between the Cp data and the linear approximation of Equation [11] is small, as shown by the difference between the end point of the 4 straight lines, and the saturation curve. The average Cp for superheating calculations was calculated in Table IV, and shown as a bold number.

The heat required to superheat the steam was calculated from these average Cp values, and is shown in column AN of Table II. These values represent stage 3 of the process. The total heat for all 3 stages is the sum of values in columns AI and AN, and is shown in column AO and plotted in Figure 3. A trendline analysis of the total heat showed excellent agreement to a linear equation:

Heat for 1 kg water to SHS = 0.957t + 2418

^{*} See, for example, a typical Mechanical Engineering Thermodynamics textbook. or the NBS/NRL steam tables published by Hemisphere Press (1984). For more serious steam table calculations, a steam table calculator is available from Archon Engineering (http://www.archoneng.com).

The volume of saturated steam (m^3/kg) is shown in Table II in column AJ, and in liters in column AQ. Comparison volumes were calculated assuming ideal behavior (column AR) and van der Waals behavior (column AS). The cubic form of the vdW equation was set up with the vdW parameters for steam taken from text Table 8.1:

 $pV^3 - (0.0237p + 0.08314T)V^2 + 5.46V - 5.46(0.0237) = 0$ [13] where p is in bars and V is the molar volume (molar volume = volume of 1 kg/55.51). Goal Seek was used to calculate the vdW volume (liters/kg) for each case, as shown in column AS and AT of Table V. The results are shown in Figure 4. Clearly the vdW equation is superior to the ideal gas law at elevated pressure.

Interpolation in the steam tables was used to estimate the volume (liters/kg) of the SHS steam, and is shown in column AL of Table II, and plotted in Figure 5. A table of results is shown below.

T Boil	р	T S-heat	Ht Stg 1	Ht Stg 2	Ht Stg 3	Total Ht	Vgas	
190°C	12.6 bar	230°C	557 kJ	1979 kJ	102 kJ	2638 kJ	175 lit	
200°C	15.6 bar	240°C	601 kJ	1941 kJ	106 kJ	2648 kJ	142 lit	
210°C	19.1 bar	250°C	647 kJ	1899 kJ	111 kJ	2657 kJ	110 lit	
220°C	23.2 bar	260°C	693 kJ	1856 kJ	117 kJ	2666 kJ	98 lit	

<u>Assignment</u>

Calculate the maximum work obtainable from 1 kg of superheated steam when it is expanded reversibly to the pH_2O in equilibrium with water at 60°C.

Calculation of the boiling point of an Au-Cu alloy and construction of the gas-liquid phase diagram. *See text, Section* 9.3, 9.9 and Example #1.

Example Description

The vapor pressure of an alloy is the sum of the partial pressures of each constituent. The normal boiling point is defined as that temperature where Ptotal = 1 atm. This example shows how to calculate the boiling point of an Au-Cu alloy and plot the gas/liquid phase diagram for the system.

Calculations and Results

Liquid Au-Cu alloys exhibit nearly regular behavior, according to:* $RT(ln\gamma_1) = -5750(X_2)^2$

This is negative deviation from Raoult's Law, so the pAu and pCu are less than for an ideal solution.

Required data for the calculations is shown in Table I of worksheet ABP. Gold boils at 3124 K, and copper at 2839 K. A p-T expression was obtained for each element by plotting log(p) vs. 1/T, as shown in Figure 1. The trendline tool was used to fit the data to a linear equation ($R^2 \cong 1$) as shown on the legend box. For Au, the temperature range was entirely *below* 3124 K, hence no extrapolations of vapor pressure data were needed. In contrast, for Cu the b.p. of the alloy was all *above* 2839 K and hence pCu was extrapolated well beyond the values listed in Table I.

An expression for log p was written in Table II for each element as a function of T and alloy composition (row 37 and 38). The Goal Seek tool was used to calculate a temperature such that Ptotal (row 41) was equal to 1 atm. (Naturally, no expression was needed for XAu = 0 or 1). The results were plotted in Figure 2. The trendline tool was used to develop an expression for the b.p. of the alloy. The equation is given in row 79 of the worksheet.

The XAu in the gas phase is the same as the pAu, since Ptotal = 1 atm. This is displayed in row 42 (same as row 40), and plotted in Figure 2. The gas is clearly enriched in Cu, hence the separation of Cu from Au by boiling the alloy is conceptually feasible. However, the extent of separation is such that several stages would be required.

<u>Assignment</u>

Calculate the composition of the vapor phase of solid Au-Cu alloys at 1150 K. Solid alloys have thermodynamic properties that can be adequately expressed as follows (data in calories, from Hultgren):

$$\begin{split} \Delta \mathrm{H}^{\mathrm{-M}} \, Cu &= -10605 X^3 \, Cu + 17274 X^2 \, Cu - 3880 X_{Cu} - 2790 \\ \Delta \mathrm{S}^{\mathrm{-}XS} \, Cu &= -2.212 X^3 \, Cu + 4.576 X^2 \, Cu - 2.964 X_{Cu} + 0.30 \\ \Delta \mathrm{H}^{\mathrm{-M}} \, Au &= -13590 X^3 \, Au + 15090 X^2 \, Au + 2640 X_{Au} - 4140 \\ \Delta \mathrm{S}^{\mathrm{-}XS} \, Au &= 8.24 X^3 \, Au - 14.13 X^2 \, Au + 7.04 X_{Au} + 1.15 \end{split}$$

[14]

^{*} R. Hultgren et. al., "Selected Values of Thermodynamic Properties of Metals and Alloys", John Wiley, New York, 1963. The thermodynamic data listed in this book, and in this example, is in <u>calories</u>. There are 4.184 J/cal, and R = 1.987 cal/mol•K.

Vacuum Refining of Zinc from an Aluminum-Zinc Alloy (Example AVR)

Calculation of the change in temperature during vacuum refining of Zn from Al. See text, Section 9.2-9.3.

Example Description

Vacuum refining can be used when the impurity has a much higher vapor pressure than the host metal. Therefore, Zn can be removed from recycled Al scrap by a vacuum treatment. One technique is called *spray refining* because the metal is exposed to the vacuum in the form of tiny droplets. The large surface area of the droplets enhances mass transfer to the gas, so the assumption of gas-liquid equilibrium is reasonable. The scrap contains 9 wt.% Zn, and is to be refined to 0.1% Zn. The evaporation of Zn is endothermic, so the initial temperature must be high enough to provide the necessary sensible heat, and still be molten at the end of the refining process. Another restriction is that the pZn at the end (0.1% Zn) must be above 0.0001 atm to give a satisfactory rate of evaporation. This example shows how to calculate the desired initial alloy temperature to properly refine the metal. Since the spray is exposed to the surroundings for only a few seconds, heat losses were neglected (adiabatic process).

Calculations and Results

The mol fraction of Zn in the alloy is calculated from:

$$XZn = \frac{1}{1 + \frac{2.424 (\% Al)}{\% Zn}}$$
[15]

Therefore, the XZn at 9 wt% Zn = 0.0392, and at 0.1% Zn is 0.000413. At these low concentrations of zinc, it is reasonable to assume the Zn solute obeys Henry's law in the solvent alloy. Based on the compilation of Hultgren, the Henry's Law activity coefficient for liquid Zn in an Al-Zn alloy is:

 $\log(\gamma^{\circ} Zn) = 555/T - 0.22$ [16]

The vapor pressure of pure liquid Zn is obtained from thermodynamic data on Zn(g), shown in Table I on worksheet AVR. A linear relationship was developed from data between 850 and 1180 K in Figure 1 of the worksheet:

 $\log(p^{\circ}Zn) = -6124/T + 5.193$ [17]

A combination of these 2 equations gives an expression for the pZn as a function of XZn:

 $\log(pZn) = -5570/T + 4.973 + \log(XZn)$

A plot of pZn vs. temperature is shown as Figure 2 on the worksheet for 0.1% Zn (XZn = 0.000413). The restriction of minimum pZn means that the temperature of the refined alloy must be \approx 725°C, or \approx 65° above the melting point of Al. This is confirmed by solving Equation [18] at XZn = 0.000413.

Making a heat balance on the process is somewhat complicated, since we know the final alloy temperature, but not the initial one. This is resolved by starting with liquid Al at 725°C and adding Zn in increments until the alloy has reached 9% Zn. There is a very minor approximation in starting with pure Al as opposed to an alloy of 0.1% Zn, but as will be seen, other even larger approximations are required in order to make the arithmetic manageable. Although the actual process occurs continually, a stepwise calculation will be used to simplify the arithmetic.

The calculations were made with mass unit of grams and temperature unit of °C. The basis was 1000 g of 9% Zn alloy, or 910 g of pure Al at 725°C. The mass of Zn condensed was calculated at each increment of 15° rise in temperature.* The detailed calculations are shown in Table IV of the worksheet, with comments on each row to indicate the meaning of the numbers. The steps in making a calculation were as follows:

- 1. Start with 910 g Al(l) and X \hat{g} Zn(g) at 725°C.
- 2. Heat these two substances 15°.
- 3. Condense X g Zn(g) to Zn(l) at 740°C. The heat of condensation of Zn is a minor function of T, and the
- appropriate relationship was determined by use of the trendline tool in Figure 3, from data in Table III.
- 4. Dissolve X g of Zn(l) in the Al(l) to make an alloy. The partial molar heat of solution of Zn in Al is taken from Hultgren and assumed not to vary with temperature. The partial molar heat of solution was a slight function of composition; as an approximation, an average value of heat of solution was 10140 J/mol.
- 5. X was calculated by dividing the heat to raise the Al(l) 15° by the sum of the heats for heating Zn(g), condensing it, and dissolving it in the Al(l). 910 + X gave a new alloy weight, and the composition of the alloy at 740°C was calculated.
- 6. The steps were repeated, except that in step 1, X grams of Zn(l) were also heated to 755°C. Lacking a value for Cp of the alloy, the Cp for Al(l) and Zn(l) were used.
- 7. The results were plotted in Figure 4. The starting temperature for the 9% Zn alloy is shown to be at least 865°C. It should probably be 10-15° higher as a safety factor to allow for some mass transfer limitations and heat losses.

