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Problems to be solved on the Thermo-Calc data bank system

Based on the textbook by Mats Hillert:

Phase Equilibria, Phase Diagrams and Phase Transformations
2nd edition, Cambridge University Press, 2007

About Thermo-Calc:

This is a commercial data bank system. The students of the above textbook have been promised to register free-of-charge to get access to a DEMO version of T-C and a limited number of databases. The license is for a limited time but the license may be renewed.

It may take a few days to be given a license.

The present collection of problems was not designed to make a general instruction to the use of the Thermo-Calc package but will introduce the student to features essential for solving the special questions raised by the present problems. Often these problems are not of the kinds of interest to the ordinary customers and Thermo-Calc may not always be designed to give the most direct way of finding the answer to such questions. On the other hand, a more detailed path to a solution may be instructive for the student and may give her/him a deeper insight in how thermodynamics works.

The problems are designed as exercises to various sections in the textbook and are collected Chapter-wise.

Chapter 1. Basic concepts of thermodynamics

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1.1A. External state variables

a) Consider a system of pure carbon. Define the conditions in sufficient detail to allow the state of equilibrium to be computed, using a thermodynamic data bank. Choose the conditions any way you like, except that P=1 bar should be chosen. Then, evaluate the volume.

b) Use that volume when redefining the conditions and exclude another piece of information from the conditions. Then, evaluate the state of equilibrium, which should be the same as before. Check that by inspecting the value of the excluded property. It should be the same as before.

Hint

1) The conditions can be defined using the values of c+2=1+2=3 independent variables. So far we have discussed T, P and V but it is evident that another one is the amount of material, e.g. the number of moles of components (usually atoms), N. Since you are asked to evaluate V, it is evident that among those four variables you must give the values to all three of T, P and N to define the conditions. You may take 1000^{o}C, 1 bar and 1 mol. 1 bar is 100000 Pa.

2) There can never be more than c+1 independent *intensive* variables, in this case T and P, whereas V and N are *extensive* variables and at least one of them is required in order to have a complete definition of the conditions. It serves to define the size of the system. However, you could use more than one extensive variable. When including V in the new set of independent variables, you could exclude N but it may be more interesting instead to exclude one of the potentials, say T, and use two extensive variables, V and N, together with P.

1.1B. External state variables

Calculate and plot the function ($V(P,T_1,N_1)$ for graphite between 1 bar and 1 kbar (i.e. 100000 to 1E8 Pa) at 1000°C and for 1 mol.

Hint

The method of computing and plotting a curve depends on your particular data bank system.

1.2. Internal state variables

Consider an Ag-Cu alloy with 10 mass% Cu at 600°C and 1 atm (101325 Pa). Compute the equilibrium and find the values of some internal variables. Then, use one of those values when redefining the conditions and instead exclude one of the external variables. Again calculate the equilibrium and check that the excluded variable got the same value as it had before.

Hint

You can certainly make your program present the calculated state of equilibrium. It will then give a long list containing the external variables but also some internal variables, e.g. the fractions of phases and their compositions if there is more than one phase. Choose any of these values when redefining the conditions for a new computation of the same of equilibrium.

1.3A. The first law of thermodynamics

1 kg of a steel (Fe+0.8 mass% C) is heated from a state of equilibrium at 500°C to a new state of equilibrium at 800°C. The pressure is kept at 1 atm. How much heat was needed for this operation?

Hint

Since there is no change of P, you should use the first law for the enthalpy, which yields $Q = \Delta H - \int VdP = \Delta H$ for constant P. You should thus compute the equilibria for the two sets of conditions, show the enthalpy and take the difference. It does not matter if you don't understand what reference state the values refer to because that does not affect the difference.

1.3B. The first law of thermodynamics

A mixture of 2 mol of H_2 and 0.1 mol of O_2 is kept in a very strong cylinder at 25°C. The cylinder has a moveable piston, working against an outside atmosphere of 1 atm. The mixture is ignited and reacts quickly to a state of equilibrium, containing mostly H_2O molecules, and without giving time for any exchange of heat. Calculate the new temperature. In order to simplify the computation you may reject all species except for H_2, O_2 and H_2O.

Hint

The internal energy is not directly affected by an internal reaction. It can be changed only by interactions with the surroundings as described by the first law, dU=dQ-PdV. In the present case dQ=0 but dV>0. It would thus be more convenient to consider the enthalpy, dH=dU+d(PV)=dQ+VdP=0 since dQ=0 and dP=0. One should thus evaluate H for the initial state (which is not at equilibrium) and then search for an equilibrium state that has the same H value.

1.4. Freezing-in conditions

0.5 kg of a white cast iron with 3.5 mass %C (which contains no graphite due to insufficient rate of reaction during fast cooling) has been heat treated at 1100^{o}C to equilibrium (without graphite). Then it is cooled to 800^{o}C. Calculate the amount of “liberated” heat during the cooling under two experimental conditions. (A) The state at 1100^{o}C is completely frozen-in during the cooling. (B) A new state of full equilibrium has been established when 800^{o}C is reached due to slow cooling. Also (C) evaluate the heat evolution if the frozen-in state equilibrates isothermally at 800^{o}C if it were first retained during cooling to 800^{o}C.

Hint

1) Suppose the pressure is the same. Then ΔH=Q+$\int$VdP=Q, where ΔH is the difference of H between the initial and final states.

2) After the equilibrium at 1100^{o}C has been computed, you should like to freeze-in the constitution and only change T. Thus, you should not compute equilibrium before evaluating H of the frozen-in state at 800^{o}C. The question is what facility your data bank system has for frozen-in states.

3) For (B) it does not matter how close to equilibrium the system was at various temperatures during the cooling because H is a state function.

1.5. Reversible and irreversible processes

Consider a cylinder that can be in contact with any of two heat reservoirs of 20 and 50^{o}C. There is a piston by which the volume can be changed. The cylinder contains pure N_2 gas and is initially at a pressure of 1 atm.

(a) Using the first heat reservoir one compresses the gas slowly and isothermally at 20^{o}C to a pressure of 10 atm.
(b) One continues by compressing adiabatically (i.e., with no heat exchange) until a temperature of 50^{o}C has been reached.
(c) Using the second heat reservoir one releases the pressure to a value P_3 slowly and isothermally at 50^{o}C.
(d) One continues releasing the pressure to 1 atm adiabatically. The pressure P_3 was chosen in such a way that the final temperature was 20^{o}C. It is thus possible to repeat this cycle any number of times.

Evaluate the heat and work received by the system for each one of the four steps. Then add up the net work, *W*, done *by the system* on the surroundings and calculate the ratio of that work and the heat drawn *from the warm reservoir,* Q_3. Assume that all the four processes are carried out in a reversible fashion.

