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Calculations of Composition Boundaries of Saturated Phases

by

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Calculations of Composition Boundaries of Saturated Phases

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ABSTRACT

A program for the HP-41CV calculator is presented for calculating the equilibrium composition boundaries of pairs of saturating solids, liquids, or a combination of a solid and liquid. The activity coefficients must be represented in the form \( \ln \gamma_1 = (b_h/T - b_s)x_2^2 + (c_h/T - c_s)x_2^3 \) where \( h \) refers to an enthalpy contribution and \( s \) refers to an excess entropy contribution. For solid-liquid equilibria, enthalpies and entropies of fusion are required. For all equilibria, provision is made for use of hypothetical standard states such as the Henry's Law standard states. For example, in treating solid solutions of molybdenum in face-centered cubic metals such as Ni, Rh, or Pt, it is sometimes convenient to use a hypothetical fcc standard state of Mo which represents the limiting Henry's Law behavior of Mo in the fcc metal and has much different properties than a real fcc molybdenum solid.
Calculation of Composition Boundaries of Saturating Phases

Such calculations require that Gibbs energy of solution be expressed in analytical form as a function of temperature and composition. The functional form of the regular solution equation is the most practical for most systems.

The regular solution derivation\(^1,2\) gives the Gibbs energy in terms of volume fraction. If the volume fraction is expanded as a truncated power series in mole fraction, one obtains

\[
\Delta G_1^{E}/RT = b_g x_2^2 + c_g x_2^3 \quad \text{and} \quad \Delta G_2^{E}/RT = [b_g + 3 c_g] x_1^2 - c_g x_1^3
\]

\(\Delta G_1^{E}\) is the excess partial molal Gibbs energy of component 1 and \(V_1\) is the molal volume of component 1. As the regular solution equation is derived under constant volume conditions, an excess entropy term arises from the volume change upon mixing. In addition, since \(b_g = (V_2^2 / V_1) [\Delta E_1 / V_1]^{1/2} - (\Delta E_2 / V_2)^{1/2} / RT\), the temperature coefficients of the molal volume and of the energy of vaporization, \(\Delta E\), also result in an excess entropy.\(^1\) The enthalpy and excess entropy can be expressed as similar functions of mole fraction.

Their combination to give the partial molal Gibbs energy equation yields for each component in its standard state dissolving in the solution

\[
\ln y_1 = \Delta G_1^{E}/RT = (b_h / T - b_s) x_2^2 + (c_h / T - c_s) x_2^3 = \Omega_1 x_2^2 \\
\ln y_2 = \Delta G_2^{E}/RT = [b_h / T - b_s + 3 (c_h / T - c_s)] x_1^2 - (c_h / T - c_s) x_1^3 = \Omega_2 x_1^2
\]

where the signs of the \(b_h, c_h, b_s\) and \(c_s\) terms are the same as the signs of the corresponding enthalpy and entropy terms in the Gibbs energy equation. Thus, \(b_g T\) at a temperature \(T\) equals \(b_h - b_s T\), etc. These equations average out the contributions of \(\Delta C_p\) values to the Gibbs energy by using the average enthalpy and entropy values over the temperature range of interest. Analytical equations of this form are found to reproduce, within the range of experimental uncertainty, the thermodynamic properties of many metallic solutions over a considerable range of temperature and composition.

When a miscibility gap exists in the solution at a given temperature, the partial molal Gibbs energies of both components are equal in both saturating phases. If the mole fractions are expressed as \(x_1 = 1 - y\) and \(x_2 = y\) in the phase with excess component 1 and as \(x_1 = x\) and \(x_2 = 1 - x\)
in the phase with excess component 2, the equilibrium condition can be expressed as

\[ \ln x + b(1-x)^2 + c(1-x)^3 = \ln(1-y) + by^2 + cy^3 \]
\[ \ln y + (b+3c)(1-y)^2 - c(1-y)^3 = \ln(1-x) + (b+3c)x^2 - cx^3 \]

where \( b = (b_1/T - b_2) \) and similarly for \( c \). When the same values of \( b \) and \( c \) are not applicable for both phases, the equations become

\[ \ln x + b_x(x-1)^2 + c_x(x-1)^3 + e_x = \ln(1-y) + (b_y+3c_y)y^2 - cy^3 = -d_x \]
\[ \ln y + b_y(1-y)^2 + c_y(1-y)^3 + e_y = \ln(1-x) + (b_x+3c_x)x^2 - cx^3 = -d_y \]