[18]

<u>Assignment</u>

Scrap aluminum containing 10% Zn is refined by injecting Ar in a continuous reactor fed with 1 kg/sec of alloy. The alloy enters at 920°C and is kept there by electrical heat. Calculate the % Zn in the alloy leaving the reactor as a function of the flow rate of Ar, and the amount of heat required. The Ar is initially at 25°C.

^{*} The selection of 15° was made to give a value of X close to 10 g. This allowed the process to be carried forward over about 10 steps. The larger the number of steps, the more closely the calculation simulates the continuous removal.

Gas Carburization of Steel at 1425 K (Example FEC)

Calculation of the relationship between the composition of a CO/CO₂ gas mixture and the wt. %C in Austenite at 1425 K. *See text, Section 9.9.*

Example Description

Gas carburization of steel can take place by contacting the steel with a gas containing CO and CO₂. The gas transfers carbon to the surface of the steel, and the surface reaches equilibrium with the gas such that the aC in the gas = aC at the steel surface. The object of this example is to show how the thermodynamic properties of the gas can be related to the composition of carbon at the steel surface. the temperature is set at 1425 K, and the pCO + pCO₂ = 1 atm. Control of the carbon content in the steel is achieved by measuring the gas composition, and relating that to the thermodynamics of the Fe-C system.

Calculations and Results

Equilibrium between the gas and carbon dissolved in the steel is represented by:

 $CO_2 + C \rightarrow 2CO; \ aC = (pCO)^2/Krx(pCO_2)$ [19] One control strategy is to measure the CO₂ content of the carburizing gas, and calculate the aC from the thermodynamics of Equation [19]. Another strategy is to use a solid-state sensor to measure the pO₂ in the carburizing gas, and use that to calculate the CO and CO₂ gas composition according to:

$$CO_2 \rightarrow CO + 0.5O_2; \ pO_2 = Krx(pCO_2/pCO)$$
 [20]

The aC is related to the pO₂ by an algebraic combination of Equations [19] and [20]:

$$aC = \frac{\frac{(K20)^2}{pO_2}}{K19\left[1 + \frac{K20}{\sqrt{pO_2}}\right]}$$
[21]

Note that Equation [21] is valid only when pCO + pCO₂ = 1 atm. Data for K19 and K20 are given on worksheet FEC at 1425 K. They were calculated by interpolation in $\Delta G^{\circ}rx$ between 1400 and 1450 K. K19 = 741 and K20 = 1.492 x 10⁻⁶.

The gas composition provides a way to calculate the aC from the pO₂, as shown in columns B, C, and D of Table III. But the desired control objective requires that we have a relationship between the aC and the %C in the steel. Hultgren^{*} has a table of γ C as a function of XC at 1425 K, but provides no equation for the variables. His results were used to derive a 2-parameter Margules relation^{**} of the type:

$$Ln(\gamma C) = \alpha(XFe)^2 + \beta(XFe)^3$$
^[22]

Table II of the worksheet lists values of γC at 0.01 XC intervals, and values of the function $\ln(\gamma C)/(XFe)^2$ were calculated and plotted in Figure 1. The trendline tool was used to develop a linear relationship between the function and XFe, thereby generating values of α and β . Equation [23] relates the aC (calculated from the gas composition) and the composition of the steel (in terms of XFe):

 $Ln(aC) = ln(1-XFe) + 16.16(XFe)^2 - 14.61(XFe)^3$

This equation was solved in Table III using the goal seek tool. Goal Seek varied the XFe in column F until the ln(aC) in column G equaled that in column E (yellow highlight on the worksheet). The rest of the cells were filled with simple formulas to obtain complete information about the gas and steel. The relationship between $log(pO_2)$ and %C in steel is plotted in Figure 2. A 4-term polynomial trendline fit gave excellent agreement between the two variables, and the equation could be used in the development of a control strategy for steel carburization by CO/CO_2 mixtures.

A corresponding relationship between $%CO_2$ in the gas and %C in the steel was plotted in Figure 3. The curve in Figure 3 shows rapidly changing slope, and was fitted by the trendline tool to a power function. However, the fit is not as good as that relating %C and log(pO₂).

<u>Assignment</u>

Calculate the %C in Austenite at carbon saturation. What is the log(pO₂) and %CO₂ in the gas at that point?

[23]

^{*} R. Hultgren et. al., "Selected Values of Thermodynamic Properties of Metals and Alloys," John Wiley, New York, 1963. ** See Section 9.9 of the text.

Calculation of activity coefficients from a phase diagram assuming regular solution behavior. *See text, Section 10.6 and 10.7.*

Example Description

Chapter 10 of the text gives many examples of the relationship between the appearance of the phase diagram and the thermodynamic properties of the two components. Example 10.9 shows how the phase diagram can be calculated from data on the thermodynamics of the components. In this example, the phase diagram will be used to obtain values of γ of liquid Cu (liquid Cu is designated as *Cu* here), assuming the liquid conforms to regular solution behavior.

Calculations and Results

The ASM Metals Handbook contains phase diagrams of many alloy systems. The Cu-Bi system has a eutectic temperature very close to the m.p. of Bi, and a eutectic composition of nearly pure Bi. There is almost no solid solubility of Bi in Cu. Values of the composition and temperature of the liquidus line were read from the diagram, and plotted in Figure 1 of worksheet CuBi. The values were less accurate at the composition extremes because of the slope of the line. At the liquidus condition, the activity of Cu(solid) = 1, but the activity of Cu is \neq 1. From text equation 10.22:

 $Cu(solid) \to Cu; \ \Delta G^{\circ} = -RTln(aCu) = -RTln(\gamma Cu) + ln(XCu)$ [24]

The value of ΔG° for the reaction can be obtained from data on the thermodynamic properties of supercooled liquid Cu. Table I shows such a table from the FREED database, which was calculated by assuming that the Cp for *Cu* remains the same below the m.p., and calculating all other parameters from that. Section 10.5 of your text discusses this procedure. (Also see Example SNF).

The values of ΔG° for Equation [24] = ΔG° f of *Cu* from Table I, and are listed for temperatures between 550 K and the melting point of 1357.6 K in Table II. An equation for ΔG° f vs. T was obtained with the regression tool. A 3-term equation was chosen as being able to give a satisfactory fit, considering the error in reading values from the phase diagram. The equation parameters are shown in cells H61-H63 of the worksheet.

Table III shows phase diagram values, which were converted to mol fraction and degrees K. For each temperature, a value of $\Delta G^{\circ}f$ of *Cu* was calculated from the regression equation. This allowed the calculation of RTln(γCu) according to Equation [24], and the regular solution parameter α (called α' in text Equation 9.68). If the Cu-Bi system were truly regular, the value of α would be a constant. Owing to some combination of non-regular behavior, error in determination of the phase diagram, error in assuming constant Cp of supercooled *Cu*, and error in reading the liquidus values from the Handbook, the α values fluctuate around an average of 14,930. Thus,

 $\operatorname{RTln}(\gamma Cu) \cong 14,930(\operatorname{XBi})^2$

[25]

and of course the equivalent equation holds for RTln(γ Bi).

The γCu was calculated at 1360 K in two different ways. First, from the value of RTln(γCu) obtained from the phase diagram, and setting T = 1360. These values are designated RS' in Table III. Second, with Equation [25], which uses the average value of α . In the latter case, a value of $\gamma^{\circ}Cu$ (the so-called Henry's Law constant) was calculated to be 3.74. The results are plotted in Figure 2. They are in close agreement at all but the two lowest temperature values, which is not surprising in view of the error sources mentioned above.

Assignment

Calculate how much heat is required to completely melt a mixture of 50 g of Cu and 50 g of Bi, for an initial temperature of 400 K.

Reaction Equilibria in the System N-O (Example NOX)

Calculation of the composition of NOx species in N₂-O₂ mixtures. See text, Chapter 11.

Example Description

At temperatures below about 1000 K, N_2 and O_2 have a negligible tendency to react to form oxides of nitrogen (collectively called "Nox" in this example). At higher temperatures, NOx species do form, and although in small amounts, they are of concern to the environment because of their contribution to smog. This example explores the tendency to form NOx as a function of N_2/O_2 ratio, temperature, and pressure.

Calculations and Results

The reactions between N_2 and O_2 to form NOx are favored by increased temperature. The relevant reactions are shown below. The value of Keq at 2500 K is also listed, as obtained from Table I in worksheet NOX.

$N_2 + 0.5O_2 \rightarrow N_2O$; Keq = 3.36 x 10 ⁻⁶	[26]
$0.5N_2 + 0.5O_2 \rightarrow NO; \text{ Keq} = 5.95 \times 10^{-2}$	[27]
$N_2 + 1.5 O_2 \rightarrow N_2O_3$; Keq = 3.81 x 10 ⁻¹²	[28]
$N_2 + 2O_2 \rightarrow N_2O_4$; Keq = 6.74 x 10^{-16}	[29]
$0.5N_2 + O_2 \rightarrow NO_2$; Keq = 1.05×10^{-4}	[30]
$N_2 + 2.5O_2 \rightarrow N_2O_5$; Keq = 1.03 x 10 ⁻¹⁸	[31]
In addition, N_2 and O_2 tend to disproportionate slightly, according to:	
$N_2 \rightarrow 2N$; Keq = 8.45 x 10 ⁻¹⁴	[32]
$O_2 \rightarrow 2O$: Keg = 2.07 x 10 ⁻⁴	[33]

At temperatures up to 2400 K, the extent of these reactions is so slight that the amount of N_2 and O_2 do not change appreciably. Up to that temperature the Keq expressions for all reactions can contain the same values of pO_2 and pN_2 before and after reaction. This makes it easy to calculate the equilibrium pNOx, pN and pO. The calculations using this approximation were carried to 2800 K, even though the discrepancy between correct and approximate values is increasingly noticeable above 2400 K. Above 2400 K, accurate answers require a different approach, such as THERBAL. The THERBAL results are shown in worksheet NOX-TH, and may be compared to those from worksheet NOX to see the extent of difference.