Hint

Let conditions of the initial state be T_0,P_0 and after the first, second and third step T_0,P_1, T_2,P_2 and T_2,P_3, respectively. After the fourth step it is again T_0,P_0. P_2 and P_3 are not known but may be evaluated because the entropy is not changed by an adiabatic process. For the second step you thus have $S_2 = S_1$, i.e. $S(T_2,P_2) = S(T_0,P_1)$, which yields P_2. For the fourth step you have $S_3 = S_0$, i.e. $S(T_2,P_3) = S(T_0,P_0)$, which yields P_3. Denote the heat and work received by the system during the first step by Q_1 and W_1 etc. The heats received during the isothermal steps, i.e. the first and third steps, are according to the definition of entropy for a reversible and isothermal process $Q_1 = \int T_0 dS = T_0(S_1 - S_0) = T_0(S(T_0,P_1) - S(T_0,P_0))$ and $Q_3 = \int T_2 dS = T_2(S_3 - S_2) = T_2(S(T_2,P_3) - S(T_2,P_2))$. The change of internal energy for the first step is equal to the work plus the heat, which yields $W_1 = U_1 - U_0 - Q_1 = U(T_0,P_1) - U(T_0,P_0) - Q_1$ and for the third step $W_3 = U_3 - U_2 - Q_3 = U(T_2,P_3) - U(T_2,P_2) - Q_3$. For the adiabatic steps $Q_2 = 0$ and $Q_4 = 0$ and $W_2 = U_2 - U_1 = U(T_2,P_2) - U(T_0,P_1)$ and $W_4 = U_0 - U_3 = U(T_0,P_0) - U(T_2,P_3)$. You can finally evaluate $W / Q_3 = -\Sigma W_i / Q_3$.

1.6. The second law of thermodynamics

When you in problem 1.3B calculated the final temperature when a gas mixture of 2 mole of H_2 and 0.1 mole of O_2 was reacting adiabatically after being ignited, you relied on an algorithm hidden inside the program. Check that the final state was really the state expected from the second law. To make a decisive test you may now use 2 mole of H_2 and 1 mole of O_2 but again under a constant pressure of 1 atm and with an initial temperature of 25^{o}C. The adiabatic temperature would then be very high and, although all of H_2 and O_2 could in principle form H_2O, some would be dissociated into H_2 and O_2 and one could easily introduce some deviation from the equilibrium constitution at one temperature by first computing the equilibrium at a different temperature.

Hint

1) Equilibria are usually computed by minimizing a function called Gibbs energy. However, it applies only under constant T and P and in the present case T varies during the reaction.

2) For a closed system the second law gives $dS=dQ/T+d_{ip}S$ and for adiabatic conditions $dS=d_{ip}S$. In Problem 1.5 you considered reversible, adiabatic processes, for which $d_{ip}S=0$ and the entropy does not change. The present process is adiabatic but not reversible because the formation of H_2O molecules occurs spontaneously. For each H_2O molecule formed, the temperature will rise and that should continue until $d_{ip}S/dN_{H2O}=0$, i.e., until S reaches a maximum where $dS/dN_{H2O}=0$. The problem is thus to examine if the amount of H_2O, formed

when the final temperature is reached, gives a higher S value than any other amount of H_2O would do if evaluated at the temperature reached when that amount has formed. You should test a slightly higher amount and a slightly lower.

3) The SER reference is based on the pure elements in their stable states, e.g. H_2 and O_2, and at 25^{o}C and 1 atm. Furthermore, in ideal gases there is no heat of mixing. Thus H=0 for our initial gas mixture because no H_2O has yet formed. The final state under adiabatic conditions and constant pressure can thus be obtained from the condition H=0.

1.7. Condition of internal equilibrium

Most programs for the computation of equilibria work by minimizing a function G, called Gibbs energy, under constant T and P. So far you have only learned that equilibrium is found where $d_{ip}S$ has a maximum. Use that criterion in order to check that the state obtained from an available program is actually a state where $d_{ip}S$ has a maximum. Make the test with an Al alloy with 50 mass% Si at 500^{o}C and 1 atm.

Hint

The constitution of the alloy is varied when the program searches for the minimum of G. You should use the program to evaluate the equilibrium and examine how the equilibrium constitution is described. Then you can vary the constitution around the equilibrium constitution and check that $d_{ip}S$ has a maximum there. You know that $d_{ip}S=dS-dQ/T$. From the first law you know $dU=dQ+PdV$ and thus $d_{ip}S=dS-dQ/T=dS-(dU+PdV)/T$. For constant P you get $d_{ip}S=d[S-(U+PV)/T]$. You should thus define a function FUNC=S-(U+PV)/T and test if the equilibrium state obtained from the program actually is a maximum of FUNC when the constitution is varied around the equilibrium constitution. Since you are going to compare situations at the same temperature, 500^{o}C, you could just as well multiply by T and define the function as FUNC=ST-U-PV.

1.8. Driving force

Consider an Fe alloy with 30 mol% Cr at 650^{o}C and 1 atm. It is in a state of homogeneous bcc and is supersaturated with respect to the sigma phase of an approximate 50/50 composition. Evaluate the driving force for the precipitation of sigma, using the basic definition $D = T \cdot d_{ip}S / d\xi$.

Hint

From Problem 1.7 you know that $d_{ip}S=d[S-(U+PV)/T]$. You may thus evaluate the function S-(U+PV)/T for the initial state and for a state with a minute amount, ΔN, of sigma, measured per mole. Take the difference, multiply by T and divide by ΔN because the amount of sigma expressed in mole can be used to represent the progress of the process, ξ.

1.9. The combined first and second law

Evaluate the quantity $(\partial S/\partial N)_{U,V}$ from a tabulation module that can list H and S for a series of temperatures. Choose Al_2O_3 at 1 atm.

Hint

1) The combined law can be written as $dS = (1/T)dU + (P/T)dV - (G_m/T)dN + (D/T)d\xi$ and $(\partial S/\partial N)_{U,V} = -G_m/T$. Thermodynamic tables usually give values under a given P and for a series of T and, as a consequence, they usually list values of H and S. It would have been nice to have a table of U and S but if that is not available one could usually approximate U with H for condensed materials. Use that approximation here.

2) Primarily one should expect both S and H to increase if the size, N, is increased because they are both extensive quantities. In order to vary S but keep H constant it seems necessary to allow T to decrease to a level where the tabulated value, which may be given for 1 mole of formula units, has decreased by a factor equal to the one by which N has increased. Denoting the two temperatures by 1 and 2, we get $H=N_1H_1=N_2H_2$ where $N_1=1$. On the other hand, for the entropy we have $\Delta S=N_1S_1-N_2S_2=N_1(S_1-S_2N_2/N_1)=N_1(H_2S_1-H_1S_2)/H_2$. However, $\Delta N=N_2-N_1=N_1(N_2/N_1-1)=N_1(H_1/H_2-1)=N_1(H_1-H_2)/H_2$. We find $\Delta S/\Delta N=(H_2S_1-H_1S_2)/(H_1-H_2)$. From the table one should thus examine the H and S values for two neighbouring temperatures and evaluate $(\partial S/\partial N)_{U,V} \cong \Delta S/\Delta N = (H_2S_1 - H_1S_2)/(H_1 - H_2)$. That should be a reasonably correct value in the middle of the range of T. Make the test at 1000 and 1100 K.

3) Sometimes a table also gives the values of G but all values given in a table of properties are molar quantities. G should thus be identical to G_m as given under (1), provided that N is expressed in the same kind of mole, in the present case mole of formula units. You may thus check your result by comparing with G_m/T at the two temperatures.

1.10. General conditions of equilibrium

At the melting point of a pure element the liquid and solid phases are in equilibrium with each other and each potential should thus have the same value in both phases. It should be possible to evaluate the melting point by comparing tables of properties of the two phases. Do that for molybdenum.