The subscript \( x \) indicates the constants apply in the phase region for which \( x = x_1 \) is small and \( y \) indicates applicability in the phase region for which \( y = x_2 \) is small. These general equations may be reduced to the first set if \( b_x = b, b_y = b + \frac{3c}{2}, c_x = c, \) and \( c_y = -c \). When the solubilities are small, the cubic terms can be dropped with the constants of the quadratic terms being \( \Omega_x = b_x + c_x \) and \( \Omega_y = b_y + c_y \). The \( e_x \) and \( e_y \) terms are discussed below.

For a symmetrical immiscibility gap when the molal volumes of the two components are closely the same, \( c = 0 \) and \( b_x = b_y \) resulting in equal values of \( x \) and \( y \). The two equations reduce to \( \ln[x/(1-x)] + b(1-2x) = 0 \), which is readily solved by Prgm. IM, with \( e = 0 \). If the excess entropy is neglected, \( b \) will be inversely proportional to \( T \) and the calculations can be repeated at a new temperature \( T_2 \) by multiplying \( b \) by \( T_1/T_2 \). This can be done by

\[ T_1 \uparrow T_2 / \text{STO} \times 1 \rightharpoonup \text{STO} \times 2 \times \text{EQS} \]  

To obtain the value of \( x = y \) at \( T_2 \). The temperature that brings \( b \) down to 2 will be the critical temperature. For \( b < 2 \), the system will be miscible.

Program IM carries out the simultaneous solution of these two equations for \( x \) and \( y \) to yield the compositions of the saturating phases. The iterative solution using the secant method is based in part on a portion of Prgm. SD-ll of the HP-67 Standard Pac. Program IM first assumes that the solubilities are small enough to neglect \( d_x \) and \( d_y \) and to approximate \( 1-x \) by 1. This yields as the first approximation \( x' = e^{-(b_x+c_x)} \). \( x' \) is used to calculate the first approximation of \( d_y \).

\[ \ln y + b_y(1-y)^2 + c_y(1-y)^3 + d_y + e_y = 0 \]

is then solved by iteration to yield \( y'' \). If flag 0 is set, the value of \( y \) obtained by each iteration is flashed. The process continues until the fractional change in \( y \) in the last iterative step rounded to the number of
places after the decimal designated in step 2 is displayed as zero. The same process is then used in step 7 to calculate \( x'' \). The value of \( x'' \) is used to calculate a new value of \( d_y \) and the equation for \( y \) is solved again to obtain \( y''' \). Steps 6 and 7 are alternately repeated until the values of \( x \) and \( y \) show no additional change. To speed convergence, step 2 should be set initially at \( \text{FIX} 2 \) and no change in \( x \) and \( y \) will be noted after \( \Delta x/x \) or \( \Delta y/y < 0.005 \). For \( x \) and \( y \sim 0.1 \), the values of \( x \) and \( y \) will be accurate to 0.0005 and can be read to 4 places by keying \( \text{FIX} 4 \). If it is desired to calculate \( x \) and \( y \) more accurately, steps 7 and 6 can be repeated with \( \text{FIX} 3 \) or \( 4 \). If there is no interest in the progress of the iteration at each step, \( \text{CFO} \) will stop the flashing of successive \( x \) or \( y \) values. \( \text{SFO} \) will change back to flashing.

If the same standard states are not used for both phases, a constant term would be added to \( d_x \) or \( d_y \) or both corresponding to the Gibbs energy difference between the standard states divided by RT. The equilibrium between the solidus and liquidus portions of a phase diagram will be considered as an example. For solid with largely component 1 in equilibrium with the liquid phase, then \( e_x = \Delta G^\circ_{f,1}/RT = \Delta H^\circ_{f,1}/RT - \Delta S^\circ_{f,1}/R \) and \( e_y = -\Delta G^\circ_{f,2}/RT = -\Delta H^\circ_{f,2}/RT + \Delta S^\circ_{f,2}/R, \) where \( \Delta H^\circ \) and \( \Delta S^\circ \) are the average enthalpies and entropies of fusion of the two components over the temperature range of interest. In the equations given on the previous page, \( b_x \) and \( b_y \) will be considerably different, in general, for the example of solid-liquid equilibria.