The first set of calculations was done to determine the effect of temperature on the p of each product gas for an initial $O_2/N_2 = 1$, at Ptotal = 1 atm. The array is set up as Table II, and the results plotted in Figure 1. Owing to the large range of values, the results are plotted on a logarithmic scale. Clearly, the only species that are present in significant amounts are NO, NO₂, and O. The second set of calculations was done at 2500 K and Ptotal = 1 atm for various initial concentrations of N₂. The results are shown in Table III, and Figure 2. Clearly, some species are affected much more by the initial gas composition than others. Finally, the effect of Ptotal at 2500 K was examined for an initial $O_2/N_2 = 1$. High pressures occur during combustion in an internal combustion engine. The results are shown in Table IV and Figure 2. Each point on the graph represents a doubling of Ptotal. The greatest effect is shown at the lower pressures. The effect of Ptotal is to increase the p of each NOx gas, and also the vol % of each NOx gas *except for N and O*; their vol. % **decreases** with P. This is explained by Le Chatelier's Principle.

The wt % NOx was calculated vs. temperature in column L on a basis of 1 mol of initial gas of $N_2/O_2 = 1$ (30 grams of gas), and assuming that the mols of each gas was equal to the partial pressure of each gas. As discussed earlier, this assumption is very good up to about 2400 K.

Assignment

Calculate the grams of NOx formed by the combustion of 1 kg of gasoline in an internal combustion engine operating at 1600 K and 15 atm. The gasoline has 14 wt % H, rest C, and is burned with 120% of stoichiometric air. To simplify the arithmetic, consider only the 3 most abundant NOx species in the calculation. Calculation of the composition of gas species in various mixtures. See text, Chapter 11, Section 11.6.

Example Description

Gas-phase reactions that involve a change in volume make the equilibrium arithmetic complicated. Sample calculations for the reaction between SO₂ and O₂ are described in the text. The first part of this example will show how Excel's goal seek tool can simplify the calculations in the S-O system. In the second part of the example, an approach different from Gaskell's is used to calculate the equilibrium when a third element (N) is added to the system.

Calculations and Results

 SO_2 reacts with O_2 to form SO_3 according to:

 $2SO_2 + O_2 \rightarrow 2SO_3$; Krx = $(pSO_3)^2/(pSO_2)^2 (pO_2)$ [34]

The text example explores the effect of T and P on the equilibrium gas composition produced when 1/2 mol of O2 reacts with 1 mol of SO₂. The cubic equations used in the text were written as formulas in worksheet SON, and goal seek was used to find the mols of SO₃. The stoichiometry relationships were then used to calculate the partial pressures of each gas, and the % of initial SO₂ that reacted.

Data for SO₂ and SO₃ are shown in Table I. The value of log(Krx) for Equation [34] was plotted vs. 1/T to develop a linear relationship between log(Krx) and 1/T, as shown in Figure 1. Such a relationship is particularly useful for calculating the temperature for a specific gas composition. The first set of calculations was made to explore the effect of T at Ptotal = 1 atm. The value of Krx was calculated from the $\log(Krx)$ vs. 1/T equation developed from Figure 1, and listed for several T values in Table III. Goal seek varied the mols of SO_3 (row 10) until the Krx (row 11) was the same as that calculated earlier (row 9). The 2 rows involved are tinted yellow. The text equations were then used to calculate the vol.% of each species in the equilibrium gas, and the result plotted in Figure 2. A trendline fit was developed to express the $\%SO_2$ converted as a quadratic equation. Lower temperatures favor the formation of SO_3 because Equation [34] is very exothermic.

A similar calculation was carried out at 1000 K to show the effect of P. Again, the goal seek tool was used to vary the moles of SO₃ until the value of Krx reached 3.296 (i.e., the value at 1000 K). The results are shown in Table IV and Figure 3. The trendline tool was used to find an expression that represented the % SO₂ converted vs. P, and is shown on the Figure. Higher pressures favor the formation of SO₃ because Equation [34] has a volume decrease.

Introducing nitrogen increases the number of species, and makes the arithmetic even more complex. In this part of the example, SO_2 will be oxidized to SO_3 by the addition of air. A procedure different from that in your text will be used to make the calculations. This procedure solves directly for partial pressures instead of mols, and is based on the principle that the ratio of mols in = ratio of partial pressures in the equilibrium gas. On the basis of 1 mol of SO_2 in, plus varying amounts of air, the following equations can be written:

d + t + x + n = P; (total pressure equation)	[35]
S/O = (d + t)/(2d + 3t + 2x) = 1/(2 + 0.42A); (S/O ratio based on 1 mol SO ₂ in)	[36]
S/N = (d + t)/2n = 1/1.58A; (S/N ratio based on 1 mol SO ₂ in)	[37]

S/N = (d + t)/2n = 1/1.58A; (S/N ratio based on 1 mol SO₂ in)

 $t^2/x(d^2) = \text{Krx};$ (equilibrium constant expression)

where d, t, x, and n refer to the partial pressures of SO₂, SO₃, O₂, and N₂, and A refers to the mols of air added to 1 mol of SO₂. This example requires specification of A (the mols of air in), P, and T. All other variables are calculated from the above 4 equations.

Excel cannot directly solve the above 4 equations. Instead, they must be resolved by hand calculation into a set of single equations, after which Goal Seek can be used. For this example, P = 1 atm. First, to eliminate *n*:

based on Eqn. [37]: n = 0.79A(d + t); [39]

based on Eqn. [35] & [39]: d + t + x + 0.79A(d + t) = 1[40]

Further algebraic manipulation results in the following:

 $t = \frac{[1 - (1 + A)d]}{(0.5 + A)}$ [41a]

 $x = 0.21 \mathrm{A}d + t(0.21 \mathrm{A} - 0.5)$ [41b] The values of d, x, and t were determined by using goal seek in a stepwise manner. Table V in worksheet SON shows a sample calculation at 1060 K, where Keq = 0.873. Column AJ contains a series of values of A, from 0.6 to 5. Column AK contained initially an estimate for d (entered as 0.5 for all cases). Column AL contains the formula expressed as Equation [41], and thereby calculates t. Columns AM and AN are d^2 and t^2 , which are used in calculating Krx. Column AO calculates *x* from the formula in Equation [42]. Column AP contains the denominator for Equation [38]. Column

[38]

AQ is the expression for Keq (Equation [38]). Goal Seek is used by setting *d* (the value in column AK) to a value that will give 0.873 (\pm 0.0002) in column AQ. Thus all values of *d*, *x*, and *t* are calculated at 1060 K. The process was repeated for the other 3 temperatures, and the results were copied to Table VI. Partial pressures were converted to mols by knowing that the mols of N₂ remain constant, so the mols of SO₃ formed were calculated in column AW. Then the % conversion of SO₂ to SO₃ was calculated.

The results of the gas pressure calculation are shown in Figure 4, and the % conversion in Figure 5. Note the interesting trend in pSO_3 with added air (blue curves in Figure 4). The greatest pSO_3 is at the lowest temperature, as expected from the trend in Krx with T. A maximum pSO_3 occurs at about 1 mol of air added. More SO_3 is produced as more air is added, but eventually the added air overwhelms the increasing amount of SO_3 formed, which results in a maximum in pSO_3 that is dependent on T.

THERBAL Calculations

Worksheet SON-TH contains results of using THERBAL on the S-O-N system. Table I shows an output sheet of products formed when 2.5 mols of air + 1 mol SO₂ react at 950 K and 1 atm. The heat balance is based on reactants in at 300 K, and is endothermic at 950 K. Table II shows results from a series of calculations at variable air, with the results plotted in Figures 1 and 2. Table III shows the results from a series of calculations at different temperatures, for 2.5 mols of air + 1 mol SO₂. These results determine the adiabatic reaction temperature, and the 90% SO₂ conversion temperature.

Assignment

SO₃ is to be produced by burning S with air, then cooling the resulting gas until 90% of the contained S is present as SO₃. 8 mols of air is added to 1 mol of S, combusted at 1000 K, then cooled. What is the gas composition at 1000 K, and to what T will give the desired 90% conversion?

Preparation of Steel Carburization Gas (Example CRB)

<u>Example Objective</u>: Develop a relationship between the dew point of a carburizing gas and the aC in the gas at various steel carburizing temperatures. *Concepts: gas-phase equilibria. See text, Example 3, end of Chapter 11.*

Example Description

Gases rich in CO and H₂ have the ability to transfer C to the surface of steel. The carburizing gas can be prepared in various ways, one of which is the reaction between air and CH₄ at temperatures near 1000°C. Typically, the gas-phase reaction is carried out in an electrically heated furnace with a catalyst to assure complete reaction, then passed into the carburizing furnace, which may be at temperatures between 970-1030°C. It is important to control the aC in the carburizing gas in order to attain the desired %C in the steel. This example will show how certain approximations may be made in calculating the aC in the carburizing gas, and relating it to the so-called "dew point" of the gas (i.e., the temperature at which the moisture in the gas starts to condense). Using "dew point" was a common way to measure the pH₂O in a gas before the advent of more sophisticated gas analyzers. In this example, with gases having a high aC, the dew point will be below 0°C, so technically it should be called the "ice point." All calculations are carried out assuming an ambient pressure of 1 atm.

