Title

Calculations of Composition Boundaries of Saturated Phases

Permalink

https://escholarship.org/uc/item/3f29k5sj

Authors

Brewer, L.
Hahn, S.

Publication Date

1983-09-01

LBL-16726 c.2

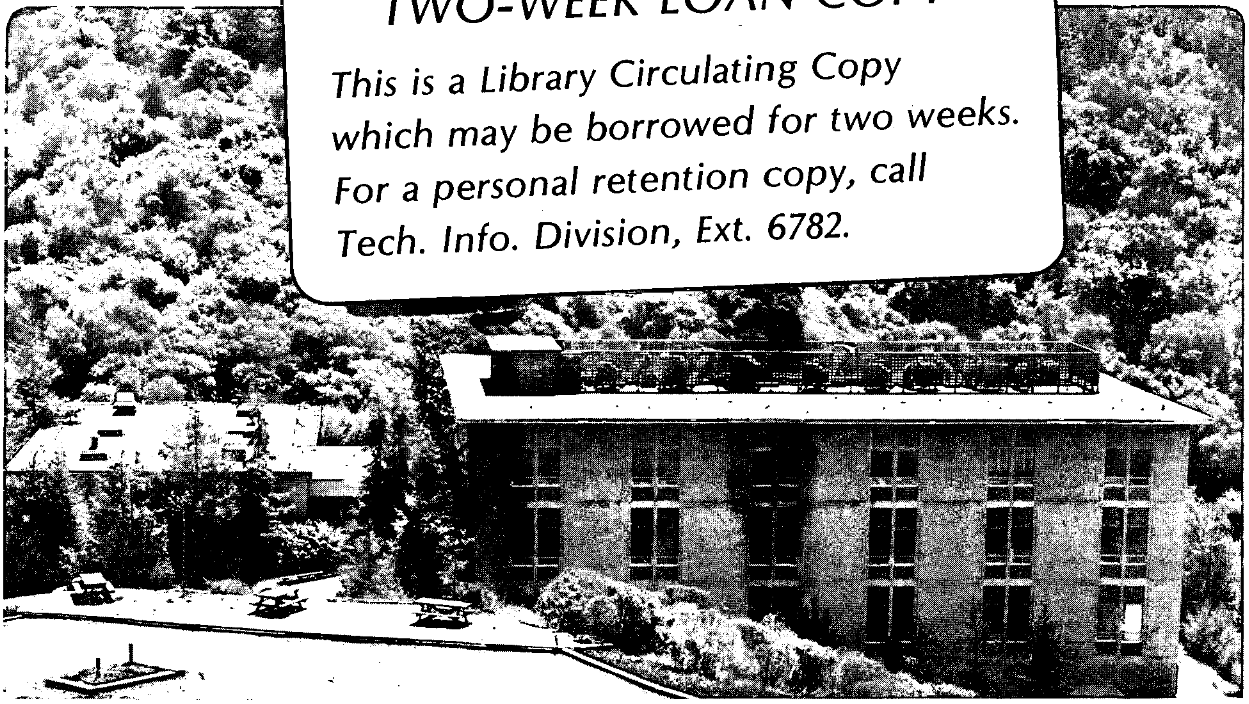
Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

CALCULATIONS OF COMPOSITION BOUNDARIES OF SATURATED PHASES

L. Brewer and S. Hahn

September 1983



Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

DISCLAIMER

LBL-16726

Calculations of Composition Boundaries of Saturated Phases

by

Leo Brewer and Susie Hahn

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
and
Department of Chemistry
University of California
Berkeley, California 94720

September 27, 1983

This work was supported by the Division of Materials Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract Number DE-AC03-76SF00098.

This manuscript was printed from originals provided by the authors.