Program IM provides for insertion of the enthalpy and entropy terms to allow calculation of \( b_x \), \( c_x \), \( e_x \), \( b_y \), \( c_y \) and \( e_y \) at various temperatures and then to solve for \( x \) and \( y \) values for the saturating phases at the given temperature. When the \( b \), \( c \) and \( e \) values are already known for the desired temperature, the enthalpy values are inserted as zero and the \( b \), \( c \) and \( e \) values are inserted with reversed sign for the entropy terms as illustrated in one of the test examples.

For mutual solubilities of two liquid phases or two solid phases for which there are no \( e_x \) or \( e_y \) terms due to differences in standard states, \( \Delta H^\circ_{f,1} \Delta S^\circ_{f,1} \Delta H^\circ_{f,2} \) and \( \Delta S^\circ_{f,2} \) are entered as zero. When the difference in standard states corresponds to the solid phase transition, then \( \Delta H^\circ \) and
\( \Delta S^2 \) are replaced by the corresponding values for the transition. For liquid immiscibility with small enough solubilities for the approximation

\[
\ln \gamma_1 = \left( \frac{b_x + c_x}{b_x + \frac{1}{2} c_x} \right) y^2 \quad \text{and} \quad \ln \gamma_2 = \left( \frac{b_x + c_x}{b_x + \frac{1}{2} c_x} (1-y)^2 \right)
\]

in the phase rich in component 2, the regular solution theory predicts 

\[
\frac{b_x + c_x}{b_x + \frac{1}{2} c_x} = \frac{\gamma_2}{\gamma_1}.
\]

This is sometimes useful, but, in practice, the value of \( c \) is often more dependent upon change in character of the bonding across the solution range than upon the volumes of the pure materials, especially with change in electronic configuration upon solution. One can sometimes obtain a useful value of \( c \) by comparison of \( \frac{(\ln \gamma_1)}{x_2} = b + c \) at large \( x_2 \) with \( \frac{(\ln \gamma_2)}{x_1} = b + \frac{1}{2} c \) at large \( x_1 \). If \( c = 0 \) is used in Prgm. IM, \( \frac{(\ln \gamma_1)}{x_2} \) and \( \frac{(\ln \gamma_2)}{x_1} \) are taken equal for a given solution, but their value can be greatly different on opposite sides of the miscibility gap.

**Directions:**

1. Insert Prgm. IM
2. Fix \( x \), usually \( n=2 \) initially
3. \( \Delta H^0_{1,1}/R \uparrow \Delta S^0_{1,1}/R \uparrow b_h^x + b_s^x \quad \text{Display} \quad \Delta H^0_{1,1}/R \)
4. \( -\Delta H^0_{1,2}/R \uparrow -\Delta S^0_{1,2}/R \uparrow b_h^y + b_s^y \quad \text{or} \quad \Delta H^0_{1,2}/R \)
5. \( c_h^y + c_s^y + c_h^x + c_s^x \quad R/S \quad \text{(or} \quad b) \quad \text{or} \quad c_h^y \)
6. T B (or \( t^\circ C \ D) \)
7. C Repeat 7 and 8 alternately until \( x \) and \( y \) show no change in successive steps; read final values with Fix \( x \) \( n+1 \)
8. R/S \quad \text{Print Out} \quad \frac{\tau}{x'''} \quad y'''

**If** \( y \) **is known;** after step 7, Fix \( x \) \( n \) to desired accuracy followed by

\( y \) STO \( d \)

\( x'''' \) \( x'''' \)

\( x \)

\( y \)

\( \text{If} \ x \text{ is known; after step 6, Fix} \ x \text{ to desired accuracy followed by} \)

\( x \) STO \( d \)

\( d_y \)

\( y'''' \)

\( y'''' \)