Calculations and Results

Example 3 of the text contains a good description of 2 different techniques for calculating the gas composition in the C-O-H system. This procedure could be adapted to the C-O-H-N system, with Excel making the necessary calculations. However, a simpler approach is appropriate in this example because *at high aC*, the carburizing gas contains very little CH₄, H₂O, or CO₂. This is shown by a THERBAL calculation where different amounts of CH₄ are mixed with 10 mols of dry air, and reacted at 1000°C. Table II shows a THERBAL output for 4.2 mols of CH₄ and 10 mols of air; note the very low amounts of CH₄, CO₂, and H₂O in the product gases. Table III lists the product gas pressures as a function of amount of CH₄, and the values are plotted in Figure 1. Over the range shown, the pCO and pH₂ are almost constant at 0.203 and 0.406 atm respectively (note Ptotal = 1 atm). This constancy of pCO and pH₂ is the basis for the simplified calculational approach used here.

The aC and pH₂O are related by the following reaction:

 $C + H_2O \rightarrow CO + H_2$; Krx = (pCO)(pH₂)/(aC)(pH₂O)

The numerator in the Krx expression $\cong 0.0824$, hence to a good approximation, a measure of pH₂O can be directly related to the aC at a given carburizing temperature. This is true regardless of the temperature at which the carburizing gas was prepared, so long as the aC in the carburizing gas was initially above about 0.2. Table IV gives values for log(Krx) for Equation [42], and Figure 2 shows a fit to reciprocal temperature:

 $\log(Krx)$ for Eqn. [42] = -7076/T + 7.479 [43]

Since we know the pCO and pH₂, we have the following:

 $7076/\text{Tcarb} - 8.563 - \log(pH_2O_i\text{ce}) = \log(aC)$

The vapor pressure of ice is given by the data in Table V of the worksheet. Figure 3 gives the following equation: $log(pH_2O,ice) = -2665/Tdew + 8.534$ [45]

A combination of Equations [44] and [45] relate the dew point of a gas sample extracted from the carburizing furnace to the aC in that gas:

log(aC) = 7076/Tcarb + 2665/Tdew - 17.097

The dew point of a gas is typically measured by passing a gas sample over a cooled mirror. A light beam reflects off the mirror to a sensor. When the mirror is cooled to a point where ice starts to form on the surface, the light beam becomes diffuse, and thus the sensor indicates incipient ice formation. In practice, a gas sample is continually withdrawn from the carburizing furnace, passed through the dew-point meter, and at intervals, the mirror is cooled until ice forms. Knowledge of the carburizing furnace and dew-point temperatures allows calculation of the aC. In practice, corrections in Equation [46] are required if the ambient pressure is not 1 atm, or if the carburizing gas contained other hydrocarbons than CH₄. Also, information on the activity coefficient of C in steel is required to complete the control strategy for carburizing. (See Example FEC).

Assignment

An alternate way of producing a carburizing gas is to react a mixture of steam and CH₄ over a catalyst. Make calculations on the pCO and pH₂ from this method of preparing a carburizing gas, then modify Equation [46] for this condition.

[46]

[44]

[42]

Thermodynamics of the Carbon-Oxygen-Nitrogen System (Example CON)

Example Objective: Construct a spreadsheet to calculate all of the important variables in the C-O-N system, and display the results graphically. Concepts: gas-solid equilibria, phase rule. See text, Section 12.6.

Example Description

The C-O-N system is very important in the production and processing of materials. Most applications of the system are for conditions where the pO₂ is <10⁻⁶ atm, which means that O₂ is not a significant contributor to the total pressure in the system. This is the part of the system covered by this example. Here we will look in more detail at the relationships between all of the thermodynamic variables involved in defining the system. These variables are:

- Temperature (designated T, in degrees K).
- Total pressure (designated P, in atm).
- Activity of carbon (designated aC).
- Partial pressures of gases (designated pCO, pCO₂, pO₂, and pN2, in atm).
- Sum of partial pressures of CO and CO₂ (designated pt, in atm. P = pt in the absence of N₂, and if pO₂ < 10⁻⁶).
- pCO/pCO₂ (designated R).

Calculations and Results

For the C-O system with only a gas phase, the phase rule indicates 3 degrees of freedom. Thus one may arbitrarily select (for example) the pCO₂, and pO₂, and all other variables will be fixed.^{*} Adding nitrogen to the system (such as by burning carbon with air) gives another degree of freedom.

The basic equations for the system are those for the formation of CO and CO₂ from the elements. However, for practical applications, the following equations are more useful:.

$$2CO_2 \rightarrow 2CO + O_2; \text{ Krx} = R^2 pO_2$$

$$C + CO_2 \rightarrow 2CO; \text{ Krx} = R(pCO)/aC$$
[47]
[48]

$$C + CO_2 \rightarrow 2CO; Krx = R(pCO)/aC$$

A 3-term equation for log(Krx) for the above reactions was developed on worksheet CON based on data in Table II and is shown as green cells in row 57 and 88 in worksheet CON. This gives explicit relationships between T and the other variables.

Reaction [47] is important in systems where oxidation/reduction processes are taking place. The relationships between R, pO2 and T are independent of P at pO2<10⁻⁶, so specifying any 2 allows the other to be calculated. This computational procedure is shown in cells D59:D60, D65:D66, and D71:D72 in the worksheet. In the first 2 cases, the calculation is explicit for any values entered into the 2 cells. But for the third case (solving for T), Goal Seek must be used. As mentioned in the footnote, some arbitrarily selected entries in the spreadsheet cells will specify a system where the aC is >1, which is an unstable system. This must be tested, as described below.

Reaction [48] is important where carburizing/decarburizing processes are taking place. Here pressure (both P and pt) is involved in the calculations. Therefore, 3 variables must be selected in order to calculate the rest. The procedure was set up in cells D90:D92, D98:D100, D106:D108, and D116:D118. In the first 3 groups, the calculations are explicit, but for the 4th set, Goal Seek must be used. The values of R, pt, and T obtained from Reaction [48] should be used to calculate the aC in cells D90-92 to be sure that the aC is <1**.

The special case of the burning of C with air uses up one of the degrees of freedom for the C-O-N system because air fixes the O/N ratio. Air is assumed to be 21% O₂, 79% N₂ by volume. This assumption ignores trace gases, and includes the Ar with the N₂. This fixes the O/N ratio for the system to 0.2658. A number of relationships can be derived between the variables by using this ratio. One used in the formula bar of the worksheet is:

 $aC = [0.347R^{2}(P)] / [(R + 1.652)(K48)]$

[49]

where K48 is the value of Krx for Reaction [48].

The calculation of system variables for this condition is similar to that already described. Cells D136-138, D144-146, and D152-154 are used to explicitly calculate system variables, while cells D162-164 (to calculate the temperature) require Goal Seek.

An array of selected values of aC was calculated from the methods described above, and plotted in Figure 1. The results show a number of interesting features of the system. First, note the position of the aC = 1 line at pt = 1 atm (heavy black). (Compare to Figure 12.15 of text). This shows that below about 950 K, CO₂ is the most abundant species, while above 950, CO predominates. The reaction between air and C at aC = 1 (*dashed black line*) produces a gas having a relatively higher amount of CO than a gas produced by reacting O_2 with carbon. This is explained by applying

LeChatelier's principle to Reaction [48], and noting the effect of pressure on the extent of a volume change reaction. As a general rule:

- <u>In the presence of carbon</u>: Lowering P will raise R and lower pO_2 . Thus for example the gas formed by the burning of C with air at aC = 1 will give a lower pO_2 than for burning of C with O_2 . Raising T will raise pO_2 and raise R.
- <u>In the absence of carbon</u>: Lowering P will lower the aC, and have no effect on pO₂. Raising T will raise pO₂ more than if carbon was present, and lower the aC. R will not be affected. Lowering the T will raise the aC; eventually the aC will be >1, and the system will be unstable with respect to sooting of C. Sooting C lowers R.

Assignment

1. Calculate R and $log(pO_2)$ for various values of T between 900 & 1200 K for aC = 0.1 at pt = 1 atm, and similarly for the burning of C with air at P = 1 atm. Plot the results.

2. Calculate R for the equilibria of $Fe_{.947}O$ and Fe, and plot the result on Fig. 1 of the worksheet. (Hint: look at Eqn [12]). At what temperature will pt = 1 atm for a mixture of wustite and iron with C?

^{*} Not all values are permissible selections. In some cases, the resulting system will have a calculated aC >1, which will cause carbon to form, thus changing the specified values.

^{**} Carbon does ot normally soot out from a gas unless there is a catalyst, or the aC>>1. It is sometimes useful to make calculations where the aC >1 to examine the metastable situation.

Example Objective: Determine the relative effects of using CO, H₂, or CO/H₂ mixtures on the reduction of iron oxide to iron. *Concepts: gas-solid equilibria. See text, Section* 12.7.

Example Description

Iron is commonly produced in a liquid form using the blast furnace, where reduction occurs in the upper part of the stack by a CO-rich gas. Another common way to produce iron is as a solid using a reducing gas containing CO and H₂. The reduced iron (called DRI, for *direct reduced iron*) is melted in an electric furnace to produce steel. The objective of this example is to calculate the amount of Fe_2O_3 that can be reduced by different CO/H₂ mixtures, as a function of temperature.