Hint

The combined law expressed in terms of dU shows that G_m is a potential and is conjugate to N, the amount of matter. There would thus be a driving force for the transfer of matter between the two phases if G_m did not have the same value in both phases. One of them would grow at the expense of the other. You should thus examine at what temperature the two phases have the same G_m value.

Chapter 2. Manipulation of thermodynamic quantities

2.1. Evaluation of one characteristic function from another

1) Test if your system can yield the value of a state variable that in principle could be used as a characteristic state function.

2) Test if it can accept values of a set of variables that are the natural set for another characteristic state function.

3) Try to use the value of a site fraction as condition.

Hint

An advanced data bank systems may be composed of modules, one of which stores thermodynamic properties of individual phases as fundamental equations representing some characteristic state function, usually the Gibbs energy, G, as function of its natural set of variables, e.g. T, P and N for G of a pure substance. However, since G is an extensive state function it can be expressed with the molar Gibbs energy, $G = N \cdot G_m$, and it is sufficient to store $G_m(T,P)$ for a pure substance. Multiplying with N is a trivial matter. For a phase with more components, G may be stored as a function of T, P, N_1, N_2 etc. and, in principle, one could then evaluate G for a set of values of these variables, the natural set for G. However, one still prefers to store the information on G as a function of the molar Gibbs energy. For a simple case one would use a function $G_m(T,P,x_1,x_2,...)$ and it is a trivial matter to evaluate N and all the x_i from the set of N_i values. For a phase with sublattices one prefers $G_m(T,P,y_1',y_2'... y_1'',y_2''...)$ where y_i are the site fractions, i.e., mole fractions defined for each sublattice. In a simple case one can also evaluate the site fractions from the set of N_i values. In more complicated cases there is one or more degrees of freedom and there is not only one set of y_i values that satisfies the set of N_i values. The equilibrium set of y_i values is then found by minimizing the Gibbs energy. In the same way, when there is more than one phase and each has no degree of freedom, there is a degree of freedom for the material to be distributed between the phases. The equilibrium composition and amount of each phase are then again found by minimizing the Gibbs energy.

To the customer all this is like a black box and he simply trusts that it contains information stored as a fundamental equation based on the Gibbs energy. He will thus give the values of T, P, N_1, N_2, etc. when setting the conditions or he will use T, P, N and x_1, x_2 etc. Your data bank system will probably accept the mass, B_i, instead of N_i and the mass fraction, w_i, instead of x_i.

The above conditions are all based on the natural set of variables for G and it is an interesting question whether your data bank system can also accept other sets of variables as conditions. Could it even behave as if it were based on another characteristic state function?

Start with a unary system of your choice and set conditions for the state to be studied. Evaluate S after computing equilibrium. Then, enter the S value as a condition and remove one of the initial conditions. First, remove the initial T value, which makes a conjugate pair with S. Compute equilibrium and evaluate T. Then, enter the T value and, instead, remove the initial P value, which is part of another conjugate pair. Compute equilibrium and evaluate P. Again you should obtain its initial value if the equilibrium module can accept a set of conditions that does not contain one variable from each pair of conjugate variables.

2.2. Internal variables at equilibrium

At equilibrium D=0 and the driving force, D, can be evaluated in different ways that all should give the same result. For instance, $D = -(\partial G / \partial \xi)_{T,P} = -(\partial F / \partial \xi)_{T,V}$ where ξ is an internal variable. Demonstrate this by a numerical calculation.

Hint

1) First you must choose a system with an internal variable. For systems with more than one phase, the fraction of a phase is such a variable. For one-phase systems with a variable degree of order, one can choose some site fraction as the internal variable. For a gas, there may be a variable constitution due to reactions between molecules. For the present demonstration it may be convenient to choose a binary system with two phases, which can both dissolve the two components.

2) With a binary bcc+fcc alloy you may establish two slightly different constitutions by computing equilibrium at two temperatures, 1 K apart. Define this difference as $\Delta\xi = Nfcc2 - Nfcc1$ where Nfcc is the amount of the fcc phase. Examine their properties at a quite different temperature where they are far from equilibrium. In order not to change their constitutions at that temperature you must evaluate the bcc and fcc phases separately and for extensive properties you can then add the contributions from the phases.

3) For the first constitution you evaluate V_1, G_1 and F_1. For the second one you evaluate G_2 and approximate the driving force according to G as DFG=-(G_2-G_1)/(Nfcc2-Nfcc1) for the values of T and P used as conditions. To get the corresponding quantity for the Helmholtz energy, F, you must compare two states of the same T and V, not P. When you first evaluate V_2 for the second constitution you find that it differs from V_1 because of the difference in constitution, mainly in the amounts of the phases. You must find a new pressure that makes the volume of the second constitution equal to V_1. Just try a different P and evaluate its effect on V_2. Then you may find the proper P by extrapolation.

2.4A. Experimental conditions

Evaluate C_V and C_P for pure Cr at 500°C and 1 atm.

Hint

The heat capacities can be obtained from the second derivatives of F and G with respect to T but can also be obtained from first derivatives, e.g. $C_P = -TG_{TT} = (\partial H / \partial T)_P = T(\partial S / \partial T)_P$ and $C_V = (\partial U / \partial T)_V = T(\partial S / \partial T)_V$.

2.4B. Experimental conditions

One mole of N_2 gas at 400°C and 1 atm is compressed adiabatically and reversibly to 100 kbar. Evaluate the new temperature.

Hint

$\Delta S = Q/T + \Delta_{ip} S = 0+0=0$. The final state should thus have the same entropy as the initial state. You should evaluate S for the initial state and then find the temperature where S has the same value at the higher P.

2.4C. Experimental conditions

One mole of diamond at 400°C and 1 atm is compressed adiabatically and reversibly to 100 kbar. Evaluate the work.

Hint

$\Delta S = Q/T + \Delta_{ip} S = 0+0=0$. The final state should thus have the same entropy as the initial state. The work is equal to the change of U since there is no exchange of heat.

2.6A. Use of various derivatives

Evaluate α and κ_T for an Fe alloy with 0.5 mass% C at 850 and 750°C under 1 atm.

Hint

1) Expressed with first-order derivatives we find $\alpha = (\partial V / \partial T)_P / V$ and $\kappa_T = -(\partial V / \partial P)_T / V$.

2) At 850°C the alloy is inside the fcc one-phase field. At 750°C it is inside the bcc+fcc two-phase field. There you may evaluate the properties for the whole as well as for each phase.

2.6B. Use of various derivatives

Test numerically the relation $(\partial U/\partial V)_T = T(\partial P/\partial T)_V - P$ on two Cr alloys with 5 or 10 mass% Fe, both kept at 800^o C and 1 atm.

Hint

Both partial derivatives are based on the same two independent variables, T and V, but the experimental conditions are given through T and P. You should thus compute equilibrium and then introduce the computed V value as a condition for a new computation of equilibrium. Both partial derivatives can then be evaluated from the new description of the equilibrium based on the correct set of independent variables.

2.7. Comparison between C_V and C_P

Evaluate C_V and C_P for Cr at 500 K and 1 bar.