Calculations of Composition Boundaries of Saturated Phases

Leo Brewer and Susie Hahn

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

$$\Delta\bar{G}_1^E/RT = b_g x_2^2 + c_g x_2^3 \qquad \text{and} \qquad \Delta\bar{G}_2^E/RT = [b_g + \tfrac{3}{2}c_g]x_1^2 - c_g x_1^3$$

$\Delta\bar{G}_1^E$ 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 $b_g = (V_2^2/V_1)[\Delta E_1/V_1)^{\frac{1}{2}} - (\Delta E_2/V_2)^{\frac{1}{2}}]^2/RT$, the temperature coefficients of the molal volume and of the energy of vaporization, ΔE, 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

$$\ln\gamma_1 = \Delta\bar{G}_1^E/RT = (b_h/T - b_s)x_2^2 + (c_h/T - c_s)x_2^3 = \Omega_1 x_2^2$$
$$\ln\gamma_2 = \Delta\bar{G}_2^E/RT = [b_h/T - b_s + \tfrac{3}{2}(c_h/T - c_s)]x_1^2 - (c_h/T - c_s)x_1^3 = \Omega_2 x_1^2$$

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_gT at a temperature T equals $b_h - b_sT$, etc. These equations average out the contributions of ΔC_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

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

$$\ln y + (b+\tfrac{3}{2}c)(1-y)^2 - c(1-y)^3 = \ln(1-x) + (b+\tfrac{3}{2}c)x^2 - cx^3$$

where $b = (b_h/T - b_s)$ and similarily for c. When the same values of b and c are not applicable for both phases, the equations become

$$\ln x + b_x(1-x)^2 + c_x(1-x)^3 + e_x = \ln(1-y) + (b_y+\tfrac{3}{2}c_y)y^2 - c_y y^3 = -d_x$$

$$\ln y + b_y(1-y)^2 + c_y(1-y)^3 + e_y = \ln(1-x) + (b_x+\tfrac{3}{2}c_x)x^2 - c_x x^3 = -d_y$$

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 $b_x = b$, $b_y = b+\frac{3}{2}c$, $c_x = c$, 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 $T_1 \uparrow T_2$ / STO*8 STO*28 XEQ5 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-11 of the HP-67 Standard Pac.[3] 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 iteraction 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 **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 ~0.1, the values of x and y will be accurate to 0.0005 and can be read to 4 places by keying **FIX** 4. If it is desired to calculate x and y more accurately, steps 7 and 6 can be repeated with **FIX** 3 or 4. If there is no interest in the progress of the iteration at each step, CFO will stop the flashing of successive x or y values. 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 ΔH°_f and ΔS°_f 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 ΔH°_f and

ΔS^o_f are replaced by the corresponding values for the transition. For liquid immiscibility with small enough solubilities for the approximation $\ln\gamma_1 = (b_x+c_x)y^2$ and $\ln\gamma_2 = (b_x+\frac{1}{2}c_x)(1-y)^2$ in the phase rich in component 2, the regular solution theory predicts $(b_x+c_x)/(b_x+\frac{1}{2}c_x) = (V_2/V_1)$.

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 $(\ln\gamma_1)/x_2^2 = b+c$ at large x_2 with $(\ln\gamma_2)/x_1^2 = b+\frac{1}{2}c$ at large x_1. If c = 0 is used in Prgm. IM, $(\ln\gamma_1)/x_2^2$ and $(\ln\gamma_2)/x_1^2$ are taken equal for a given solution, but their value can be greatly different on opposite sides of the miscibility gap.

Directions:

			Display
(1)	Insert Prgm. IM		
(2)	FIX n, usually n=2 initially		
(3)	$\Delta H^o_{f,1}/R \uparrow \Delta S^o_{f,1}/R \uparrow b^x_h \uparrow b^x_s$ A		$\Delta H^o_{f,1}/R$
(4)	$-\Delta H^o_{f,2}/R \uparrow -\Delta S^o_{f,2}/R \uparrow b^y_h \uparrow b^y_s$ R/S (or a)		$-\Delta H^o_{f,2}/R$
(5)	$c^y_h \uparrow c^y_s \uparrow c^x_h \uparrow c^x_s$ R/S (or b)		c^y_h
(6)	T B (or t°c D)		x', y' ..... y"
(7)	C	Repeat 7 and 8 alternately until x and y show no change in successive steps; read final values with FIX n+1	x" .... x'''
(8)	R/S		y" .... y'''
(9)	E		Print Out T x''' y'''

If y is known; after step 7, FIX n to desired accuracy followed by

(8')	y STO 26 d	d_x
(7')	C	x" .... x_{final}

If x is known; after step 6, FIX n to desired accuracy followed by

(7")	x STO 06 d	d_y
(8")	C	y" .... y_{final}

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 °C can be inserted followed by D to convert to °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_g and c_g. Immediately after steps 6 or 8, e^x, b_g^x, and c_g^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 $d_x = -\ln a_1$ and RCL35 will give the value of $d_y = -\ln a_2$. 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' XEQ8, 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, 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