Calculations and Results

There are 3 solid forms of iron oxide: Fe_2O_3 (hematite), Fe_3O_4 (magnetite), and Fe_xO (wustite), where x varies from about 0.95 in equilibrium with Fe, to about 0.85, depending on temperature, in equilibrium with magnetite. Your text Figure 13.23 shows the range of stability of these oxides. When hematite is exposed to a reducing gas, it is reduced in stages. The final stage is reduction of wustite to iron, according to:

 $CO + Fe_{.947}O \rightarrow CO_2 + 0.947Fe; Krx = pCO_2/pCO$ [50]

 $H_2 + Fe_{.947}O \rightarrow H_2O + 0.947Fe$; $Krx = pH_2O/pH_2$ [51] The Krx expression refers to the gas composition in equilibrium with wustite and iron. This gas composition is the one that governs the calculated consumption of reducing gas for any form of iron oxide that is being reduced. This is because it is the critical value at the final stage of reduction. Therefore, the first part of this exercise requires a study of the above equilibria as a function of temperature. One additional reaction must also be considered, which is the con-

dition where aC = 1. This has already been described in connection with Example CON (please see Reaction [48]). The above equilibria are calculated in Table II, III, and IV of worksheet DRI. In all cases, the variable chosen for examination was the %CO or %H₂ in the equilibrium gas, calculated over the temperature range 800-1450 K, which covers the range of most DRI processes. The results are shown in Figure 1 of the worksheet. This figure illustrates some note-worthy aspects of the C-O-Fe system:

- CO is of limited value as a reducing gas below about 950 K because of the tendency for C to form (see heavy dashed black line on Figure 1). But sometimes the T is deliberately lowered in a separate reactor to add carbon to the DRI. In this example, the minimum reduction temperature will be set at 1000 K.
- The CO/CO₂ ratio becomes larger with increasing T because Reaction [50] is exothermic. This means that CO is a <u>less-effective</u> reducing agent with increasing T.
- The H₂/H₂O ratio becomes smaller with increasing T because Reaction [51] is endothermic. H₂ thus becomes more effective as a reducing agent with increasing T.
- CO is a more effective reducing agent for wustite than H₂ up to about 1090 K.

The effect of using CO/H₂ mixtures for reduction is shown in Table V, over the range 1000-1450 K. The results are shown in Figure 2, with pure CO and pure H₂ shown as heavy lines, and various mixtures shown as thinner lines. Interpolating between the 40% and 60% CO lines shows that temperature will have little effect on reduction potential of a 50% CO/H₂ mixture. About 3 mols of this gas will be required to reduce 1 mol of wustite, regardless of temperature. About 1 mol of the input gas is used for reduction, while the other 2 mols remains unreacted to fulfill the requirements of the Krx expression

The final part of this example makes a calculation on the amount of hematite that can be completely reduced to iron. Consider a fluidized-bed reactor fed with hot hematite at the top, and hot reducing gas fed into the bottom. DRI (100% Fe) exits at the bottom, and spent reducing gas exits at the top. A sketch of a FB reactor is shown below. The most efficient operation is an exit gas that is in equilibrium with both iron and wustite, which will have CO/CO_2 and H_2/H_2O rations given by Reactions [50] and [51], and as listed in Tables III and IV. Based on 1 mol of reducing gas put in, the mols of CO, CO_2 , H_2 , and H_2O in the exit gas are shown in Table VI. This table was constructed so that any entry between 0 and 1 in cell AJ50 will recalculate all values in the table for the selected amount of CO in. Figure 3 will also be automatically re-plotted.



The overall mass balance reaction for the reduction of hematite with 1 mol of gas of 50% CO is give n by:

 $0.5CO + 0.5H_2 + XFe_2O_3 \rightarrow 2XFe + MCO + DCO_2 + WH_2O + YH_2$

[52]

At 1000 K, for example, M/D = 1.602, Y/W = 2.297, M + D = 0.5, and H + W = 0.5 A mass balance gives M = 0.3079, D = 0.1921, H = 0.3484, and W = 0.1516. This results in X = 0.11457, or 0.229 mols Fe produced by 1 mol of reducing gas. The process is slightly endothermic (\approx 500 J required) which could be provided by reactants in at >1000 K. Note that increasing the proportion of CO causes the process to become exothermic, but less Fe is reduced. Contrast the above result of 0.229 mols of Fe produced using hematite as the oxide feed, vs. 0.326 mols of Fe that would be possible using wustite as the oxide feed.

Assignment

(A) Modify Table VI for the use of magnetite as the oxide feed.

(B) A gas composed of 35% CO, rest H_2 is used to reduce hematite at 1200 K. The hematite enters at 1200 K. Calculate the required input gas temperature to maintain the process temperature at 1200 K. (Cp for H_2 is not listed in worksheet DRI, but can be found in the workbook ThermoTables.xls).

The Calcination of Dolomite (Example DOL)

<u>Example Objective</u>: Calculate the products formed by the thermal decomposition of dolomite and mixtures of dolomite with calcite and magnesite. *Concepts: gas-solid equilibria, the Phase Rule, and thermal decomposition. See text, Chapters 12 and 13.*

Example Description

Calcination is the decomposition of complex compounds into simpler ones, plus the evolution of a gas. This occurs when the compound is heated to a point where the decomposition products are more stable than the original compound. The simplest case is the calcination of a carbonate to form an oxide and CO_2 . Another name for calcination is thermal decomposition, because thermal energy is the only driving force for the reaction (i.e., no reactant is necessary, just heat). The thermal decomposition temperature is defined as the temperature where the sum of the partial pressures of the gaseous decomposition products is 1 atm. The calcination of MgCO₃ is discussed in Section 12.2 of the text. This example will show the procedure for calculating the decomposition temperature for mixtures of the 3 carbonates in the CaO-MgO-CO₂ system

Calculations and Results

The calcination of dolomite $CaMg(CO_3)_2$ is more complex than for a single carbonate. The CaO-MgO-CO₂ system is effectively a 3-component system because the gas phase can be considered as containing only CO₂.^{*} Thermal decomposition of dolomite could produce a mixture of CaO + MgCO₃, or a mixture of MgO + CaCO₃. The correct situation can be determined by calculating the ΔG° for the following 2 reactions:

$$CaMg(CO_3)_2 \rightarrow CaO + MgCO_3 + CO_2; Krx = pCO_2$$
[53]

$$CaMg(CO_3)_2 \rightarrow MgO + CaCO_3 + CO_2; Krx = pCO_2$$
[54]

Table II of worksheet DOL shows the ΔG° results. Reaction [54] has a much lower ΔG° and hence is the first reaction to take place when dolomite is heated to the calcination temperature. Figure 1 shows a plot of ΔG° rx for Reaction [54], and a trendline equation that indicates a thermal decomposition temperature for dolomite of 691 K. The thermal-decomposition temperatures for magnesite and calcite alone are 679 and 1164 K.

The above results now permit the construction of the phase diagram for the CaO-MgO-CO₂ system as shown below. The 3-condensed-phase fields are labeled with the temperature at which the $pCO_2 = 1$ atm. The dashed lines extend from the CO₂ apex.

Calcination of an initial mixture of magnesite and dolomite occurs along line x-x'''. First the magnesite decomposes at 406°C (from x to x'), then the dolomite decomposes according to Reaction [54] at 418°C (from x' to x''), and then the calcite decomposes at 891°C (from x'' to x'''). A mixture of dolomite and calcite decomposes along line y-y'', first by decomposition of dolomite at 418°C, then calcite at 891°C. Dolomite itself decomposes in the same sequence as a mixture of dolomite and calcite.



Assignment

Dolomite is heated in a gas produced by the combustion of 1 mol of CH_4 and 10 mols of air. At what temperature will the dolomite start to decompose?

^{*} Strictly speaking, even in the presence of carbonates, the system is a 4-component one because although the gas phase is predominantly CO₂, it must also contain traces of various other gases, such as CO and O₂.

Phase Stability Diagram for the Mo-O-C System (Example MOC)

<u>Example Objective</u>: Calculate the stability criteria for the solid phases as a function of temperature. *Concepts: gas-solid equilibria, the Phase Rule, and phase stability diagrams. See text, Chapter 13.*

Example Description

Molybdenum forms stable oxides and carbides in contact with a gas containing CO and CO₂. The stability regions for the various Mo compounds is typically represented by a *Phase Stability Diagram* (PSD), which is a type of phase diagram in which all axes are restricted to being functions of the fields chemical potential and temperature, and in which the only the stability of the condensed phases is considered. Example 3 of Chapter 13 of your text shows a PSD for the Si-O-C system. This example shows how to construct 2 different types of PSDs for the Mo-O-C system.

Calculations and Results

The PSD for this example will be restricted to the region bounded by the metal and carbon (graphite), and in the temperature range of 1000-1450 K. The axis coordinates were chosen as log(aC) and $log(pO_2)$. Mo coexists with MoO₂ and Mo₂C (MoC is not stable in the abovementioned temperature range). The first steps in the construction of the PSD are construction of the log(aC) line for the Mo/Mo₂C phase boundary (*horizontal line* on the PSD), and the log(pO₂) line for the Mo/MoO₂ phase boundary (*vertical line*). Table II of worksheet MOC lists the data for these 2-phase boundaries. The next step is constructing the MoO₂/Mo₂C phase boundary according to the following reaction:

 $2MoO_2 + C \rightarrow Mo_2C + 2O_2; Krx = (pO_2)^2/aC$

[55]

The data for Reaction [55] are shown in Table III of the worksheet.

The 3-phase boundaries were plotted in Figure 1 at 1300 K (*red lines*) and 1400 K (*blue lines*). The boundaries intersect at the ternary univariant point where 3 solids coexist with a gas. The one degree of freedom at the univariant point is taken by specifying temperature. The $log(pO_2)$ and log(aC) at that point are the same as those calculated for the binary equilibria (Mo/MoO₂ and Mo/Mo₂C). The other ternary univariant point is where Mo₂C, MoO₂, and C coexist. The table below lists the univariant points at 1300 and 1400 K. Figure 1 contains metastable lines, so of the 6 lines radiating from point P, only 3 are stable. Example 3, Chapter 13 of your text discusses how to select the stable phase boundaries. This has been done in Figure 2a and 2b.