Hint

C_P is usually measured at 1 atm and can be evaluated from a database as $(\partial H/\partial T)_{P,N}$. For clarity it may be denoted $C_P(T,P_0)$ where P_0 represents 1 atm. For C_V the situation is not quite so clear. Experimentally, one prefers to work under constant pressure and C_V is usually obtained by calculation from other properties, mainly but not only from C_P. C_V may be evaluated from a database as $(\partial U/\partial T)_{V,N}$ and it is evident that one must allow P to change in order to keep V constant when making the small variation of T. However, one could still be interested in the values of C_V when starting from 1 atm at different temperatures. For each temperature one should then first compute the equilibrium at 1 atm as condition. Then one could instead introduce the current volume as condition and compute equilibrium, which should result in the same state of equilibrium. Then one could evaluate $(\partial U/\partial T)_{V,N}$. That quantity could be described as $C_V(T,P_0)$. The alternative would be to keep V constant at its value from room temperature for all temperatures and that would require that P increases with temperature in order to balance the natural thermal expansion. That quantity could be described as $C_V(T,V_0)$. Since all the experimental information usually used when C_V is evaluated from C_P has been obtained from 1 atm, the C_V values usually reported would most probably be $C_V(T,P_0)$.

2.8. Changing independent variables

Show numerically that $C_V\kappa_T = C_P\kappa_S$ for Cr at 1500 K and 1 atm.

Hint

Remember that $C_V = (\partial U/\partial T)_V$, $C_P = (\partial H/\partial T)_P$, $V\kappa_T = -(\partial V/\partial P)_T$ and $V\kappa_S = -(\partial V/\partial P)_S$. You have to be careful with the sets of independent variables that are not the same for all the partial derivatives.

2.9. Maxwell relation

Prove numerically that $(\partial S/\partial V)_T = (\partial P/\partial T)_V$. Use an Fe alloy with 10 mass% Cr at 900 and 700^{o}C under 1 atm.

Hint

1) These partial derivatives use the same three independent variables, including N that is omitted.

2) This alloy is bcc at those temperatures.

Chapter 3. Systems with variable composition

3.1. Chemical potential

Evaluate a chemical potential of a component in a state of equilibrium in a binary system with two phases, one of which is stoichiometric. Also, evaluate it for each one of the phases.

Hint

1) You may choose the Fe-C system with the Fe-rich fcc and the carbide called cementite, Fe_3C, at 1200 K and 1 atm.

2) You may define the conditions for a two-phase system in different ways. One way is to give the composition of the system but it will not fall into the two-phase field unless the composition is chosen within a certain range. It would be safer to give no condition regarding the composition but require that the two phases must be present. When the two-phase equilibrium has been computed, the composition of each phase will be known. In order to identify the equilibrium you may record its chemical potential of C.

3) In order to study fcc you should remove cementite. Then you will find that you must add another condition and it should define the composition of fcc in some way. Test that you get the same result as before if you give system the same composition that fcc had before.

4) Then take back cementite, remove fcc and give the system the composition of cementite, $x_C=0.25$. Compute equilibrium and test if you get the same chemical potential of C as before. Comment the result. Remember that the chemical potential of a component j is defined by varying its content, N_j.

3.2. Molar and integral quantities

Gibbs defined size as mass, not as number of moles. Choose a simple binary solution of a given composition and at given T and P. Evaluate $\Sigma\mu_i N_i$ in both ways and check that the result is the same.

Hint

1) Denoting mass by B, you can evaluate Gibbs' chemical potential of j as U.B$_j$ but only if you have used S, V, B$_1$ and B$_2$ when defining the conditions because $\mu_1 = (\partial U / \partial B_1)_{S,V,B_2}$ according to Gibbs, rather than $\mu_1 = (\partial U / \partial N_1)_{S,V,N_2}$.

2) You may choose an alloy of 200 gram Fe and 20 gram Cr in the bcc state at 800 K and 1 bar. After computing the equilibrium, you can read the values of S and V and then use them for a new computation of the same equilibrium.

3.3. Characteristic state functions

There is a characteristic state function which can be defined as $\Omega = U - TS - \Sigma\mu_i N_i = -PV$ and its natural state variables are *T, V* and μ_i because $d\Omega = d(-PV) = -SdT - PdV - \Sigma N_i d\mu_i$ under reversible conditions. It is called "Grand Potential" and is much used in modelling, one advantage being that it is well suited for conditions under constant volume in simple models, which implies that the distances between atoms should stay constant. On the other hand, the Gibbs energy, $G = \Sigma\mu_i N_i$, is well suited for describing experimental results and applications because it is most easy to keep its natural variables, *P* and *T*, constant in experiments. Suppose the grand potential as function of its natural variables, *T*, *V* and μ_i, is available. Evaluate Gibbs energy for a simple binary solution of a given composition.

Hint

1) For the user of a thermodynamic data bank system it may not be evident what characteristic state function is used for storing the thermodynamic information. What matters is the choice of variables in the definition of the conditions because they will thus become independent variables. One may thus mimic the grand potential by giving the values of *T*, *V* and μ_i as conditions.

2) You may use the same system as in the preceding problem, i.e. an alloy of 200 gram Fe and 20 gram Cr in the bcc state at 800 K and 1 bar.

3) Accepting the preceding system and conditions it is necessary first to evaluate the values of *V* and μ_i to be used for mimicking the grand potential. As usual, it is necessary first to compute equilibrium for the conditions given primarily.

4) The grand potential yields $N(Fe) = -(\partial\Omega / \partial mu(Fe))_{T,V,mu(Cr)} = V(\partial P / \partial mu(Fe))_{T,V,mu(Cr)}$ since $\Omega = -PV$ and *V* is constant for this partial derivative.

3.4. Additivity of extensive quantities. Free energy and exergy.

Consider 1 m^3 of pure H_2 at 600^oC and 1 atm being burned to H_2O with air containing 20 mol% O_2 and 1.5 mol% H_2O of 18^oC and the resulting gas being cooled to 18^oC. Evaluate the free energy that could theoretically be extracted from that system if the air can be regarded as an infinite reservoir of O_2 and recipient of H_2O, i.e., the exergy. Assume that one can neglect the minute amount of H_2 that is not oxidized.

Hint

One way to solve this problem is to define an initial system with the final content of matter, i.e., including the oxygen required for oxidizing the H_2 gas. Initially, there are thus two subsystems, the H_2 gas and the proper amount of oxygen in the surrounding reservoir, and one should add the Gibbs energy of them. The value of the H_2 gas must be evaluated from U(873 K,101325 Pa) – 291*S(873 K,101325 Pa) + 101325*V(873 K,101325 Pa). The value of the oxygen is obtained directly from μ_{O_2} of the atmosphere. The Gibbs energy of the final state is obtained from the H_2O gas at μ_{H_2O} of the atmosphere.

In reality one would not be able to make use of all that exergy because the local conditions in the surroundings will change by the loss of O_2 and the receipt of H_2O. The most critical information would be the local H_2O pressure. This is evident if one realizes that the decrease in Gibbs energy would be infinite if there were no moisture in the atmosphere initially and one would wait until the H_2O would spread infinitely far away. Of course, there would be no practical method to utilize that part of the process. A method to obtain a value of the practically available Gibbs energy decrease could be to calculate the amount of air that is needed for oxidizing the H_2 and assume that the H_2O will stay in the amount of nitrogen left. However, now you are not required to consider that case.

3.6A. Calculation of equilibrium

Consider a ternary system with three solution phases, e.g. Fe-Cr-C with fcc, bcc and liquid. One may define the conditions by presenting the values of T and P and further require that all three phases take part in the equilibrium. Compute the compositions of the three phases at given values of T and P but without prescribing an average composition of the system. Then, define a composition within the three-phase triangle you have found and determine the solidus and liquidus temperatures for that alloy.