$e_x = e_y = 0,\ b_g^x = 2.5,\ b_g^y = 3,\ c_g^x = .5,\ c_g^y = .1$

(3) 0 ↑ 0 ↑ 0 ↑ -2.5 A 0.00

(4) 0 ↑ 0 ↑ 0 ↑ -3 R/S 0.00

(5) 0 ↑ -.1 ↑ 0 ↑ -.5 R/S 0.00

(6) 1 B x=.05, y=.04, .06,.06,.06,.06

(7) C .08, .08, .08, FIX 3, .075; (8) R/S .062, .062, .062, FIX 4, .0618

(7) C .0755, .0755, .0755, .0755

```
 01♦LBL "IM"

 02♦LBL A
STO 17  RDN  STO 16  RDN
STO 14  RDN  STO 13
SF 00  004.024016
STO 00  REGSWAP  RDN
RTN

 16♦LBL a
XEQ A  RTN

 19♦LBL b
STO 19  RDN  STO 18  RDN
STO 39  RDN  STO 38  RTN


 28♦LBL B
STO 01  XEQ 00  XEQ d
XEQ 00  GTO C

 34♦LBL 00
7.1  STO 02  13.1
STO 03  XEQ 06  ISG 03
XEQ 06  +  XEQ 06  +
CHS  E↑X  PSE  STO 10
1.5  *  STO 06  STO 11
RTN

 54♦LBL C
RCL 11  XEQ 02  XEQ 03
STO 06  XEQ 01  RCL 06
XEQ d  RCL 26  RTN
GTO C

 65♦LBL D
273.15  +  GTO B

 69♦LBL 06
RCL IND 03  ISG 07
RCL 01  /  RCL IND 03
ISG 03  -  STO IND 02
ISG 02  RTN
```

```
 80♦LBL d
RCL 09  *  LASTX  1.5  *
RCL 08  +  -  RCL 06
X↑2  *  1  RCL 06  -  LN
-  RCL 00  REGSWAP  RDN
STO 15  RTN

102♦LBL 01
RCL 11  RCL 11  RCL 10
-  STO 12  2  /  -
STO 10  RTN

113♦LBL 02
RCL 11  XEQ e  STO 05
RCL 10  XEQ e  STO 04
RTN

121♦LBL 03
RCL 05  GTO 04

124♦LBL 05
RCL 11  XEQ e  STO 05



128♦LBL 04
RCL 10  RCL 11  -
RCL 05  RCL 04  -  /  *
ST+ 11  RCL 11  FS? 00
PSE  /  RND  X≠0?
GTO 05  RCL 11  RTN



147♦LBL e
LN  1  LASTX  -  X↑2
LASTX  RCL 09  *  RCL 08
+  *  +  RCL 15  +
RCL 07  +  RTN

165♦LBL 08
STO 30  RDN  STO 10
XEQ 09  RCL 10  XEQ 09
RTN
```

```
173♦LBL 09
1 E-4  +  STO 06  STO 11
RDN  XEQ d  RTN

181♦LBL E
RCL 01  PRX  RCL 06  ACX
RCL 26  ACX  PRBUF  END
```

43 registers
189 steps
298 bytes

0	1	2	3	4	5	6	7	8	9
Index 004.024016	T	7.1 to 10.1	13.1 to 20.1	f(y')	f(y")	x'"	e_x	b_g^x	c_g^x
10	11	12	13	14	15	16	17	18	19
x'	x"		$\Delta H^0_{f,1}/R$	$\Delta S^0_{f,1}/R$	d_x	b_h^x	b_s^x	c_h^x	c_s^x
20	21	22	23	24	25	26	27	28	29
				f(x')	f(x")	y'"	e_y	b_g^y	c_g^y
30	31	32	33	34	35	36	37	38	39
y'	y"		$-\Delta H^0_{f,2}/R$	$-\Delta S^0_{f,2}/R$	d_y	b_h^y	b_s^y	c_h^y	c_s^y

REFERENCES

(1) G. N. Lewis, M. Randall, K. S. Pitzer and L. Brewer, Thermodynamics, 2nd Ed., McGraw-Hill, New York, 1961.

(2) J. W. Hildebrand and R. L. Scott, Regular Solutions, Prentice-Hall, Englewood Cliffs, NJ, 1962.

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