\( \text{If} \ x \text{ is known; after step 6, Fix} \ x \text{ to desired accuracy followed by} \)

\( x \) STO \( d \)

\( d_y \)

\( y'''' \)

\( y'''' \)

**NOTE 1:** The alternatives \( a \) and \( b \) for \( R/S \) in steps 3 and 4 allows alteration of part of the data without need to reinsert all of the data. For step 6, temperature in \( ^\circ C \) can be inserted followed by \( D \) to convert to \( ^\circ K \) and initiate the calculations.
NOTE 2: The display control of step 2 can be changed at any time, but is best started with only two places. If higher than three place accuracy is desired, n can be increased at each successive repeat of steps 7 and 8. For each new T, start at step 6 following step 8. If step 7 was the last step, key RCL00 REGSWAP RDN before starting again at step 6.

NOTE 3: C can be used in place of R/S for step 8, but alternating between C for the x calculation and R/S for the y calculation helps one keep track of which value is being calculated.

NOTE 4: If it is desired to repeat step 7' to obtain a value to a larger number of places, change FIX n and repeat steps 8' and 7'. Similarly, if x is known, repeat steps 7'' and 8''.

NOTE 5: At any time after step 6 has been carried out, registers 7-9 and 27-29 can be recalled to check the values of e, b^x, and c^x. Immediately after steps 6 or 8, e^x, b^x, and c^x will be in R7-9 and the corresponding y values in R27-29. After step 7, the registers are reversed. After step 7, RCL15 will give the value of d_x = -ln a_x and RCL35 will give the value of d_y = -ln a_y. After step 8 with the x values in the low-numbered registers, the order is reversed.

NOTE 6: Step 6 assumes x and y are small. If they are not, follow step 6 by x' + y' XEQ 8, where x' and y' are estimates of the solution. Then continue with steps 7 and 8.

TEST:

(2) FIX 2 GTO IM;
(3) 5127 + 1.774 + 4X10^3 + .3 A 5127.00;
(4) -1371 + -.762 + 8X10^3 + .2 R/S -1371.00;
(5) 500 + .1 + 500 + .1 R/S 500.00;
(6) 2X10^3 B (or 1726.85 D) x=.07, y=.02, .02, .02, .02, .02;
(7) C x=.10, .10, .10, .10;
(8) R/S y=.02, .02, FIX 4, .0190;
(7) C x=.1014, .1014, .1014, .1014, FIX 5, .10138;
(8) R/S y=.01902, .01902, .01902, FIX 6, .019022.
(9) E

Print Out
2000.000000
0.101381 0.019022

y = .019022 known
Steps 2-7 the same as above; (8') FIX 4, .019022 STO 26; d, d_x=.0177;
(7') C .1014, .1014, .1014, .1014, FIX 5, .10138
x = .10138 known
Steps 2-6 the same as above; (7'') FIX 4 .10138 STO 06; d, d_y=.0873;
(8'') C .0190, .0190, .0190, .0190, FIX 6, .019022
\[ e_x = e_y = 0, \quad b^x_g = 2.5, \quad b^y_g = 3, \quad c^x_g = 0.5, \quad c^y_g = 0.1 \]

(3) \( 0 \times 0 \times 0 \times -2.5 A 0.00 \)

(4) \( 0 \times 0 \times 0 \times -3 R/S 0.00 \)

(5) \( 0 \times -1 \times 0 \times -0.5 R/S 0.00 \)

(6) \( 1 B x = 0.05, \quad y = 0.04, \quad 0.06, \quad 0.06, \quad 0.06 \)

(7) \( c = 0.08, \quad 0.08, \quad 0.08, \quad \text{FIX 3}, \quad 0.075; \quad (8) R/S 0.062, \quad 0.062, \quad 0.062, \quad \text{FIX 4}, \quad 0.0618 \)