Hint

It is most common to store experimental information in the form of a fundamental equation for the Gibbs energy, using T, P and N_i as the independent state variables. The computation of equilibrium when the values of other state variables are prescribed as conditions must be made by iteration. However, when such a procedure is available in a data bank system, it is not necessarily evident to the user.

There have already been a number of problems involving iteration and here is another one. It may serve to demonstrate the great flexibility that may be available in a data bank system. As an example, one could have evaluated at what temperature the liquid has a particular content or amount.

In complicated cases it may be difficult for the program to locate the equilibrium compositions of the phases. It may then help to give reasonable start values if one has a feeling for the properties of the system. There may also be ways of making the system more efficient in finding good start values for the compositions of the phases. A final possibility could be to start with an alloy composition close to a lower-order system, in this case a binary system.

3.6B. Calculation of equilibrium

Compute and plot a curve showing what happens to the alloy considered in Problem 3.6A when cooled from pure liquid state down to 500°C.

Hint

Hopefully, your databank system has a special facility for this kind of plotting. The composition of your alloy may have been 0.05319 mass% Cr and 0.002913 mass% C.

3.7. Evaluation of the driving force

Calculate numerically the driving force for the precipitation of a phase from a supersaturated solid solution under three different conditions but all under constant T and P. (a) Consider the formation of the very first, minute amount of the new phase. (b) Consider the situation where the precipitation is halfway. (c) Consider the integrated driving force for the whole reaction. (d) You may finally evaluate the driving force per mole of the new phase averaged for the whole reaction.

Hint

a) This case was considered already in Problem 1.8. It was concluded that the driving force depends on the exact composition of the new phase. In order to predict the rate of nucleation of the new phase one is interested in the composition that yields the largest driving force. That was not done in Problem 1.8. Your data bank system may have a facility for evaluating the driving force for the most favourable composition directly.

b) Here it is necessary first to compute the final equilibrium and evaluate the composition of the parent phase when the reaction is halfway. Then the problem is of the same kind as under (a).

c) Here you should simply compare the Gibbs energy of the initial and the final states. The initial state can be treated as a state of equilibrium if you can require that the new phase cannot form, i.e., as you did under (a).

For convenience you may solve this problem for the system used in Problem 1.8, the Fe-Cr system at 1 atm.

3.8. Driving force for molecular reactions

Consider a gas mixture of 60% H_2, 30% O_2 and 10% H_2O at 2000 K and 1 bar. (a) What is the driving force for the formation of more H_2O? (b) What is the average driving force per mole of H_2O for the whole reaction.

Hint

Most data bank systems have a facility for the tabulation of properties as functions of temperature, e.g. the Gibbs energy of reaction. However, when applied to reactions such tables generally assume that all the species occur in their standard states, usually the pure form at 1 atm. You would here have to look for another way to obtain the information wanted but it could be different in different systems. Try to use your facility to solve this problem by comparing the Gibbs energy for two states.

Chapter 4. Practical handling of multicomponent systems

4.1. Partial quantities

Evaluate the diffusion potential in CuZn with 50 mass% Zn at 700°C and 1 atm.

Hint

It could be evaluated directly if it could be expressed as a partial derivative of G with respect to a state variable while a set of other state variables are kept constant. That is indeed possible.

The diffusion potential is defined as the change of Gibbs energy when one component is exchanged for another. That may be accomplished by adding N_{Zn} and removing the same amount of Cu, $dN_{Cu} = - dN_{Zn}$. The total number of moles, N is thus constant. It should be easy to check the result if there is a facility for evaluating partial derivatives directly.

4.2. Relations for partial quantities

Evaluate H_{Mg} for an fcc alloy of Al-2 mass% Mg at 500°C and 1 atm.

Hint

From G = H – TS one can derive $H_{Mg} = G_{Mg} + TS_{Mg} = \mu_{Mg} + TS_{Mg}$. Remember to define the proper set of independent state variables when evaluating partial derivatives.

4.3. Alternative variables for composition

Calculate the fcc+cementite two-phase equilibrium for an Fe alloy with 4 mass% Cr and 3 mass% C at 800°C and 1 atm, assuming that no other carbide forms. Then, calculate this two-phase phase field in the phase diagram at 800°C and 1 atm. Plot the tie-lines in two diagrams with the axes x_C, u_{Cr} and x_C, z_{Cr} where $u_{Cr}=x_{Cr}/(x_{Fe}+x_{Cr})$ and $z_{Cr}=x_{Cr}/x_{Fe}$.

Hint

Each data bank system may have its own method of mapping boundaries between phase fields and also different facilities for plotting the results.

4.5. The tie-line rule

Calculate and plot diagrams similar to Figs. 4.7 (a) and (b) for the liquid Al-Mg phase at 700°C and 1 atm. Furthermore, change the references for Al and Mg to their solid states.

Hint

To be able to use the solid states as references, you should fetch data for those phases from the database.

4.6. Different sets of components

Explore what facilities your data bank system has for changing the set of components and try it on the gas with the H_2, O_2 and H_2O species.

Hint

In general, the atoms of the elements are defined as the components but there may be a possibility to change this choice. At equilibrium it would be a trivial change because the chemical potential of a species containing several atoms is equal to the sum of the chemical potentials of all the atoms. However, there may sometimes be a practical advantage, e.g. for a system containing a stoichiometric phase or for the gas phase where one may like to treat a species as a component.

4.7. Constitution and constituents

Consider an Fe alloy with 5 mass% Cr and 2 mass% C at 1000°C and 1 atm. Compute the equilibrium and evaluate all the state variables that are required to describe (1) the composition and (2) the constitution.

Hint

Of course, one must first compute the equilibrium. The method of showing the composition and the constitution may be different in different data bank systems.

4.8. Chemical potentials in a phase with sublattices

Evaluate the equilibrium distribution of Cu and Zn between the two sublattices in an ordered bcc alloy of Cu with 50 mass% Zn at 400^{o}C and 1 atm. Then, apply this distribution to 500^{o}C and evaluate the driving force for redistribution of the elements in the direction of the new equilibrium distribution by evaluating the diffusion potentials in each sublattice and taking the difference.

Hint

The method may be different in different data bank systems.

Chapter 5. Thermodynamics of processes

Problem 5.1A. Thermodynamic treatment of kinetics of internal processes
Problem 5.1B. Thermodynamic treatment of kinetics of internal processes
Problem 5.5. Chemical reaction

5.1A. Thermodynamic treatment of kinetics of internal processes

Evaluate the thermodynamic force for the solidification of pure liquid Mo to bcc at 2800 K and 1 atm. The melting point of Mo is 2896 K. Suppose the reaction is so rapid that there is no heat exchange with the surroundings.

Hint

1) The first law gives dH=dQ+VdP=0 in this case and the second law gives dS=dQ/T+d$_{ip}$S= d$_{ip}$S=(d$_{ip}$S/df)*df=X*df where X is the thermodynamic force. Suppose a small fraction, Δf , solidifies. Some heat of melting will be deliberated and will heat the system to a temperature determined by the condition that H is constant. After finding that temperature you may evaluate $X = d_{ip}S/df = dS/df \cong \Delta S/\Delta f$.