	Mo/MoC	D_2/Mo_2C	C/Mo ₂ C/MoO ₂		
Temp, K	1300	1400	1300	1400	
$log(pO_2)$	-14.27	-12.63	-13.11	-11.54	
log(aC)	-2.32	-2.19	0	0	

In worksheet CON, it was pointed out that CO-CO₂ gas mixtures generate both a pO₂ and aC, and hence at every point in Figures 2a and 2b, there must be some unique pCO and pCO₂. The PSD is enhanced by superimposing isobars of pCO + pCO₂ (called pt isobars here). Table IV gives calculated results for various values of pt at 1300 K, and Table V for 1400 K. Simply changing cell AE31 gives a new array at a different pt, and re-plots the line on Figures 2a and 2b.

One of the drawbacks of an isothermal PSD is that it does not indicate the effect of temperature (unless a 3-D plot is made). A different type of PSD can be constructed by fixing pt (at 1 atm. for this example) as one of the degrees of freedom instead of T, and then using T as one of the axes. The first step in constructing this sort of PSD is to calculate the T where pt = 1. The following 2 reactions are involved in the calculation:

$$Mo_2C + MoO_2 \rightarrow 3Mo + CO_2; Krx = pCO_2$$
 [56]

$$2Mo_2C + MoO_2 \rightarrow 5Mo + 2CO; Krx = (pCO)^2$$
[57]

The values of pCO, pCO₂, and pt were calculated in Table VI, and plotted in Figure 3 in the usual log(p) vs. 1/T format to give a straight line. A trendline equation gave T = 1328 K at the 1 atm univariant point.

A convenient way to plot the pt = 1 atm PSD is to use log(R) (where R = pCO/pCO₂) vs. T as axes. There will be two phase boundary lines above 1328 K: one for Mo/Mo₂C and one for Mo/MoO₂. There will be one phase boundary line below 1328 K, for MoO₂/Mo₂C. We also need thermodynamic data for the relevant species at 1328 K, which was obtained by interpolation in the $\Delta G^{\circ}f$ column of Table I. This information is listed in Table VI. The following 3 reactions were then used to calculate log(R) over a range of temperatures for each 2-condensed-phase equilibria:

$$Mo + 2CO_2 \rightarrow MoO_2 + 2CO; Krx = (pCO)^2 / (pCO_2)^2$$
[58]

$$2MoO_2 + 6CO \rightarrow Mo_2C + 5CO_2; Krx = (pCO)^5/(pCO)^6$$
 [59]

$$2Mo + 2CO \rightarrow Mo_2C + CO_2; Krx = pCO_2/(pCO)^2$$
[60]

These results are shown in Table VII. Owing to the higher powers of gas pressure in Reactions [59] and [60], Goal Seek was used to solve for log(R). In addition, pO₂ isobars (at 10^{-13} , 10^{-14} , and 10^{-15} atm) were also constructed using the procedure developed in worksheet CON, and added to the PSD. The results are shown in Figure 4. One of the implications of the PSD is that MoO₂ cannot be reduced to the metal by CO at temperatures below 1328 K at pt = 1 atm. Any attempt to do so would result in the formation of Mo₂C instead. The 2 types of PSDs have their respective advantages, and alternate PSDs with still different axes can be constructed.

Assignment

Calculate the values of pCO, pCO₂, and pO₂ at 1300 K at the univariant point where MoO₂, Mo₂C, and C coexist. At what temperature would pt = 10 atm?

Desulfurization of CaSO₄ (Example DES)

<u>Example Objective</u>: Calculate the process conditions for the conversion of CaSO₄ to CaO Concepts: gas-solid equilibria, the Phase Rule, and phase stability diagrams. See text, Chapter 13.

Example Description

Gas collected from coal-fired boilers or non-ferrous smelters often has levels of SO₂ that exceed pollution levels, but too low to warrant treatment in a sulfuric acid plant. One way of removing SO₂ to acceptable limits is to pass the hot gases through a bed of lime, which absorbs SO₂ and forms CaSO₄. However, this process requires the disposal of CaSO₄ (which is a nuisance), and the production of CaO (which is energy-intensive and expensive). This example will show how the CaSO₂ can be desulfurized back to CaO, while producing a gas high enough in SO₂ that it could be treated to produce sulfuric acid. Heat is provided by combustion of CH₄ and air.

Calculations and Results

When CaSO₄ is heated, it tends to decompose by the reverse of the reaction that formed it:

$$CaSO_4 \rightarrow CaO + 0.5O_2 + SO_2 \quad Krx = (pO_2)^{0.5}(pSO_2)$$
[61]

This reaction is very endothermic, and so requires the combustion of a fuel. It is enhanced by adjusting the air/fuel ratio such that the pO_2 is low, but not so low that CaS forms. For example, the pCO and pCO₂ in the process gas should be adjusted so that Reaction [62] occurs, but not Reaction [63]:

$$CaSO_4 + CO \rightarrow CaO + CO_2 + SO_2$$
[62]

$$CaSO_4 + 4CO \rightarrow CaS + 4CO_2$$

The combustion process for CaSO₄ desulfurization requires calculation of gas-solid equilibrium and a heat balance so that process characteristics are attained. Owing to the complexity of these calculations, THERBAL will be used instead of Excel alone.

A PSD for the CaO-CaSO₄-CaS system was constructed with the aid of the HSC program. The diagram at 1000°C is shown in the figure below, with the details on worksheet DES as Table I and Figure 1. The point where the 3 solids coexist (univariant point) gives the highest pSO_2 for the system, so the process should operate as close as possible to this point. The activity of CaS should be very close to 1, but no CaS should form. The pSO_2 and pO_2 at the univariant point is a function of temperature only, according to:

$$0.75\text{CaSO}_4 + \frac{1}{4}\text{CaS} \rightarrow \text{CaO} + \text{SO}_2$$

$$[64]$$

$$CaSO_4 \rightarrow CaS + 2O_2$$

$$[65]$$

At 1000°C, the pSO₂ is about 0.08 atm, and the pO₂ is about $10^{-10.4}$ atm.



[63]

The next step was to calculate the $log(pO_2)$ and $log(pSO_2)$ at the univariant point over the temperature range 900°-1000°C using THERBAL's Reaction option. The results of these calculations are shown in Table II on the worksheet, and plotted in Figure 2. Note that since the HSC and FREED database is slightly different, the values in Table I and in Table II at 1000°C are a little different. These results show that the highest pSO₂ is obtained by operating at the highest temperature, and as close as possible to the univariant point conditions, but still in the CaO region.

The third step was to calculate the equilibrium conditions and heat balance for the desulfurization of CaSO₄ in a reactor heated by combustion of CH₄ with air. For an adiabatic condition, there must be some unique combination of input amounts such that the heat balance will close, CaO is the only solid present, and the gas composition is at the univariant point. The calculation was done at 25° intervals, starting at 925°C, at Ptotal = 1 atm. THERBAL's EQG option was used, with the results shown in Table III. The basis was set at 100 mols of combustion air and 15 mols of CaSO₄ in.

THERBAL calculated the amount of each product present at equilibrium as a function of the amount of CH_4 used. During these calculations, it was determined that the heat balance required that the upper temperature limit should be <990 K, so the last interval was set at 10°. The point of incipient formation of CaS was noted, and the value just preceding that point was given a yellow cell color. This assures that the aCaS is <1.

A full THERBAL calculation (remember—basis is 100 mols of air for combustion, with air and CH₄ in at 30°C) was made using these values. The results are shown in Table IV. Note that the presence of toxic gases such as H₂S and COS are negligible. (SO₃ is present in even smaller amounts, so was not calculated). The aCaS is listed in row 40 for each part of Table IV, and is always <1. A trace of CaSO₄ is always present, which means the gas composition lies on the CaO-CaSO₄ phase boundary, at a slightly higher pO₂ and slightly lower pSO₂ than the univariant point.

A summary of the results from Table IV is listed in Table V, which was used to construct Figure 3. The trendline tool was used to develop a polynomial equation for each variable. A process calculation array is shown in Table VI, which uses the trendline values to calculate all input variables. The heat effect (heat loss = + number, heat gain = - number) is entered in cell AM62, and all other values are calculated. For example, if the heat loss was 40,000 cal, and the air was preheated by adding 100,000 cal, a value of -60,000 would be entered in cell AM62. This would require 13.6 mols of CH₄ and 11.9 mols CaSO₄ in, which would result in an operating temperature of 989°C. The product gas would contain 9% SO₂. A typical sulfuric acid plant can operate efficiently at \geq 5% SO₂.

This example shows how THERBAL can be used for what would otherwise be a very arithmetically complex problem. The results can be expressed graphically, and Excel's trendline tool used to develop a process control strategy dependent only on the heat loss or input.

Assignment

Calculate the required air preheat temperature if the feed to the reactor consisted of half CaO and half CaSO₄, and a 40,000 cal heat loss per 100 mols of combustion air.

Segregation During Solidification of a Plain Carbon Steel Ingot (Example ING)

<u>Example Objective</u>: Calculate the composition of the liquid phase during solidification of steel containing dissolved C and O, and the point where gas bubbles might form. *Concepts: interactions between dissolved solutes and nonequilibrium solidification.* See text, Example 2, Chapter 13.

Example Description

After refining, a low-carbon steel contains dissolved oxygen, in addition to the carbon. These two impurities segregate during solidification. One model for solidification is that during solidification, the solutes are "locked" in the solid as it forms, and no longer equilibrate with the liquid. Diffusion in the liquid is assumed to be rapid, and it remains homogeneous. This example shows how to calculate the segregation of dissolved O and C, and the pCO and pCO₂ generated during solidification. The steel contains initially 0.11% C and 0.011% O, and is at 1560°C.