(7) \( C = 0.0755, \quad 0.0755, \quad 0.0755, \quad 0.0755 \)

\[
\begin{align*}
01 & \text{LBL "TH"} \\
02 & \text{LBL A} \\
03 & \text{STO 17 RDN STO 16 RDN} \\
04 & \text{STO 14 RDN STO 13} \\
05 & \text{SF 00 004.024016} \\
06 & \text{STO 00 REGSWAP RDN} \\
07 & \text{RTH} \\
16 & \text{LBL a} \\
17 & \text{XEQ a RTH} \\
19 & \text{LBL b} \\
20 & \text{STO 19 RDN STO 18 RDN} \\
21 & \text{STO 39 RDN STO 38 RTH} \\
28 & \text{LBL B} \\
29 & \text{STO 01 XEQ 00 XEQ d} \\
30 & \text{XEQ 00 GTO C} \\
34 & \text{LBL 00} \\
35 & \text{STO 03 XEQ 06 ISG 03} \\
36 & \text{XEQ 06 + XEQ 06 +} \\
37 & \text{CHS ETX PSE STO 10} \\
38 & \text{1.5 * STO 06 STO 11 RTH} \\
54 & \text{LBL C} \\
55 & \text{RCL 11 XEQ 02 XEQ 03} \\
56 & \text{STO 06 XEQ 01 RCL 06} \\
57 & \text{XEQ d RCL 26 RTH} \\
58 & \text{GTO C} \\
65 & \text{LBL D} \\
66 & \text{273.15 + GTO B} \\
69 & \text{LBL 06} \\
70 & \text{RCL IND 03 ISG 07} \\
71 & \text{RCL 01 / RCL IND 03} \\
72 & \text{ISG 03 - STO IND 02} \\
73 & \text{ISG 02 RTH}
\end{align*}
\]

\[
\begin{align*}
88 & \text{LBL d} \\
89 & \text{RCL 09 * LASTX 1.5 *} \\
90 & \text{RCL 08 - RCL 06} \\
91 & \text{X*2 * 1 RCL 06 - LH} \\
92 & \text{- RCL 00 REGSWAP RDN} \\
93 & \text{STO 15 RTH} \\
102 & \text{LBL 01} \\
103 & \text{RCL 11 RCL 11 RCL 10} \\
104 & \text{- STO 12 2 / -} \\
105 & \text{STO 10 RTH} \\
113 & \text{LBL 02} \\
114 & \text{RCL 11 XEQ e STO 05} \\
115 & \text{RCL 10 XEQ e STO 04 RTH} \\
121 & \text{LBL 03} \\
122 & \text{RCL 05 GTO 04} \\
124 & \text{LBL 05} \\
125 & \text{RCL 11 XEQ e STO 05} \\
128 & \text{LBL 04} \\
129 & \text{RCL 10 RCL 11 -} \\
130 & \text{RCL 05 RCL 04 - / -} \\
131 & \text{ST+ 11 RCL 11 FS? 00} \\
132 & \text{PSE / RND X*0?} \\
133 & \text{GTO 05 RCL 11 RTH} \\
147 & \text{LBL e} \\
148 & \text{LN 1 LASTX - X*2} \\
149 & \text{LASTX RCL 09 * RCL 08} \\
150 & \text{+ * + RCL 15 +} \\
151 & \text{RCL 07 + RTH} \\
165 & \text{LBL 08} \\
166 & \text{STO 30 RDN STO 10} \\
167 & \text{XEQ 09 RCL 10 XEQ 09 RTH}
\end{align*}
\]

43 registers
189 steps
298 bytes
| Index | 004.024016 | T | 7.1 | 13.1 | f(y') | f(y'') | x'' | e_x | b^x | c^x | g
|-------|-----------|---|-----|------|-------|--------|-----|-----|-----|-----|----
|       |           | 10.1 | 20.1 |      |       |        |     |     |     |     |    |
|       | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 |    |
| x' | x'' | ΔH^0_{f,1/R} | ΔS^0_{f,1/R} | d_x | b^x | b^y | c^x | c^y | g |
| 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 |    |
| f(x') | f(x'') | y'' | e_y | b^y | c^y | g |
| 30 | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 |    |
| y' | y'' | -ΔH^0_{f,2/R} | -ΔS^0_{f,2/R} | d_y | b^y | b^y | c^y | c^y | g |

**REFERENCES**


(3) Hewlett-Packard HP-67 User's Library, 1000 N.E. Circle Boulevard, Corvallis, OR, 97330.
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