2) The new temperature may be found by introducing Δf and guessing a value of the adiabatic T and evaluating ΔH there. By extrapolation you can then find the correct temperature where $\Delta H = 0$. Then you can evaluate S at that temperature and obtain $X \cong \Delta S/\Delta f$.

5.1B. Thermodynamic treatment of kinetics of internal processes

Do the same under isothermal conditions. Compare the results and explain.

Hint

For the isothermal case you can start by evaluating the driving force, DF, from the difference in Gibbs energy. Then you get the thermodynamic force TF=DF/T.

5.5. Chemical reactions

Evaluate the driving force for the formation of more H_2O molecules in a gas with the constitution 5 mol% H_2O, 40 mol% H_2 and 55 mol% O_2 at 1 atm and 2000 K.

Hint

The driving force for the formation per mole of more H_2O is $\mu_{H_2} + 0.5 \cdot \mu_{O_2} - \mu_{H_2O}$ according to Eq. 5.62. The question is how your data bank system can give you values for the chemical potentials of a non-equilibrium gas.

Chapter 6. Stabiliy

Problem 6.5A. Limit of stability
Problem 6.5B. Limit of stability
Problem 6.5C. Limit of stability
Problem 6.6. Limit of stability of alloys
Problem 6.9. Le Chatelier's principle

6.5A. Limit of stability

Compare numerically the values of $(\partial T / \partial S)_{V,N}$ and $(\partial T / \partial S)_{P,N}$ for pure diamond at 1000 K and 1 atm. Both expressions are use to define stability.

Hint

The only difference between the two partial derivatives is that different quantities are kept constant. They are thus based on different sets of independent state variables.

6.5B. Limit of stability

Evaluate the stability of a supersaturated fcc alloy of Fe with 20 mol% C at 1200 and 1000 K and 1 atm.

Hint

A system is least stable against fluctuations of one extensive state variable while all but one of the other conjugate pairs are represented by the potential. The exception is one that has been chosen to define the size of the system, e.g. N_i where i is the main component. The preferable expression for the stability of the system would thus be $B = 2(\partial \mu_c / \partial N_c)_{T,P,\mu_2,....\mu_{c-1},N_1}$. However, it should be remembered that inside an unstable region this quantity may again turn positive while other expressions of stability have turned negative. It should thus be used only inside a stable region and when approaching an unstable region.

6.5C. Limit of stability

The stability can be defined in many ways. Each method expresses the stability in its own way and the resulting values for the same case may differ appreciably. However, there are two general principles. 1) A method using a set of independent variables containing a potential gives a lower value than a method using the conjugate extensive variable. 2) At the limit of stability all methods using potentials except for two extensive variables give the value zero. Test if your data bank system can confirm the first principle. The second one will be tested in Problem 6.5D.

Hint

You may consider the bcc phase in the Fe-Cr-C system at 1 atm and 700 K and for 1 mol% C and 5 mol% Cr.

6.5D. Limit of stability

Test the second principle defined in Problem 6.5C.

Hint

As for Problem 6.5C you may again consider the bcc phase in the Fe-Cr-C system at 1 atm and 700 K and for 1 mol% C. There is a bcc miscibility gap and the stability limit, i.e., the spinodal, falls close to 6 mol% Cr. You may thus examine the stability for 5, 6 and 7 mol% Cr.

6.6. Limit of stability of alloys

Compare the value of $\begin{vmatrix} G_{22} & G_{23} \\ G_{32} & G_{33} \end{vmatrix}$ with $(\partial\mu_2/\partial N_2)_{T,P,N_1,\mu_3}$ and $(\partial\mu_3/\partial N_3)_{T,P,N_1,\mu_2}$ for the fcc phase in an Fe alloy with 1 mol% C and 5 mol% Cr at 1200 K and 1 atm.

Hint

The determinant is equal to $G_{22}G_{33} - G_{23}G_{32}$ where G_2 is identical with $\mu_2 = (\partial G/\partial N_2)_{T,P,N_1,N_3}$. The set of independent variables are thus T, P, N_1, N_2 and N_3 for all the quantities in the determinant. Each partial derivative involves a chemical potential.

6.9. Le Chatelier's principle

Consider the internal process $2H_2 + O_2 \rightarrow 2H_2O$ when a gas with 2 mole of H and 1 mole of O from the equilibrium at 1800 K and 1 atm is (a) compressed adiabatically to 10 bar so rapidly that no reaction can occur. Evaluate T and the molar volume, V_m. Then, suppose (b) there is time for the process to go to a new equilibrium under 10 bar but still without any exchange of heat. Finally suppose (c) the temperature will eventually return to 1800 K but still under 10 bar. Evaluate the final V_m. Compare the resulting T and V_m with initial values and discuss how the results can be used as examples of Le Chatelier’s principle.

Hint

For the adiabatic compression, S is not changed because there is no internal reaction. That can be used as a condition for finding the new state after compression. However, it is a frozen-in state and would have to be evaluated from a module that can handle states of non-equilibrium. S will change during (b) due to the internal process but not H because there is no exchange of enthalpy with the surroundings during an isobaric adiabatic change. The final state (c) is easily found as the state of equilibrium at 1800 K.

Chapter 7. Applications of molar Gibbs energy diagrams

7.2. Instability of binary solutions

Calculate and plot a molar Gibbs energy diagram for the fcc phase in the Fe-Cr system at 500°C under 1 atm.

Hint

1) Since pure Fe and Cr are both bcc, there will be only one phase to be fetched from the database. From your first run you may get a Gm curve with two minima. The bcc phase should thus have a miscibility gap at this low temperature and your equilibration module may have a procedure for identify two bcc phases, an Fe rich phase, bcc#1, and a Cr rich phase, bcc#2. Try to accomplish this if it does not happen automatically.

2) On the other hand, it may be instructive to see the two minima. If you don't get them on your first run, try to inactivate the automatic procedure.

3) Use the pure elements at the actual temperature as references.

7.3. Illustration of the Gibbs-Duhem relation.

Define a system at 1000 K and 1 atm, with the elements Fe, Cr and C and with the phases bcc, graphite and cementite, (Fe,Cr)3C. Then, define Fe3C1 and Cr3C1 as new components instead of Fe and Cr. Make bcc and graphite dormant and compute the equilibrium between cementite, with equal amounts of Fe and Cr, and graphite. Evaluate the potential of a hypothetical component Fe1Cr1. Finally, evaluate the same potential if the C activity is just half as high as for graphite. Evaluate the difference in Fe1Cr1 potential with what one should expect. Fig. 7.6 can be used as an illustration.

Hint

1) Equilibrium with graphite simply means that the C activity is 1, if graphite is used as reference. The second case can then be treated in exactly the same way but with a C activity of 0.5.

2) The potential of Fe for an equilibrium is equal to the potential of Fe3C1 minus the potential of C and divided by 3. Similarly for Cr and the potential for Fe1Cr1 is the sum of the two.

7.4. Two-phase equilibria in binary systems

The database lists four carbides in the Cr-C system, Cr23C6, Cr3C Cr7C3 and Cr3C2, and together with the end-members, bcc-Cr and graphite, it makes six phases. Examine the phase equilibria by computing the equilibrium for alloy compositions in all the regions between phases.

Hint

For all the alloy compositions, let all the phases be present and note the degree of instability, i.e. the negative value of the driving force for formation, of all the phases not taking part in the equilibrium.