Calculations and Results

The solubility of most impurities in steel is greater in the liquid than the solid (δ -Fe) that forms initially in low-carbon steel. This difference is expressed as a *segregation coefficient* κ^* , which is the ratio between concentration in the solid/concentration in the liquid. For C, $\kappa = 0.17$, and for O, $\kappa = 0.054$. This means that most of the C and virtually all the O segregates to the liquid.

The steel starts to solidify when the temperature drops below the liquidus. As solid forms, the liquid becomes enriched in O and C, thereby increasing the pCO and pCO₂ in equilibrium with the melt. Eventually, the P reaches a point where bubbles of gas (mostly CO, with a little CO₂) tend to form. A rule of thumb is that bubbles tend to form for $P \ge 1.5$ atm. If solidification were very slow, the solutes would have time to diffuse in the solid and equilibrate with the liquid as solidification proceeded. But practically this does not occur, so a different set of assumptions is required to track the change in composition of the liquid during solidification. The first assumption is that once a solid has formed, its composition does not change. A second assumption is that convection flow in the liquid causes it to remain homogeneous during solidification. This model results in the following equation** for the concentration of a solute in the liquid during segregation solidification:

$$C(liq) = C_0(1-f_S)^{(\kappa-1)}$$
^[66]

where C(liq) is the concentration in the liquid, C_0 is the original concentration, and fs is the fraction solidified. Table I of worksheet ING uses Eqn. [66] to calculate the composition of the remaining liquid as a function of the fraction solidified. Eqn. [66] is invalid below about 1500°C because of the peritectic transformation in the Fe-C system.

Both C and O lower the liquidus temperature of the steel. Based on phase diagrams for the Fe-C and Fe-O system, and assuming that the contribution to liquidus temperature lowering is a linear combination of each solute's effect, we have:

$$\Delta T = 80(\% C) + 60(\% O)$$
[67]

where ΔT is the drop in liquidus temperature below that of the melting point of pure Fe (1811 K, or 1538°C). Inserting the initial steel composition gives the liquidus composition of 1528°C. In other words, the steel will start to solidify at 1528°C. The value of ΔT is calculated in Table I for each of the fractional solidification entries. For example, the ingot is half solidified about 7° below the liquidus temperature.

The buildup of C and O during solidification means that they can react to form CO and CO₂ according to:

C + O
$$\rightarrow$$
 CO; log K = 1168/T + 2.07 = log(pCO) - log(%C) - log(%O) [68]

where underlining an element indicates it is a dissolved element. The above two equations use the 1 wt % solution as the standard state for solutes in metal melts, which is discussed in your text. Thus in the beginning, the steel is in equilibrium with pCO of 0.62 atm, and pCO₂ = 0.012 atm. These values change only a little during cooling to the point where solidification begins, but they change rapidly once solidification (and segregation) occur. Table I shows a calculation of the pCO, pCO₂, and total pressure as a function of fs. The results from Table I are summarized in Figures 1a and 1b, up to fs = 0.8. Clearly Ptotal becomes so high that bubbles will form well before reaching 80% solidification, which is why Figure 1 has an upper limit of 0.6 for fs. Commonly bubbles nucleate and form when P exceeds about 1.5 atm. This would occur near 1524°C and near 40% solidification.

^{*} In some references, the segregation coefficient is expressed as 1-k. The value for O is somewhat uncertain.

^{**} This is the Scheil Equation, and is derived in a number of textbooks. See for example "Fundamentals of Solidification" by W. Kurz and D. J. Fisher, Trans Tech Publications (1986), p 129 and 232.

The composition change for the liquid phase follows the liquidus surface during solidification. This surface is drawn in Fig. 2, based on data from Table II using Eqn. [67]. The solid straight black lines are liquidus isotherms, based on Equation [67]. Next, Table III and IV were used to calculate the liquidus composition for Ptotal isobars using a combination of Eqns [67], [68], and [69]. Owing to the complex nature of the combined equations, Goal Seek was used to find the %O that satisfied the P and T restrictions. At higher values of %O, the isobar slope for 0.5 and 1.0 atm approached the isotherm slope, and Goal Seek could not find a solution. For this limited case, the isobar was extended by noting that the product (%O)(%C) is a constant at a given temperature. The results were copied to Table IV, where the %C was calculated. The isobars are shown as colored lines on the diagram at 0.5 atm intervals.

The liquid composition during solidification was then plotted on Fig. 2 using values from Table I up to fs = 0.5. This path is shown on Fig. 2 as a black dashed line. If bubble formation is suppressed (such as deep in an ingot by the high ferrostatic head), the path of the liquid continues in the direction of the dashed line. Higher in the ingot, bubble formation might start at $P \ge 1.5$ atm, in which case the liquid composition would follow the 1.5 atm isobar (shown as a dotted line in Fig. 2). The evolution of gas along the 1.5 atm isobar (about 4% CO₂) means that 1.4 times more O is removed than C. Therefore, solidification with gas evolution enriches the liquid in C but depletes it in O.

<u>Assignment</u>

Steel in a ladle is at 1567°C, and contains 0.13% C and 0.023% O. It is to be degassed (assume gas removed is CO) to 0.004% O. How many m³ (STP) CO must be removed per tonne of steel, and what is the pCO at the end of degassing? What is the liquidus temperature of this steel?

Iron Removal from Zinc Electrolyte (Example FEZ)

Example Objective: Calculate the extent to which iron ions can be removed from a zinc sulfate solution by oxidation. Concepts: oxidation-reduction reactions in ionic solutions. See text, Chapter 15.

Example Description

Zinc is obtained by electrowinning from a sulfuric acid solution. This is possible only because the hydrogen overvoltage on the cathode allows zinc to be deposited instead of hydrogen. This requires that the solution be free of impurities that affect the hydrogen overvoltage, therefore, extensive solution purification is required before electrowinning. One of the first steps is iron removal, which involves oxidation of Fe^{+2} to Fe^{+3} , and precipitating the Fe^{+3} as a finely divided compound. The high surface area of the precipitate absorbs a number of other unwanted impurities. This example will show the extent to which Fe^{+2} can be converted to Fe^{+3} and then precipitated.*

Calculations and Results

The overall reaction for the oxidation of Fe^{+2} by O_2 in an acid solution is given by:

$$Fe^{+2} + O_2 + 4H^+ \rightarrow 4Fe^{+3} + 2H_2O$$
 [70]

Thermodynamic data on various reactions associated with this example were obtained from the HSC program database, and are listed in Table I of worksheet FEZ. Eqn. [70] is composed of the following half-reactions (the standard reduction potential at 25°C is listed for each reaction):

$$Fe^{+2} \rightarrow Fe^{+3} + e^{-}; \ \mathbf{E}^{0} = -0.771 \text{ V}$$
 [71]

$$2H^+ + 2e^- \rightarrow H_2; \ \mathbf{\hat{E}}^o = 0.00 \ V$$
 [72]

$$0.5O_2 + H_2 \rightarrow H_2O(liq); \ \epsilon^0 = 1.23 \ V$$
 [73]

This gives \mathbf{E}° for Eqn. [70] = 0.459 V. The value of Keq at 25°C is obtained from:

$$Log(Keq) = \frac{4(0.459)(96,485)}{19.145(298.15)} = 31.0$$
[74]

$$Log(aFe^{+2}/aFe^{+3}) = 0.5log(aH_2O) - 7.75 + pH - 0.25log(pO_2)$$
[75]

In practice, the $aH_2O \approx 1$, and O_2 gas or air ($pO_2 = 0.2$) are used as oxidizing agents for ferrous iron. The $\log(aFe^{+2}/aFe^{+3})$ is calculated in Table II of worksheet FEZ for different ranges of pH and pO₂. at 300 and 315 K. The results are plotted in Figure 1. The degree of oxidation of Fe⁺² increases with pO₂, and decreases with pH. The temperature clearly has a major effect on the extent of oxidation. In practice, oxidation is carried out at about 30°-40°C between a pH of 3 to 4.5.

The removal of iron occurs by the precipitation of various iron compounds. For example the precipitation by Goethite is:

$$Fe^{+2} + 0.25O_2 + 1.5H_2O \rightarrow FeOOH + 2H^+$$
[76]

$$Fe^{+3} + 2H_2O \rightarrow FeOOH + 3H^+$$
[77]

Iron precipitation is carried out above 70°C to obtain a suitably filterable precipitate. Table III shows a calculation of the extent of iron removal by these 2 reactions, with the results plotted in Figure 2. The equilibrium amount of iron still in solution is vanishingly small, but for practical reasons, such low levels are not attained in practice. However, iron can be consistently removed to <4 mg/liter by the above process.

<u>Assignment</u>

An alternate iron precipitation scheme involves heating the solution to 180°C in an autoclave with oxygen to form Fe₂O₃. Calculate the expected molality of Fe⁺³ and Fe⁺² under these conditions, based on FREED data for Fe₂O₃ and the following:

$$Fe \to Fe^{+3} + 3e^{-}; V = 0.1878 - 0.0004625T$$

$$Fe \to Fe^{+2} + 2e^{-}; V = 0.489 - 0.0000468T$$
[78]
[79]

^{*} The standard state for ions is unit molality. The activity coefficient is affected by the concentration of the ion, other species in solution, the pH, and temperature.

P-T Diagram for the Cd-Zn System, and Vacuum Refining of a Cd-Zn Alloy (Example PTX)

<u>Example Objective</u>: Calculate a P-T diagram for the Cd-Zn system, and determine the change in temperature necessary to remove Cd from an alloy containing initially XZn = 0.5 by vacuum refining at 10^{-3} and 10^{-4} atm. *Concepts: phase equilibria with pressure as a variable, and refining of non-ideal solutions. See text, Chapter 14.*

Example Description

The display of phase relations in P-T space is useful when pressure is an important variable. The construction of P-T diagrams is discussed in Chapter 14 of your text, and this example involves the Cd-Zn system, as discussed in Section 14.10. The binary phase diagram is shown in Figure 14.46 of the text. The first part of the example involves calculating the position of the phase boundaries for the system, creating the P-T diagram, and then making calculations for the effect of P and T to selectively remove Cd from the melt.

Calculations and Results

Calculations require thermodynamic data on the activity coefficients of Cd and Zn in liquid melts and solid solutions. Hultgren's compilation indicates that the liquid phase is adequately simulated by using a 2-coefficient Margules equation,* which is an extension of the regular solution formalism with an extra concentration term. For the liquid phase:

$$Ln(\gamma Zn) = (1262/T)X^{2}Cd - (312/T)X^{3}Cd$$

 $Ln(\gamma Cd) = (794/T)X^2Zn + 312/T)X^3Zn$

The solute activity coefficients in the solid solutions can adequately be simulated by assuming they obey Henry's Law, which means the solvents obey Raoult's Law. Based on the composition of the Cd-rich and Zn-rich solid solutions at 539 K (from text Figure 14.46), the solute equations are:

 $Ln(\gamma^{\circ}Zn) = 1680/T; Ln(\gamma^{\circ}Cd) = 2340/T$

[82a, 82b]

[80]

[81]

The phase boundaries in an L + SS region are the compositions where the chemical potential of the element is the same in the two phases. However, below the respective melting points, the activity of Cd(liq) and Zn(liq) are based on a metastable standard state (supercooled liquid), and so the arithmetic for calculating the solidus and liquidus curves is rather complex. For that reason, THERBAL was used in most of the calculations for this example. The data for the various forms of Cd and Zn are given in Table I of worksheet PTX. The normal standard state is designated Cd, (c,l,g) and Zn, (c,l,g). The data for Cd, (l) and Zn, (l) have been extrapolated below the melting points and above the normal boiling points. The data for Cd, (g) and Zn, (g) has been extrapolated below the boiling points. For this example, the mp of Cd was set as 594 K, and that of Zn as 693 K.

The vapor pressures of Cd and Zn were calculated by using Excel's regression tool over a span of about 200°. The data used is shown in Table II, and the equations developed are:

$\log(pCd, liquid) = -5371/T + 5.198$	$\log(pCd, solid) = -5781/T + 5.890$	[83a, 83b]
$\log(pZn, liquid) = -6245/T + 5.330$	$\log(pZn, solid) = -6722/T + 6.020$	[84a, 84b]

The first step in calculating the phase boundaries was to set up THERBAL with the appropriate activity coefficient expressions, and then make 3 sets of calculations. First, in the L + Cd(SS) region, next in the L + Zn(SS) region, and third in the Cd(SS) + Zn(SS) region. In the first 2 cases, the temperature and mol fraction of input Cd and Zn were varied together so that the overall composition fell between the liquidus and solidus lines for the 2-phase regions. In the third case, a 50:50 mixture of Cd and Zn was used over a range of temperatures. A sample THERBAL output is shown for the 3 regions (at 550 and 500 K) as Table III in the worksheet. The result of the 3 sets of calculations is shown in IV. A light green highlight indicates the conditions where log(Ptotal) \approx -4; this value will be important in a later section of the example. The phase boundaries were plotted in Figure 1 of the worksheet. Excel's trendline tool was used to develop an equation relating T and composition for the phase boundaries (except for the Zn-rich SS boundaries, which are nearly pure Zn); these equations are listed on the diagram.

The calculations showed that the eutectic temperature was 540 K, which is within 1° of the temperature listed on Figure 14.45. The eutectic composition was XZn = 0.22, as compared to 0.266 in Figure 14.45. One possible reason for this discrepancy is the approximations involved in selecting or fitting the non-ideal solution model parameters. Lines representing the log(p) of each element along the liquidus conditions were superimposed on the phase diagram; a red

^{*} The Margules equation is discussed in Section 9.9 of your text. A 2-term Margules equation is sometimes referred to as a sub-regular solution.

line was used to represent Zn and a blue line for Cd. The pCd is larger over most of the composition range except for XZn> 0.98. For that reason, the Ptotal \approx pCd for most compositions. The log(Ptotal) along the liquidus is shown on Figure 1 as a black dashed line. The shape of the lines shows that temperature has the greatest effect on partial pressure until the concentration of an element approaches zero. The log(p) of each element approaches negative infinity as the mol fraction of that element approaches 0.

The data in Table IV was used to plot the P-T diagram shown in Figure 2A, which corresponds to Figure 14.46 in the text. Compare the Ptotal lines from Figure 1 to those in Figure 2. Some lines are so close together that it is difficult to discern the difference. To help, an expanded P-T diagram is shown in Figure 2B, near the eutectic temperature of 540 K. (Even more detail can be seen if the screen view is set to 200%). Point 3 on the two figures (equivalent to point 3 on text Figure 14.46) represents the eutectic point, where a liquid, 2 solid-solutions, and a gas phase coexist. There are 0 degrees of freedom (invariant situation) at this point. Points 1 and 2 are the melting points of Cd and Zn respectively, and of course are also invariant points.*

A main objective of this example is to calculate the 10^{-3} and 10^{-4} isobars for the system, but this is not an easy task using THERBAL (or most any thermodynamic software program) because the pressure must be specified as an input variable for the system. This is resolved by making a number of calculations at different XZn, and plotting the results to obtain a linear relationship between log(Ptotal) and 1/T. The results of such calculations are shown in Table V, along with the log(pCd and Zn). A plot of the results is shown in Figure 3, with the results of a linear trendline equation for each mol fraction. The XZn values were chosen closer together as XZn $\rightarrow 0$ because P changes so rapidly there.

The trendline equations were used to develop data for the log(P) = -3 and -4 isobars, with the results shown in Table VIa. These results were plotted in Figure 4 with the assumption that both isobars were in the stable liquid phase over the whole range of composition. However, an inspection of Figure 1 showed that this was not true for the 10^{-4} isobar, which appeared to intersect the liquidus line at XZn of about 0.45 and 0.04. An enlarged version of Figure 1 (Figure 5) shows the intersection to be at 591 K and XZn = 0.48. A similar plot (not shown on the worksheet) indicates that the 10^{-4} isobar, as shown in Table VIb. Note that the isobar is horizontal in the 2-phase region, and sloped in the liquid, Cd(SS) and Zn(SS) regions. To complete the isobar calculations, the data in Table IVc was used to calculate the 10^{-5} isobar (calculation not shown on the worksheet), and is listed in Table VIb.

The T-X diagram for the system with Ptotal isobars is shown in Figure 6. This figure is a reproduction of Figure 1, with the pCd, pZn, and Ptotal lines deleted, and the isobars added. This information can be used to determine the conditions for vacuum refining an alloy at 10^{-3} and 10^{-4} atm. The results are shown in the following table for refining at 10^{-3} atm. The temperature must increase to 708 K to attain an XZn of 0.96 in the alloy, but by that time, the gas leaving the system contains over 30 vol.% Zn. If the refining is carried out at 10^{-4} atm, the initial alloy contains a small amount of Zn(SS) phase, and all refining is carried out at 591 K; the removed gas contains XZn = 0.045. During refining, the amount of liquid phase decreases while the amount of Zn(SS) increases.

Table showing changes in melt composition and temperature during vacuum refining at 10^{-3} atm.

X Zn	0.5	0.85	0.93	0.96
Т, К	665	678	695	708
pCd	0.0009337	0.000882	0.000793	0.000684
pZn	0.000662	0.000116	0.000207	0.000312
X Zn in gas	0.066	0.116	0.207	0.313

In conclusion, the gas removed at lower temperatures has a higher Cd content, but the pressure has to be lower. Some practical problems would be encountered in trying to vacuum refine at 10⁻⁴ atm when the system contains a large fraction of solid. The most efficient refining process might be to follow the liquidus line (increasing the temperature as Cd is removed), while raising the refining pressure. This would follow the black dashed line in Figure 1. The refining process could be carried out until the gas being removed reaches some practical limit on XZn.

^{*} The vertical lines on text Figure 14.46 were omitted in the construction of Figure 2.

Assignment

1. Calculate the T-X values for conditions of $log(pZn) = 10^{-4}$, and plot the line on Figure 6. Note that THERBAL is not necessary or particularly useful for this calculation.

2. Investigate the refining of an alloy containing initially XZn = 0.5 and 700 K by injecting air into the melt. You will need to make a heat balance for each increment of air added in order to track the temperature change. Assume adiabatic conditions, and air entering at 300 K. Assume the Cp for the alloy is the molar average for pure Zn and Cd. The integral heat of formation for 1 mol of the liquid phase (from pure liquid elements) is well-expressed by the following equation:

 $\Delta H^{\rm M} = -8410({\rm X}^2{\rm Zn}) + 8410({\rm X}{\rm Zn})$

[85]

Conclusion

The above examples were developed to give you an overview of the way a spreadsheet can be used to solve problems that would otherwise be too complex arithmetically. The approaches used were selected to give a broad overview of Excel's capabilities, but even so, there are many other Excel features not used in the examples, but which could have been used to good advantage.

The assignments were developed to build on the techniques used in each example. Some of these assignments require assumptions that are implicit in the system, but are not explicitly stated (such as assuming a certain value for total pressure). Assignments may require the use of equations from your text that were not covered in the example.

This author (AEM) welcomes additional examples from instructors or students using the text. These will be posted on the Thermart web page, along with examples developed for other texts.