7.5. Allotropic phase boundaries

Fcc and bcc Fe have the same Gibbs energy at 1 atm and 911^{o}C. That phase equlibrium represents an end-point of a T_o line that extends into all binary Fe-X phase diagram. Compute and plot that line for the Fe-C system up to 1 mass% C.

Hint

The T_o line is sometimes regarded as an allotropic phase boundary. In principle, it is evaluated from the condition G_m(fcc) = G_m(bcc) but different data bank systems may have different methods of computing that kind of equilibrium.

7.6. Effect of a pressure difference on a two-phase equilibrium

Compute the effect of a pressure increase of 100 atm on the bcc phase when in equilibrium with fcc of 1 atm in the Fe-C system at 1000^{o}C.

Hint

One way to compute the equilibrium between two phases, when only one of them is under an increased pressure, would be to go to the module where the properties are stored and change the molar volume of the other phase to zero. With T-C one you have another possibility.

7.7. Driving force for the formation of a new phase

An fcc phase of Fe with 1.5 mass% C at 1000°C and 1 atm is supersaturated with respect to graphite and cementite. Compute the driving forces for their nucleation. Plot the driving forces as functions of the C content of fcc up to 2 mass% C.

Hint

You should remember the difference between the driving force for the first stage of formation, the so-called nucleation, and the driving force for the whole reaction until equilibrium has been established, i.e. the integrated driving force.

7.8. Partitionless transformation under local equilibrium

Consider the partitionless solidification of an Al-Mg alloy with 2 mass% Mg under 1 atm. Suppose heat conduction is very efficient and the system is thin enough to be kept at a homogeneous temperature, which is decreased until the right temperature for partitionless solidification has been established. Compute the driving force for diffusion in the liquid in front of the solidification front if there is local equilibrium.

Hint

You must first find the temperature where the conditions for partitionless solidification are fulfilled. It is required that the new phase should grow with the composition of the bulk of the liquid. You should thus start by computing at what temperature the solid phase with that composition is in equilibrium with liquid. That should also yield the composition of the liquid at the interface. Then it is easy to take the difference in Mg content inside the liquid, i.e., between the interface to solid and the bulk, which has the initial content.

7.9. Problem on activation energy for a fluctuation

Long ago one had the idea that a small coherent particle could precipitate by a fluctuation in the parent phase first reaching the correct composition and size for a nucleus and then transforming without any diffusion. Consider an fcc Fe alloy with 0.5 mass% C at 1000 K and 1 bar and calculate the activation energy for such a fluctuation being a precursor of a critical nucleus of the new phase.

Hint

You have to know the composition and size of the fcc fluctuation. Suppose they have the same values as the critical nucleus of the new phase according to ordinary nucleation theory. You should then start by evaluating the critical nucleus. 1 J/m^2 may be a reasonable value for the specific surface energy.

Chapter 8. Phase equilibria and potential phase diagrams

Problem 8.1. Gibbs' phase rule
Problem 8.2. Fundamental property diagram
Problem 8.4. Potential phase diagrams in binary and multinary systems
Problem 8.5. Sections of potential phase diagrams
Problem 8.7. Ternary systems

8.1. Gibbs' phase rule

CaO and MgO are both stoichiometric and they can form a solution (Ca,Mg)O. Evaluate the chemical potential of MgO in a 50/50 alloy at 1500 K and 1 atm, using pure MgO as the reference.

Hint

For a data bank specialized to oxide systems it would be possible to use only oxides bas components. The present system would then have two components. A more general kind of data bank should be capable of combining information on different kinds of systems. It is then essential also to describe chemical potentials of elements. It may be an advantage to build such a data bank on an algorithm based on the chemical potentials of the elements. That does not prevent the use of compounds as components but the number of components must be the same as the number of elements.

8.2. Fundamental property diagram

Plot the complete property diagram T,P,μ_{Fe} for pure fcc Fe in order to show that it is convex.

Hint

In principle, it should be a trivial matter to compute equilibrium over a T,P area and to evaluate a property, e.g. μ_{Fe}, for each point. In order to plot the result one should place those points along a series of constant T or P values. One would thus get two series of more or less parallel curves but in order to see the shape of the surface in a two-dimensional diagram, one should redefine the axes. The result should resemble Fig. 8.2 or 8.4. Any point for $\mu(T,P)$ should be placed at (XX,YY) where $XX = T - AA \cdot P$ and $YY = \mu_{Fe} - BB \cdot P$, and the values of AA and BB may be obtained by trial and error. Reasonable starting values could be $AA = 0.2(T_{\max} - T_{mn})/(P_{\max(} - P_{\min})$ and $BB = 0.9(\mu_{\max} - \mu_{\min})/(P_{\max} - P_{\min})$.

8.4. Potential phase diagrams in binary and multinary systems

Examine if there is any combination (T,P) where the invariant four-phase equilibrium bcc/fcc/Fe_3C/graphite exists in the Fe-C system? If you find it, examine the region around it. In principle, it should be similar to Fig. 8.11 but instead of constructing a three-dimensional diagram, you may show projections from three directions.

Hint

When mapping the region around the invariant equilibrium, it may be difficult to start from the invariant equilibrium, which cannot be followed. It may be better to start from a point on a three-phase line.

8.5. Sections of potential phase diagrams

Compute the μ_O, μ_S phase diagram for the Cu-O-S system at 1 atm. Then make a section at 1000 K, using P_{O_2} to express μ_O and P_{S_2} to express μ_S.

Hint

You are invited to try to interpret the resulting potential diagram before sectioning. It may then be helpful to consult the long list of print-outs from the computations of equilibria.

8.7. Ternary systems

Consider the possible oxidation of Cu in water without any extra oxygen present. There are two possible oxides, Cu_2O and CuO, in addition to H_2O.

Hint

Cu would first oxidize to Cu_2O and O would have to come from H_2O. Free hydrogen would thus form and dissolve in the water or form gas bubbles if the H potential is high enough, i.e. if the partial pressure of H_2 would be high enough compared to the external pressure. It would thus be interesting to compute the equilibria and express the result as partial pressure of H_2 in a hypothetical gas phase. Do that from 0 to 100°C.

It is conceivable that oxidation continues and results in CuO. First you should thus consider the equilibrium $H_2O/Cu_2O/Cu$ and then $H_2O/CuO/Cu_2O$.

When you have completed this problem you have obtained a diagram which may be regarded as a potential phase diagram for the Cu-O system with the H potential in water as an expression of the O potential. The diagram has three phase fields, one each for Cu, Cu_2O and CuO. In Section 8.7 there is already a diagram showing the equilibrium between CuO and Cu_2O although it is more complicated but does not show Cu. Furthermore, it uses the O potential instead of the H potential.

Chapter 9. Molar phase diagrams

9.1. Molar axes

Compute and plot the phase diagram for Fe-C at 1 atm and between 1650 and 1850 K and 0 and 0.03 mol% C. Then, try to use enthalpy and C content as axes in the diagram.

Hint

You should realize that you may have to declare that you are not interested in the values for two-phase mixtures but for the individual phases present in the mixtures.

9.2. Sets of conjugate variables containing molar variables

Compute the phase equilibria for pure Fe between 500 and 1000 K and between 8E9 to 14E9 bar. Plot the results as phase diagrams with various pairs of axes. In particular combine H_m with other quantities.

Hint

As shown in Table 9.1, all combinations of axes don't give true phase diagrams.

9.4. Sections of molar phase diagrams

Consider a carbon free Fe-6 mass% Cr alloy being carburised. Demonstrate with a diagram how the alloy would move from phase field to phase field as the C content is increasing. Construct the diagram for temperatures between 650 and 1550^{o}C. Then, try to figure out the number of phases in the various phase fields. Finally, compute diagrams showing how the amounts of the phases change with the C content during carburisation and with temperature during cooling.

Hint

Evidently, you are asked to compute a so-called isopleth with a constant ratio of Fe to Cr. It will give the same result whether you define this ratio with mass fractions or mole fractions.

9.6. Topology of sectioned molar diagrams

Compute a zero-phase-fraction line of your own choice through the isopleth obtained in the first part of Problem 9.4. Plot this line in a diagram with the same axes as the isopleth.

Hint

Your data bank system should offer some method of requiring that a selected phase should take part in all the equilibria that are computed, but with the zero amount.

Chapter 10. Projected and mixed phase diagrams

10.1A. Schreinemakers' projection of potential phase diagrams.

Consider the ternary Al-Mg-Si system at 1 atm and in the region 400 to 700°C. It should obey the same topological rules as a binary system with a variable *P*, as Fig. 10.1(a). Calculate the three-dimensional phase diagram. Plot the result with the axes a_{Mg}, a_{Si}, which should yield a projection in the T direction with the same topology as Fig. 10.1(b). Produce a stereographic pair of pictures by using $a_{Si} \pm \varepsilon \cdot T$ instead of a_{Si} as an axis. You have to find a conveniently small value of the ε constant. That pair should give an impression of the three-dimensional structure. Another method was used in Fig. 10.1(a).

Hint

Your data bank system certainly has a standard procedure for mapping phase diagrams with axes for two components. Hopefully, it is then possible to plot the results with the activity axes. It may be most convenient to use activities based on the pure elements in their stable solid states and at the current temperature as references.

10.1B. Schreinemakers’ projection of potential phase diagrams

Compute and plot all the liquidus surfaces for the Fe-Cr-C system at 1 atm. Then, add isotherms on the liquidus surfaces.

Hint

In principle, the first part of this problem is solved by mapping the complete potential phase diagram after sectioning at the constant pressure. However, the condition liq=fix must be used in order to avoid all other univariant lines (also called monovariant). To add isotherms actually means to map isothermal sections, which might require a new mapping operation for each section.

10.2. The phase field rule and projected diagrams

The fundamental property diagram of a ternary system has 3+2=5 axes, e.g. μ_A, μ_B, μ_C, T and P. By projecting in one direction one obtains a four-dimensional potential phase diagram and those four potentials then make a set of independent state variables. In order to obtain a two-dimensional phase diagram, which can be plotted on paper, one can project in the directions of three potentials and could thus obtain 5x4x3=60 different projections. An alternative would be to project in one direction and section at constant values of two potentials. That would give another 60 alternatives. Finally, one could project in two directions and section at a constant value of one. That would add yet another 60 alternatives. You are asked to make two two-dimensional phase diagrams of the Fe-Cr-C system.

Hint

1) Each time you decide to make a section, you must make a new mapping of the phase equilibria at the chosen value of the sectioned potential. On the other hand, once you have mapped the equilibria for variable conditions for all the potentials, you can directly plot any projection you like. For convenience, you should thus choose to make two projections.

2) Since only four of the potentials are independent due to the Gibbs-Duhem relation, you should choose one to be dependent, say μ_A.

3) After mapping all the univariant equilibria you should choose two pairs of potentials to be used as axes in the two diagrams. It may be most illustrative to choose T and P as one pair and μ_B and μ_C as the other.

10.4. Coincidence of projected surfaces

Compute the Fe+FeO+Fe_2O_3+FeS equilibrium at 1 atm. In order to simplify the problem, include only the fcc phase as an Fe phase. Compute the connecting four three-phase equilibria in a reasonably large region around the invariant point. Plot those four-phase lines using T and $\mu_{O_2} - \mu_{O_2}^{ref}$ as axes. Use O_2 gas of 1 atm and the current temperature as reference for O_2. Then change the latter axis to $\mu_{O_2} - \mu_{O_2}^{ref} \pm \varepsilon \cdot (\mu_S - \mu_S^{ref})$ where ε is a conveniently small number.

Hint

1) It may be convenient also to use pure S as at the current temperature as reference.

2) You may find that the modified axis made a new line appear. From where did it come?

10.7A. Selection of axes in mixed diagrams

Compute the phase diagram for Pb-Sn at 1 bar. Plot the result in a diagram with the μ_{Pb}, S_m axes. It should look as Fig. 10.18. Plot the diagram with the following pairs of axes, μ_{Pb}, S_{Pb}; μ_{Pb}, T; x_{Pb}, S_m; x_{Pb}, S_{Pb}; $(\mu_{Pb} - \mu_{Sn}), S_m$.

Hint

In order to obtain a true phase diagram you must choose a pair of axes that belong to the same set of conjugate variables.

10.7B. Selection of axes in mixed diagrams

Compute the isothermal section of the Fe-Cr-C system at 1200^{o}C and 1 atm. Then, plot the result with the axes u_{Cr}, μ_C as in Fig. 10.19. The diagram probably shows swallow tails. Try to get rid of them by changing the axes. It may be worth trying x_{Cr}, μ_C; u_{Cr},($\mu_C - \mu_{Fe}$); u_{Cr},($\mu_C - \mu_{Cr}$); u_{Cr},ln(a_C/a_{Fe}) and x_{Cr},a_C.

Hint

Consult Tables 9.1 and 3 regarding the ways of combining variables for the axes in a true phase diagram.

10.8. Konovalov's rule

In the T-x diagram for the Fe-Cr system there is a bcc+fcc two-phase field showing a congruent transformation. Use an isothermal section to examine how the phase field extends into the ternary diagram when C is added. First, choose axes for the mole fractions of Cr and C. Show what kind of diagram you should then use in order to obtain a congruent transformation point. With what experimental technique could one observe it?

2) There is another pair of axes that would give a similar diagram. Compare the Cr content of the congruent point in the two diagrams. Explain the difference by studying a diagram with two potential axes.

Hint

You may get some inspiration from Problem 10.7B. There you obtained two true phase diagrams with one potential axis. Only one of them seemed to indicate a congruent transformation.

Chapter 11. Direction of phase boundaries

Problem 11.5. Congruent melting points
Problem 11.6. Vertical phase boundaries

11.5. Congruent melting points

Determine the curvatures of the two phase boundaries at the congruent transformation point for bcc/sigma in the Fe-Cr system.

Hint

You may evaluate the curvature of a curve from three points. The transformation point is one and you may compute one point on each side by requiring that T should be 0.1 K lower, for instance.

11.6. Vertical phase boundaries

The phase boundary bcc/fcc in the Fe-C system is retrograde, i.e., the solubility of C in bcc which starts from zero at the transition point of 911^{o}C reaches a maximum value at some lower temperature and then decreases and approaches zero at low temperatures. Evaluate the temperature of maximum solubility with high accuracy.

Hint

Rather than just comparing the solubility at various temperatures it may be more accurate to evaluate the slope of the phase boundary and evaluate where it goes through zero.